Platinized tin oxide: A low-temperature oxidation catalyst

Erik Joshua Kielin

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PLATINIZED TIN OXIDE:
A LOW-TEMPERATURE OXIDATION CATALYST

A Dissertation
Presented to
The Faculty of the Department of Applied Science
The College of William and Mary in Virginia

In Partial Fulfillment
Of the Requirement for the Degree of
Doctor of Philosophy

by
Erik Joshua Kielin
1998
APPROVAL SHEET

This dissertation is submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

Erik Joshua Kielin

Approved, November 1998

Floyd L. Klavetter, Ph. D.
(Chairman)

Kenneth G. Brown, Ph. D.
(Co-Chairman)

Robert L. Vold, Ph. D.

Robert A. Ortwoll, Ph. D.

William E. Cooke, Ph. D.
(Department of Physics)
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ABSTRACT

Some combinations of a noble metal with a reducible metal oxide, an NMRO catalyst, possess a synergistic level of activity for the catalytic oxidation of CO at lower temperatures and partial pressures of O\textsubscript{2} than can be obtained by either component alone. These properties make NMRO catalysts candidates for use in recycling of CO\textsubscript{2} laser gas, purification of breathing air in enclosed spaces, purification of compressed air and other oxygen-containing gases, CO removal from automobile emissions during cold start, personal safety masks, and selective chemical sensors.

The activity for the reaction between CO and O\textsubscript{2} on a variety of noble metal-metal oxide combinations was measured. The most promising candidates, Au on MnO\textsubscript{2} and Pt on SnO\textsubscript{2}, were investigated for the effects on activity of noble metal loading, of reductive pretreatment at elevated temperature, and of reaction gas mixture composition. Optimum activity was obtained at 28% Au/MnO\textsubscript{2} and 17% Pt/SnO\textsubscript{2}. Both catalysts benefitted from reductive CO pretreatment at 125°C while showing no change in activity from pretreatment in He or O\textsubscript{2} in He. Both catalysts showed enhanced activity when the reaction gas mixture contained excess O\textsubscript{2}, and both were inhibited somewhat by excess CO. Au/MnO\textsubscript{2} was severely inhibited by CO\textsubscript{2} in the reaction gas mixture whereas Pt/SnO\textsubscript{2} showed no inhibition by CO\textsubscript{2}.

A method for coating Pt/SnO\textsubscript{2} onto various substrates was developed. The SnO\textsubscript{2} layer was applied to the substrate via thermal decomposition of tin(II) 2-ethylhexanoate, SnEH. The decomposition of SnEH was followed using DRIFTS. The effects of surface area and pore size distribution of both substrate and of the SnO\textsubscript{2} layer on the CO oxidation activity of the final catalyst coating were investigated. Low-surface area, high-pore diameter substrates provided the highest activity catalyst coatings. The activity also increased as the total SnO\textsubscript{2} loading and surface area were increased. Activity correlated with total Pt and SnO\textsubscript{2} surface areas.

Small amounts of H\textsubscript{2}O in the reaction gas mixture enhanced the low-temperature, CO-oxidation activity over Pt/SnO\textsubscript{2}; large amounts eliminated the activity unless the catalyst was mildly heated. The activity-enhancing effect of water is due, in part, to the formation of surface hydroxyl groups. Hydroxyl groups may function in the dissociative adsorption of O\textsubscript{2} or as oxidizing agents themselves. Silylation of the hydroxyl groups of Pt/SnO\textsubscript{2} destroyed the CO-oxidation activity. Changes in the catalyst surface from silylation were analyzed using DRIFTS. In addition, molecular water enhances the activity by aiding in the breakdown of surface-bound CO\textsubscript{2} consistent with the creation of more acidic sites on SnO\textsubscript{2} with the addition of H\textsubscript{2}O.

The conversion of formaldehyde, acetaldehyde, and the C\textsubscript{1} to C\textsubscript{3} alcohols over Pt/SnO\textsubscript{2} was investigated and compared to that over Pt. Differences in product mixtures were attributed to the presence of higher concentrations of surface oxygen provided by SnO\textsubscript{2}. The oxidation of the C\textsubscript{1} to C\textsubscript{5} hydrocarbons to CO\textsubscript{2} and H\textsubscript{2}O over Pt/SnO\textsubscript{2} was found to occur at significantly lower temperatures than reported for noble metal catalysts. The reduced temperature was attributed to the presence of SnO\textsubscript{2}. Mechanisms are discussed.
PLATINIZED TIN OXIDE:
A LOW-TEMPERATURE OXIDATION CATALYST
CHAPTER 1
NMRO CATALYST COMPOSITION

1.1. INTRODUCTION

Pulsed CO\textsubscript{2} lasers are finding increased use in industrial, medical, and military
applications. Consequently, means for improving the power, stability, and lifetime, while
minimizing the expense of operation are under constant investigation. All CO\textsubscript{2} lasers suffer
from one main problem: dissociation of the CO\textsubscript{2} into CO and O\textsubscript{2} during the electrical
excitation phase. Although sensitivity to O\textsubscript{2} is laser dependent, the build up of small
amounts of O\textsubscript{2} to partial pressures greater than 1\% causes arcing, rapid power loss, and
eventual laser failure. Typically, to maintain high power and continuous operation, fresh
CO\textsubscript{2} gas is pumped into the laser cavity and the spent gas containing CO and O\textsubscript{2} is
exhausted. This requires that a tank of gas accompany the laser. For applications where
weight is costly and space is limited (i.e. satellites, tanks), it is desirable or even necessary
to eliminate the unnecessary size and weight penalty of tanks. A means for eliminating the
tanks would be to use an appropriate catalyst to recombine the CO and O\textsubscript{2} back into CO\textsubscript{2}
and thereby enable sealed or closed-cycle operation of the laser.

A candidate catalyst for CO oxidation in the laser cavity must operate (1) in low
partial pressures of O\textsubscript{2} (<< 1\%), (2) unhindered by other components—CO\textsubscript{2} in particular,
(3) without input of energy (e.g. at ambient laser temperature), (4) with a minimum of
forced circulation; and (5) without dusting. The first three requirements dictate
composition, the last two form (e.g. powder, pellet, monolith).

Catalyst development at NASA Langley Research Center (LaRC) originated from a
need to operate a high-power, sealed CO\textsubscript{2} laser for spaceborne and remote sensing
applications. The Laser Atmospheric Windsounder (LAWS) was to employ a sealed CO\textsubscript{2}
laser to monitor wind speeds in the upper atmosphere from an orbiting satellite for a period of five years. For use in such remote sensing applications, it was necessary for the laser to use rare-isotope CO$_2$, such as $^{12}$C$^{18}$O$_2$, $^{13}$C$^{16}$O$_2$, or $^{13}$C$^{18}$O$_2$. For this application, the additional requirement was imposed that the catalyst operate without scrambling the rare-isotope CO$_2$. In other words, any common-isotope oxygen in the catalyst could not react with the C$^{18}$O produced during the decomposition of C$^{18}$O$_2$. In addition, the military desired use of sealed CO$_2$ lasers for remote sensing of toxic chemical weapons.

The commercially available CO-oxidation catalysts consist of either single metal oxides (generally the transition metal oxides) or noble metals dispersed on an inert support (e.g. Pt, Pd, Rh, or Au). Examples of inert supports are carbon, Al$_2$O$_3$, ZrO$_2$, TiO$_2$, or SiO$_2$. They do not, themselves, participate in the catalytic process but only better disperse the catalyst to provide more active sites for an equal amount of material. This class of one-component catalysts require elevated temperatures or high concentrations of O$_2$ to work efficiently. Under conditions of excess O$_2$, Pt and Pd metals do not show substantial oxidation of CO until temperatures of about 150°C are reached. For Rh and Au about 300°C is required. Under stoichiometric conditions even higher temperatures are required. The oxides traditionally used to support these noble metals such as Al$_2$O$_3$ and SiO$_2$ show no substantial activity at these temperatures. Under similar oxidizing conditions, however, some metal oxides show substantial oxidation of CO at temperatures equal to or below that of the aforementioned noble metals. Under stoichiometric or reducing conditions, on the other hand, the activity over metal oxides is either non-existent or short-lived due to reduction of the metal oxide. The metal oxides such as SnO$_2$, NiO, CuO, MnO$_2$, Fe$_2$O$_3$, and Co$_3$O$_4$ can oxidize CO at between 100°C and 200°C in excess O$_2$ atmospheres. These metal oxides will be given the special name of “reducible oxide” for their ability to oxidize CO at relatively low temperature.

Bimetallic and mixed metal oxides have been used as CO-oxidation catalysts as
well. Pd-Ag supported on Al₂O₃ shows somewhat reduced temperature for CO-oxidation by comparison to either component alone.⁴ Hopcalite®, a mixed metal-oxide catalyst discovered and commercialized by Mine Safety Appliances Co., is capable of normal room-temperature oxidation of CO. It consists of the oxides of copper and manganese interspersed at the atomic level in an amount of about 10-20% CuO to 80-90% MnO₂—without noble metal. Hopcalite is capable of oxidizing CO at normal room temperatures but requires excess oxygen, is fouled by moisture below 200°C, and is irreversibly poisoned by NOₓ and SOₓ.⁵ A similar composition exhibiting similar activity and fouling is copper oxide/tin oxide.⁶

During the last twenty years a new class of two-component catalysts has emerged, some of which meet the first three requirements listed above for candidate, CO₂ laser catalysts. These catalysts consist of one or more noble metals dispersed on a reducible oxide and have been given the acronym NMRO for “noble metal-reducible oxide catalyst.”⁷ For the reducible oxides mentioned above, combining any with Pt, Pd, or Au, reduces the temperature at which substantial CO oxidation can be obtained to between 0°C and -70°C, far below that of either component alone.²,⁸,⁹

The purpose of this chapter is to present the low-temperature CO-oxidation capacity of several NMRO catalysts along with their benefits and potential problems. The NMRO compositions investigated include Pt, Pd, Ag, Ru, Au, and Cu on MnO₂; Pt, Pd, and Au on SnO₂; and Au on Fe₂O₃, CeO₂, and Pt on Fe₂O₃. The notation used to designate these catalysts will be, for example, 2% Au/Fe₂O₃, to represent Au deposited on or co-precipitated with Fe₂O₃. The quantity preceding the noble metal refers to the weight percent of noble metal in the overall composition.

It should be noted that the chemical nomenclature just used to describe the noble metals and metal oxides does not necessarily indicate the composition of either component at the surface of or at the interface between the noble metal and metal oxide. It is simply
based on the bulk materials and is for the purpose of convenient nomenclature. Of the metal oxides presented here, due to the relative ease with which surface oxygen can be removed, attaining stoichiometric purity is nearly impossible.\textsuperscript{10} There will be metal atoms without their full complement of coordinated oxygen atoms and vice versa. In other words, the surface region can behave as though two oxidation states are present. Based on the stoichiometry of the oxygen present, the oxides of both manganese and cerium behave as though both +3 and +4 oxidation states are present.\textsuperscript{9} For tin oxide, the near surface region is complex. SnO\textsubscript{2} can be enriched with oxygen at the surface due to adsorption of water as hydroxide groups and show oxygen depletion from a few atomic layers into the material into the bulk, SnO\textsubscript{x} where x is between 1.84 and 2.\textsuperscript{11} Such nonstoichiometry may also be essential to the catalytic capacity of the metal oxides.\textsuperscript{9} The degree of nonstoichiometry depends upon the identity of the parent metal and the conditions under which the metal oxide was manufactured or treated prior to analysis.

Similarly, Herz and Shinouskis have shown that all finely divided noble metals can be oxidized to some degree either during preparation or under reaction conditions, perhaps with the exception of gold.\textsuperscript{12} Even finely divided gold "retains an amount of oxygen by adsorption, which varies according to the degree of subdivision, the nature of the precipitation reagent, and the environmental atmosphere during heating."\textsuperscript{13} It has also been proposed that tin oxide stabilizes the oxidized forms of Pt and Pd against reduction by carbon monoxide.\textsuperscript{14,15}

To date one of the most promising compositions for CO oxidation at normal room temperature, under stoichiometric CO and O\textsubscript{2} concentrations, without interference of CO\textsubscript{2}, is Pt/SnO\textsubscript{2} or Pt-Pd/SnO\textsubscript{2}. The first demonstration of synergy for CO oxidation at low temperature was reported by Bond, Fuller and Molloy in 1976 for the catalytic system composed of palladium and tin(IV) oxide. The combination of Pt and SnO\textsubscript{2} for oxidation of
CO in CO₂ lasers was first patented by Wright and Sampson in 1985. Then and today, the most promising materials for use in CO₂ lasers remain Pt/SnO₂-based catalysts.

1.2. EXPERIMENTAL

1.2.1. Pt-based catalyst preparation. Preparation of the Pt/SnO₂, Pt/Fe₂O₃, and Pt-Pd/SnO₂ catalyst powders and silica sphere-supported and high surface area silica gel-supported catalysts has been explained in detail earlier. Briefly, tin is oxidized to metastannic acid via dilute nitric acid oxidation of 30-mesh tin granules (Alfa/AESAR).

\[
\text{Sn} + 2\text{HNO}_3 \rightarrow \text{H}_2\text{SnO}_3 + \text{NO} + \text{NO}_2
\]

To ensure removal of excess nitric acid and water, the slurry is heated to dryness using a hotplate temperature of about 150°C. This heating converts metastannic acid to tin(II)oxide via dehydration.

\[
\text{H}_2\text{SnO}_3 + \text{heat} \rightarrow \text{H}_2\text{O} + \text{SnO}_2
\]

For coating silica spheres or high surface-area silica gel with metastannic acid, tin is oxidized in the presence of the support which has been vacuum deaerated to remove any air from the pores.

For Pt/Fe₂O₃ on silica gel, the Fe₂O₃ coated silica gel was prepared by thermally decomposing Fe(NO₃)₃·9H₂O in a stirred slurry of 60-80 mesh silica gel (Davison).

Before deposition of platinum or palladium, the supported or unsupported substrate is vacuum deaerated in the presence of a solution of either tetraamineplatinum(II)hydroxide (PtAH) or tetraaminepalladium(II)nitrate (PdAN). Platinum and palladium are then deposited on the oxide surface via formic acid reduction.
\[
\text{Pt(NH}_3\text{)}_4(\text{OH})_2 + \text{HCO}_2\text{H} + \text{heat} \longrightarrow \text{Pt} + 4\text{NH}_3 + \text{CO}_2 + 2\text{H}_2\text{O}
\]

Again the slurry is heated to dryness to remove excess water, formic acid, and the volatile byproducts. The preparation is completed by drying the catalyst in a convection oven in air at 150°C.

The above preparation has the beneficial characteristic of using reagents which form volatile by-products and leave behind no residues. By contrast, CO-precipitation techniques make Pt/Sn\textsubscript{O}_2 by peptizing mixtures of H\textsubscript{2}PtCl\textsubscript{6} and SnCl\textsubscript{4} followed by extensive rinsing to remove residual chloride which may poison the catalyst.\textsuperscript{18}

1.2.2. Mn\textsubscript{O}_2-based and Au-based catalyst preparation. The Mn\textsubscript{O}_2-based and Au-based catalysts were prepared by Steve Gardner, a member of the research group of Gar Hoflund at the University of Florida, Gainesville. As discussed previously (page 3), a variety of metal oxides had shown activity for CO oxidation between 100°C and 200°C alone and in combination with gold. A variety of noble metals were combined with Mn\textsubscript{O}_2 and a variety of metal oxides with gold. The materials investigated were synthesized using established impregnation and co-precipitation techniques.\textsuperscript{19} The samples prepared include Mn\textsubscript{O}_2, Pt/Mn\textsubscript{O}_2, Ag/Mn\textsubscript{O}_2, Pd/Mn\textsubscript{O}_2, Au/Mn\textsubscript{O}_2, Au/Ce\textsubscript{O}_2, and Au/Fe\textsubscript{O}_3.

The Mn\textsubscript{O}_2 was used as received from the Kerr-McGee Company, U.S.A. It was prepared by the electrolytic oxidation of manganous sulfate and has a BET surface area of 74 m\textsuperscript{2}/g. The Mn\textsubscript{O}_2 served as a sample itself as well as impregnation support for other materials.

The Pt/Mn\textsubscript{O}_2, Pd/Mn\textsubscript{O}_2, and Ag/Mn\textsubscript{O}_2 samples were prepared by impregnation of the as received Mn\textsubscript{O}_2 using an aqueous solution of Na\textsubscript{2}Pt(OH)\textsubscript{6}, PdCl\textsubscript{2}, or AgNO\textsubscript{3}. Each impregnated sample was dried in air at 280°C for 4.5 hours.

A technique in which Mn(OH)\textsubscript{2} was precipitated in the presence of ultra-fine Ru powder was used to prepare a 2% Ru/Mn\textsubscript{O}_2 sample. A solution of Mn(NO\textsubscript{3})\textsubscript{2} was added.
drop-wise to a stirred mixture of Ru powder in NH$_4$OH. The resulting product was dried and calcined at 400°C for 2 hours.

Four supported Au samples were synthesized via co-precipitation from aqueous HAuCl$_4$ and the nitrate of the corresponding support metal. The compositions of the materials are approximately 10% Au/MnO$_2$, 20 at% Au/MnO$_2$, 22% Au/ CeO$_2$ and 12% Au/Fe$_2$O$_3$. In each case the appropriate precursor solutions were added drop-wise to a stirred solution of sodium carbonate at room temperature. After washing and drying the precipitates were calcined in air at 400°C for 4 hours. Two Au/Fe$_2$O$_3$ samples were prepared which differed only in the temperature of the wash water utilized (25°C and 80°C).

1.2.3. Measurement of activity. Figure 1.1 shows a schematic of the system used to measure catalyst activity. The general flow through the system is as follows. The gases flow from high pressure tanks to Hastings mass flow controllers where the flow rate is regulated. Each of the four catalyst reactors and bypass has an independent flow controller. From the flow controller, the flow passes through the bypass or catalyst reactors, which are housed in a Thermolyne convection oven, to the automated sample loop and then to a Shimadzu gas chromatograph for analysis. In the case of the catalyst reactors, prior to passing through the sample loop, the flow passes through a 9-port, continuous-flow, stream-selection valve which enables automated control of which reactor is connected to the sample loop.

In a typical test, the catalyst is purged with He for 1 hour while the oven is heated to the run temperature. While the catalyst samples are being flushed with He, the test gas flows through the bypass to the GC for analysis of the reaction gas mixture in the absence of catalyst. After the He purge, the reaction gas mixture is diverted to the catalyst samples in the reactors. At preset times, a 1-mL sample of the effluent gas from the reactor is directed to the GC for analysis of the concentrations of CO$_2$, O$_2$, and CO. The activity is determined by calculating the loss of CO or O$_2$ and the gain in CO$_2$. 

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Figure 1.1. Schematic representation of plug flow reactor system with automated stream selection, sample loop, and data collection.
The catalyst sample was supported between plugs of quartz wool in a glass tube with glass-metal unions at either end. This is shown in Figure 1.2. A 50-mg to 150-mg sample of catalyst was used for activity measurements and will be indicated where appropriate. The temperatures at which activity was measured were between 35°C and 80°C and will be indicated as appropriate. Unless otherwise indicated, the catalysts were tested at a flow rate of 10 standard cm³/min (sccm) using one of the following reaction gas mixtures whose concentrations were nominally, (1) stoichiometric: 1.00% CO, 0.500% O₂, balance He; (2) stoichiometric with 16% CO₂, balance He; (3) twice the stoichiometric amount of CO: 2.00% CO, 0.500% O₂, balance He; and (4) twice the stoichiometric amount of O₂: 1.00% CO, 1.00% O₂, balance He. All test gases had a 2.00% Ne internal standard and were gravimetric standards obtained from either Scott Specialty Gases or MG Industries.

Catalyst pretreatment. For some of the tests, the catalyst samples were reductively pretreated prior to testing. A typical pretreatment proceeded as follows. The catalysts were heated to the desired temperature under He flow for 1 hour. Then the gas was switched to 10 sccm of 5% CO (or H₂) in He for 1 hour. Helium was reintroduced and the oven temperature reduced to the desired test temperature for 1 hour. The pretreatment temperatures used varied from 55°C to 225°C and will be indicated where appropriate. Once the pretreatment was completed, the gas was switched from He to the reaction gas mixture and the analysis was started. Unless otherwise indicated, all of the Pt/SnO₂ catalyst samples were pretreated at 125°C for 1 hour prior to testing.

1.3. RESULTS

1.3.1. Effect of catalyst composition on CO oxidation activity. The activity of a catalyst can be expressed in a variety of ways. In this section, it is expressed in terms of conversion efficiency of CO to CO₂. Conversion efficiency is a measure of the fraction of the limiting reagent in the reaction gas mixture converted to product by the
Figure 1.2. Catalyst reactor tube with powder 2% Pt/SnO$_2$ catalyst.
catalyst. When stoichiometric amounts of CO and O₂ are in the reaction gas mixture, the conversion efficiency can be expressed as the fraction loss of either CO or of O₂. It can also be expressed as the fraction yield of CO₂. Percent loss or yield is obtained simply by multiplying the conversion efficiency by 100. Each is calculated as follows.

\[
\text{% loss CO} = 100 \left( \frac{[\text{CO}]_0 - [\text{CO}]_t}{[\text{CO}]_0} \right) = 100 \left( 1 - \frac{[\text{CO}]_t}{[\text{CO}]_0} \right) \tag{1}
\]

\[
\text{% loss O}_2 = 100 \left( \frac{[\text{O}_2]_0 - [\text{O}_2]_t}{[\text{O}_2]_0} \right) = 100 \left( 1 - \frac{[\text{O}_2]_t}{[\text{O}_2]_0} \right) \tag{2}
\]

\[
\text{% yield CO}_2 = 100 \left( \frac{[\text{CO}_2]_t}{[\text{CO}]_0} \right) = 100 \left( \frac{[\text{CO}_2]_t}{2[\text{O}_2]_0} \right) \tag{3}
\]

where the term in brackets, [], is the concentration or partial pressure of that species, the subscripted 0 and t refer to the concentrations of the species in the reaction gas mixture and in the effluent stream from the catalyst as a function of time, respectively.

**Au-based and MnO₂-based catalysts.** Several combinations of Au with metal oxides and noble metals with MnO₂ were prepared and tested for activity using the stoichiometric reaction gas mixture containing 1.00% CO and 0.500% O₂ in He, as per Section 1.2.3. Figure 1.3 shows the conversion efficiencies plotted as a function of time for each 150-mg sample of catalyst prepared by impregnating the electrolytically produced MnO₂, as well as the MnO₂ itself. Each of the catalysts is active at 75°C for the oxidation of CO. Both Ag/MnO₂ and 0.2% Pt/MnO₂ catalysts show slightly greater conversion efficiency than the MnO₂ itself. The Pd/MnO₂ catalyst showed substantially lower conversion efficiency. The conversion efficiency of the MnO₂ appears to level out in activity although a longer testing period would be necessary to ascertain this.
Figure 1.3. The effect of various noble metals on high surface area MnO$_2$ on the percent conversion of CO to CO$_2$ at 75°C.

If the conversion efficiency of MnO$_2$ were truly leveling out, then it is possible that exposure of the MnO$_2$ to other reagents or thermal treatment during the noble metal impregnation, rather than the noble metal itself, may have enhanced or reduced the activity of the MnO$_2$. An example of this is provided by the Pd/MnO$_2$ sample. Recall from Section 1.2.2 that the Pd was deposited from a solution containing PdCl$_2$. Since chloride is a known inhibitor of CO oxidation over noble metals,$^{18}$ it is possible that the reduced activity is merely a result of contamination from chloride rather than by the Pd. By contrast, Ag and Pt were deposited from non-chloride-containing reagents and demonstrated no such inhibition in conversion efficiency.

The differences in conversion efficiency amongst the samples are nonetheless real and within the experimental error of less than 2% of the calculated percent yield of CO$_2$. Consequently, it remains possible that the effects provided by the noble metal are real but may be short-lived. Also note that increasing the amount of Ag from 0.2% to 1% reduced,
rather than improved, the conversion efficiency and increased the rate of decay. A decrease in conversion efficiency with an increase in noble metal loading suggests that Ag may contaminate rather than enhance the activity of MnO₂. If Ag does provide an enhanced activity, it does so only when small amounts are present. With the available data, none of the combinations presented here can be verified as more catalytically active than MnO₂ itself.

Figure 1.4 shows the percent yield of CO₂ at 80°C, 55°C, and 35°C for a variety of Au-based catalysts produced by co-precipitation techniques rather than by impregnation of MnO₂. All of the Au-based catalysts are active for CO oxidation to some extent at all temperatures. The Au/MnO₂ catalyst showed essentially complete conversion of CO to CO₂ at 80°C and 75% conversion at 35°C. The Au/CeO₂ and both Au/Fe₂O₃ samples showed significantly lower conversion efficiencies than Au/MnO₂. Both Au/CeO₂ and Au/Fe₂O₃-1

![Figure 1.4. The effect of metal oxide on the CO oxidation activity of several Au-based catalysts; 12% Au/Fe₂O₃-1 washed in 80°C water and Au/Fe₂O₃-2 in 25°C water.](image)

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showed decreases in conversion efficiency of 1/2 during the 25°C temperature drop to 55°C and an additional decrease in activity by slightly greater than 1/2 during the drop to 35°C. The Au/MnO$_2$ catalyst showed a significantly higher conversion efficiency at each temperature, dropping to about 90% conversion at 55°C and to 75% conversion at 35°C.

The only difference between the Au/Fe$_2$O$_3$-1 and -2 was the wash water temperature during rinsing of the CO-precipitate, 80°C and 25°C, respectively. Because the Au was deposited via HAuCl$_4$, it is possible that residual chloride was left behind on the sample washed with 25°C water. The increasing conversion efficiency at 80°C may have been an indication of removal of the contaminant by the reaction gas mixture.

**Pt-based catalysts.** Platinum was deposited on several metal oxides which resulted in "catalysts" with no significant CO-oxidation activity near room temperature. Among these were oxides of vanadium, tungsten, bismuth, molybdenum, and lead. Figure 1.5 shows the activities of several Pt-based catalysts prepared as per the instructions in the experimental section. All samples were pretreated for 1 hour except for the silica gel-supported 2% Pt/Fe$_2$O$_3$ sample which was pretreated for 6 hours to ensure complete activation.

Each of the catalysts, except for the silica gel-supported Pt, 5% Pt/SiO$_2$, showed some activity for CO-oxidation, with increased activity at each higher temperature. The 5% Pt/SiO$_2$ catalyst showed no activity which demonstrates that Pt is not responsible for the activity of either of the silica gel-supported 2% Pt/Fe$_2$O$_3$ or 15% Pt/SnO$_2$ catalysts nor the unsupported 10% Pt/MnO$_2$. The 15% Pt/SnO$_2$ catalyst showed the highest activity of the Pt-based catalysts. It is interesting that the 2% Pt/Fe$_2$O$_3$ catalyst showed as high an activity as the 15% Pt/SnO$_2$ catalyst at 35°C. Unfortunately, the activity of the 2% Pt/Fe$_2$O$_3$ catalyst drops to about 1/3 its pretreated value upon exposure to excess oxygen (not shown). The 15% Pt/SnO$_2$ shows only small losses upon exposure to air. Although this O$_2$ sensitivity is not a problem for actual laser operation, it encumbers preparation, storage,
The activity of all of the catalysts presented thus far depends on, not only catalyst composition, but also the physical characteristics of the catalyst such as the surface area of the support oxide and the degree of dispersion of the noble metal. Haruta reported that the activity for gold-based catalysts was inversely related to the particle size of the Au crystallites.\(^2\) Figure 1.6 shows the effect of mean Au particle diameter on the resulting activity of three gold based catalysts, Au/Fe\(_2\)O\(_3\), Au/Co\(_3\)O\(_4\), and Au/TiO\(_2\), at 0°C. The activity is expressed in turn over frequency in (s\(^{-1}\)), which is the number of molecules converted per active Au site. For the catalysts prepared by Haruta using co-precipitation techniques, the critical diameter of the Au crystallites appears to be about 3.5 nm. Above this diameter, none of the three catalysts shows much activity, but below this diameter the activities take an almost vertical climb in activity. From this observation, it is apparent that

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for Au-based catalysts, the Au particle size determines the catalyst activity. For this reason, comparing the activities amongst the various catalysts presented in this chapter, without knowledge of the Au crystallite size can, at best, provide qualitative information. Haruta also noted that CO-oxidation activity of Pt-based catalysts were independent of the size of the Pt crystallite. This suggests that Pt-based catalysts may operate in a different manner than the Au-based catalysts. This is in contrast to the data to be presented in Chapter 2.

**Effect of noble metal loading.** Because Pt/SnO₂ and Au/MnO₂ showed the highest conversion efficiencies in each group, further investigation into the effect of noble metal loading on the activity was investigated. In order to compare the effect of noble metal loadings, a more revealing measure of activity is the conversion of CO normalized to the weight of catalyst. Figures 1.7 and 1.8 show the activity expressed as standard cubic centimeters of CO converted to CO₂ per gram of catalyst at 55°C, or "sccm CO conv/g catalyst." The data for Pt/SnO₂ on silica spheres has been published previously.²⁰ For both
Figure 1.7. The effect of Pt loading on the CO activity of Pt/SnO$_2$ catalysts on 10-μm silica spheres.

Figure 1.8. The effect of Au loading on the CO activity of Au/MnO$_2$ catalyst powders.
catalysts, the activity increases with increasing loading of noble metal until a maximum is reached. The Pt/SnO$_2$ catalysts gave a maximum activity at a Pt to SnO$_2$ ratio between 11 and 17% Pt, whereas the group of Au/MnO$_2$ catalysts gave a maximum activity at between 20 and 28% Au. The Au/MnO$_2$ catalysts prepared by co-precipitation techniques provide an overall greater activity per unit weight of catalyst than the Pt/SnO$_2$ catalysts deposited on silica spheres. It is interesting that the Pt/SnO$_2$ catalysts show a bimodal distribution of activities with Pt loading showing a second maximum in activity between 32 and 39% Pt. This phenomenon may be the result of differences in catalyst production rather than the result of loading. Further characterization of the catalyst surface might reveal the cause for the bimodal distribution.

Another means of comparing the activities of these catalysts uses the activities normalized to noble metal weight. This indicates how efficiently the noble metal is used. Figures 1.9 and 1.10 show the activities of each group of Pt/SnO$_2$ and Au/MnO$_2$ catalysts normalized to the noble metal weight, respectively. The Au/MnO$_2$ catalysts show about twice the activity per gram of noble metal than the Pt/SnO$_2$ catalysts. Although the total activity increases with increasing weight of noble metal, as shown in Figures 1.7 and 1.8, the activity per gram of noble metal decreases. This indicates that more activity could be gained from each unit weight of noble metal by using smaller amounts relative to the metal oxide. Along with the increase in total activity, as the noble metal increases, the likelihood of forming larger aggregates of noble metal, rather than NMRO sites, also increases. In this manner some noble metal is wasted due to lack of sufficient metal oxide area on which to disperse. This point will be taken up in considerable detail in Chapter 2.

1.3.2. Effect of pretreatment. This section presents the effect on CO conversion efficiency of pretreating the Pt/SnO$_2$ and Au/MnO$_2$ catalysts in various reaction gas mixtures: He, 5% O$_2$ in He, and 5% CO in He.
Figure 1.9. The effect of Pt loading on the efficiency of use of the Pt in Pt/SnO$_2$ catalysts on 10-μm silica spheres.

Figure 1.10. The effect of Au loading on the efficiency of use of Au in Au/MnO$_2$ catalyst powders.
Pt/SnO$_2$. As explained in the experimental section, the Pt-based catalysts were pretreated at 125°C in a flowing stream of 5% CO in He. The effects of reductive CO and H$_2$ pretreatments on Pt/SnO$_2$ catalyst have been reported before.$^{21,22}$

Figure 1.11 shows the activity versus time profile for a 2% Pt/SnO$_2$ catalyst before and after a reductive pretreatment at 100°C, 125°C, 175°C, and 225°C. The catalyst was prepared by Engelhard Corporation according to the method prescribed in Section 1.2.1 with the exception that the catalyst was calcined at 400°C. After the in situ pretreatment at any temperature, the 2% Pt/SnO$_2$ initially showed a high conversion efficiency which decreased rapidly and then recovered to a level about two times greater than that of the unpretreated catalyst. This has been referred to as the “dip” in activity.$^{21}$ The initially high conversion efficiency was probably the result of the reaction of O$_2$ from the reaction gas mixture with chemisorbed CO remaining on Pt after the pretreatment process. This

![Graph showing the effect of pretreatment temperature on the resulting conversion efficiency of a commercial 2% Pt/SnO$_2$ catalyst.](image)

**Figure 1.11.** The effect of pretreatment temperature on the resulting conversion efficiency of commercial 2% Pt/SnO$_2$; Van Norman, et al.$^{21}$

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phenomenon is commonly observed and can be used as a means for determining noble metal dispersions.

Both the extent of the dip in activity and the eventual steady-state activity are a function of pretreatment time and temperature. Figure 1.12 shows the first 500 minutes of Figure 1.11, the "dip"-region expanded. Increasing the pretreatment temperature increased the length of duration of the dip in activity, but no dip occurred if the catalyst was pretreated below 125°C. Pretreatment temperatures of 125°C, 175°C, and 225°C resulted in equal catalytic activity, for the catalyst tested, but pretreatment at 100°C yielded somewhat lower activity. Catalyst activity after a 20-hour CO pretreatment was found to be lower than after a 1-hour pretreatment. Too short a pretreatment period also diminished catalyst activity. For optimum results the effluent gas from the pretreatment was analyzed, and the

![Figure 1.12. The effect of pretreatment temperature on the extent of the "dip" in CO-oxidation activity over commercial 2% Pt/SnO₂.](image)

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pretreatment terminated, when no significant yield of CO₂ was detected (or H₂O when H₂ was used as the reducing gas).

By comparison to the reductive pretreatment, O₂ or He pretreatments at elevated temperature showed no effect on activity relative to the as prepared catalyst. This is reasonable since the calcining in air at 400°C was used during its preparation.

Because of the rather mild temperature at which the catalyst showed a dip, loss of adsorbed water was investigated as a cause. Figure 1.13 shows the activity versus time of two 0.15-g samples of commercial 2% Pt/SnO₂ catalyst at 85°C. Both samples were pretreated at 225°C using 5% CO in He. For one sample, the pretreatment gas was humidified by passing the 5% CO mixture over calcium chloride dihydrate. Exposure to moisture during pretreatment completely eliminated the initial dip in activity. It should be noted that in many cases moisture not only eliminated the initial dip in catalyst activity, but

![Figure 1.13. The effect of water in the pretreatment gas on the initial dip in CO-oxidation activity over commercial 2% Pt/SnO₂; Van Norman, et al.](image)
also enhanced the activity of the catalyst. Moisture added to the reaction gas mixture in the same manner as for the reductive treatment also alleviated the dip. In fact, addition of moisture has been shown to increase the activity even of an unpretreated Pd/SnO₂ catalyst. As will be discussed in Chapter 4, this is believed to be due to conversion of surface oxide to more-active surface hydroxide groups. Furthermore, this suggests that hydrogen in some form, probably as hydroxide groups, plays a key role in the mechanism of low-temperature oxidation of CO.

As a result of the activity-enhancing effect of water, silica gel, a support which would provide water was incorporated into the catalyst system. Silica gel could serve as a source and sink for the water thereby eliminating the initial dip in activity without interfering with laser performance which can be degraded by water vapor. Patents were issued for the understanding the impact of water on catalyst activity and by incorporating a means for controlling its administration to the catalyst. The subject of water's impact on catalyst activity will be taken up in more detail in Chapter 4.

Surface characterization of as-prepared and pretreated Pt/SnO₂. Surface characterization studies of the Pt/SnO₂ catalysts before and after pretreatment provide some insight into why the reductive pretreatment improves the CO-oxidation activity. Hoflund et al., at the University of Florida in conjunction with NASA Langley Research Center investigated the aforementioned, commercial 2% Pt/SnO₂ and the silica gel-supported 15% Pt/SnO₂ using Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and ion-scattering spectroscopy (ISS), before and after the reductive CO pretreatment. The 2% Pt/SnO₂ catalyst discussed above was examined as a function of pretreatment temperature (air exposed, 75°C, 100°C, 125°C, and 175°C) under 4 and 40 Torr of CO. The silica gel-supported Pt/SnO₂ catalyst of the Figure 1.5 was analyzed as-prepared and after reduction for 1 hour in 10 Torr of CO at 125°C and 250°C.
During the reduction of the 2% Pt/SnO₂, XPS data indicated that the O/Sn ratio decreased indicating removal of surface oxygen in either bound or adsorbed form. Corroborating evidence came from ISS data indicating a reduction in surface hydroxide concentration. For the silica gel-supported Pt/SnO₂, the 125°C reduction resulted in a slight increase in the O/Sn ratio while the 250°C reduction resulted in a decrease.

For both catalysts, XPS data also indicated that the initially present forms of platinum, PtO and PtO₂, were reduced in surface concentration while the Pt(OH)₂ surface concentration increased. Increasing the reduction temperature to 250°C, however, reduced a large fraction of the Pt(OH)₂ to zero-valent Pt. There was also evidence of zero valent Sn and Pt/Sn alloy formation from the CO reduction as low as 75°C. It might be expected that a higher temperature would be required to reduce SnO₂ to Sn metal and then to alloy with Pt. In a similar system, Pd/SnO₂, however, Bond, Fuller, and Molloy believed the catalytic mechanism to involve the Pd catalyzed reduction of SnO₂ in the presence of CO. The alloy formation observed during the reductive pretreatment of Pt/SnO₂ is consistent with this observation.

Au/MnO₂. Due to the beneficial impact of reductive pretreatment on the CO-oxidation activity of Pt/SnO₂, the effect of various pretreatments on Au/MnO₂ was also investigated. Figure 1.14 shows the CO-oxidation activities of 20% Au/MnO₂ at 55°C after having had inert and oxidative pretreatments at 55°C in He and in 5% O₂, and reductive pretreatments at 55°C and 125°C in 5% CO. The samples pretreated in He and 5% O₂ showed equal conversion efficiencies of about 70% yield of CO₂ within experimental error. Both samples pretreated in 5% CO showed 15% higher conversion efficiency, or approximately 85% yield of CO₂. The temperature of the 5% CO pretreatment had little effect on the conversion efficiency.

The conversion efficiency of the inert- and O₂-pretreated samples at the start of the test was 30% and levelled off at about 70%. That of the 55°C CO-pretreated sample started

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only 15% below its steady-state level of 83%, and that of the 125°C CO-pretreated sample started less than 10% below its steady state level of 85%. The difference in starting conversion efficiency between the He- and O₂-pretreated samples and the CO-pretreated samples was likely due to loading of the Au surface with CO. This suggests that CO adsorption might be a rate-limiting step in the oxidation of CO on Au/MnO₂. Because the difference in conversion efficiency between the He- and O₂-pretreated samples and the CO-pretreated samples shows no signs of diminishing, however, the CO pretreatment must provide real changes to the catalyst. As stated earlier, He and O₂ pretreatments show no effect on conversion efficiency of the Pt/SnO₂ catalyst. As for Au/MnO₂ only a reductive pretreatment was beneficial.

It is also possible that the Au/MnO₂ catalysts experienced some loss of water during the pretreatments and that water was migrating from the bulk to the surface. This would parallel what has already been hypothesized as a side-effect of the pretreatment of Pt/SnO₂.
It might also be hypothesized that the induction period for Au/MnO$_2$ was due carbonate retention. DRIFTS studies of the reaction between CO and O$_2$ on Au/MnO$_2$ indicated that large amounts of CO$_2$ were retained as carbonate.$^{28}$ Mass balance was, however, maintained at all times during the activity measurements. In other words, both the percentage loss of O$_2$ and of CO are equal to the percentage yield of CO$_2$ at all times during the test within experimental error. If retention were indicated, then at least the CO loss and possibly the O$_2$ loss should be greater than the CO$_2$ yield during the induction period, but this was not observed. Due to the time required to complete an analysis of a sample of effluent gas using GC (9 minutes), early measurements of mass balance could not be made.

1.3.3. Effect of reaction gas mixture composition. This section presents the effects of various reaction gas mixtures on the activity of both Au/MnO$_2$ and Pt/SnO$_2$ catalyst. The effect of O$_2$ and CO in excess of their stoichiometric concentrations as well as that of added CO$_2$ are discussed.

Effect of excess O$_2$ or CO. For all cases except very low CO concentrations (low ppm range), it is generally observed that noble metal catalysts exhibit CO oxidation rates that are first order in O$_2$ and zero order in CO.$^{29}$ This is due to CO saturation of the noble metal surface at normal room temperature. Consequently, the activity of a given catalyst improves when O$_2$ is present in excess of the stoichiometric concentration. Conversely, excess CO in the reaction gas mixture reduces the activity. For NMRO catalysts the situation is the same. Figures 1.15 and 1.16 show the CO-oxidation activities of 20% Au/MnO$_2$ and 15% Pt/SnO$_2$ on silica gel under stoichiometric, excess O$_2$, and excess CO in the reaction gas mixture at 35°C. In the presence of excess O$_2$, both catalysts show higher activity. For the Au/MnO$_2$ catalyst, the activities under stoichiometric and excess O$_2$ reaction gas flows are about parallel with the latter giving about 15% higher activity. With excess CO in the reaction gas mixture, both catalysts show reduced activity. The Au/MnO$_2$ catalyst shows a decay in activity that is absent under the other conditions.

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Figure 1.15. The effect of excess $O_2$ or CO in the reaction gas mixture on the CO-oxidation activity of Au/MnO$_2$.

Figure 1.16. The effect of excess CO or $O_2$ in the reaction gas mixture on the CO-oxidation activity of Pt/SnO$_2$.

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For the Pt/SnO$_2$ catalyst, the effect of excess O$_2$ in the reaction gas mixture is dramatic. The presence of CO does not cause Pt/SnO$_2$ to decay at any greater rate than under stoichiometric concentrations of CO and O$_2$.

**Effect of CO$_2$.** Both Au/MnO$_2$ and Pt/SnO$_2$ meet the first two requirements of candidate CO-oxidation catalyst for CO$_2$ laser applications. On the basis of the activities presented above for both Au/MnO$_2$ and Pt/SnO$_2$ catalysts, Au/MnO$_2$ appears to be a better candidate since, in addition to showing higher activity and lower decay, it requires no pretreatment. Because the laser gas mixture used in most CO$_2$ lasers contains from 8% to 16% CO$_2$, it is important to know the effect of CO$_2$ on the CO-oxidation activity of candidate laser catalysts. Figure 1.17 shows the conversion efficiency at 35°C in percent yield CO$_2$ of both the Au/MnO$_2$ and Pt/SnO$_2$ catalysts in the presence and absence of 16% CO$_2$, a common concentration used in CO$_2$ laser applications. In the absence of CO$_2$,

![Graph showing conversion efficiency at 35°C](image)

Figure 1.17. The effect of added 16% CO$_2$ on the CO-oxidation activity of Pt/SnO$_2$ and Au/MnO$_2$ catalysts at 35°C.
Au/MnO_2 clearly performs better. In the presence of CO_2, however, its activity drops to about 1/6 of that without CO_2. By contrast, Pt/SnO_2 shows no inhibition in activity, making it the choice for CO_2 laser applications. Au/MnO_2 is only about 1/3 as active as Pt/SnO_2 on silica gel under laser gas concentrations of CO_2.

The hindering effect of gas phase CO_2 on Au/MnO_2, suggests that an adsorption-desorption equilibrium exists between the gas phase and the active sites of the Au/MnO_2 catalyst. When CO_2 is absent from the reaction gas mixture, the equilibrium is shifted toward desorption. When CO_2 is present, the equilibrium is shifted toward adsorption and the reaction rate lowers by comparison. Consequently, it appears that CO_2 competes with CO and/or O_2 for active sites. This is consistent with DRIFTS studies on Au/MnO_2 catalysts which show carbonate retention.\textsuperscript{28}

Temperature-programmed desorption of Au/MnO_2 in a flowing He stream after exposure to the reaction gas mixture showed that both CO_2 and O_2 desorbed from the catalyst, but not CO. Figure 1.18 shows the mole percent of CO_2 and O_2 plotted as a function of time. The temperature curve is shown on the right-hand axis. The CO_2 began desorbing between 80°C and 100°C, a temperature range in which MnO_2 can maintain CO oxidation in the presence of O_2. The O_2 began desorbing at about 150°C when the CO_2 concentration started to decrease. The results are consistent with both reduction of MnO_2 by CO chemisorbed on Au

$$\text{CO•Au + MnO}_2 \rightarrow \text{CO}_2 + \text{MnO} \quad (4)$$

and release of excess O_2 resulting from carbonate decomposition

$$2 \text{CO}_3^{2-}\text{•site} \rightarrow 2 \text{CO}_2 + \text{O}_2 + 4 \text{e}^- + 2 \text{site} \quad (5)$$
Figure 1.18. The reaction of adsorbed CO as a function of temperature over Au/MnO₂ catalyst under He flow.

where the “site” probably includes manganese. It is possible that both reactions are occurring on the catalyst.

CO₂ outgassing studies provide more information on the possible CO₂ retention on Au/MnO₂ and Pt/SnO₂. Figure 1.19 shows the response of both Au/MnO₂ and Pt/SnO₂ to switching from an 11,000-minute exposure to stoichiometric reaction gas mixture—without CO₂—to He for 1 hour at the reaction temperature of 55°C and then switching back to the reaction gas mixture. During the outgassing period, no CO or CO₂ is observed in the effluent He stream from Au/MnO₂. Except for a slight and temporary increase in activity, the Au/MnO₂ catalyst is unaffected by the outgassing. Based on the results of the temperature-programmed desorption study, the Au/MnO₂ would not be expected to show CO₂ outgassing and is consistent the data presented in Figure 1.19.

The Pt/SnO₂ catalyst, on the other hand, desorbs CO₂ under He flow. No CO is observed, consistent with chemisorption on Pt. Upon re-exposure to the reaction gas
mixture, the initial high activity of Pt/SnO₂ is restored, followed by a sharp decrease to its pre-outgassing level. This suggests that Pt/SnO₂ retains CO₂. Similar behavior is observed if air rather than He is used as the outgassing medium. Figure 1.20 shows the effect of outgassing CO₂ on the conversion efficiency of 15% Pt/SnO₂ on silica gel for six consecutive outgassing cycles. The entire process was carried out over nearly a seven-week period. The outgassing was conducted by switching the flow over the catalyst from the reaction gas mixture (stoichiometric: 1% CO, 0.5% O₂ in He) to He at 10 sccm at 55°C for 1 hour increments and then returning the flow to the reaction gas mixture. Giving the catalyst time to desorb CO₂ enables the Pt/SnO₂ to restore its initial high activity. The initial high activity rapidly decreases, however, to the pre-outgassing curve.

The slight downward slope of this curve indicates that Pt/SnO₂ displays another, slower mode of decay in activity. The reason for the slower mode of decay is not known at this time. It has been speculated that it may be due to drying out of the catalyst.. Another
speculation is that the decay is due to encapsulation of the Pt by oxides of tin.\textsuperscript{31} That oxides of tin could be mobile at such low temperature seems unlikely, but so does the low temperature at which CO can be oxidized. It might be possible the there exists a chemically-induced surface rearrangement during the extended use of the catalyst.

There is a paradox evident in the data on Au/MnO\textsubscript{2}. Both the temperature-programmed desorption study and the DRIFTS study\textsuperscript{28} suggest CO\textsubscript{2} retention as carbonate. Both the inhibition of CO-oxidation activity caused by gas phase CO\textsubscript{2} and the lack of CO\textsubscript{2} outgassing suggest an absence CO\textsubscript{2} retention. The paradox can be resolved by hypothesizing the presence of two forms of CO\textsubscript{2}: chemisorbed, as carbonate, and physisorbed, as CO\textsubscript{2}. The chemisorbed form does not inhibit CO-oxidation, the physisorbed form does.

Raman studies of SnO\textsubscript{2} in the presence of gas phase CO\textsubscript{2} indicate that surface carbonate does not form until heated to a temperature of at least 500°C. (REFERENCE)
This indicates that SnO$_2$ does not adsorb CO$_2$ at the temperatures used in these studies. Pt does not adsorb CO$_2$ either. It would not be expected for gas phase CO$_2$ to inhibit CO oxidation on Pt/SnO$_2$, consistent with observations. This indicates that carbonate retention and the consequent inhibition of CO oxidation on Pt/SnO$_2$ can only arise from carbonate formed from the reaction of surface adsorbed CO and O$_2$. By contrast, carbonate formed similarly on Au/MnO$_2$ does not appear to inhibit CO oxidation, but gas phase CO$_2$ does.

1.4. DISCUSSION

It has been shown that several combinations of noble metal with reducible oxide demonstrate a synergistic capacity for catalyzing the reaction between CO and O$_2$ at normal room temperatures and lower, in low partial pressures of O$_2$—a feat unmatched by the individual components. Because a wide variety of combinations show this capacity, the combination of a noble metal with a reducible metal oxide establishes itself as a unique class of catalysts which has been given the acronym NMRO for “noble metal-reducible oxide” catalyst.

A closer look at the thermodynamics provides some insight into what might make these metal oxides active components in NMRO catalysts whereas the traditional support oxides remain inert and serve only to disperse the noble metal. Consider first the reduction of the surface of the metal oxide, MO, by CO.

\[
\text{MO}_x + \text{CO} \rightarrow \text{MO}_{x-1} + \text{CO}_2
\]  

(6)

The standard free energy of reaction at 298.15 K, $\Delta G^\circ_{\text{rxn}}$, is

\[
\Delta G^\circ_{\text{rxn}} = \sum_i v_i \Delta \overline{G}^\circ_{fi}
\]  

(7)
where $\Delta \overline{G}^\circ_{fi}$ is the free energy of formation of species $i$ from the elements at 298.15 K and $\nu_i$ is the stoichiometric coefficient of species $i$. For reaction (6) where the MO is $\text{MnO}_2$, the $\Delta G^\circ_{rxn}$ is

$$
\Delta G^\circ_{rxn} = \Delta \overline{G}^\circ_{\text{MnO}} + \Delta \overline{G}^\circ_{\text{CO}} - \Delta \overline{G}^\circ_{\text{MnO}_2} - \Delta \overline{G}^\circ_{\text{CO}_2}
$$

$$
= -86.74 + (-94.254) - (-111.18) - (-32.780) \text{ kcal/mol}
$$

$$
= -37.03 \text{ kcal/mol}
$$

The negative free energy indicates that the CO can reduce $\text{MnO}_2$ to $\text{MnO}$ spontaneously at 298.15 K. Looking at $\text{TiO}_2$, one of the “non-reducible” metal oxides, we have

$$
\Delta G^\circ_{rxn} = \Delta \overline{G}^\circ_{\text{TiO}} + \Delta \overline{G}^\circ_{\text{CO}} - \Delta \overline{G}^\circ_{\text{TiO}_2} - \Delta \overline{G}^\circ_{\text{CO}_2}
$$

$$
= -118.3 + (-94.254) - (-211.4) - (-32.780) \text{ kcal/mol}
$$

$$
= +31.6 \text{ kcal/mol}
$$

By contrast, the positive free energy indicates that CO cannot reduce $\text{TiO}_2$ to $\text{TiO}$ at 298 K.

The reduction of the metal oxide, however, is only half of the story. For sustained catalysis, the partially-reduced metal oxide surface must then be re-oxidized by gas-phase $\text{O}_2$. In order for this to happen the $\text{O}=\text{O}$ double bond must be broken. The $\Delta G^\circ$ for dissociation of $\text{O}_2$ is

$$
\Delta G^\circ_{\text{rxn}} = 2\Delta \overline{G}^\circ_{\text{O}} - \Delta G^\circ_{\text{O}_2} = 2( +55.389 \text{ kcal/mol}) = +110.778 \text{ kcal/mol}
$$

and, as such, represents an energy barrier to re-oxidation. The equation used to determine the $\Delta G^\circ_{\text{rxn}}$ for the re-oxidation of the metal oxide is
although this does not reflect the mechanism of re-oxidation of the partially-reduced metal oxide surface in a surface catalyzed reaction. Using again the examples of MnO and TiO, we have

\[
\Delta G^\circ_{\text{rxn}} = \Delta G^\circ_{\text{f,MnO}_2} - \Delta G^\circ_{\text{f,MnO}} - \Delta G^\circ_{\text{f,O}_2} \\
= -111.18 - (-86.74) \text{ kcal/mol} \\
= -24.44 \text{ kcal/mol}
\]

\[
\Delta G^\circ_{\text{rxn}} = \Delta G^\circ_{\text{f,TiO}_2} - \Delta G^\circ_{\text{f,TiO}} - \Delta G^\circ_{\text{f,O}_2} \\
= -211.4 - (-118.3) \text{ kcal/mol} \\
= -93.1 \text{ kcal/mol}
\]

Table 1.1 shows \(\Delta G^\circ_{\text{rxn}}\) for the CO reduction and for the \(\text{O}_2\) re-oxidation of selected metal oxides. For the “non-reducible” metal oxides, \(\text{Al}_2\text{O}_3\), \(\text{ZrO}_2\), and \(\text{TiO}_2\) mentioned earlier, the positive \(\Delta G^\circ_{\text{rxn}}\) indicates that the CO reduction does not occur spontaneously at normal room temperature. The high free energy barriers for the reduction of the \(\text{Al}_2\text{O}_3\) and \(\text{ZrO}_2\) may exist because the Al and Zr do not have a second stable oxidation state in combination with oxygen. Instead, these oxides would have to be reduced to the zero-valent metal. The \(\Delta G^\circ_{\text{rxn}}\) for re-oxidation, although highly negative, is less relevant if the metal oxide cannot be reduced initially by CO. The thermodynamics say nothing the mechanism of the surface reaction, yet no room temperature-catalyzed oxidation of CO is observed over these oxides, consistent with the restriction imposed by the positive \(\Delta G^\circ_{\text{rxn}}\) for CO reduction. For the “reducible” oxides, on the other hand, several stable oxides exist and the free energy for CO reduction is negative indicating that the reaction is
thermodynamically allowed at 298 K. This may be the reason that the reducible oxides are active components in NMRO catalysts whereas the non-reducible support oxides remain inert.

The reducible metal oxides are believed to catalyze the oxidation of CO by a redox mechanism wherein the metal oxide is reduced by CO and then re-oxidized by gas-phase $O_2$. With both the CO reduction and the $O_2$ re-oxidation yielding negative $\Delta G^o_{\text{rxn}}$, sustained catalysis at room temperature might be expected to occur, but this is not observed. Instead, the reducible metal oxides require temperatures around 100°C to 200°C and excess $O_2$ for sustained catalysis. The reason generally given for the absence of low-temperature activity is that the parent metal-oxygen bond of the reducible oxide is too strong to be broken at low temperature. In short, as the $\Delta G^o_{\text{rxn}}$ approaches zero and goes

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^o_{\text{rxn}}$ kcal/mol CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3 (s) + 3 \text{CO (g)} \rightarrow 2 \text{Al (s)} + 3 \text{CO}_2 (g)$</td>
<td></td>
</tr>
<tr>
<td>$2 \text{Al (s)} + 3/2 \text{O}_2 (g) \rightarrow \text{Al}_2\text{O}_3 (g)$</td>
<td>$+$64.59</td>
</tr>
<tr>
<td>$\text{ZrO}_2 (s) + 2 \text{CO (g)} \rightarrow \text{Zr (s)} + 2 \text{CO}_2 (g)$</td>
<td>$+$63.14</td>
</tr>
<tr>
<td>$1/2 [\text{Zr (s)} + \text{O}_2 (g) \rightarrow \text{ZrO}_2 (s)]$</td>
<td></td>
</tr>
<tr>
<td>$\text{TiO}_2 (s) + \text{CO (g)} \rightarrow \text{TiO (s)} + \text{CO}_2 (g)$</td>
<td>$+$31.6</td>
</tr>
<tr>
<td>$\text{SnO}_2 (s) + \text{CO (g)} \rightarrow \text{SnO (s)} + \text{CO}_2 (g)$</td>
<td>$+$1.3</td>
</tr>
<tr>
<td>$\text{SnO (s)} + 1/2 \text{O}_2 (g) \rightarrow \text{SnO}_2 (s)$</td>
<td></td>
</tr>
<tr>
<td>$3 \text{Fe}_2\text{O}_3 (s) + \text{CO (g)} \rightarrow 2 \text{Fe}_3\text{O}_4 (s) + \text{CO}_2 (g)$</td>
<td>$-$14.7</td>
</tr>
<tr>
<td>$2 \text{Fe}_3\text{O}_4 (s) + 1/2 \text{O}_2 (g) \rightarrow 3 \text{Fe}_2\text{O}_3 (s)$</td>
<td></td>
</tr>
<tr>
<td>$\text{Mn}_2\text{O}_3 (s) + \text{CO (g)} \rightarrow 2 \text{MnO (s)} + \text{CO}_2 (g)$</td>
<td>$-$24.35</td>
</tr>
<tr>
<td>$2 \text{MnO (s)} + 1/2 \text{O}_2 (g) \rightarrow \text{Mn}_2\text{O}_3 (s)$</td>
<td>$-$37.12</td>
</tr>
<tr>
<td>$2 \text{CuO (s)} + \text{CO (g)} \rightarrow \text{Cu}_2\text{O (s)} + \text{CO}_2 (g)$</td>
<td>$-$34.37</td>
</tr>
<tr>
<td>$\text{Cu}_2\text{O (s)} + 1/2 \text{O}_2 (g) \rightarrow 2 \text{CuO (s)}$</td>
<td>$-$27.10</td>
</tr>
<tr>
<td>$\text{MnO}_2 (s) + \text{CO (g)} \rightarrow \text{MnO (s)} + \text{CO}_2 (g)$</td>
<td>$-$37.03</td>
</tr>
<tr>
<td>$\text{MnO (s)} + 1/2 \text{O}_2 (g) \rightarrow \text{MnO}_2 (s)$</td>
<td>$-$24.44</td>
</tr>
</tbody>
</table>

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negative, the probability for low-temperature catalytic activity of the metal oxide increases. It is interesting that mixtures of the oxides of Mn and Cu and of Sn and Cu show room-temperature activity for the oxidation of CO whereas their individual components do not, but excess $O_2$ and low $H_2O$ concentrations are required. Their low-temperature activity is consistent with the favorable thermodynamics.

Because the method of catalysts preparation can have an impact on the resulting activity of the catalyst, it is difficult to draw conclusions about which combinations are better than others on the basis of activity measurements alone. For this reason it is important to gain information on a catalyst’s physical characteristics such as the surface area of noble metal or noble metal particle size. Surface characterization using high vacuum techniques can also provide valuable information about changes occurring in both the bulk and surface of the catalyst as a result of various processing steps.

It has been shown that both Au/MnO$_2$ and Pt/SnO$_2$ with high noble metal loading benefit from concentrations of $O_2$ in excess of stoichiometric and suffer inhibition in reaction rate from concentrations of CO in excess of stoichiometric. This CO inhibition is similar to that found over noble metals catalysts without a participating metal oxide.

Some combinations of noble metal and reducible oxide appear to be better than others for CO oxidation under certain conditions. For instance, Au/MnO$_2$ might be better than Pt/SnO$_2$ in the absence of CO$_2$, but is clearly worse in its presence. The differences in behavior under the same reaction gas mixtures also suggest that the mechanism of reaction between CO and $O_2$ over each catalyst may be different. For CO$_2$ laser applications, Pt/SnO$_2$ remains the most promising candidate and, as such, will be the focus of the remainder of the text.
CHAPTER 2
COATING TECHNOLOGY

2.1. INTRODUCTION

As demonstrated in Chapter 1, a catalyst composed of Pt/SnO₂ met the first three requirements for a candidate laser catalyst. Unfortunately, powdered catalysts dust and cause a high pressure drop across the catalyst bed due to the low void volume. The need to develop a coating technology for CO₂ laser applications resulted from the failure of the catalyst to meet the last two requirements. Consequently, finding a means for bonding the catalyst to a substrate was necessary. This chapter presents the development of a technology for preparing well-bonded, thick-layer coatings of Pt/SnO₂ on suitable substrates. The term “thick-layer” is used here to express that the catalyst layer is approximately one micrometer thick or greater.

In addition to the composition, the textural properties of the substrate and the catalyst coating can have a profound impact on the level of activity. Measurement of the surface area and pore size distribution of the substrate and of the catalyst coating during each step in the production provides insight into how these textural factors affect the activity of the final product.

2.1.1. Substrates. Substrates generally used for catalyst coatings come in a variety of shapes and sizes including pellets, spheres, monoliths, and more recently, reticulated foams. Pellets provide for a lower pressure drop than powders but pellets, like powders, are still mobile in a reaction chamber. Such movement can be severe during the take-off of a rocket and ultimately lead to breakage and dusting. Monolithic substrates like honeycombs and foams, on the other hand, can easily be secured in a reaction chamber and can be constructed so as to provide the lowest pressure drop across the catalyst bed of all
substrates. Honeycomb monoliths resemble the honeycombs found in beehives, hence the name, with the exception that the channels or cells are open on both ends. The shape of the cell and the cell density can be customized to the parameters of a given application. Because the channels are necessarily straight and open, catalyst coatings deposited on monoliths have the potential problem of poor interaction with the reactant gas due to the possible occurrence of laminar flow. Laminar flow (as opposed to turbulent flow) can exist in the channels when the reaction gas mixture is flowing at a high rate. Under laminar flow conditions, transfer of the reactive species to the surface of the catalyst is controlled by diffusion. Consequently the reaction rate is more likely to be limited by diffusion than by the intrinsic rate of the catalyst.

Refractory ceramics such as alumina, zirconia, titania, and cordierite are common materials used to prepare catalyst substrates and can be easily coated with oxides and noble metals. In the automotive industry, cordierite is favored because it has a low thermal expansion coefficient and high durability in a corrosive environment with heavy temperature cycling. Cordierite is a magnesium aluminum silicate of the form \(2\text{MgO}\cdot2\text{Al}_2\text{O}_3\cdot5\text{SiO}_2\). Figure 2.1 (a) shows a sample of uncoated cordierite honeycomb monolith. It is cylindrical in shape has 400 cells/in\(^2\) and measures 3 inches in diameter by 1/2 inch long. Figure 2.1 (b) shows same substrate coated with 2% Pt/SnO\(_2\).

Due to the potential differences in flow and diffusion in a reactor system resulting from substrates with different geometries (i.e. pellet versus honeycomb monolith), the substrate geometry can have an impact on the observed activity of the catalyst coating. In order to eliminate the differences in activity due to differences in substrate geometry from those differences due to changes in the preparation of the catalyst coating, comparisons are only drawn for catalyst samples with the same geometry. In other words, only the activities of catalyst coatings deposited on the same substrate can be compared (i.e. pellets versus pellets or monolith versus monolith). Because the coating technology is applicable to many
Figure 2.1. Samples of 400 cell/in\(^2\) cordierite honeycomb monolith.
oxide supports, the coating of both cordierite monolith and alumina pellets is presented.

2.1.2. Tin oxide coating. In the preparation of noble metal catalysts for the automotive industry, it is common to first apply a washcoat of high surface area alumina. The alumina washcoat has many purposes but is not—itself—an active catalyst component. First it anchors the noble metal to substrate. Second it provides a barrier to sintering of the noble metal crystallites at the elevated temperatures and thereby prevents loss of active sites. Third and most importantly, it enhances dispersion of the noble metal over a much larger area than that of the substrate alone thereby generating more active sites. More active sites means higher activity. It could be said that the tin oxide is the washcoat for the platinum and, as such, provides for dispersion of the Pt. Because the SnO$_2$ is also an active catalyst component, this is where the analogy ends. As will be discussed in Chapter 4, SnO$_2$ is responsible for the dissociative adsorption of O$_2$ and this process may be aided by the presence of surface hydroxide groups. This section presents information pertinent to the preparation of a high surface area, hydroxylated tin oxide layer on cordierite and alumina substrates that is well-bonded.

How might a tin oxide layer be deposited on and bonded to a substrate with channels? Commercially, the least expensive method for coating such a substrate is a dip-coating technique where the substrate is dipped into a solution containing the precursor of the SnO$_2$ followed by draining of excess solution, thermal decomposition, and sintering. Inexpensive, commercially available reagents that might be suitable for producing a tin(IV) oxide layer are tin metal itself, the tin chlorides (SnCl$_2$ and SnCl$_4$), tin(IV) oxide sol, and tin(II) 2-ethylhexanoic acid, a carboxylic acid salt of tin.

Nitric acid digestion of tin metal to produce SnO$_2$ is a convenient means of producing a powder catalyst and, perhaps, for coating small particles such as silica spheres or silica gel of small mesh size. It is a poor method, however, for coating cordierite or alumina because the residual nitric acid required to completely oxidize the tin metal to SnO$_2$
deteriorates or dissolves many of the materials from which substrates are composed.

SnCl₄ is volatile and can evaporate from a substrate rather than decompose. SnCl₂ decomposes in water to produce oxides of tin making solution preparation difficult. In addition, residual chloride is a known inhibitor of the CO-oxidation reaction over noble metals. Consequently, chloride free reagents are preferred. Because noble metal catalysts are traditionally processed and/or used at high temperatures (>300°C), the residual chloride usually decomposes as HCl gas. For required low-temp processing and/or ambient temperature use, on the other hand, the chloride would not be removed.

Tin(IV) oxide sol, a colloid suspension of oxide particles approximately 15 nm in diameter, produces a high surface area tin(IV) oxide, but one that dusts unless excessive sintering is used. Sintering, however, causes a loss of valuable surface area. There are few commercially available, inexpensive tin salts. Tin(II) 2-ethylhexanoate, SnEH, is one such salt. Its finds considerable use commercially as a catalyst in the polymerization of various classes of monomers, more frequently than as a material for producing SnO₂ coatings. Other ethylhexanoate salts, such as that of Fe(III), have been used for metalorganic deposition (MOD) of α-Fe₂O₃ films.¹ Use of SnEH as a reagent for preparing SnO₂ coatings on both cordierite and alumina substrates will be discussed in detail.

In recognizing the importance of the tin oxide coating for dispersing the noble metal, for preserving the hydroxide group concentration, and for bonding the catalyst to the substrate without dusting, it is important to understand several factors in the production of the oxide coating from SnEH that affect the resulting activity of the catalyst coating. Consequently, the following factors were investigated: (1) the mechanism of decomposition of SnEH; (2) the concentration of SnEH deposition solution on the bonding of the tin(IV) oxide layer; (3) the effect of decomposition temperature; and most importantly (4) the effects of the physical properties of the substrate itself on the SnO₂ layer and the resulting activity of the catalyst.
2.2. EXPERIMENTAL

The general coating method is presented below. Modifications to the coating method that were used to determine their effects on the activity of the resulting catalyst coating will be described where appropriate.

2.2.1. Catalyst preparation. The preparation is divided into sections, one for each step. Not all of the steps are carried out for each sample prepared. When differences exist between samples, they will be noted.

Substrate etching. For the preparation of some catalyst samples, the cordierite substrates were etched to increase the surface area in hopes of producing a higher surface area catalyst. Substrate etching proceeded as follows. Twelve rectangular pieces, 2.5 to 2.8 inches (or 34 by 37 cells) on a side by 1/2-inch thick, were cut from larger pieces of 400 cells/in² cordierite and dried in a muffle furnace at 300°C for 4 hours. They were then cooled in a desiccator and weighed. Next the samples were stacked in a 3-L resin flask and covered with 1.6 M HNO₃ (a 1 to 10 dilution of concentrated HNO₃), about 1.5 L, and refluxed in the nitric acid solution at about 95°C. The nitric acid solution was refreshed every 16 hours to more efficiently dissolve the MgO and Al₂O₃. After each 16-hr period, the HNO₃ was drained from the samples. Hot DI H₂O was added to the resin flask and allowed to boil for 15 minutes to rinse the samples. The rinse water was drained and the rinse repeated. In the last step, all 12 pieces were placed into a muffle furnace overnight at 300°C for drying and decomposition of any remaining HNO₃. The samples were etched in 16 hour increments to produce three sets of four samples with etching times of 16, 32, and 48 hours. The samples were cooled in a desiccator and weighed to determine the weight loss. The surface area and pore size distribution of the etched and unetched pieces were determined via the BET method with N₂ as the adsorbent at liquid N₂ temperature using a Micromeritics, ASAP 2010 Porosimetry Analyzer.
Tin oxide coating. SnEH was used to coat all of the catalyst samples presented in this chapter. SnEH is a liquid at room temperature and has about the viscosity of maple syrup. Acetone can be used to reduce its viscosity and ultimately provide thinner layers or perhaps even micro-droplets of SnEH on the surface of the substrate once the acetone has evaporated. Each substrate was vacuum deaerated in SnEH either pure or diluted with acetone. Deaeration facilitates exchange of trapped air in the pores of the monolith with the desired solution ensuring a thorough coating with the starting material. After deaeration, the excess solution was shaken, drained, or blown from the substrate, the method used depending on the type of substrate being coated. Next the SnEH-coated substrate was placed in a muffle furnace and heated from ambient to 200°C at 1°C/min and held for 3-6 hr and then heated to 300°C at 1°C/min for 2-6 hr to decompose the SnEH to tin oxide and remove residual organic material, respectively. The above steps were repeated until the desired loading of tin oxide was obtained.

Etching SnO$_2$-coated substrate. When desired, the SnO$_2$-coated substrate was etched to increase the surface area of the SnO$_2$ layer which ultimately provides better dispersion of the noble metal. The SnO$_2$-coated substrates were submerged in 1.5 to 1.6 M nitric acid and heated to near boiling. As with the uncoated cordierite, etching time varies depending on the desired surface area of the SnO$_2$-coated substrate. Once etched, the substrates were rinsed with hot DI water to remove any residual nitric acid. Finally the substrates were placed into a muffle furnace and dried at 100°C for 1 hour then at 250°C for 2 hour to decompose any nitric acid.

Platinum coating. Platinum was incorporated into the catalyst by deaerating the coated substrate in a solution of tetraamineplatinum(II) hydroxide, PtAH, followed by draining, thermal drying, and decomposition to Pt metal and its oxides and hydroxides. The amounts of PtAH used to prepare the solution in which the substrate was vacuum deaerated were determined from water uptake, tin oxide loading, and the desired platinum
loading.

**Reductive treatment.** The final step in the preparation of catalyst coating was a reductive treatment step where the dry coated substrate was heated to 125°C in a flowing stream of gas containing either 5% carbon monoxide or 5% hydrogen in helium, generally the former. The absence of oxygen was essential. This process was continued until only a small amount of CO$_2$ was formed (H$_2$O, if H$_2$ was used as the reducing gas.) The length of time for this process depended on the total amount of catalyst being reduced and on the concentration of reducing gas.

**2.2.2. DRIFTS analysis of SnEH decomposition.** The Nicolet 5PC Infrared spectrometer was fitted with a diffuse reflectance attachment equipped with a High Temperature Environmental Chamber, HTEC, (both from Spectra Tech, Inc.). The sample stage is a refractory ceramic embedded with a resistive wire heating element. A type K thermocouple feeds into the sample cup for temperature measurement. The heating element and thermocouple work in concert for temperature control. During high temperature applications the body of the HTEC is cooled via a stainless steel coil through which water is circulated. The HTEC also has input and output lines to enable gas flow to the sample being analyzed. The entering infrared beam is defocused over the sample cup and recollected by parabolic mirrors. The infrared beam enters and exits the HTEC through KBr or BaF$_2$ windows. The intensity ratio of input to the reflected infrared light is expressed in all spectra in Kubelka-Munk units.

To analyze the decomposition, a small amount of SnEH was spread on a freshly sanded Al disc measuring 3/8" in diameter and then placed onto the sample stage and sealed in the HTEC environmental chamber. Spectra were taken as the sample was slowly ramped from ambient temperature to 350°C under flowing dry air or ambient air. Dry air was provided to the SnEH coated sample at 10 sccm from a tank of zero air (MG Industries) using a Hastings mass flow controller. For the ambient air studies, room air at about
50% relative humidity was pulled over the sample at 10 sccm using a small mechanical pump.

Because the presence of hydroxide groups on the tin(IV) oxide surface is important to the mechanism of CO oxidation, it was also important to see what the film looked like after exposure to air. Consequently, the film prepared from SnEH was exposed to ambient air by removal from the HTEC for 24 hours and then resealed within it. The SnO₂ film was then exposed to dry air flow. DRIFTS spectra were then taken at each of the following temperatures 25°C, 100°C, 200°C, 300°C, and 350°C until there was no change in the intensity of the OH stretch region at that temperature, generally 30 minutes.

To aid in the assignment of the bands of the SnEH-produced tin oxide film, DRIFTS spectra of tin(IV) oxide and tin(II) oxide powder on Al were collected from room temperature to 350°C. In addition, a tin(IV) oxide film was prepared on an Al metal disc by evaporating a SnO₂ colloidal suspension. The colloid was composed of 15% by weight of 15-nm SnO₂ particles at a pH of 10-11 and was obtained from Alfa Aesar.

2.2.3. Activity measurements. The activity measurement for catalyst coatings follows that described in the experimental section of Chapter 1. Differences will be noted in the text that follows, where appropriate.

2.2.4. Surface area and pore size distribution measurements. The N₂ adsorption isotherm at liquid N₂ temperature was obtained using a Micromeritics ASAP 2010, a static system. Each point in the isotherm was obtained admitting known amounts of N₂ into the sample chamber in a pulse-equilibrate manner until a predetermined pressure was reached. Using PVT relations, the amount of N₂ adsorbed on the sample was determined. Accompanying software was used to reduce the data. The surface area was calculated from the isotherm using the method of Branauer, Emmet, and Teller (BET). The fraction that was microporous area (pores less than 20 Å) was estimated using the t-plot method. And the pore size distribution of mesopores (pores between 20 and 600 Å) was
calculated by considering condensation of a liquid in a capillary pore given by the Kelvin equation.²

2.3. RESULTS

2.3.1. Tin(II) 2-ethylhexanoate decomposition. The first step in preparation of the catalyst coating is dipping and deaerating a substrate in a solution of acetone-thinned SnEH followed by thermal decomposition in a muffle furnace. SnEH starts to decompose between 150°C and 200°C with the evaporation of 2-ethylhexanoic acid, EHA. This was determined by condensing the vapor exiting the muffle furnace stack during the thermal decomposition of SnEH-coated cordierite monolith at 200°C onto a watch glass and then obtaining an FTIR spectrum. The spectrum was consistent with that of 2-ethylhexanoic acid matching all of the peaks in location and approximate relative intensity.³

Figures 2.2 and 2.3 show the DRIFTS spectra of EHA and SnEH run neat on an aluminum metal disc for the regions 750 to 2000 cm⁻¹ and 2200-3600 cm⁻¹, respectively. Of importance in the spectrum of EHA are the strong carbonyl stretch band at 1700 cm⁻¹ and the broad hydroxyl stretch between 2200 cm⁻¹ and 3600 cm⁻¹ which are absent in the spectrum of SnEH. The spectrum of SnEH shows two strong absorption peaks around 1409 cm⁻¹ and 1623 cm⁻¹ which are characteristic of the symmetric and asymmetric stretch of the three-atom carboxylate groups, respectively.⁴ These two peaks are notably absent in the spectrum for 2-ethylhexanoic acid. When chelating a metal ion, the two carbon-oxygen bonds of the carboxylate group become equivalent, rather than remaining as discrete double and single bonds. Consequently, the carbonyl stretch band at 1700 cm⁻¹ should be absent from the SnEH spectrum. Its presence and low intensity indicate some small amount of a carboxylic acid in the technical grade SnEH. This is further confirmed by gravimetric studies of the thermal decomposition of SnEH up to 800°C which showed this lot to be
Figure 2.2. DRIFTS spectra of (a) EHA and (b) SnEH run neat on an aluminum metal disc; fingerprint region.

Figure 2.3. DRIFTS spectra of (a) EHA and (b) SnEH run neat on an aluminum metal disc; 3600 to 2200 cm\(^{-1}\).

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about 97% pure. These data are also consistent with the Material Safety Data Sheet, MSDS, for technical grade SnEH which contains excess alkyl acetic acid. FTIR spectra of coated samples taken to 300°C show no evidence of organic compounds on the SnO₂-coated surface. Consequently, exposing the SnO₂-coated substrate to a temperature of 300°C ensures removal of organic residue.

In order to follow the mechanism of decomposition of SnEH more closely, the decomposition of SnEH was followed as a function of temperature. Figures 2.4 and 2.5 show the spectra of the SnEH-coated Al disc taken at temperatures of 25, 50, 75, and 100°C during the decomposition under dry air for the fingerprint region and the region from 3500 to 2250 cm⁻¹, respectively. As the temperature was increased from 25°C to 100°C, there was a corresponding decrease in the intensities of the OH-stretch and the CO-stretch bands. This suggests that the some of the residual acid may have been evaporating. Between 75 and 100°C there was also a loss in the intensities of all peaks, but the relative rate of loss of the OH- and CO-stretch bands was far greater. This is consistent with an evaporation hypothesis for residual acid, but not the SnEH. Furthermore, SnEH decomposes prior to evaporating in air. The loss of intensity between 75 and 100°C of all bands might have been due to thinning of the SnEH film on the Al disc.

Figure 2.6 shows the spectra of the SnEH-coated Al disc taken at temperatures of 150°C, 175°C, and 200°C for the fingerprint region. As the temperature was increased from 150°C to 200°C, there is a corresponding decrease in the symmetric and asymmetric carboxylate stretch bands to below detectable levels concurrent with an increase in the carbonyl stretch band and also a slight increase in the intensity of the OH stretch band (the OH band, not shown). Also becoming apparent at 200°C is the appearance of peaks at around 1520 cm⁻¹ and 1650 cm⁻¹ which are characteristic of oxides or hydroxides of tin. In combination, these events indicate that the chelating 2-ethylhexanoate moieties of SnEH hydrolyze at temperatures below 200°C to EHA rather than combust to CO₂ and water.
Figure 2.4. DRIFTS spectrum of SnEH on Al between 25 and 100°C for the fingerprint region.

Figure 2.5. DRIFTS spectrum of SnEH on Al between 25 and 100°C for the region between 3500 and 2250 cm\(^{-1}\).
Figure 2.6. DRIFTS spectra of SnEH on an Al metal disc between 150°C and 200°C.

As the temperature was increased further to 300°C and held for an extended period of time (145 minutes), the remainder of the peaks associated with the EHA disappeared except for the weak CH-stretch bands. When the temperature was increased to 350°C, the CH-stretch band disappeared with the corresponding temporary appearance of a band at 2350 cm⁻¹ characteristic of carbon dioxide (See Figure 2.10). This indicates that the residual hydrocarbon combusted to CO₂ and H₂O.

With information on how the SnEH decomposed in dry air environment, it was necessary to see what might happen in the presence of humid air as the cordierite monoliths would be submitted to a humid environment in the muffle furnace. Figures 2.7 and 2.8 show the DRIFTS spectra in the region of 1200 to 1800 cm⁻¹ of the SnEH decomposition under the flow of both dry and ambient air (about 50% relative humidity) at 25°C and 100°C, respectively. At 25°C the asymmetric carboxylate stretch band at 1623 cm⁻¹ is almost absent from the SnEH film under humid air flow appearing only as a shoulder,
Figure 2.7. Comparison of DRIFTS spectra of SnEH films on Al metal discs at 25°C under flow of dry and humid air.

Figure 2.8. Comparison of DRIFTS spectra of SnEH films on Al metal discs at 100°C under flow of dry and humid air.
while it remains intense in the film under dry air flow. By 100°C, the 1623 cm⁻¹ absorption band is absent along with the disappearance of all bands associated with the SnEH. Only the C=O stretch band remains indicating that the SnEH is hydrolyzed to EHA and hydroxides of tin at a lower temperature than under dry air flow. As the temperature was increased to 300°C and then 350°C, the spectra of the samples under wet and dry air flow became equal, the overall intensities remaining different. The differences in intensity after decomposition might have been due to spreading of the SnEH film over the Al giving a less intense signal where the IR beam was focused. The presence of H₂O might have facilitated such spreading.

Figure 2.9 shows the DRIFTS spectra of the tin oxide films at 350°C in the region of 1000 to 2000 cm⁻¹. The spectra in this region are essentially identical suggesting that the films are composed of essentially the same kinds of bonds in similar ratio to each other. For the film prepared under humid air, there are bands evident at 1750 cm⁻¹, 1650 cm⁻¹, 1535 cm⁻¹, and shoulders at 1300 cm⁻¹, and 1200 cm⁻¹. By comparison, the bands for the film prepared under dry air shows about a 10 cm⁻¹ shift to lower energy. That the spectra have similar slopes in this region indicates similar IR radiation scattering phenomenon and therefore similar particle size of the tin oxide making up each film. The similarity of the spectra for these suggest that the resulting character of the SnO₂ film can be reproduced regardless of how rapidly the SnEH decomposes.

Because the presence of hydroxide groups on the tin(IV) oxide surface is important to the mechanism of CO oxidation, it is also important to see what the film looks like in the region of the OH-stretch band after exposure to air. Figure 2.10 shows the spectra of the SnO₂ film prepared from SnEH under dry air flow after exposure to air at various temperatures between ambient and 350°C. The strong broad OH stretch band of the spectrum at 25°C indicates that the surface adsorbs water upon exposure to ambient air. Based on the work of Harrison on SnO₂ gels, most of the adsorbed water desorbs at
Figure 2.9. DRIFTS spectra of tin oxide films on Al metal at 350°C created from thermal decomposition of SnEH under dry air and ambient air.

Figure 2.10. DRIFTS spectra versus temperature of the SnO₂ film prepared from SnEH after exposure to ambient air, followed by re-exposure to flowing dry air.

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100°C. Above this temperature, only tin-bound OH groups remain.\(^5\) As the temperature increases, the OH band decreases in intensity but remains even at 350°C. This is consistent with the literature which indicates that SnO\(_2\) remains hydroxylated to over 900°C.\(^6\) The absorption band between 2800 cm\(^{-1}\) and 3000 cm\(^{-1}\) is from the C–H stretch of hydrocarbon residue as discussed above. By comparison to the intensity of the C–H stretch prior to thermal decomposition, about 3.5 Kubelka-Munk, the amount of residual hydrocarbon after thermal decomposition is extremely small.

To aid in the assignment of peaks, the DRIFTS spectra of SnO and SnO\(_2\) powders and a SnO\(_2\) film prepared from a SnO\(_2\) sol, each on Al metal, were collected over a range of temperatures. The spectra of these samples at 350°C in the region of 1800 cm\(^{-1}\) to 700 cm\(^{-1}\) appear in Figures 2.11. Each sample shows absorption bands in the range of 1200 cm\(^{-1}\) to 1700 cm\(^{-1}\), but no peak is common to all spectra. Considering that there are only two types of bonds, Sn–O and O–H, and that no adsorbed water should be present, only a few possible vibrational modes can exist: those for the symmetric and asymmetric stretches of Sn-O-Sn and O-Sn-O, and various deformation modes of surface Sn-O-H. Combination bands with lattice modes might also appear. It should also be noted that all spectra show strong broad peaks in the OH stretch region as shown above in Figure 2.10, but not shown here.

Harrison and Guest analyzed tin(IV) oxide discs prepared from compressed tin(IV) oxide gel which had been made by hydrolyzing SnCl\(_4\) with ammonia.\(^5\) They assigned the peaks in the region of 820 cm\(^{-1}\) to 1400 cm\(^{-1}\) to deformation modes of hydroxide groups and peaks at 770 cm\(^{-1}\), 1430 cm\(^{-1}\), and 1530 cm\(^{-1}\) to the symmetric and asymmetric stretching modes of bridging Sn-O-Sn bonds, the latter two possibly being overtones of the 770-cm\(^{-1}\) band and another likely existing around 715 cm\(^{-1}\) but unobserved in their spectrum.\(^4\) It is interesting to note by comparison that the film prepared from the SnEH shows no specific bands in the region that Harrison and Guest attributed to O–H
Figure 2.11. DRIFTS spectra of SnO and SnO powders and tin oxide films on Al metal prepared from thermal decomposition of SnEH and SnO powders, SnO from SnOH2 sol after treatment at 350°C.

deformations, yet the film is apparently hydroxylated even at 350°C. The film prepared from colloidal SnO2 and the SnO2 and SnO powders, on the other hand, do show absorption bands in this region. Although the bands at 1430 cm⁻¹ and 1530 cm⁻¹ are present in the film prepared from SnEH, they decreased in intensity as the film temperature was increased. Because dehydroxylation of adjacent Sn-OH groups occur at temperatures above 300°C to form Sn-O-Sn bonds, the intensity of these peaks should have increased rather than decreased. It must then be concluded then that these bands are associated with OH in some manner, rather than with overtones of bridging oxygen.

It is possible that the spectral differences amongst the various samples shown here and those presented by Harrison and Guest result from differences in method of sample preparation. None of the methods of preparation employed high temperature calcination and consequently should have produced amorphous or polymorphous materials rather than
well-defined crystals, except for the commercial SnO powder which was calcined at high temperature. This was verified by Harrison and Guest for their samples using XRD.\(^5\)

These differences could lead to differences in the relative quantities of hydroxyl groups and of bridging Sn–O–Sn bonds, among others, or to differences in site symmetry which would ultimately lead to spectral differences.

It should also be noted that the film of SnEH on cordierite and the resulting SnO\(_2\) layer is much thicker than that on Al. The cordierite material consists of reticulated pores, in contrast to the nonporous Al metal discs. The SnEH can easily soak into and through the porous network much like water in a sponge. This makes the SnEH layer very thick. Furthermore, the oxides making up cordierite—SiO\(_2\), in particular—have strong absorptions in the fingerprint region which interfere with most of those of tin oxide. Consequently it was not as informative to analyze the SnEH decomposition on cordierite as it was on Al metal. Considering that the SnEH layer is thicker on cordierite than on Al discs during preparation of SnO\(_2\)-coated cordierite, the outer surface of the SnEH layer is probably hydrolyzed while the bulk decomposes more slowly since it would be somewhat shielded from moisture in the surrounding air. Consequently, both modes of SnEH decomposition presented in this section probably occur during the preparation of the SnO\(_2\)-coated cordierite.

2.3.2. \textbf{SnO}_2 \textit{coating}. The SnO\(_2\) layer is the most important element of catalyst coating. Both its physical and chemical nature can have a profound influence on determining the activity of the catalyst coating. Aside from being an active catalyst component itself, the tin oxide layer serves both to anchor the catalyst to the substrate and to physically disperse the Pt. As such it is important to understand those factors in preparation of the SnO\(_2\) coating that impact the activity of the final catalyst coating.

The majority of the remainder of this chapter presents a series of experiments which investigate the impact of the SnO\(_2\) coating on the catalyst activity. Due to the quantity of
information presented, a brief statement of the main conclusions will be presented in order to help organize the information for the reader. First, the concentration of SnEH-dipping solution used for coating does not have a significant impact on the catalyst activity once a high enough concentration is used to provide a continuous SnO₂ layer over the surface of the substrate. Second, the activity of the catalyst coating is inversely related to the precoated surface area of the substrate. Third, the Pt apports itself according to the total available surface area, both SnO₂ and substrate. Fourth, the activity of the catalyst coating increases as the SnO₂ loading and surface area increase. Fifth, the surface area of the SnO₂ layer can be increased by etching the SnO₂-coated cordierite in dilute nitric acid. And sixth, the manner in which residual SnEH thermally decomposes can lead to temperature increase which can reduce valuable SnO₂ surface area.

**SnEH concentration.** The concentration of SnEH used to coat the substrate was investigated to determine its effect on the physical nature of the SnO₂ coating as well as on the resulting activity of the catalyst. Four catalyst samples were prepared on unetched cordierite monolith using a single SnEH coating cycle with different solution concentrations: 25, 50, and 75 vol% SnEH in acetone, and pure SnEH. Only one coating cycle was performed. Then the Pt was deposited as per Section 2.2.1. The acetone diluted SnEH was easier to work with from a production standpoint since the reduced solution viscosity allowed draining of excess solution from the narrow monolith channels and from between and around a mass of small pellets. One disadvantage of using a dilute SnEH solution was that more coating cycles are required to attain the same SnO₂ loading as with pure SnEH. Another disadvantage of using dilute SnEH was the increased rate of decomposition from atmospheric moisture. Acetone can absorb atmospheric moisture. When the SnEH fraction fell below about 40 vol%, it decomposed rather rapidly, via hydrolysis.

Figure 2.12 shows the observed activity of each catalyst coating, R.obs, in units of
CO₂ produced per gram of Pt. The activity of the catalyst coatings prepared from the 50%, 75%, and 100% SnEH solutions all show similar, high activities. The catalyst sample prepared using the 25% SnEH in acetone solution showed a significantly lower activity.

The difference in activity of the catalyst coating of this one sample can be explained from information provided by SEM micrographs of the SnO₂-coatings produced from each different solution concentration. Figure 2.13 (a) shows the SEM micrograph of the SnO₂ layer on unetched cordierite produced from the 25% SnEH solution. The tin oxide appears as islands upon the incompletely covered cordierite surface. Island formation may have been induced by poor wetting of the cordierite surface by the SnEH. This is not unreasonable since the SnEH is a nonpolar compound in contrast to the polar cordierite. It is also possible that the appearance is due in part to the partial hydrolysis of the SnEH in the solution, as described above, producing particulate or aggregates of tin oxide in EHA.

![Graph showing the effect of SnEH concentration in acetone on the activities of the Pt/SnO₂ catalyst coatings on unetched cordierite monolith.](image)

Figure 2.12. The effect of SnEH concentration in acetone on the activities of the Pt/SnO₂ catalyst coatings on unetched cordierite monolith.

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rather than a uniform SnEH layer.

Figures 2.13 (b), (c), and (d) show the SEM micrographs of the SnO$_2$-coatings prepared from the 50%, 75%, and 100% SnEH solutions. The coatings from the 50% and 75% solutions appear to completely cover the cordierite, and no other features are apparent. When 100% SnEH was used, the resulting SnO$_2$ layer developed cracks, possibly due to differences between the thermal expansion coefficients of SnO$_2$ and cordierite. Although this cracking did not apparently affect catalyst activity, a cracked surface can lead to loss of catalyst from the substrate with only minor agitation. This process is known as dusting and is undesirable for just about any application for which the catalyst would be used. To attain complete coverage, but prevent cracking of the SnO$_2$ layer, a solution concentration between 50% and 75% SnEH is favorable.

Although the physical appearance of the SnO$_2$ coating was affected by the solution concentration of SnEH, the activity of the resulting catalyst itself was apparently unaffected. Many series of samples have been prepared on a variety of substrates including cordierite honeycomb monolith, alumina pellets, and silica gel with varying concentrations of SnEH in acetone. Differences in the CO-oxidation activities of the resulting catalyst coatings were absent as long as the same kind of substrate was coated. If the substrate was changed, however, then the activity changed. In other words the activities of catalyst coatings on cordierite were different from coatings prepared in a similar manner but on alumina pellet or silica gel. This substrate effect on activity is the next topic of discussion.

**Effect of substrate surface area on catalyst activity.** Substrates do not normally participate in the catalytic reaction; they merely serve to disperse and bond the catalyst components in a more convenient geometry for the desired application. In this respect, their physical properties are more important than their chemical properties. Substrates such as pellets and honeycomb monolith are made by mixing oxide powders with binders and a liquid to form a clay-like mass which is then extruded in the desired
Figure 2.13. SEM micrograph of the SnO$_2$ film on cordierite monolith produced from the thermal decomposition of (a) 25 vol% SnEH and (b) 50 vol% SnEH.
Figure 2.13. SEM micrograph of the SnO$_2$ film on cordierite monolith produced from the thermal decomposition of (c) 75 vol% SnEH and (d) 100 vol% SnEH.

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shape, dried, and fired at high temperature. For example, cordierite is prepared from the oxides of Mg, Al, and Si in a specific ratio (2 to 2 to 5, respectively). The required firing temperature is around 1450°C to allow bonding of the oxide aggregates to one another, a process called "sintering." The as-received cordierite used in these experiments has very low surface area, < 1 m²/g, and very large pores, about 3.5 μm. This arrangement is common for a porous material: large size pores generally accompany low surface area; small pores generally accompany high surface area.

It is generally preferred, however, that a substrate have a high surface area in order to better disperse the catalyst components and consequently generate a greater number of active sites than possible on a low surface area substrate. This is especially important for optimum use of expensive noble metal components. In the production of automobile emissions catalysts for instance, a high surface area alumina washcoat is first added to the low surface area substrate to better disperse the noble metals, Pt, Pd, and Rh. For the same reason, the as-received cordierite honeycomb monoliths were etched, as described in Section 2.2.1, to increase the surface area prior to coating. Figure 2.14 shows the activities of a series of catalysts prepared as above, with varying concentrations of SnEH in acetone, but deposited, instead, on etched cordierite. The steady-state activities of each catalyst coating were very nearly the same, about 3 to 4 sccm CO₂ produced/g Pt at around 4000 minutes. By contrast, the catalyst coatings on unetched cordierite (Figure 2.12) showed activities in the range of 20 to 26 sccm CO₂ produced/g Pt, except for the sample with incomplete SnO₂ coverage of the cordierite which showed an activity of about 10 sccm CO₂ produced/g Pt.

Comparing the activities of these two groups of samples (etched versus unetched) suggests that the catalyst coatings on the etched cordierite might have some degree of incomplete coverage with catalyst as was observed for the sample prepared from the 25% SnEH solution. How the physical nature of the etched substrate can affect the activity of the
resulting catalyst coating can be understood by investigating the surface area and pore size distribution of the etched substrate. The changes to the cordierite material created by the etching process indicate that incomplete coverage is indeed the case.

During the etching process, the nitric acid dissolves some of the Al and Mg oxides, thereby removing atoms and/or aggregates from the cordierite ceramic. Table 2.1 shows the changes in the cordierite due to etching as instructed in Section 2.2.1. The as-received or unetched cordierite had no detectable surface area in micropores. For the etched samples, both the weight loss and surface area increase with increasing etch time. Regardless of the increased loss of cordierite material, however, all of the surface area created is microporous. Therefore, etching increased the total number of micropores but not the average size of the pores. As noted earlier, the as-received cordierite substrates had an average pore diameter of 3.5 μm or 35,000 Å—three orders of magnitude larger than the pores created by etching. Combining the two pore sizes gives a picture of what is
happening during the etching process. Etching pits the 3.5 μm pores with extremely small pores about 1/1000th the size.

If we next consider the size of the SnEH molecules that we are trying to fit in to the pores, the problem of incomplete coverage of the etched cordierite surface area by SnO₂ becomes apparent. From simple geometric considerations and readily available bond lengths, the size of the SnEH molecule Sn(OOCC₇H₁₄)₂, can be conservatively estimated to have a length of 11 Å and a width of about 3.5 Å. This size factor in conjunction with surface tension, viscosity, and polarity differences between the SnEH and cordierite indicate that the pore volume created by etching might not be coated by SnEH and, as a result, SnO₂.

If a portion of the cordierite remains exposed prior to the deposition of Pt, the Pt may coat the exposed cordierite making both active Pt/SnO₂ sites and inactive Pt/cordierite sites. PtAH ions in water are smaller than SnEH and more polar. Following this hypothesis, the total mass of PtAH, and consequently of Pt, should apportion itself on both cordierite and SnO₂ according to the respective amount of surface area of each that is available. The observed activity, $R_{obs}$, can be adjusted to account for the fraction of catalyst that is actually active, that which is Pt/SnO₂. Table 2.2 shows the data necessary to make the adjustment to observed activity of the catalyst coatings on etched cordierite, $(R_{obs})_{etched}$, to give the adjusted activity $(R_{adj})_{etched}$. The table has the data for both sets of catalyst coatings, those on etched and on unetched cordierite, that are required to make the

<table>
<thead>
<tr>
<th>Etch time</th>
<th>% weight loss</th>
<th>A, m²/g</th>
<th>% µporous area</th>
<th>µpore dia, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unetched/0 hr</td>
<td>0</td>
<td>&lt; 1</td>
<td>&lt;2</td>
<td>—</td>
</tr>
<tr>
<td>16 hr</td>
<td>14%</td>
<td>60</td>
<td>&gt;98</td>
<td>32.4</td>
</tr>
<tr>
<td>32 hr</td>
<td>30%</td>
<td>188</td>
<td>&gt;98</td>
<td>26.4</td>
</tr>
<tr>
<td>48 hr</td>
<td>42%</td>
<td>224</td>
<td>&gt;98</td>
<td>31.0</td>
</tr>
</tbody>
</table>
adjustment to \((R_{\text{obs}})_{\text{etched}}\). The activities were determined once the catalysts reached a near steady-state level, around 10,000 minutes for the unetched and 4,000 minutes for the etched.

The ultimate number required to make the adjustment to \((R_{\text{obs}})_{\text{etched}}\) is the ratio of the SnO\(_2\) surface area to the total surface area in the etched samples. As described above, this ratio determines the active fraction of Pt. The ratio can be determined only if the surface area of the tin oxide layer itself is known. Because the measured surface area of the SnO\(_2\) coating on etched cordierite arises from both uncoated cordierite and SnO\(_2\), it cannot be used to determine the surface area of the SnO\(_2\) itself. Instead, the data from the SnO\(_2\) coating on unetched cordierite must be used. Because the unetched cordierite has less than 1 m\(^2\)/g surface area, it does not contribute significantly to the measured surface area of the SnO\(_2\)-coated cordierite, \((A_{\text{SnO2-cord}})_{\text{unetched}}\). Dividing this surface area by the fraction that is tin oxide, \((X_{\text{SnO2}})_{\text{unetched}}\), gives the surface area of the tin oxide layer itself. For example, unetched cordierite coated one time with the 75\% SnEH solution gave an SnO\(_2\) loading of

Table 2.2. Observed and Adjusted CO-Oxidation Rates for Catalyst Coatings on Etched and on Unetched Cordierite

<table>
<thead>
<tr>
<th>Vol% SnEH used</th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>((A_{\text{SnO2-cord}})_{\text{unetched}}) m(^2)/g</td>
<td>5.05</td>
<td>5.29</td>
<td>11.0</td>
<td>14.6</td>
</tr>
<tr>
<td>((X_{\text{SnO2}})_{\text{unetched}})</td>
<td>0.4466</td>
<td>0.6376</td>
<td>0.1175</td>
<td>0.1321</td>
</tr>
<tr>
<td>(A_{\text{SnO2}}) m(^2)/g</td>
<td>113</td>
<td>83.0</td>
<td>93.6</td>
<td>111</td>
</tr>
<tr>
<td>((X_{\text{SnO2}})_{\text{etched}})</td>
<td>0.7185</td>
<td>0.7893</td>
<td>0.1122</td>
<td>0.1602</td>
</tr>
<tr>
<td>((\text{total } A_{\text{SnO2}})_{\text{etched}}) m(^2)</td>
<td>8.12</td>
<td>6.55</td>
<td>10.5</td>
<td>17.8</td>
</tr>
<tr>
<td>((A_{\text{SnO2-cord}})_{\text{etched}}) m(^2)/g</td>
<td>38.9</td>
<td>48.1</td>
<td>52.0</td>
<td>34.0</td>
</tr>
<tr>
<td>active fraction of Pt</td>
<td>0.209</td>
<td>0.136</td>
<td>0.202</td>
<td>0.523</td>
</tr>
<tr>
<td>((R_{\text{obs}})_{\text{etched}}) scnm CO(_2)/g Pt</td>
<td>2.90</td>
<td>3.89</td>
<td>3.20</td>
<td>3.75</td>
</tr>
<tr>
<td>((R_{\text{adj}})_{\text{etched}}) scnm CO(_2)/g Pt</td>
<td>14</td>
<td>29</td>
<td>16</td>
<td>7.2</td>
</tr>
<tr>
<td>((R_{\text{obs}})_{\text{unetched}}) scnm CO(_2)/g Pt</td>
<td>12.4</td>
<td>25.8</td>
<td>20.5</td>
<td>21.9</td>
</tr>
</tbody>
</table>

\(^{\dagger}\)In order to prevent confusion, the rows have been labeled with a subscripted title of "etched" or "unetched" to indicate on which substrate the catalyst coating data pertains.

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11.75% and a surface area which measured 11.0 m²/g. Then the surface area of the SnO₂ layer, A_{SnO₂}, is \((11.0 \text{ m}^2/\text{g})/0.1175 = 93.6 \text{ m}^2/\text{g} \text{ SnO}_2\). Data for the other samples are presented in Table 2.2.

Now, if the SnEH cannot penetrate the pores of the etched cordierite, the SnEH should produce an SnO₂ layer on the etched cordierite with a surface area nearly equal to that on the unetched counterparts. Multiplying \((A_{SnO₂})_{unetched}\) by the SnO₂ loading on the etched cordierite, \((X_{SnO₂})_{etched}\), should give a good approximation to the area of the SnO₂ layer, \((total \ A_{SnO₂})_{etched}\). Assuming a 1-gram sample of SnO₂-coated etched cordierite, the equation is

\[
(tot_{A_{SnO₂}})_{etched} = (1 \text{ g}) \times (X_{SnO₂})_{etched} \times (A_{SnO₂})_{unetched}
\]

which for the 75% SnEH sample is

\[
(1 \text{ g}) \times \left( \frac{11.22 \%}{100} \right) \times (93.6 \text{ m}^2/\text{g}) = 10.6 \text{ m}^2 \text{ SnO}_2
\]

If we now invoke the assumption that the Pt apportions itself on the SnO₂ and cordierite according to the available surface area of each, then the resulting fraction of active Pt is the ratio of total SnO₂ surface area, \((total \ A_{SnO₂})_{etched}\), to the measured surface area of the SnO₂-coated etched-cordierite, \((A_{SnO₂-cord})_{etched}\). Continuing with the 75% SnEH sample, and again using the 1 gram basis, the active fraction of Pt is

\[
\text{active fraction of Pt} = \frac{10.6}{52.0} = 0.203
\]

For every 1 g of Pt only 0.203 g is active. The remainder is wasted forming Pt/cordierite sites. Normalizing \((R_{obs})_{etched}\) to 1 g of Pt gives
Results of this calculation for the other three samples can be found in Table 2.2.

For comparison to \((R_{\text{adj}})_{\text{etched}}\), the final row in the Table 2.2 shows the observed activity for the catalyst coatings on the \textbf{unetched} samples, \((R_{\text{obs}})_{\text{unetched}}\). They should be equal. The adjustment accounts for a large portion of the discrepancy between the activities of the samples described above and lends evidence to the hypothesis that the differences arise from the physical differences between the substrates. Even the samples prepared from the 25% SnEH solution, whose substrates were incompletely covered with tin oxide, show good agreement. However, as the Pt loading increases, the dispersion would decrease making fewer active sites. Because the SnO\textsubscript{2}-coated \textbf{etched} cordierite had a higher total surface area than the SnO\textsubscript{2}-coated \textbf{unetched} cordierite, better dispersion and hence higher activity per gram of Pt would be observed. For this reason, the adjustment made above to \((R_{\text{obs}})_{\text{etched}}\) should have over compensated. For the catalyst coatings prepared with 25% and 50% SnEH, this was observed. Those adjustments for the samples prepared from 75% SnEH and 100% SnEH, on the other hand, appear to under compensate, the 100% sample worse than the 75% sample. This can be explained on the basis of the viscosity of the SnEH solution in which the substrates were coated. The more dilute the SnEH solution, the lower its viscosity and the smaller the pores that could be coated. Consequently, less total cordierite area would remain exposed and less Pt would be lost to cordierite for the samples. As the concentration of the SnEH increased, on the other hand, the amount of exposed cordierite would increase. The assumptions made above could not account for the extent to which the surface area of the etched cordierite could be coated with SnO\textsubscript{2}. The trend in the adjustment with solution viscosity suggests that some of the surface area created by etching the cordierite can, in fact, be coated by SnO\textsubscript{2} if the solution viscosity is low enough.
The above observations provide evidence that the Pt apportions itself according the total available surface area and that solution viscosity plays a role in how much of the etched cordierite can be coated with SnO₂. In terms of production then, this suggests that only substrates having "coatable" surface area should be used for holding the catalyst coating prepared via this method. Such substrates should preferably have pores with diameters on the order of µm—not 10's of Å.

**Alumina pellet surface area, another example.** As further evidence of the phenomenon discussed above, and to demonstrate that the suppressed activities of the catalyst coatings on etched cordierite were not a result of the etching process itself, a similar study was carried out on a series of alumina pellets whose only differences were their starting surface area and pore size distribution. Catalyst coatings were deposited on alumina pellets with surface areas of 2.6, 99, and 270 m²/g. Using the same assumptions as above for the samples on cordierite, similar results were obtained: the activity decreased as the surface area of the uncoated substrate increased. Some differences, however, exist and are discussed. First, the SnO₂ coating was prepared from 2 SnEH coating cycles in a solution that was 2 parts SnEH to 1 part acetone. Second, it was assumed that the alumina did contribute some to the measured surface area of the SnO₂-coated sample. This is reasonable as the alumina has a surface area of 2.6 m²/g and composed about 83% of the sample, the SnO₂ the remaining 17%. This can only be done for the 2.6-m²/g sample because its pores were large enough to be accessible to the SnEH, greater than 1500 Å. (Remember that the etched cordierite had a large portion of the pore volume in pores smaller than about 30 Å.) For a 1-g sample, the total SnO₂ surface area is the difference between the measured surface area and the surface area of the alumina or

\[
SA_F - SA_{\text{alumina}} = \frac{17.7 \text{ m}^2}{g} - \left[ (1 - 0.1699)(2.6 \text{ m}^2 \text{ g}^{-1}) \right] = 15.4 \text{ m}^2 \text{ SnO}_2 \quad (5)
\]
where the internal bracketed term is the alumina surface area. For the same gram basis, the surface area per gram of tin oxide is equal to 15.4 m$^2$ divided by 0.1699 g SnO$_2$, or 90.6 m$^2$/g. This surface area is similar to that found for the SnO$_2$ coating on the unetched cordierite samples discussed above.

For the 99-m$^2$/g and 270-m$^2$/g samples, knowing the fraction that is SnO$_2$ and using the calculated value of 90.6 m$^2$/g for the SnO$_2$ surface area, the total surface area of SnO$_2$ could be determined. For these higher surface area samples, a fraction of the pore volume, is composed of pores whose dimension is too small for the SnEH to coat. The uncoatable fraction is, however, unknown. For the 2.6-m$^2$/g sample, on the other hand, the uncoatable fraction is much smaller and was taken into account. It is reasonable to use the SnO$_2$ surface area calculated from the 2.6-m$^2$/g sample because the pellets are all alumina and experienced the thermal history. Consequently, the tin oxide—itself—should have the same surface area regardless of the surface area and porosity of the alumina on which it was deposited. In other words, the SnEH gives and SnO$_2$ layer with an independent matrix.

Table 2.3 shows these calculated surface areas and the adjusted rates for each sample. If the poor coverage of the substrate material was again observed, then the adjusted activities should be closer to each other on a percentage basis than the observed activities. If the correction were exact, equal values for $R_{adj}$ would be observed among the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>270 m$^2$/g</th>
<th>99 m$^2$/g</th>
<th>2.6 m$^2$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{SnO_2-alumina}$, m$^2$/g</td>
<td>217 ± 2</td>
<td>90.7 ± 0.3</td>
<td>17.7 ± 0.1</td>
</tr>
<tr>
<td>$X_{SnO_2}$</td>
<td>0.1245</td>
<td>0.2381</td>
<td>0.1699</td>
</tr>
<tr>
<td>total $A_{SnO_2}$, m$^2$</td>
<td>11.3</td>
<td>21.6</td>
<td>15.4</td>
</tr>
<tr>
<td>$R_{obs}$, sccm CO/g Pt</td>
<td>3.8</td>
<td>6.5</td>
<td>35</td>
</tr>
<tr>
<td>$R_{adj}$, sccm CO/g Pt</td>
<td>73</td>
<td>27</td>
<td>40</td>
</tr>
<tr>
<td>$R'_{adj}$, sccm CO/g Pt</td>
<td>51</td>
<td>no correction</td>
<td>no correction</td>
</tr>
</tbody>
</table>
R_{obs} for the catalyst coating on 2.6 m^{2}/g alumina is almost 6 times higher than that of the catalyst coating on 99 m^{2}/g alumina, but R_{adj} is only 1.5 times higher. Similarly, R_{obs} for the coating on the 2.6 m^{2}/g alumina is 10 times higher than that of the coating on 270 m^{2}/g alumina, but R_{adj} is only 1/2 the activity. That the values are closer suggests that a fraction of the alumina pore volume cannot be coated by SnO_{2} but can be coated by Pt thereby creating inactive catalyst.

As with the cordierite samples, R_{adj} for the catalyst coating on 270-m^{2}/g alumina seems to have been over-corrected on the basis of surface area alone. Looking more closely at the differences between the pore volumes calculated by H_{2}O uptake and by N_{2} adsorption may provide the reason for the over-correction. The pore volume as determined by H_{2}O uptake and by N_{2} adsorption is provided in the Table 2.4. There exist differences between the pore volumes determined by the two techniques. The differences suggest how much pore volume and therefore surface area is available to the catalyst reagents. Because of the limits in physical properties, N_{2} adsorption can only provide information about the surface area and pore size distribution for pores between about 20 and 600 Å.\textsuperscript{2} Using the t-plot method, the data can be extended to pores less than 20 Å.\textsuperscript{2} For reason of similar limitations, H_{2}O can only be used to determine the pore volume in pores ranging from 10 to 1500 Å.\textsuperscript{2} The water uptake method suffers from water adsorbed to the outermost surface of the pellet and at contact points between pellets, so there is a greater potential for error using this method. By using probes capable of penetrating different pore size ranges, more

<table>
<thead>
<tr>
<th>Sample</th>
<th>by H_{2}O uptake cm^{3}/g Al_{2}O_{3}</th>
<th>by N_{2} uptake cm^{3}/g Al_{2}O_{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>271 m^{2}/g</td>
<td>0.26</td>
<td>0.36</td>
</tr>
<tr>
<td>99 m^{2}/g</td>
<td>0.41</td>
<td>0.26</td>
</tr>
<tr>
<td>2.6 m^{2}/g</td>
<td>0.28</td>
<td>0.0076</td>
</tr>
</tbody>
</table>
detailed information about the pore size distribution can be obtained about the alumina substrates in Table 2.4.

For the 2.6 m²/g alumina, the pore volume for N₂ adsorption is only 0.0076 cm³/g, in stark contrast to that determined from water adsorption, 0.285 cm³/g. This indicates that only a small amount of pore volume exists in pores less than 600 Å, approximately 0.0076/0.285 or 2.7%. Instead, the majority of the measured pore volume is composed of pores between 600 Å and 1500 Å. Pore volume in pores greater than 1500 Å remains unknown.

For the 99 m²/g alumina, the N₂ adsorption method yields a lower value for the pore volume than that determined by water uptake but in the same order of magnitude. The pore size distribution as determined for this substrate indicates that a significant fraction of the pore volume is composed of pores with diameters between 20 than 600 Å. The difference between that determined by H₂O uptake and N₂ adsorption is the amount of pore volume composed of pores between 600 and 1500 Å, or

$$0.41 \text{ cm}^3/\text{g} - 0.26 \text{ cm}^3/\text{g} = 0.15 \text{ cm}^3/\text{g}$$  \hspace{1cm} (6)

The fraction of the pore volume composed of pores with diameters between about 600 and 1500 Å is

$$\frac{0.15 \text{ cm}^3/\text{g}}{0.41 \text{ cm}^3/\text{g}} = 0.37$$  \hspace{1cm} (7)

or about 37% of the pore volume.

For the 270 m²/g sample, the measured pore volumes were reverse of that found for the other alumina samples, larger by N₂ adsorption and smaller by H₂O uptake. Following the reasoning used in (6) and (7), the difference between the pore volumes as determined by the different methods divided by the total pore volume gives that fraction of
the pore volume which is less than about 20 Å, or

\[
\frac{(0.36 \text{ cm}^3/\text{g} - 0.26 \text{ cm}^3/\text{g})}{0.36 \text{ cm}^3/\text{g}} = 0.28
\]  (8)

or about 28% of the pore volume.

Because 28% of the pore volume is unavailable to water, it is likely uncoatable by Pt. Consequently, more Pt would have coated the SnO₂ than expected based on the first correction that only SnO₂ was unable to coat all of the pore volume. As a result, \( R_{\text{adj}} \) should be much smaller than \( R_{\text{adj}} \) than originally calculated for the catalyst coating on 270-m²/g alumina. Correcting for the 28% that cannot be coated by Pt requires calculation of the fraction of the sample that is alumina surface area. The total alumina area for a 1-g, SnO₂-coated sample would be the weight fraction of the SnO₂-coated alumina that is alumina, multiplied by the surface area of the uncoated alumina, or

\[
(1 - 0.1245) \times (270 \text{ m}^2/\text{g}) = 236 \text{ m}^2/\text{g}
\]  (9)

Of this amount, 28% cannot be coated, or

\[
(0.28) \times (236 \text{ m}^2/\text{g}) = 66 \text{ m}^2/\text{g}
\]  (10)

This amount must be subtracted from the measured surface area of the SnO₂-coated alumina, or

\[
217 \text{ m}^2/\text{g} - 66 \text{ m}^2/\text{g} = 151 \text{ m}^2/\text{g}
\]  (11)

to give the total available surface area which can be coated by the Pt. Adjusting the CO-oxidation activity, \( R_{\text{obs}} \), in Table 2.3 with the coatable surface area, 151 m²/g rather than
the measured surface area, 217 m²/g, gives

\[ R'_{\text{adj}} = \frac{151 \text{ m}^2/\text{g}}{11.3 \text{ m}^2/\text{g}} (3.8 \text{ sccm CO/g Pt}) = 51 \text{ sccm CO/g Pt} \] (12)

The correction brings \( R'_{\text{adj}} \) much closer to \( R_{\text{adj}} \) for the catalyst coatings on the 2.6-m²/g and the 99-m²/g alumina (Table 2.3). The correction is still too large suggesting that more Pt is in contact with SnO₂ or less is lost to alumina. It is possible that some of the pores were blocked by SnO₂ making the coatable portion of Al₂O₃ by Pt even less than 28%. This would effectively reduce the correction even more.

In summary, the data presented in this section suggest that a portion of the problem in coating high surface area substrates is the unavailability of the small pores. The same problem has been encountered by others in the chemical coating of coconut charcoal whose pore volume and hence surface area exist largely in pores with diameters less than 20 to 30 Å.⁷ Since high surface area necessarily coincides with small pore dimensions, catalyst coatings of Pt/SnO₂ applied via the described methodology require a low surface area, large pore volume substrate. For the cordierite, in spite of creating additional substrate surface area, HNO₃-etching creates uncoatable area. Similarly, a large fraction of the surface area on the high surface area alumina is unavailable to not only the SnEH, but also to the PtAH.

**Effect of SnO₂ loading.** In order to make Pt/SnO₂-based catalysts economically viable for mass production, a means of reducing the platinum requirement was essential. The original catalyst formulation was designed for a one-time spaceborne laser application where its activity was maximized per unit weight of catalyst since total weight was the driving cost. Its composition, 15% Pt/SnO₂, would not be economically viable at such a high Pt content. For commercialization or mass production, the problem shifted to maximizing the activity per unit cost of catalyst. In short, this meant maximizing the activity per unit weight of platinum as platinum remains the driving material cost in the production.
Consequently, it was important to look at the catalyst activity on a per gram of platinum basis. Changes to the production or composition which directly affected how efficiently the platinum was used became immediately evident.

Although somewhat of a contradiction to established findings, using a high surface area substrate did not provide better dispersion of the catalyst components for the coating method employed to make Pt/SnO$_2$ coatings. Other means for providing better dispersion of the catalyst components was necessary. One means of providing better Pt dispersion might be to increase the total tin oxide loading. This would give more total SnO$_2$ surface area on which the Pt could disperse. To this end, a series of catalysts was prepared whose only significant difference was the weight of the tin oxide coating. The tin oxide loading on each of 4 samples was incremented via increasing the number of coating cycles with SnEH as described in Section 2.2.1. Then, a constant Pt loading of about 0.034±0.002 g/in$^3$ of Pt was added to each sample.

Table 2.5 shows the SnO$_2$ loading, surface area, and the resulting activity of this group of catalyst samples. The total surface area of the SnO$_2$-coated substrate, $A_{\text{SnO}_2}$, increases as the SnO$_2$ loading increases, but the surface area of the SnO$_2$ layer, $A_{\text{SnO}_2}$, remains about a constant 150 m$^2$/g SnO$_2$ until the highest loading is reached. The activity normalized to the weight of platinum, $R_{\text{obs}}$, increases as the total surface area of SnO$_2$ increases. Remember that the Pt loading for each sample is nearly equal. Any slight

<table>
<thead>
<tr>
<th>SnO$_2$ loading (g/in$^3$)</th>
<th>$A_{\text{SnO}_2}$-cord (m$^2$/g total)</th>
<th>$A_{\text{SnO}_2}$ (m$^2$/g SnO$_2$)</th>
<th>total $A_{\text{SnO}_2}$ (m$^2$)</th>
<th>$R_{\text{obs}}$ (scm CO/g Pt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.26</td>
<td>22.9</td>
<td>104</td>
<td>10.7</td>
<td>44.6</td>
</tr>
<tr>
<td>1.33</td>
<td>15.3</td>
<td>155</td>
<td>9.53</td>
<td>30.3</td>
</tr>
<tr>
<td>1.03</td>
<td>17.4</td>
<td>151</td>
<td>7.37</td>
<td>20.5</td>
</tr>
<tr>
<td>0.713</td>
<td>12.4</td>
<td>149</td>
<td>4.83</td>
<td>14.0</td>
</tr>
</tbody>
</table>

Table 2.5. Surface Area and Activity Data for Catalysts with Varying SnO$_2$ Loading

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differences in Pt loading were removed by normalizing $R_{obs}$ to the weight of Pt.

Figure 2.15 shows a plot of $R_{obs}$ versus $A_{SnO2}$. It is apparent that the activity of the group of catalysts is not a linear function of the SnO$_2$ surface area. Combining Langmuir-Hinshelwood (L-H) kinetics with a few simple geometric relations provides a good explanation of the observed relation. L-H kinetics for the reaction between two species that have separate adsorption sites (here CO on Pt and O$_2$ SnO$_2$), suggests that the reaction rate is described as

$$R = k \cdot \theta_{CO} \cdot \theta_{O2}$$  \hspace{1cm} (13)

where $k$ is the rate constant, and $\theta_{CO}$ and $\theta_{O2}$ are the fractions of available sites occupied

![Graph showing $R_{obs}$ versus $A_{SnO2}$](image)

**Figure 2.15.** $R_{obs}$ versus $A_{SnO2}$ for a series of Pt/SnO$_2$ catalyst coatings on cordierite with increasing SnO$_2$ loadings and constant Pt loadings.
by CO and O₂. If there are quantities of both CO and O₂ in gross excess of that necessary
saturate all of the available sites, then the gas concentrations are essentially constant and
become part of k, and θ_A and θ_B can be replaced by the number of adsorption sites for each
CO and O₂, we have

\[ R = k' \cdot N_{Pt} \cdot N_{SnO2} \] (14)

where \( N_{Pt} \) and \( N_{SnO2} \) are the number of adsorption sites of Pt and SnO₂, respectively. This
is consistent with the manner in which Pt/SnO₂ were tested with at less than 70%
conversion across the catalyst bed. It is also reasonable to assume that \( N_{SnO2} \) and \( N_{Pt} \) are
directly proportional to the surface areas of each and can be replaced by including
appropriate constants making equation (14)

\[ R = k'' \cdot A_{Pt} \cdot A_{SnO2} \] (15)

where \( A_{Pt} \) and \( A_{SnO2} \) are the surface areas of Pt and SnO₂, respectively.

Since \( A_{Pt} \) is not known, we must consider what happens to it when \( A_{SnO2} \) is
increased. This follows from dividing a given mass or volume of material into smaller parts
over a surface and observing the change in total area. Let's assume that the shape of the
object is spherical although it does not matter. A sphere of radius \( r \), has volume \( V \) and area
\( A \) of

\[ V = \frac{4}{3} \pi r^3 \quad A = \pi r^2 \] (16)

If we divide this volume into \( n \) smaller hemispheres of radius \( s_i \), the total volume must
remain constant because the total mass of material remains constant, and the volume can be

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rewritten as

\[ V = v_1 + v_2 + \ldots + v_n = \sum_{i=1}^{n} v_i = \frac{1}{2} \cdot \frac{4}{3} \pi \sum_{i=1}^{n} s_i^3 \]  \hspace{1cm} (17)

and the new area, \( A_n \), resulting from \( n \) new islands becomes

\[ A_n = a_1 + a_2 + \ldots + a_n = \sum_{i=1}^{n} a_i = \pi \sum_{i=1}^{n} s_i^2 \]  \hspace{1cm} (18)

For the sake of simplicity let each sphere be of equal radius, or \( s_1 = s_2 = \ldots = s_n = s \), then (17) and (18) simplify to

\[ V = \frac{4}{3} \pi \sum_{i=1}^{n} s_i^3 = \frac{4}{3} \pi ns^3 \quad A_n = \pi \sum_{i=1}^{n} s_i^2 = \pi ns^2 \]  \hspace{1cm} (19)

Since the total volume remains constant, the relation between the radii of the smaller spheres and the radius of the original sphere can be equated and the resulting relation between the radii of the larger and smaller hemispheres becomes

\[ \frac{1}{2} \cdot \frac{4}{3} \pi r^3 = V = \frac{1}{2} \cdot \frac{4}{3} \pi ns^3 \Rightarrow r = n^{1/3} \quad s \]  \hspace{1cm} (20)

Finally, taking the ratio of the new area formed to that of the old and substituting in for \( r \) from (20) gives

\[ \frac{A_n}{A} = \frac{n \pi s^2}{\pi r^2} = \frac{ns}{n^{2/3} s} = n^{1/3} \]  \hspace{1cm} (21)

Equation (20) indicates that \( A \propto n^{1/3} \) so large increases in the number of spheres are give...
only modest gains in the surface area. It is reasonable to assume that the surface area of SnO\textsubscript{2} will provide the impetus for the division of the Pt into smaller islands, so \( n \) can be replaced by \( A_{SnO2} \) and the relation between the tin oxide surface area and that of Pt is

\[
A_{Pt} = c \left( A_{SnO2} \right)^{1/3}
\]  

(22)

where \( c \) is the constant of proportionality. Large increases in \( A_{SnO2} \) are required to give only modest increases in \( A_{Pt} \). Finally, equation (15) can be rewritten as

\[
R = k''' \cdot (A_{SnO2})^{1/3} \cdot A_{SnO2} = k''' \cdot (A_{SnO2})^{4/3}
\]  

(23)

indicating that \( R \) is predicted to have a 4/3 power dependence on \( A_{SnO2} \). This is reasonable because increasing the surface area of the SnO\textsubscript{2} should increase the number of adsorption sites for both O\textsubscript{2} and CO and consequently the activity.

Returning now to Figure 2.15, the solid line is the least squares fit through the data points assuming a power relation, \( R = \text{constant} \cdot (A_{SnO2})^{\text{power}} \). The error bars are based on a 10% relative error in determining the surface area. This is reasonable based on the assumptions inherent in the BET relation. There is also about 2% relative error in determining the relative activities of the catalyst samples, but this is less than or equal to the size of the symbol used to plot the data. The resulting power is 1.37 which is very near 4/3 suggesting this simple geometric model is a reasonable explanation of changes occurring in the activity with changes in the surface area of the SnO\textsubscript{2} layer of the catalyst.

**Surface area and pore size distribution data.** Another important point to note from the data presented in Table 2.5 is that \( A_{SnO2} \) remains nearly constant until the highest loading of SnO\textsubscript{2} is reached. One might expect the SnO\textsubscript{2} surface area to fall off with each additional coating step since SnO\textsubscript{2} would potentially cover existing SnO\textsubscript{2}. The surface area and porosimetry data taken between each coating step provides insight into the
observed behavior. To this end, the N$_2$ adsorption isotherm of the SnO$_2$-coated cordierite layer was taken after each of six coating cycles. The data are summarized in Figure 2.16. The total pore volume (solid circles; right axis) increases with the first two dips and then decreases almost linearly with subsequent dips. During the second dip, then, new SnO$_2$ pore structure was created without a loss of that created during the first dip. For subsequent dips, only a portion of the existing SnO$_2$ was covered up. The SnO$_2$ loading (open squares; left axis) increases almost linearly with each dip in SnEH. The slight downward curvature, however, indicates that the amount of SnO$_2$ added on each subsequent dip decreases slightly. The reason for this decrease is probably that, although new pore volume is being created with each coating, some of the existing pore volume is lost in subsequent coatings either by filling of pore volume or by sintering.

Figure 2.16. Changes in SnO$_2$ loading and total pore volume as a function of the number of SnEH coating cycles.
Figure 2.17 shows the total surface area of the SnO₂-coated cordierite, $A_{\text{total}}$, as a function of tin oxide loading. The surface area increases with SnO₂ loading for the first three coats (or until about a 20% SnO₂ loading is reached) and then remains approximately constant thereafter. The first three points are linearly related and indicate that surface area increases about 1.4 m²/g of SnO₂-coated cordierite. Extrapolating to zero SnO₂ loading, the intercept of 0.52 m²/g should be the surface area of the cordierite monolith which shows good agreement with that determined by N₂ adsorption to be <1 m²/g.

Figure 2.18 shows the SnO₂ surface area and the average pore diameter of the SnO₂ layer as a function of tin oxide loading. $A_{\text{SnO}_2}$ was calculated as before by assuming a negligible contribution from the cordierite. $A_{\text{SnO}_2}$ remained relatively constant until a 20% SnO₂ loading was reached and then fell off with higher loadings. This indicates that during the first three coating cycles, the SnEH does not penetrate the SnO₂ pore structure created.
in the previous steps. This behavior is reasonable as the average pore diameter of the pores in the SnO\textsubscript{2} layer is small enough to prevent the SnEH from penetrating the majority of the porous framework during subsequent coating steps. This phenomenon was observed in trying to coat the etched cordierite and high-surface-area alumina pellets whose pores were too small to enable complete coverage with SnEH. Because SnEH generates an essentially microporous SnO\textsubscript{2} layer, each subsequent dip in SnEH can provide additional SnO\textsubscript{2} surface area without sacrificing the existing, valuable surface area. After the first three steps, however, the surface area begins to fall off indicating some covering up of existing SnO\textsubscript{2} area or, perhaps, a loss of SnO\textsubscript{2} surface area due to repeated thermal processing. This coincides with the leveling off of \( A_{\text{total}} \) shown in Figure 2.17.

The average pore diameter (right axis in Figure 2.18) of the SnO\textsubscript{2} layer shows a similar trend with SnO\textsubscript{2} loading except that it peaks at the second coating step and then falls

Figure 2.18. The effect of SnO\textsubscript{2} loading on the surface area and on the average pore diameter of the SnO\textsubscript{2} layer.
off rapidly and changes little after the fourth coating cycle. This decrease may indicate some filling of the some of the larger pores in the SnO$_2$ layer created in previous steps. The change is not important for the most part in that the porosity in the SnO$_2$ network is still very small.

These data suggest that either a 20 weight percent loading of SnO$_2$ or three coating cycles using the 2-to-1 SnEH-to-acetone solution may be optimum in terms of gaining the highest number of active sites per gram of SnO$_2$ on the cordierite substrate.

It is apparent from the data presented thus far that improved catalyst activity comes from increasing the total SnO$_2$-layer surface area. It is also known that the surface area of the SnO$_2$ layer cannot be increased by coating a high surface area substrate. Instead increasing the geometric surface area of the substrate can increase the total catalyst activity by reducing loss of SnO$_2$ area by coating in subsequent cycles. For example, spreading out the same amount of SnO$_2$ over twice the geometric area should give a catalyst with greater than twice the activity. Because building the SnO$_2$ layer thicker via more coating cycles causes a loss of some SnO$_2$ surface area with each coat, a more efficient use of the SnO$_2$ can be obtained by spreading it out over a larger geometric area. The volume restraints for a given application will decide the optimum catalyst coating per unit volume of substrate.

**Increasing the SnO$_2$ layer surface area.** The above data demonstrate that increasing the total SnO$_2$ loading increases the activity per gram of Pt. due in part to increasing the SnO$_2$ surface area. There exists, however, a limit as to how much SnO$_2$ can be added to the substrate. As could be seen from the physical characterization, there was a loss in SnO$_2$ surface area with increasing loading. Because of this limit, the direction of research shifted to modifying the SnO$_2$ layer so as to increase its surface area without also increasing the total amount of tin oxide. The approach was to add magnesium 2,4-pentanedioniate (Mg-acac, hereafter) to the SnEH-acetone coating solution which, upon thermal decomposition, would give a composite oxide coating on the cordierite substrate.
consisting of two components, MgO and SnO2. MgO is soluble in dilute HNO3; SnO2 is not. The coated substrate would be etched with dilute nitric acid to dissolve out some of the MgO leaving behind a higher surface area SnO2 layer. This experimental design follows the same reasoning used to increase the cordierite surface area: the Al and Mg oxides of cordierite are soluble in dilute HNO3, whereas SiO2 is not soluble.

In keeping with good experiment controls, as two variables would be changed at one time, it was necessary to prepare 4 samples. In order to subtract the impact of the Mg-acac on the activity of the resulting catalyst, oxide coatings with and without Mg-acac were prepared. In order to subtract the effect of HNO3 etching, both pure SnO2-coated and MgO-SnO2-coated substrates had to be etched. The etching process was described in Section 2.2. Sample etching lasted 4 hours followed by rinsing with DI H2O, drying at 100°C and decomposition of residual nitric acid at 250°C. A Pt loading of 1% relative to the oxide coating was aimed for; the Pt loading per unit volume varied by no more than ±10% relative to the average loading.

Table 2.6 shows the percentage weight loss and the surface areas before and after the etching process—prior to the addition of the Pt—as well as the activities, \( R_{obs} \), of each catalyst after 11,000 minutes of testing, expressed in units of CO converted to CO2 per gram of platinum. The samples are labeled according to the composition and processing of the oxide coating. All samples were coated with about equal amounts of Pt. Both of the etched samples showed similar weight losses, about 9%, and correspondingly similar gains in surface area, 3.3 or 2.6 times greater, by comparison to their unetched counterparts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SnO2 unetched</th>
<th>SnO2 etched</th>
<th>MgO-SnO2 unetched</th>
<th>MgO-SnO2 etched</th>
</tr>
</thead>
<tbody>
<tr>
<td>% weight loss</td>
<td>—</td>
<td>9.2219</td>
<td>—</td>
<td>8.9641</td>
</tr>
<tr>
<td>SA, m²/g</td>
<td>16.7</td>
<td>55.6</td>
<td>18.7</td>
<td>.48.4</td>
</tr>
<tr>
<td>( R_{obs} ), sccm CO/g Pt</td>
<td>10</td>
<td>42</td>
<td>3.9</td>
<td>16</td>
</tr>
</tbody>
</table>
Two observations are immediately apparent from comparing \( R_{\text{obs}} \): (1) etching improves the catalyst activity, and (2) MgO is apparently a hinderance to the activity of Pt/SnO\(_2\) catalysts. As to the extent of improvement, it is near that predicted by equation (23), or \( R \propto A_{\text{SnO}_2}^{4/3} \). Here, however, the ratios are validly taken or

\[
\frac{R_2}{R_1} = \left( \frac{n_2}{n_1} \right)^{4/3}
\]

than might be expected by comparing the ratios of the surface areas. For the SnO\(_2\) samples, etching yielded a catalyst with 4.2 times the activity as the unetched counterpart, whereas the surface area increased by a factor of 3.3. For the MgO-SnO\(_2\) samples, the activity increase was 4.1 times greater and the surface area 2.6 times greater. Applying relation (24) to the samples prepared on etched and on unetched SnO\(_2\)-coated and MgO-SnO\(_2\)-coated cordierite, gives respectively

\[
\frac{R_{\text{etched}}}{R_{\text{unetched}}} = \left( \frac{55.6}{16.7} \right)^{4/3} = 4.97 \quad \frac{R_{\text{etched}}}{R_{\text{unetched}}} = \left( \frac{48.4}{18.7} \right)^{4/3} = 3.55
\]

The theoretical and observed values for the samples are about in 15% relative error. The observed value for the SnO\(_2\)-coated sample is less than the theoretical value. A possible reason for this discrepancy could be the result of the etching process during which some cordierite may have been exposed causing a loss of Pt to inactive Pt/cordierite sites upon Pt deposition. For the MgO-SnO\(_2\) sample the observed value is greater than the theoretical value. Some Pt is apparently already lost to MgO prior to etching thereby giving a lower than expected \( R_{\text{unetched}} \) and making the ratio higher.

Surprisingly, the MgO was completely unnecessary for increasing the surface area of the oxide layer. It is possible that, even though SnO\(_2\) is insoluble in dilute nitric acid, small bits of the coated substrate are lost in a manner similar to that for the cordierite, in
which the aluminum and magnesium oxide portions are soluble, but the silica portion is not thereby enabling etching away of some of the insoluble silica.

In summary, the surface area of the tin oxide layer can be increased in three ways: (1) by increasing the total SnO₂ loading, (2) by etching the SnO₂-coated cordierite substrate, and (3) by increasing the geometric area over which the SnO₂ is deposited. It is also clear from the data that because SnO₂ is an active catalyst component as well as a dispersant for the Pt, that maximizing its surface area is essential for producing a catalyst with optimum activity.

**Processing temperatures used during SnEH decomposition.** As can be seen from the data in the former section, a high surface area SnO₂ layer is essential to high catalyst activity. It is well documented that the surface area of hydrous tin(IV) oxide falls off rapidly above temperatures of 300°C. Consequently, it is important to keep the temperatures used during preparation of the catalyst below 300°C. This section investigates what happens thermally during the preparation of the SnO₂-coating process by placing type K thermocouples in the muffle furnace during the decomposition of the SnEH on cordierite monolith.

After the standard decomposition at 200°C, the catalyst has a medium to light brown appearance. This could be due to partially combusted hydrocarbon but is more likely due to tin(II) oxide which is brown to black. This is reasonable as the tin ion in the SnEH is in its +2 valence state, and the reduction in available O₂ due to any increased amount of SnEH may lead to incomplete oxidation to tin (IV) oxide, SnO₂. After treatment at 300°C, the smaller monolith samples were uniform in color being a bit lighter than the original cordierite. When larger pieces were coated, however, they showed varying shades of brown with none having uniform color depending on the temperature which the area of a given piece reached. Differences in temperature are due to the temperature gradient in the muffle furnace. Subsequent dips in the SnEH solution showed that some of the brown
material came off in the dipping solution, exhibiting poor bonding to the substrate.

Three type K thermocouples were placed around the monoliths in the muffle furnace: one at an intersection point between monoliths placed next to each other, a second inside a center channel of a monolith, and a third on an outer cylinder surface, non-intersection point. The temperatures were collected every 3-5 minutes using a Fluke/Hydra Data Bucket. Figures 2.19 and 2.20 show the temperature as a function of time for spaced and unspaced monoliths, respectively. When the monoliths were placed close together, and ramped at 2°C/min there was an exothermic reaction which increased the temperature between the monoliths and within the channel to 400°C. The temperature on the outer, non-intersection point, on the other hand, never reached 300°C. The probable cause for the temperature excursion was the oxidation of residual hydrocarbon to CO₂ and H₂O.

The samples did not remain brown if given enough time at 300°C, namely about 8 hours. Consequently, extended time at 300°C is sufficient to alleviate the problem with any residual brown material on the SnO₂-coated samples. The smaller samples probably could not exhibit such increases in temperature because they were only 1/2-inch thick and could easily dissipate the heat generated during the reactions occurring from 200°C to 300°C.

During the second, third, fourth, and fifth coating cycles, the samples were spaced and the thermocouples placed as before with the exception that the first thermocouple could not be sandwiched between the monoliths and was instead suspended in the space between them. With spacing and a temperature ramp decreased to 1°C/min, the temperature excursion did not occur. Also note that there exists a difference in the temperature excursion within the channel depending on where in the oven the monolith was placed. The excursion was greatest within the channel when the monolith was placed at the center of the oven, slightly less when placed at the back of the oven, and lowest when placed at the front of the oven. Taken together, this data suggests that the non-uniform color of the monoliths is likely be due to a non-uniform oven temperature.
Figure 2.19. The temperature at various locations in and around the SnEH-coated substrates during the thermal decomposition of tin(II) 2-ethylhexanoate with monoliths unspaced.

Figure 2.20. The temperature at various locations in and around the SnEH-coated substrates during the thermal decomposition of tin(II) 2-ethylhexanoate with monoliths spaced.
A forced or mechanical convection would even out the temperature during the second thermal dwell at 300°C and perhaps even the first dwell at 200°C unless an explosion hazard exists. Perhaps a 200°C muffle furnace step followed by a 200°C-300°C convection oven step would be best in preventing the explosion hazard as most of the ethylhexanoic acid would be lost in the 200°C muffle furnace phase. It is also possible that the convection oven might exacerbate the temperature increase by providing excess O_2 to any residual hydrocarbon. Since combustion can be a function of the O_2 concentration reaching the substrate surface, then increasing the O_2 circulation around and within the monolith may ultimately escalate the temperature.

2.3.3. Effect of Pt loading on activity. During the development of the catalyst coating technology, the project emphasis broadened from preparing a single catalyst for a single use in a satellite-mounted laser to include mass production for use in commercially produced CO_2 lasers. Potential use in air purification applications was also investigated. The original catalyst formulation prepared for spaceborne laser applications—about fifteen weight percent platinum to tin oxide, 15% Pt/SnO_2—was reformulated to maximize the catalyst activity per unit total weight of catalyst. For the other applications, the problem shifted from one of minimizing total weight to one of minimizing total cost. Because the noble metal is generally the driving cost in the production of most noble metal catalysts, reducing the total amount of platinum was essential. The original tests performed to reduce the amount of platinum involved reducing the total amount of catalyst while retaining the platinum to tin oxide ratio at fifteen percent. Unfortunately this approach produced a catalyst with inferior activity. As demonstrated above, improved results were obtained by spreading the Pt out over a larger surface area.

The effect of Pt loading on catalyst activity was investigated by preparing a series of catalysts from a single SnO_2-coated substrate with varying Pt loadings. Table 2.7 lists the Pt loading, R_{obs} without normalization, and R_{obs} normalized to the platinum weight in the
Table 2.7. Pt Loading and $R_{\text{obs}}$

<table>
<thead>
<tr>
<th>Pt loading, $\frac{\text{g}}{\text{in}^3}$</th>
<th>$R_{\text{obs}}, \text{scm CO}$</th>
<th>$R_{\text{obs}}, \frac{\text{scm CO}}{\text{g Pt}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.168</td>
<td>1.68</td>
<td>10.0</td>
</tr>
<tr>
<td>0.124</td>
<td>1.92</td>
<td>15.5</td>
</tr>
<tr>
<td>0.088</td>
<td>2.01</td>
<td>22.8</td>
</tr>
</tbody>
</table>

tested catalyst sample. The non-normalized value increased slightly with decreasing Pt loading. The normalized value increased with decreasing Pt loading. This indicates that Pt was being wasted at higher loadings. The inverse relation between Pt loading and the normalized $R_{\text{obs}}$ indicates that more activity can be gained by better dispersing the Pt.

It is obvious from the foregoing discussion on the effect of the $A_{\text{SnO}_2}$ on $R_{\text{obs}}$, that the activity per gram of Pt should increase with decreasing Pt loading. As the Pt loading increases Pt dispersion decreases as does the SnO$_2$ surface area. This should have the reverse effect on $R_{\text{obs}}$ as increasing SnO$_2$ surface area. For the catalyst samples presented in this section, the Pt loadings used were a significant portion of that catalyst weight (1.5% to 6.3% relative to the SnO$_2$). It is also known that the total catalyst area falls as the Pt loading is increased, making this observation reasonable. Using the same reasoning as that developed for the effect of SnO$_2$ surface area in Section 2.3.2, $R_{\text{obs}}$ should not be related linearly but rather as some power of the Pt loading. Figure 2.21 shows the normalized $R_{\text{obs}}$ versus Pt loading. The data were fit with a least squares regression assuming a power law relation. As per equation (23), the data would be expected to have a power of $-4/3$ consistent with observation. The negative sign comes from the inverse relation between Pt loading and $R_{\text{obs}}$ for a given surface area of SnO$_2$.

2.3.4. Catalyst activation. As discussed in Chapter 1, the reductive treatment of the catalyst enhances the activity of Pt/SnO$_2$ and might be involved in the formation of active sites involving both Pt and Sn. In that sense, the reductive treatment is intimately
involved with activating this catalyst composition. Until recently, it was believed that exposure to air—or more specifically to O₂—after the reductive treatment even at ambient temperature would "undo" the changes to the catalyst created by the reductive treatment. To investigate the validity of this, the CO-oxidation activity of a single sample was measured between each of the following consecutive conditions: (1) prior to reduction, (2) after reduction followed by a 44-hour exposure to ambient air, (3) after a 70-hour exposure to ambient air without additional reduction, and (4) after a second reduction followed by a 28-day exposure to ambient air. The composition of the catalyst sample used was a 3.4% Pt/SnO₂ coating on unetched cordierite monolith. For conditions 2 and 4, the catalyst was given a standard reduction in 5% CO in He at 125°C as described in Chapter 1.

The results of the activity measurements after each of the four conditions is shown in Figure 2.22. Without reduction, the catalyst activity decays rapidly and shows little activity after the first day of testing. By comparison, after the first reduction, the activity is
an order of magnitude higher and does not begin to show signs of decay until about 15,000 minutes (1.5 weeks) of testing. Comparison of the activities following conditions 1 and 2 shows that the reductive treatment is not only essential to the activity of the catalyst, but also that the catalyst does not revert to its unreduced condition after a short exposure to ambient air. Condition 3 was used to ensure that the gain in activity of the second reductive treatment (condition 4) was not merely a result of outgassing of CO₂, as had been explained in Chapter 1. Because the catalyst showed signs of decay within about 3,000 minutes of testing (2 days) whereas after the second reduction, there were no signs of decay until about 17,000 minutes, the second reduction actually reconditions the catalyst for further use. Furthermore, the exposure to ambient air following the second reduction indicates that the catalyst does not revert to its unreduced condition for long periods of time.

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It is reasonable that the catalyst coatings should require a reductive treatment as a normal step in the catalyst preparation. This can be easily understood by noting the differences in methods of production of the catalyst powders and the catalyst coatings. During the production of the catalyst powders, the PtAH is reduced to finely divided Pt metal on the surface of the tin oxide by adding a reducing agent, namely formic acid, to the tin oxide slurry, and the resulting catalyst is black. During the production of the catalyst coatings, on the other hand, a temperature of 275°C to 300°C is used to decompose the PtAH, far greater than the 200°C required to decompose it. The resulting appearance of the catalyst-coated monoliths, however, is only somewhat darkened—not dark black—as normally seen for finely divided Pt catalysts.

The change from a reducing to an oxidizing environment suggests that the platinum might remain largely as Pt\textsuperscript{2+} under the oxidizing atmosphere of the muffle furnace. Upon reductive treatment, however, the catalysts darken in color to very dark brown to black with Pt loadings as low as 1% relative to the tin oxide. This suggests that the Pt is in a form similar to that on the as-prepared powders. As discussed in surface characterization of Pt/SnO\textsubscript{2}, in Section 1.3.2 of Chapter 1, the Pt exists in several forms, metal, oxides and hydroxides of Pt. In short, a reductive treatment is essential as part of the production of the catalyst coatings.

Also, as explained in Chapter 1, the powdered catalysts benefitted from a reductive treatment in spite of using formic acid reduction of the PtAH during production. The reason for this is probably that they are exposed to an oxygen rich environment at an elevated temperature (150°C) which would enable some of the changes that occur during the reduction to be undone. For this reason the catalyst coatings are cooled to ambient temperature under an inert atmosphere after the reductive treatment step before exposure to air. The kinetic explanation is obvious. Exposure to oxygen at elevated temperatures will increase the rate, over that at ambient temperature, of whatever changes are O\textsubscript{2}-mediated.
Deposition of platinum using PtAH requires a reductive treatment step during the preparation of the catalyst to assure reduction of the Pt(II) to finely divided Pt metal. Only when the catalyst is reduced, does the catalyst approach its maximum activity. Also, air exposure does not undo the improvements afforded by the reductive treatment step. Nor does extended air exposure severely hurt the catalyst activity in that the catalyst never returns to the poor activity found in the pre-reduced state.

2.4. SUMMARY

It is apparent from the information presented in this chapter, that the activity of the catalyst can most be affected by modifying the SnO$_2$ layer. It is important that all of the noble metal be located on the tin oxide—not on the substrate. As a result, it is necessary to use a low surface area substrate with large size pores to enable complete coverage with tin oxide. It is also important to have good noble metal dispersion which can be accomplished by increasing the total amount of tin oxide or by etching the tin oxide-coated cordierite. To the same end, it is also important to employ low processing temperatures during preparation of the catalyst in order to prevent loss of valuable tin oxide surface area. A reductive processing step is essential for high activity and can also be used to regenerate catalyst activity after extended use for CO oxidation.
CHAPTER 3
OXIDATION OF VOLATILE ORGANIC COMPOUNDS

3.1. INTRODUCTION

With government standards on the emission of toxic gases growing ever more strict, the need to develop more effective, less expensive means for removing these gases is growing ever more important. Flue gases still contain high amounts of CO, unburned hydrocarbons, SO\textsubscript{X}, and NO\textsubscript{X}.\textsuperscript{1} Noble metal catalysts traditionally used for abatement applications and automobile emissions control require elevated temperatures to work efficiently. If the reaction temperature exceeds 400°C and only a slight excess of oxygen is present the production of NO\textsubscript{X} emission increases.\textsuperscript{2} Furthermore, 95% of the CO found in automobile exhaust is produced during the first 5 minutes of operation until the catalyst in the catalytic converter (generally a combination of platinum, palladium and rhodium) heats up to a high enough temperature to oxidize the CO to CO\textsubscript{2}.

Since the development of Pt/SnO\textsubscript{2} catalysts for CO oxidation in CO\textsubscript{2} lasers, research has been extended to investigate the passive removal of CO from ambient air in houses and other enclosed spaces—including commercial buildings, automobiles, airplanes, submarines, etc. Even with CO detectors, CO poisoning from incompletely combusted fuels in home heating systems continues to be a threat. A variety of other potential applications has been proposed, such as removal of CO from breathing gas and other oxygen-containing gases, removal of CO from internal-combustion engine exhaust during cool-engine operation, as well as use in selective chemical sensors.

In addition to the applications involving CO oxidation, the potential for oxidizing other compounds over Pt/SnO\textsubscript{2}-based catalysts has been investigated. Among these are formaldehyde, C\textsubscript{1} to C\textsubscript{3} alcohols, and the straight-chain C\textsubscript{1} to C\textsubscript{5} hydrocarbons. These
molecules serve as model molecules to generate an understanding of the trends in oxidation likely to be found for other volatile organic compounds (VOC).

The capacity for Pt/SnO\textsubscript{2} to catalyze the complete oxidation of carbon monoxide, formaldehyde, and methanol to CO\textsubscript{2} and H\textsubscript{2}O at ambient temperatures and below, as well as the saturated hydrocarbons at temperatures significantly lower than attainable on traditional noble metal catalysts, rests on two principles. First, the catalyst possesses two different kinds of sites (at least). One set of sites can adsorb the species to be oxidized while the other set of sites chemisorbs O\textsubscript{2}. Second, the catalyst possesses surface hydroxyl groups which may act as the oxidizing agents or may aid in the adsorption and dissociation of gas phase O\textsubscript{2} at ambient and sub-ambient temperatures. If the basis for ambient temperature oxidation lies in the ability of Pt/SnO\textsubscript{2} to dissociatively adsorb O\textsubscript{2}, then it ought to have a more general capacity for oxidation of other species at lower temperatures than on traditional catalysts. This chapter reports on the oxidation and conversion of compounds other than CO.

3.2. EXPERIMENTAL

3.2.1. Catalyst preparation. Catalyst samples with both high and low loadings of Pt were prepared. For the formaldehyde, methanol, and ethanol conversion studies, samples of Pt, SnO\textsubscript{2}, and Pt/SnO\textsubscript{2} on cordierite were used to investigate the effect of each on the mechanism. The SnO\textsubscript{2} and Pt/SnO\textsubscript{2} catalyst samples were prepared according to the instructions presented in Chapter 2 on unetched cordierite honeycomb monolith. The Pt was deposited on cordierite in the same manner as Pt was deposited on the SnO\textsubscript{2}-coated cordierite described in Chapter 2 except that, prior to coating, the cordierite was etched for 48 hours in 1.5 M HNO\textsubscript{3} at about 100°C to increase the surface area to about 220 m\textsuperscript{2}/g. The surface area was increased to improve the dispersion of the Pt, and thereby minimize any differences in Pt surface area between samples. The 0.5% Pt on cordierite sample
weighed 0.4765 g and contained 1.1 mg Pt. The SnO\textsubscript{2} on cordierite sample weighed 0.476 g and contained 0.112 g SnO\textsubscript{2}. The 1% Pt/SnO\textsubscript{2} on cordierite sample weighed 0.4807 g and contained 0.115 grams of catalyst of which 1.3 mg was Pt. To minimize differences in flow effects between samples, equal sample size and geometries were used, specifically a 3 by 3 channel section, 1.5-in long, cut from a larger sample with a cell density of 400 cells/in\textsuperscript{2}.

For some of the formaldehyde, alcohols and all of the hydrocarbon oxidation studies, the Pt/SnO\textsubscript{2} catalyst samples tested contained higher Pt loadings, from 10 to 12% relative to the SnO\textsubscript{2}. The weight of the samples varied from 0.4 to 0.5 g total weight giving a catalyst coating weight of from 40 to 50 mg.

3.2.2. Activity testing. Capacity for oxidation of formaldehyde, methanol, ethanol, n-propanol, iso-propanol, and the straight-chain hydrocarbons from C\textsubscript{1} to C\textsubscript{5} was examined in the reactor system described in Chapter 1. Differences exist in the manner in which the analyte being investigated was delivered to the catalyst and are discussed below.

**Formaldehyde, CH\textsubscript{2}O.** Formaldehyde was provided by the thermal decomposition of paraformaldehyde. Approximately ten grams of paraformaldehyde (Sigma Chemical) was sealed in a 1-oz glass bottle with a rubber stopper and RTV silicone sealant. The rubber stopper was fitted with 1/8-in, stainless steel, inlet and outlet tubes that fed into the head space. The CH\textsubscript{2}O and was incorporated into the test gas stream by flowing an O\textsubscript{2}-containing or a CO- and O\textsubscript{2}-containing gas mixture through the head space. The gas mixtures used were one of the following: (1) 5% O\textsubscript{2} in He, (2) 1% CO\textsubscript{2}, 1% CO, 1% O\textsubscript{2}, balance He (Scott Specialty Gases), or (3) 500 ppm CO, 20% O\textsubscript{2}, balance He (MG Industries). The first gas mixture was used to determine the oxidation of CH\textsubscript{2}O in excess O\textsubscript{2}. The second and third gas mixtures were used to study the simultaneous oxidation of CO and CH\textsubscript{2}O in a stoichiometric amount of O\textsubscript{2} and excess O\textsubscript{2}, respectively.

The gas mixture flow rate was controlled at 25±1 sccm using a Hastings mass flow
controller or a needle valve in conjunction with a Hastings mass flow meter. The temperature of the paraformaldehyde was controlled between 35°C and 55°C using a heating mantle in conjunction with a Whatman temperature controller. The temperature was adjusted to attain the desired concentration of CH$_2$O in the reaction gas mixture. The 35°C temperature gave a concentration of at least 500 ppm CH$_2$O and the 55°C temperature gave a CH$_2$O concentration of at least 5000 ppm. These values are lower limits considering potential adsorption on the catalyst. The feed gas containing the formaldehyde was passed over the catalyst sample in the plug flow reactor system and then to a Shimadzu GC-8A with TCD detection for quantitation of CO$_2$, O$_2$, CH$_2$O and H$_2$O.

**Alcohols.** Delivery of the alcohols was similar to that for the formaldehyde with the exception that the alcohols required no heating. About 40 mL of each alcohol to be tested, methanol, ethanol, 1-propanol, and 2-propanol, was sealed in a 100-mL round bottom flask with a rubber stopper fitted with 1/8-inch, stainless steel inlet and outlet lines into the head space. The rubber stopper was further sealed with RTV silicone. For the tests using high concentrations in the reaction gas mixture, the analyte was swept from the flask to the catalyst by passing a 12.5 sccm stream of 5% O$_2$ in He directly through the head space. To attain lower concentrations, the carrier gas was split into two streams allowing only a portion to pass through the head space; the streams were then consolidated. The amount of carrier passing through the head space was controlled by choking the tubing diameter at the inlet and outlet of the flask with various lengths of 1/16th-in stainless steel tubing with a 0.020-inch inside diameter. By varying the length of the tubing the concentration could be controlled.

For tests involving the effect of O$_2$ concentration, the final composition was prepared by blending a gas mixture containing 2% Ne in O$_2$ with 99.999% He using Hastings Mass Flow Controllers. The total O$_2$ concentration was held at 20% for the 1-propanol and 2-propanol. For methanol and ethanol, it was varied from 0% to 20% to
determine the effects of $O_2$ concentration on the reactions over the catalyst.

As for formaldehyde oxidation, tests for the effect of CO on the conversion of methanol were performed using the reaction gas mixture containing 500 ppm CO, 20% $O_2$, balance He.

**Hydrocarbons.** The straight-chain, saturated $C_1$ to $C_5$ hydrocarbons were oxidized over Pt/SnO$_2$ catalyst as a function of catalyst temperature in order to obtain temperature activity profiles. The $C_1$ to $C_5$ hydrocarbon test gases used were gravimetric standards obtained from MG Industries in concentrations containing nominally 1000 ppm in Ultra Zero Air.

The reactor tubes in which the catalyst samples were held were mounted in the temperature controlled oven of a GC equipped with a flame ionization detector (FID). The test gas was passed over the catalyst and directly to the FID without separation on a column. Test gas flow over the catalyst was controlled at 10 sccm using a Hastings flow transducer. The effluent gas from the reactor or bypass tube flow directly to the FID without intervening columns thus only total hydrocarbon concentration was determined.

A typical temperature-activity profile was obtained as follows: (1) The catalyst was exposed to nitrogen or air in order to establish a baseline at 35°C (0 ppm HC). (2) The air stream was switched to the HC test gas and allowed to equilibrate until a stable line was obtained indicating the total unconverted HC concentration. (3) The temperature was incremented at 2°C per minute for 5 minutes (10°C total) and then held for 15 minutes to allow equilibration. The temperature was ramped from 35°C up to a temperature high enough to completely oxidize the HC, anywhere from 190°C to 280°C depending on the HC. And (4) the final temperature is held for 15 minutes and then the system was cooled back to 35°C to check the original baseline activity.

The process was repeated for each HC from $C_5$ to $C_1$ using the same catalyst.
sample. The order of HC from C$_5$ to C$_1$ was used so that the catalyst was exposed to progressively higher temperatures versus being exposed to higher temperatures first.

3.3. RESULTS

3.3.1. Formaldehyde. Formaldehyde, CH$_2$O, is a compound used in the production of textiles, in preservation of cadavers, and in fumigation to rid enclosed spaces of pests. It is toxic in small amounts and is therefore a constituent of indoor air which must be removed to insure safe air quality. Because of its use in the textile industry, CH$_2$O is the most prevalent indoor air pollutant next to CO. It will be presented in this work, that Pt/SnO$_2$-based catalysts are capable of oxidizing CH$_2$O to CO$_2$ at temperatures as low as -5°C, perhaps lower, without the production of CO or other by-products.

The decomposition of CH$_2$O over Pt catalysts has been studied before. It has been observed that CH$_2$O decomposes at sub-ambient temperatures (-195°C) to adsorbed hydrogen atoms and CO. In the presence of excess oxygen, CH$_2$O is completely oxidized to CO$_2$ and H$_2$O with no detectable CO at ambient pressure and temperature. In the presence of CO, however, the normally observed oxidation of CH$_2$O is completely stopped as the Pt surface becomes saturated with CO. Because of this CO saturation, the temperature-activity profile for the oxidation of CH$_2$O follows that of CO. The CO must first be oxidized to CO$_2$ to free up surface sites on the Pt for CH$_2$O adsorption. Since Pt/SnO$_2$ oxidizes CO at temperatures as low as -70°C, it is reasonable to assume that the low-temperature oxidation of CH$_2$O will not be inhibited over Pt/SnO$_2$.

Effect of CO on CH$_2$O oxidation. Because Pt alone can oxidize CH$_2$O at ambient temperature to CO$_2$ and H$_2$O, it was important to determine if Pt/SnO$_2$ or Pt alone was responsible for the oxidation of the formaldehyde. Oxidation tests in which both CO and CH$_2$O were present in the reaction gas mixture provided some insight. This section reports on the effect of CO on the oxidation of CH$_2$O over Pt, SnO$_2$, and Pt/SnO$_2$. In order
to determine the active component, oxidation over the various portions of the catalyst composition were used as controls, namely, Pt on etched cordierite, SnO\textsubscript{2} on unetched cordierite, as well as Pt/SnO\textsubscript{2} on unetched cordierite.

Table 3.1 below shows a qualitative summary of the oxidation capacity of each sample under each of the test gas mixtures used. At the 23±1°C test temperature, SnO\textsubscript{2} showed adsorption of CH\textsubscript{2}O, but no oxidation of either CO or CH\textsubscript{2}O at ambient temperature. This indicated that Pt was essential for the ambient temperature oxidation of CO and CH\textsubscript{2}O. In the absence of CO, complete oxidation of CH\textsubscript{2}O to CO\textsubscript{2} and H\textsubscript{2}O occurred over both Pt and Pt/SnO\textsubscript{2}. In the presence of CO, with a stoichiometric amount of O\textsubscript{2}, on the other hand, Pt showed no oxidation of either CO or formaldehyde. This is consistent with the research of McCabe and Mitchell discussed earlier.\textsuperscript{4}

Over Pt/SnO\textsubscript{2}, some oxidation of CO and/or CH\textsubscript{2}O occurred initially and then rapidly fell to no oxidation of either species. This was not expected since CO readily oxidizes over Pt/SnO\textsubscript{2} at 23°C. Upon removing the CH\textsubscript{2}O from the test gas stream, however, spontaneous CH\textsubscript{2}O desorption from the catalyst occurred, and the CO oxidation capacity returned. This indicates (1) that a molecular adsorption-desorption equilibrium exists for CH\textsubscript{2}O on Pt and Pt/SnO\textsubscript{2} and (2) that CH\textsubscript{2}O prevents the oxidation of the CO. Because CO does not adsorb on SnO\textsubscript{2} and CH\textsubscript{2}O clearly adsorbs on SnO\textsubscript{2}, it is apparent that CH\textsubscript{2}O blocks the adsorption sites of O\textsubscript{2} on SnO\textsubscript{2}. This provides evidence that the

<table>
<thead>
<tr>
<th>Sample on cordierite</th>
<th>CH\textsubscript{2}O xs O\textsubscript{2}</th>
<th>CO xs O\textsubscript{2}</th>
<th>CH\textsubscript{2}O + CO-Stoich. O\textsubscript{2}</th>
<th>CH\textsubscript{2}O + CO-xs O\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CH\textsubscript{2}O</td>
<td>CO</td>
</tr>
<tr>
<td>SnO\textsubscript{2}</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Pt</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>initially no</td>
</tr>
<tr>
<td>Pt/SnO\textsubscript{2}</td>
<td>yes</td>
<td>yes</td>
<td>initially yes</td>
<td>yes</td>
</tr>
</tbody>
</table>
dissociative adsorption of $O_2$ occurs on $SnO_2$ sites or at the interface of Pt and $SnO_2$. The concentrations of $CH_2O$ and CO in the reaction gas mixture were high, 1% (10000 ppm) CO and 0.5% (5000 ppm) $CH_2O$. These high concentrations suggest the following events leading to the cessation of oxidation over Pt/$SnO_2$. Initially, some CO and $CH_2O$ were oxidized to $CO_2$ and $H_2O$. Because the feed rate of each surpassed the oxidation rate, however, $CH_2O$ adsorption saturated the $SnO_2$ preventing further $O_2$ dissociative adsorption and consequently CO oxidation. Then CO was able to rapidly saturate the Pt surface preventing further $CH_2O$ adsorption and oxidation.

When a gross excess of $O_2$ was present in the reaction gas mixture, CO and $CH_2O$ were completely oxidized over the Pt/$SnO_2$ catalyst for greater than 24 hours with no appreciable signs of decay. Because the concentrations of CO and $CH_2O$, about 500 ppm each, were low enough to prevent saturation of the active sites (i.e. the oxidation rate exceeded the feed rate) sustained oxidation remained possible. Over the Pt catalyst, on the other hand, initially no $CH_2O$ or CO was present in the effluent stream; $CO_2$ was present. Within about 60 minutes, CO appeared in the effluent stream, and the $CH_2O$ oxidation rate began decreasing and eventually ceased after about 16 hours. This is similar to what happened over the Pt catalyst under the stoichiometric concentrations of CO, $CH_2O$ and $O_2$. The loss of activity took longer here under low CO and $CH_2O$ concentration.

This study indicates that Pt/$SnO_2$ provides a means for the low-temperature oxidation of mixtures of CO and $CH_2O$ which Pt by itself cannot provide. In addition, the study provides evidence that SnO2 is responsible for the dissociative adsorption of O2. This will be discussed in greater detail in Chapters 4 and 5.

**Long-term $CH_2O$ oxidation study.** A long term study of a 29-mg sample of 11.8% Pt/$SnO_2$ coating on cordierite was carried out to investigate catalyst longevity. The catalyst temperature was controlled at 25°C using a refrigeration unit in conjunction with an Omega temperature controller. The temperature of the paraformaldehyde was controlled at
57°C. Based on the amount of CO$_2$ produced, the amount of CH$_2$O reaching the catalyst was estimated at roughly 7500-8200 ppm. No CO or CH$_2$O was detected.

Figure 3.1 shows the concentrations of CO$_2$ and CH$_2$O in the catalyst effluent stream over 37,000 minutes (15 days). During the first 24,000 min (17 day), the catalyst completely oxidized the formaldehyde to below detectable limits. At 24,000 min a breakthrough of CH$_2$O occurred causing the oxidation activity to decrease rapidly to about one-eighth its original level with a corresponding increase in CH$_2$O. This breakthrough suggests that the oxidation rate of CH$_2$O lagged behind its adsorption rate at 25°C. After a steady-state level of CO$_2$ production was established, the CH$_2$O was removed from reaction gas mixture for about 7 hours in order to enable adsorbed CH$_2$O to react with O$_2$ in the reaction gas mixture and thereby clean the catalyst surface. During this period, only CO$_2$ was detected in the effluent stream—no CH$_2$O. Upon re-exposing the catalyst to the

![Figure 3.1. The long-term oxidation of CH$_2$O to CO$_2$ over Pt/SnO$_2$ on cordierite honeycomb monolith at 25°C.](image-url)
CH$_2$O-containing reaction gas mixture, the activity temporarily returned to complete oxidation but rapidly decayed to a level about twice that the value after the original breakthrough and then continued to decay more slowly to the level before the He flush. This suggests that the outgassing period was insufficiently long to enable the O$_2$ to completely react with the residual CH$_2$O.

**Sub-ambient CH$_2$O oxidation.** This test was performed to determine the capacity of Pt/SnO$_2$ for the oxidation of CH$_2$O at temperatures from 25°C to -5°C. The catalyst tested was 11.8% Pt/SnO$_2$ on etched cordierite. The total sample weight tested was 0.2870 g total or 63.4 mg of catalyst of which 7.48 mg is Pt. The catalyst was tested plug-flow style in a quartz reactor tube as shown in Figure 1.2. The catalyst temperature was controlled using a refrigerator in combination with an Omega temperature controller. The temperature of the paraformaldehyde was controlled at 40°C. The gas mixture used to carry the CH$_2$O to the catalyst was 5% O$_2$ in He, and a flow rate of 25 scm was used. The amount of CH$_2$O reaching the catalyst was estimated from the amount of CO$_2$ produced estimated at 25°C, 3200±160 ppm.

The catalyst temperature was decreased from 25°C to -5°C in decrements of 5°C and monitored for 24 hours at each temperature for CO$_2$ and CH$_2$O. Figure 3.2 shows the average concentrations of CO$_2$, O$_2$, and CH$_2$O at each catalyst temperature. The error bars represent the standard deviation in the CO$_2$ concentration measured at each temperature over the 24-hour period. The measured concentration of CO$_2$ varied from 2500 to 3200 ppm from 25°C down to 5°C. This range is likely the random error resulting from poor resolution of the CO$_2$ peak on GC chromatograms rather than due to activity or adsorption fluctuations of the catalyst itself. The CO$_2$ produced during the oxidation of CH$_2$O remained relatively unchanged until the temperature was decreased to 0°C and below. At 0°C and -5°C the concentration of CO$_2$ being produced decreased. No CH$_2$O was detected until the catalyst remained at -5°C for about 24 hours. That the CH$_2$O concentration did not
increase by at least 2000 ppm, as would be expected from mass balance considerations,
verifies that the CH₂O continued to adsorb on the catalyst even after 24 hours at -5°C.
Also, because water is produced during the oxidation of CH₂O and freezes at 0°C,
irreversible water adsorption on the catalyst was likely one responsible factor in loss in the
CH₂O oxidation capacity of Pt/SnO₂.

The O₂ remained almost constant at each temperature as would be expected since
there was a gross excess of the amount required for complete oxidation of the CH₂O in the
reaction gas mixture. There was a slight but distinct increase in the O₂ concentration once
the CH₂O oxidation rate began to decrease indicating a decrease in the O₂ adsorption
capacity of the catalyst. This too may have been due to the presence of adsorbed water.
Because water is necessarily a product of CH₂O oxidation, a means for removing the water
is essential in using either Pt or Pt/SnO₂ as a catalyst for oxidation below 0°C.

Figure 3.2. The effect of temperature on the CH₂O-oxidation activity of
Pt/SnO₂ on cordierite honeycomb monolith.
3.3.2. Methanol, CH$_3$OH. Unlike the oxidation of formaldehyde, the oxidation of methanol showed the formation of a by-product which was identified as methyl formate as determined by GC. Because a by-product was formed, conversion is a more appropriate term than oxidation. The conversion of methanol over 100 mg of catalyst containing a high Pt loading, 15% Pt/SnO$_2$, showed nearly complete conversion to CO$_2$ and H$_2$O with a small amount of methylformate, CH$_3$OOCH, at 35°C. In this test, the flow rate was 12.5 sccm and the reaction gas mixture contained 1.0% methanol with 5.0% O$_2$ balance He. The formation of CH$_3$OOCH over Pt alone has been reported by McCabe and Mitchell.$^4$

Figure 3.3 shows the concentrations of CH$_3$OH, CH$_3$OOCH, and CO$_2$ in the effluent stream from the catalyst as a function of temperature. Note that the concentration of methyl formate was multiplied by a factor of 10 so that it would show up more clearly on

![Figure 3.3](image_url)

**Figure 3.3. The temperature-activity profile for methanol conversion to methyl formate and CO$_2$ over 15% Pt/SnO$_2$ on cordierite.**

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the graph. The shape of the CO₂ curve suggests that the light-off temperature (temperature required for conversion of 50% of analyte) is well below ambient temperature. As such, it cannot be determined if the oxidation process is aided or inhibited by the presence of the SnO₂.

In addition to the temperature-activity profile, the effect of O₂ concentration on the oxidation of methanol over the same catalyst sample was investigated. Figure 3.4 shows the concentration of CO₂ and CH₃OOCH in the effluent stream of the catalyst at 34°C. All of the CH₃OH was converted to CO₂, H₂O, and CH₃OOCH over the entire concentration range of O₂ down to 2% O₂. Once below 2% O₂, the concentration of CH₃OOCH increased and CH₃OH appeared in the effluent stream. The likely cause was O₂ deprivation, as the stoichiometric concentration of O₂ required for complete oxidation of 1% CH₃OH would be 1.5% O₂.

Figure 3.4. The effect of O₂ concentration on the product distribution in the oxidation of methanol over 15% Pt/SnO₂ on cordierite.
Another interesting and almost contradictory feature of the temperature-activity profile is that the production of CO$_2$ increases as the concentration of O$_2$ decreases, in particular between 5% and 2% O$_2$, until sub-stoichiometric concentrations are reached. Concurrently, the concentration of CH$_3$OOCH decreases slightly in this region. This amount of O$_2$, slightly greater than stoichiometric, suppresses the formation of CH$_3$OOCH while enhancing the formation of CO$_2$. The error in measuring the concentrations of CO$_2$ and CH$_3$OOCH are small, on the order of the size of the symbols (about ±150 ppm) used to represent them in the temperature-activity profile, so the observed behavior is real.

It would be expected that a reduction of oxygen relative to CH$_3$OH would increase the amount of the partially oxidized product, CH$_3$OOCH, over the completely oxidized product. The inhibition of conversion of CH$_3$OH to CH$_3$OOCH over Pt/SnO$_2$ is, however, consistent with the observed decomposition behavior of CH$_3$OH in vacuum over many metal surfaces having preadsorbed O atoms. It has been speculated that preadsorbed atomic oxygen on Fe, Cu, and Ag stabilizes the methoxy group, –OCH$_3$, resulting in a higher temperature decomposition into CO and H$_2$.\textsuperscript{5} On Pt(111), this stabilization amounts to a 30°C increase in the decomposition temperature (140 K to 170K).\textsuperscript{6} On the other hand, this “stabilization” may merely be a competition between O$_2$ and –OCH$_3$ for the sites required for decomposition of the –OCH$_3$. Under the pressure and temperature conditions used in this study, competition seems more valid. As the molar amounts of oxygen and CH$_3$OH approach each other, the competition between CH$_3$OH decomposition and O$_2$ adsorption would decrease thereby increasing the chance for complete oxidation to CO$_2$.

**Effect of CO on CH$_3$OH oxidation.** Adding CO to the reaction gas mixture provides additional insight into the reaction of CH$_3$OH and O$_2$ on Pt and Pt/SnO$_2$ catalysts. The results are similar to those found for competitive oxidation of CH$_2$O and CO over the same 0.47% Pt, 1% Pt/SnO$_2$, and SnO$_2$ samples on cordierite. As with formaldehyde, SnO$_2$ on cordierite adsorbed some CH$_3$OH, but showed no oxidation to CO$_2$ and H$_2$O nor
conversion to CH$_3$OOCH. After about 2 hours, the SnO$_2$ on cordierite had reached its adsorption capacity, and the CH$_3$OH concentration in the effluent stream had returned to the original concentration of the reaction gas mixture.

The conversion of CH$_3$OH in the presence and absence of CO for 0.47% Pt/cordierite and 1% Pt/SnO$_2$ at a temperature of about 22°C will be presented in the next four figures. Figures 3.5 and 3.6 show the composition of the effluent stream from the Pt and Pt/SnO$_2$ catalysts at 22°C, for the test gas mixture containing 6900 ppm CH$_3$OH and 5% O$_2$, without CO. The scales of both independent and dependent axes were kept the same in both figures for the sake of comparison. The Pt catalyst required about 200 minutes for the reaction to start producing significant quantities of CO$_2$ and CH$_3$OOCH. Upon reaching this higher oxidation rate, however, the concentrations of CO$_2$ and CH$_3$OOCH increased dramatically, and larger amounts of CH$_3$OH were adsorbed from the reaction gas stream—but were not converted. This is consistent with findings that multilayer adsorption of CH$_3$OH (and the C$_2$ to C$_4$ alcohols) after chemisorption of a partial monolayer has been reported on Pt (111) single crystals. A mass balance calculation indicates that more CH$_3$OH was adsorbed than could be accounted for in the products throughout the reaction period. In addition, the trend in the curves indicates that the reaction rate was increasing as the CH$_3$OH adsorption increased. Considering these observations it is reasonable to hypothesize that Pt requires an induction period involving chemisorption of CH$_3$OH which is then followed by a more rapid physical adsorption. The induction period is also consistent with the aforementioned stabilization and/or competition for active sites of preadsorbed oxygen on clean metal surfaces. The rate would increase as the preadsorbed oxygen is removed and replaced by CH$_3$OH.

By contrast to Pt, the Pt/SnO$_2$ catalyst reached equilibrium within 60 minutes producing about 600 ppm CO$_2$ and 850 ppm methylformate and leaving 3000 ppm methanol unoxidized. A mass balance calculation indicates that about 1600 ppm of
Figure 3.5. The effluent stream composition resulting from conversion of 6900 ppm CH₃OH and 5% O₂ in He over 0.47% Pt/cordierite at 22°C.

Figure 3.6. The effluent stream composition resulting from conversion of 6900 ppm CH₃OH and 5% O₂ in He over 1% Pt/SnO₂ at 22°C.
methanol was adsorbed from the reaction gas mixture onto the catalyst throughout the test. In spite of the greater testing period, the Pt/SnO₂ catalyst showed no signs of increasing adsorption of methanol as had the Pt catalyst. This suggests that the reaction mechanisms may be different for the Pt and the Pt/SnO₂ catalysts. Specifically, it is reasonable that the presence of the SnO₂ enabled the dissociative adsorption of O₂ thereby eliminating competition for active sites on Pt with CH₃OH. This elimination of competition would also allow the reaction to proceed more rapidly to a steady-state. More about this topic will be discussed in Chapter 5.

The effect of CO on the CH₃OH conversion over Pt and Pt/SnO₂ catalysts provides further insight into the mechanism. Figure 3.7 shows the composition of the effluent stream from 0.47% Pt/cordierite. For this test, the concentration of CH₃OH in the reaction gas mixture was reduced from 6900 ppm to about 3000 ppm. The added CO concentration

![Figure 3.7. The effect of 500 ppm CO on the oxidation of 3000 ppm CH₃OH over 0.47% Pt/cordierite catalyst.](image_url)
was 500 ppm, and that of the $O_2$ 20% (200,000 ppm). The same sample of catalyst in this test was used in the previous test without CO and was exposed to ambient air between tests. Several differences arise due to the presence of CO. First, after a period of adsorption from the reaction gas mixture, the $CH_3OH$ equilibrated to a steady-state level of around 2500 ppm rather than continuing to decline as happened in the absence of CO (Figure 3.5). Second, the $CH_3OOCH$ remained below its detection limit of about 150 ppm. And third, the CO concentration remained at 500 ppm throughout the test indicating it could not be oxidized over Pt. It should be noted that CO could not be monitored for the first 200 minutes due to interference from water eluting from the GC column at nearly the same time as CO was giving falsely high readings. It is possible that some CO was oxidized during the first 200 minutes by preadsorbed oxygen on the Pt as this is commonly used during titration experiments to determine Pt dispersion.

Figure 3.8 is an expansion of the final 200 minutes of the test shown in Figure 3.7. When the $CH_3OH$ was removed from the reaction gas mixture, the $CO_2$ concentration began declining slightly and the CO concentration remained at 500 ppm. The absence of CO oxidation throughout the test indicates that the $CO_2$ produced resulted from the oxidation of $CH_3OH$—not CO. The absence of CO oxidation even in the absence of $CH_3OH$ indicates, not surprisingly, that $CH_3OH$ was not responsible for preventing CO oxidation. When the CO was removed from the reaction gas mixture and the $CH_3OH$ returned, the concentration of $CO_2$ increased from 150 ppm to almost 800 ppm and $CH_3OOCH$ appeared at a level of about 500 ppm. These observations indicate that CO interferes with the formation of $CH_3OOCH$ and the oxidation of $CH_3OH$ to $CO_2$. It is possible that some $CH_3OOCH$ was produced in the presence of CO; detection limits prevented determining its presence. The probable reason for the interference was that, as with formaldehyde, CO preferentially adsorbed on the Pt surface preventing adsorption and conversion of methanol.
Interestingly, complete oxidation of CH$_3$OH to CO$_2$ and H$_2$O was preferred to partial oxidation to CH$_3$OOCH. This suggests that CO might prevent surface diffusion of chemisorbed formate, OOCH, and methoxy groups, OCH$_3$, and thereby prevent their reaction to form CH$_3$OOCH. It is also possible that the Pt surface is so saturated by CO that adsorption of methanol and its consequent reactions are prevented. This "stabilization" of intermediates, then, would enhance the pathway leading to complete oxidation to CO$_2$ and H$_2$O. This stabilization is similar to that provided for OCH$_3$ by preadsorbed O on metal surfaces, mentioned in the previous section.

Figure 3.9 shows the composition of the effluent stream from the 1% Pt/SnO$_2$ sample when 500 ppm CO was present in the reaction gas mixture. In this test the concentration of methanol was only about 1000 ppm and the concentration of O$_2$ 20%. Again, several points are worth noting. First, unlike Pt alone, Pt/SnO$_2$ was able to oxidize CO in the presence of CH$_3$OH and consequently, CH$_3$OH as well. Second, when CO$_2$ concentration started declining the first time (at about 200 minutes), both CO and CH$_3$OH...
Figure 3.9. The effect of 500 ppm CO on the oxidation of 3000 ppm CH₃OH over 1% Pt/SnO₂ on cordierite.

appeared in the effluent stream. Third, when the CH₃OH was removed from the reaction gas mixture, a large spike of CO₂ appeared in the effluent stream followed by a decline to about 500 ppm. Fourth, the total amount of CH₃OH can only be accounted for by speculating adsorption on the catalyst throughout the test period. And fifth, although not shown in the figure, CH₂OOCH was only detected when the CO₂ concentration fell below 500 ppm. Otherwise, methylformate remained below detectable levels or simply was absent throughout the test period. The curve for methylformate was left out so as to prevent interference with viewing the other data.

Lack of temperature control during the test allowed the catalyst temperature to change according to the room temperature as shown in the figure. This provided some interesting information. The decline in CO₂ concentration after the first 200 minutes was due to a slow drop in room temperature. As the temperature fell, both CO and CH₃OH appeared in the effluent stream indicating incomplete oxidation of CO. Mass balance
considerations indicate that the CO$_2$ arose from the oxidation of portions of both CO and CH$_3$OH. When the room temperature rose again, all CO, CH$_3$OH, and CH$_3$OOCH were removed from the reaction gas mixture again, and the CO$_2$ concentration increased.

Although not shown, the same catalyst was tested with 3000 ppm methanol in the reaction gas mixture rather than the 1000 ppm used above. In this test, the CO$_2$ concentration started at a lower concentration and fell to zero followed by a rise in the methanol concentration to near 3000 ppm. This indicates that methanol prevented oxidation of CO. Because methanol absorbs onto SnO$_2$ as well as onto Pt, it is possible that methanol adsorption prevents dissociative adsorption of O$_2$ on SnO$_2$. Formaldehyde created the same activity-extinguishing effect in the presence of CO when high concentrations of both were present in the reaction gas mixture. Ultimately, these observations indicate that adsorption of methanol and formaldehyde on SnO$_2$ is favored to dissociative adsorption of O$_2$. More on this point will be discussed in Chapters 4 and 5.

Based on the data presented thus far in the chapter, the adsorption probabilities of CO, O$_2$, methanol, and formaldehyde on Pt and SnO$_2$ can be surmised. Near ambient temperature, the order of increasing adsorption probability on Pt is O$_2$ < formaldehyde = methanol < CO. On SnO$_2$ the order is CO < O$_2$ < formaldehyde = methanol. No distinction is made between methanol and formaldehyde because such information is irrelevant here. This particular order of adsorption probability imposes two conditions for maintaining continuous oxidation of mixtures of formaldehyde and CO or methanol and CO over Pt/SnO$_2$: (1) the CO feed rate must be less than or equal to the catalyst’s capacity to oxidize it to CO$_2$, and (2) the concentration of the organic species in the reaction gas mixture must be small enough, or its oxidation rate great enough, to prevent saturation of the SnO$_2$. If the first condition is not met, then the following chain of events will occur: (1) excess CO saturates the Pt; (2) adsorption and oxidation of methanol or formaldehyde ceases; (3) methanol or formaldehyde saturates the SnO$_2$ preventing dissociative adsorption of O$_2$; and
(4) CO oxidation ceases. If the second condition is not met then a similar chain of events occurs, but in a different order: (1) methanol or formaldehyde saturates the SnO₂ preventing further dissociative adsorption of O₂; (2) CO oxidation ceases; (3) CO saturates the Pt; and (4) methanol or formaldehyde oxidation ceases.

3.3.3. Ethanol, CH₃CH₂OH. Figure 3.10 shows the temperature-activity profile for the conversion of about 3000 ppm ethanol over 1% Pt/SnO₂ on cordierite. As with methanol, the catalyst can absorb a considerable amount of ethanol. Conversion begins at a catalyst temperature of 30°C or lower, producing CO₂, H₂O, and two by-products: methane, CH₄, and ethanal (or acetaldehyde), CH₃CHO. No standard was available for ethanol, so the response factor was estimated from mass balance considerations at 175°C where residual ethanol adsorption was not likely and only CO₂ and CH₄ remained. The relative error in determining the ethanol concentration is approximately

![Figure 3.10. The temperature-activity profile for the conversion of 3000 ppm ethanol over 1% Pt/SnO₂ catalyst coating on cordierite.](image-url)
10%. As the catalyst temperature was increased, oxidation to CO₂ and H₂O increased and the concentration of CH₃CHO decreased while that of CH₄ increased. Both the ethanol and the CH₃CHO were completely converted between 125°C and 155°C.

The CH₄ concentration in the effluent stream decreased at a catalyst temperature above 125°C. It might be tempting to assume that the decrease was due to its oxidation to CO₂ and H₂O, but this is not likely. As will be shown in Section 3.3.5 below, the temperature for 50% conversion of CH₄ over Pt/SnO₂ is about 220°C. Consequently, the CH₄ concentration would not be expected to decrease until a temperature of 220°C is reached. Instead, the decrease was due to an increase in the complete oxidation of ethanol and CH₃CHO to CO₂ and H₂O rather than to CH₄.

Figure 3.11 shows a similar temperature-activity profile for the 0.47% Pt/cordierite sample. The composition of the effluent stream was similar to that of Pt/SnO₂, but

![Figure 3.11. The temperature-activity profile for the conversion of 3000 ppm ethanol over 0.47% Pt on etched cordierite monolith.](image-url)
differences existed in concentrations of CO$_2$ and CH$_3$CHO at equal temperatures. Both samples adsorbed large amounts of ethanol and mass balance never appeared to be attained until temperatures in excess of 155°C were reached. For Pt/SnO$_2$, CO$_2$ appeared at a lower temperature (55°C versus 95°C) and in higher concentrations. By 95°C, the Pt/SnO$_2$ sample was producing 1400 ppm CO$_2$ while the Pt sample only 400 ppm. The Pt catalyst required a temperature of about 115°C to produce an equal amount of CO$_2$. Between 125°C and 155°C the Pt catalyst surpassed the Pt/SnO$_2$ catalysts in CO$_2$ production. Interestingly, this is the temperature at which Pt begins oxidizing CO, one of the decomposition products of ethanol on Pt$^7$ A possible reason for this temperature difference is that SnO$_2$ may provide atomic oxygen to the reaction at a lower temperature than possible on Pt alone thereby increasing the oxidation rate. If this hypothesis is true, then the CH$_3$CHO concentration should peak earlier as well. This was, in fact, observed. The CH$_3$CHO concentration peaked somewhere between 75°C and 95°C for Pt/SnO$_2$, but between 110°C and 125°C for Pt, a difference of 30°C to 35°C. This hypothesis will be considered in further detail in Chapters 4 and 5.

It is also interesting to note that CH$_4$ appears in the effluent streams of both samples at the pinnacle of the curve for CH$_3$CHO, albeit 30°C higher for Pt than for Pt/SnO$_2$. This behavior is consistent with the formation of CH$_4$ from CH$_3$CHO. Typically when a reaction involves the following sequence, A $\rightarrow$ B $\rightarrow$ C, the temperature-activity profile takes on the form shown in 3.10 and 3.11$^8$ This particular system of curves arises because the conversion of B to C is first order in B; hence, sufficient B must be present in order for C to form. As the concentration of B increases, so does C. Here, A is ethanol, B is CH$_3$CHO, and C is CH$_4$. If CH$_4$ is produced from the decomposition of CH$_3$CHO then CH$_3$CHO must be present in sufficient quantity. Once all of the CH$_3$CHO is converted, the concentration of CH$_4$ levels off or decreases.

Further tests were carried out to determine the products in the conversion of ethanal
over Pt and Pt/SnO₂. A mixture of 460 ppm CH₃CHO plus 5000 ppm O₂ was passed over each catalyst sample as a function of temperature. Both effluent streams showed the presence of CO₂, H₂O, and CH₄ as per the temperature-activity profiles shown in Figures 3.10 and 3.11 except that both showed the presence of CO₂ at 24°C, a lower temperature than observed in the oxidation of ethanol. The appearance of CO₂ at this lower temperature suggests that physically adsorbed ethanol may inhibit its own complete oxidation by preventing adsorption of O₂. Although this does not prove that all of the ethanol is first oxidized to CH₃CHO prior to forming CO₂ and CH₄, it is one definite pathway in the oxidation of ethanol over Pt and Pt/SnO₂. It is also reasonable that the ethanol is converted directly into CO₂ and CH₄ without first being oxidized to CH₃CHO. The amount of CO₂ produced in the oxidation of either the ethanol or the ethanal was always far greater than the amount of CH₄ formed. This indicates that CH₄ is a small by-product rather than a main product in the oxidation pathway. More about this mechanism will be discussed in Chapter 5.

3.3.4. 1-Propanol and 2-propanol. Figure 3.12 shows the temperature-activity profile for the oxidation of 1-propanol over 15% Pt/SnO₂ on cordierite. As in the conversion of ethanol over Pt/SnO₂, conversion began at 30°C with the formation of two by-products. One by-product could not be reliably quantitated due to interference from other peaks and so was not included in the figure. It was, however, identified as ethane using GC comparison to an ethane standard. CO₂ was not detected until a temperature of 75°C was reached but may have been present at 30°C. Incomplete resolution from another peak eluting the column slightly prior to the CO₂ likely prevented its detection. Because no standard was available for 1-propanol, the temperature-activity data is shown in terms of percent of the maximum detector response for the 1-propanol in the effluent stream. The unknown by-product, too, is based on the percent maximum of 1-propanol. The CO₂ concentration is shown on the right-hand axis. The concentration of the unknown in the
effluent stream increased from the starting test temperature of 30°C and reached a maximum somewhere between 75°C and 100°C. 1-Propanol was completely converted by 125°C while the by-product concentrations decreased but were still present at 125°C.

Based on identity of the by-products produced during the oxidation of ethanol, it is reasonable to assume that the identity of the second unknown (the one shown in Figure 3.12) was propanal, CH$_3$CH$_2$CHO. This remains speculative, however, because the ethane appeared in its highest concentration at 30°C and then decreased to a lower concentration over the rest of the temperature range. This is nearly the reverse of the behavior observed for the by-products appearing in the ethanol conversion study where the ethanal decreased as the methane increased. Here the hypothesized propanal increased as the ethane decreased.

For 2-propanol, oxidation did not begin until a catalyst temperature of 100°C was reached. About two-thirds was oxidized to CO$_2$ by 150°C, and no by-products were
detected. Because 2-propanol required a higher temperature than 1-propanol for complete oxidation, it is possible that steric hinderance may have hindered its oxidation. This same steric effect may also have prevented the formation of by-products. By comparison to the other alcohols, the OH groups are on terminal carbons whereas for 2-propanol, the OH is on a secondary carbon.

A general trend begins to appear for the oxidation of alcohols by Pt/SnO$_2$-based catalysts. For alcohols whose OH group is on a terminal carbon some oxidation occurs at low catalyst temperatures. As the number of carbons increases, however, the alcohol requires a slightly higher temperature for complete oxidation. Oxidation of alcohols whose OH group is not on a terminal carbon (i.e. 2-propanol) require slightly higher temperature for oxidation than their unbranched counterparts.

The products formed during the conversion of the alcohols over Pt/SnO$_2$ at ambient pressure are consistent with, but somewhat different from, those formed over Pt alone in vacuum. Sexton, et. al. investigated the decomposition of the C$_1$ to C$_4$ alcohols in vacuum on clean and O-preasorbed Pt (111) surfaces. In all cases on the clean surface, the products were a mixture of CO, H, C, and CH$_X$ fragments with the only desorbing products being CO and H$_2$. When pre-adsorbed O was present, water was additionally desorbed, but not CO$_2$ or hydrocarbon. Herein lies the difference between the vacuum and ambient pressure processes. In spite of the oxidizing conditions, ethanol produced some methane and 1-propanol produced some ethane over Pt alone as well as Pt/SnO$_2$. In addition, the aldehyde, ethanal, was formed from ethanol and, likely, propanal was formed from 1-propanol at ambient pressure, but not under conditions of vacuum. The major decomposition products at ambient pressure, CO$_2$ and H$_2$O, are nonetheless consistent with the products produced under vacuum. The CO and H atom in the presence of excess O$_2$ should reasonably go on to form CO$_2$ and H$_2$O, and a small fraction of the CH$_X$ fragments could go on to form methane or ethane by combining with H.

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For 2-propanol, no by-products were formed. This too, is consistent with the decomposition in vacuum. Sexton, et. al. also found that 1-propanol and 1-butanol produced the hydrocarbon fragments ethylidyne, CH\textsubscript{3}C\textsuperscript{-}, and propylidyne, CH\textsubscript{3}CH\textsubscript{2}C\textsuperscript{-}, but not 2-propanol. The H's from the terminal carbon could serve as a source of H to form the methane and ethane observed at ambient pressure. 2-Propanol could not form such a species due to the absence of a terminal OH. Instead it could only form CH\textsubscript{3}\textsuperscript{-} and CO, but no similar source of H. Once decomposition started, lack of H would leave the preferred path of complete oxidation for the methyl groups. Here again, the data obtained in vacuum is complementary to the ambient pressure data.

3.3.5. Saturated C\textsubscript{1} to C\textsubscript{5} hydrocarbons. The saturated hydrocarbons as a group are the most difficult of the organic compounds to oxidize over noble metal catalysts. They show the highest light-off temperatures (temperature required for 50\% conversion), T\textsubscript{lo}, of all of the hydrocarbons. Methane, in particular, is the most difficult of oxidize. The T\textsubscript{lo} for methane provides an estimate of the upper limit that would be required to oxidize most volatile organic compounds, VOC, over Pt/SnO\textsubscript{2}. Consequently, it is important to know the temperature-activity profiles of the saturated hydrocarbons.

Figure 3.13 shows the temperature-activity profile of each of the C\textsubscript{1} to C\textsubscript{5} hydrocarbons over Pt/SnO\textsubscript{2}. The light-off temperatures ranged from about 150°C for pentane to about 220°C for methane. An interesting observation is that as the number of carbons increased, the light-off temperature decreased. Because the light-off temperatures get progressively closer as the carbon number gets higher, there is apparently a minimum temperature at which any HC can be oxidized. If the difference between the light-off temperatures, \Delta T\textsubscript{lo}, of successive hydrocarbon is plotted against carbon number, this minimum temperature can be estimated. (See Figure 3.14.) This is basically the derivative of the change in light-off temperature with respect to the number of carbons. Since the increments are in number of carbons, \Delta T\textsubscript{lo}/\Delta C is more appropriate than dT\textsubscript{lo}/dC. The
Figure 3.13. Temperature-activity profiles for the C₁ to C₅ hydrocarbons over Pt/SnO₂ catalyst on cordierite honeycomb monolith.

\[ \Delta T_{lo} = -8.5 \times \text{(Carbon No.)} + 45.2 \]
\[ r^2 = 0.97 \]

Figure 3.14. The change in light-off temperature, \( \Delta T_{lo} \), with the average carbon number.
average of the adjacent hydrocarbons has been used for $\Delta C$ to prevent confusion in determining from where the $\Delta T_{lo}$ on the graph came. For example, the $\Delta T_{lo}$ for ethane ($C_2$) and propane ($C_3$) is $196^\circ C - 171^\circ C = 25^\circ C$ and appears at the independent axis value of $(2 + 3)/2 = 2.5$.

Note that $\Delta T_{lo}$ between methane and ethane and between ethane and propane are about equal whereas $\Delta T_{lo}$ for the others grow closer together. Several reasons may be offered for the difference in behavior: (1) methane has no C-C bonds thereby creating a potentially different mechanism for this molecule’s oxidation; (2) the first bond to be broken for CH$_4$ would have to be a C-H bond whereas it may be a C-C bond for the other HC thereby requiring different bond energies; and most likely (3) the stability of the intermediates would increase with increasing carbon number due to surface-intermediate interactions thereby making oxidation easier. For instance more carbons gives more atom to surface bonding character. If the first $\Delta T_{lo}$ is ignored, then an approximately linear relationship forms between $\Delta T_{lo}$ and carbon number. This relationship indicates that the $\Delta T_{lo}$ should go to zero at $C_6$ or n-hexane. This is an interesting prediction as n-hexane is the first of the HC’s that is a liquid at ambient atmospheric conditions.

Although not shown, a small amount of each hydrocarbon desorbed unconverted from the catalyst from ambient temperature up to that temperature at which oxidation began, somewhere between $80^\circ C$ to $120^\circ C$ depending on the hydrocarbon. This indicates that Pt/SnO$_2$ has some adsorption capacity for each hydrocarbon even at elevated temperature. Once the catalyst had been exposed to nitrogen even at temperatures as low as $35^\circ C$, no detectable hydrocarbon remained adsorbed on the catalyst surface. This was determined by ramping the temperature under N$_2$ flow after having allowed the catalyst to equilibrate under flow of the hydrocarbon-containing reaction gas mixture at $35^\circ C$. This suggests that the hydrocarbons are not strongly bound on Pt/SnO$_2$. The absence of strong bonding to Pt/SnO$_2$ may be the reason for the difficulty in oxidizing hydrocarbons. This is in contrast...
to CO which never desorbed from the catalyst but, instead, was converted to CO$_2$.

Studies carried out at near atmospheric pressure (rather than in vacuum) on each of
the noble metals used in the three-way automotive catalysts, Pt, Rh, and Pd, indicate that
oxidation of CH$_4$ begins at around 300°C with a light off temperature of between 500°C
and 600°C depending on the identity noble metal. The rate-limiting step is believed to be
the dissociative adsorption of CH$_4$. Excess O$_2$ was found to inhibit the conversion
indicating that O$_2$ preferentially adsorbed on the noble metal at the temperature at which the
oxidation started. The lower light-off temperatures obtained for oxidation over Pt/SnO$_2$
may be due to reduction or elimination of the competition for adsorption. Because SnO$_2$
can provide dissociative adsorption of O$_2$ at the lower temperatures required for the
hydrocarbons to remain adsorbed to the catalyst, the reaction can proceed at a lower
temperature. More about the mechanism will be discussed in Chapter 5.

3.4. CONCLUSIONS

At present, there is no compelling evidence to suggest that the low-temperature
oxidation of formaldehyde, methanol, and ethanol requires Pt/SnO$_2$ over Pt alone in order
to occur. If CO is present in the reaction gas mixture, however, Pt/SnO$_2$ is required to
effect oxidation. Nonetheless some differences resulted from the presence of SnO$_2$. For
methanol, Pt/SnO$_2$ modifies the composition of the effluent stream somewhat from that of
Pt, eliminating the delay in the start-up of oxidation and providing a shorter stabilization
time. For ethanol, the temperature for conversion to CO$_2$ and the by-products appears to be
somewhat lower than over Pt alone. Differences for both methanol and ethanol are
consistent with an increased availability of oxygen at a lower temperature. As such the
results presented, here, of the oxidation of volatile organic compounds over Pt/SnO$_2$
versus Pt provide support for the adsorption and possibly the dissociative adsorption of O$_2$
on SnO$_2$. 

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With the results of the VOC tested herein, the conversion/oxidation behavior of other oxygen-containing VOC can be predicted. For compounds which have C–O bonds, similar low-temperature activity in the presence of CO should be expected. Examples, are formic acid and ethylene glycol, HOCH₂CH₂OH. This suggests that Pt/SnO₂ might be used for low-temperature, VOC-oxidation applications in the presence of CO where Pt alone cannot operate. This would include all VOC which would oxidize under about 150°C, where Pt starts oxidizing CO in significant amounts when excess O₂ is present.

Including the oxidation of by-products, Pt/SnO₂ has shown the ability to oxidize aldehydes, alcohols, and esters. It is reasonable to assume that carboxylic acids and ketones will be similarly easily oxidized alone or in the presence of CO. The study of the series of alcohols and hydrocarbons provided an indication in the likely trend in activity-temperature profiles for other VOC. Specifically, the temperature-activity profile behaves more like the associated saturated hydrocarbon as the number of carbons attached to the functional group increases. Branching of the hydrocarbon portion causes a slight increase in the temperature required to start oxidation.

Of all organic compounds, the saturated or aliphatic hydrocarbons require the highest catalyst temperatures for complete oxidation in excess O₂ over all noble metal catalysts, including Pt/SnO₂. Consequently, it is reasonable to assume that all of the olefinic or unsaturated hydrocarbons as well as the oxygen-containing organic compounds will be oxidized at temperatures less than that for the saturated hydrocarbons. Methane is the most difficult to oxidize but shows a light-off temperature of about 220°C over Pt/SnO₂. All other VOC should show a light-off temperature in excess O₂ lower than 220°C. By comparison, each of the three noble metals used in 3-way noble metal catalysts for automobile emission control, Pd, Pt, and Rh, have a light-off temperature for methane between 500°C and 600°C in the presence of CO. The possible mechanisms of conversion and oxidation of the hydrocarbons and VOC will be discussed further in Chapter 5.
CHAPTER 4
ROLE OF WATER IN CO OXIDATION

4.1. INTRODUCTION

Hydrogen, probably in the form of OH, is frequently neglected in studies of catalytic oxidation reactions, in particular, the reaction between CO and O₂ over noble metals and metal oxides. One possible reason for this neglect is that many high vacuum techniques commonly used to characterize surfaces are relatively insensitive to hydrogen.¹ Yet nature provides several examples where the presence of H in some form is necessary for oxidation to occur. Iron rusts easily in humid air but not in dry air. Water is commonly added to hydrocarbon-oxygen mixtures to aid ignition (i.e. acetylene, methane, propane).² Carbon monoxide-oxygen mixtures will not ignite when extremely dry, but will ignite readily when small amounts of water are added.³ Hydroxyl radicals—not oxygen radicals—are the oxidizing agent in almost all tropospheric reactions.⁴ And hydroxyl radicals—not oxygen radicals—are the oxidizing agents in the gas phase oxidation of CO.⁵ The reaction between CO and O is unfavored because it violates spin conservation rules.⁶ The O is triplet in its ground state and CO is singlet. Even in the presence of a third body, the reaction is unfavored.

Hydrogen, as OH, may serve a critical role in the oxidation of CO over NMRO catalysts. Because absence of dissociative adsorption of O₂ prevents CO oxidation from occurring at normal room temperature on either noble metals or metal oxides alone, dissociative adsorption of O₂ must be facilitated on NMRO catalysts, in particular on Pt/SnO₂. In the presence of CO, O₂ does not adsorb on Pt. Over fully oxidized, single crystals of SnO₂, O₂ does not adsorb at all.⁷ Nor does O₂ dissociatively adsorb on air-exposed Pt/SnO₂ until temperatures of greater than 350°C are reached.⁸ It has been shown...
from the CO-titration of adsorbed oxygen on Pt/SnO₂ and from rare-isotope reduction of Pt/SnO₂ with C¹⁸O₂, on the other hand, that either physisorbed or chemisorbed oxygen on Pt/SnO₂ reacts with CO to form CO₂ at temperatures at least as low as 24°C.⁸⁻⁹ There exists, then, some form of labile surface oxygen on Pt/SnO₂. The form has not yet been determined.

It has long been known that small amounts of gas phase water catalyze the reaction between CO and O₂, whether in the gas phase or over catalysts.¹⁰ Fuller, et. al. reported that water vapor catalyzed the oxidation of CO over Pd/SnO₂,¹¹ and Schryer, et. al. over Pt/SnO₂.¹² Boulahouache, et. al. reported that the CO-oxidation rate of Pt/SnO₂ increased with increasing water vapor concentration in amounts up to 18.2 mbar (0.0180 atm) at 60°C, but the upper limit of water concentration for which enhancement could be provided was never reached.¹³ In the present study, four series of experiments were performed to further investigate the extent to which water contributes to CO oxidation over Pt/SnO₂. One measures the effect on CO oxidation activity of adding and removing water to a silica gel-supported Pt/SnO₂ catalyst. The next two measure the effect on activity of varying water vapor concentration at constant temperature and of temperature at constant water vapor concentration. The fourth uses rare-isotope H₂¹⁸O to investigate the effect of water on the oxidation of common isotope C¹⁶O with¹⁶O₂ and also on the interaction of C¹⁶O₂ with Pt/SnO₂.

In spite of the recognized enhancement in CO-oxidation activity afforded by water, the literature seems to have few proposed mechanisms elucidating its role. There are several ways in which water might increase the rate of reaction: (1) by increasing the number of O₂ adsorption sites; (2) by forming hydroxyl groups that act as the oxidizing agent; (3) by improving the rate of dissociation of O₂; (4) by increasing the rate of surface diffusion of atomic O to the Pt-SnO₂ interface; (5) by increasing the breakdown of surface adsorbed intermediates; or (6) by some yet to be determined mechanism.
The first possibility follows from consideration of Langmuir-Hinshelwood type kinetics which indicate that the reaction rate is proportional to the amount of adsorbed CO and O₂. Boulahouache, et. al. found that, although water catalyzed the reaction between CO and O₂, it did not increase the adsorption capacity of either CO or O₂ on Pt/SnO₂. Consequently, it was concluded that water did not create extra sites for O₂ adsorption.

The next three possibilities may be different manifestations of a single phenomenon, the dissociation of water on metal oxides. Water dissociates on most metal oxide surfaces, including SnO₂, to form hydroxyl groups. It is also known that some hydroxyl groups remain present on most metal oxides until calcined at extremely high temperatures. Tin(IV) oxide, for example, must be taken to over 900°C to remove all of the hydroxyl functions. Consequently, most metal oxides possess hydrogen as hydroxyl groups even after the calcining steps used during production which seldom exceed 500°C.

It is possible that hydrogen, present as surface hydroxyl groups, facilitates the dissociative adsorption of O₂. Hydroxyl groups would enable hydrogen bonding with gas phase O₂ which might, in turn, improve the O₂ sticking probability and reduce the energy barrier to breaking the O=O double bond. It requires less energy to break the O=O double bond (494 kJ/mol) than to break the HO—OH (143 kJ/mol) single bond. In addition, hydroxyl radicals are more stable than oxygen radicals making OH a more reasonable oxidizing agent at low temperature. Evidence in support of the hydroxyl group-aided, dissociative adsorption of O₂ comes from Buyevskaya, et. al., who found that even at temperatures as high as 873K “the complete elimination of OH groups on alumina coincided with a loss of activity towards oxygen dissociative adsorption.”

If O₂ dissociates via some mechanism other than by hydrogen bonding to hydroxyl groups, it is still possible that the reaction rate increase could be due to OH-aided surface diffusion of oxygen atoms to the Pt-SnO₂ interface. Depletion of oxygen atoms near the Pt-SnO₂ interface from reaction with CO would provide impetus for surface diffusion. The
oxygen-covered SnO₂ surface might create a barrier to diffusion of adsorbed oxygen atoms because of the common negative charge. Surface defects in the SnO₂ would also be scarce in the presence of atmospheric oxygen. The presence of surface OH, on the other hand, would enable an oxygen atom to encounter a sea of hydrogen atoms across which it might more easily diffuse.

Another way in which hydroxyl groups might participate in the oxidation reaction is as an oxidizing agent itself. As stated above, small amounts of water catalyze the reaction between CO and O₂ over Pt/SnO₂. At 35°C, however, water alone cannot oxidize CO.¹⁸ This would be the equivalent of the water-gas shift reaction, H₂O + CO = H₂ + CO₂, but this does not happen. This reaction generally requires high temperatures and pressures to occur over a noble metal catalyst. Consequently, it is the combination of O₂ and H₂O that is required for oxidation of CO on Pt/SnO₂. Because Pt preferentially adsorbs CO over H₂O, it is reasonable that hydroxyl groups associated with the tin oxide are potential oxidizing agents themselves. Booker and Keiser found OH to be the oxidizing agent for CO over Rh/Al₂O₃ using FTIR.¹⁹ Gurney and Ho used TP-EELS, TPRS, and LEED to discover that OH oxidizes CO to formate on the (100) face of Rh.²⁰ And Knell, et. al. used FTIR to discover the OH-oxidation of CO to formate on Au/ZrO₂ which in another step decomposes to CO₂.²¹

Aside from the activation of O₂, what is special about the hydroxyl radicals of the "reducible" metal oxides that might enable them to act as oxidizing agents when those of the refractory oxides do not? The hydroxyl groups of all metal (metalloid) oxides are not created equal. If the sole purpose of hydroxyl groups were to dissociatively adsorb O₂, then it might be expected that all hydroxylated oxides would work equally well for CO oxidation at ambient temperature, yet not all combinations of noble metal and metal oxide or metalloid oxide show sustained ambient-temperature, CO-oxidation activity (e.g. Pt/Al₂O₃, Pt/SiO₂, Pt/TiO₂, Pt/ZrO₂). The difference is that those metal oxides which function in
NMRO catalysts are multivalent and can change oxidation state under relatively mild conditions, so to lose a hydroxyl group would be possible. If the hydroxyl groups of various metal oxides merely serve to dissociatively adsorb $O_2$, on the other hand, then it is possible that the spacing of the hydroxyl groups in the reducible oxide lattice plays an essential role.

Cox and Fryberger discovered that the surface bridging oxygen atoms in (110)-face of SnO$_2$ single crystals could be removed by evacuation at about 475°C, and then those positions could be relabeled with rare-isotope $^{18}$O atoms with 85% efficiency. This indicates both that the surface O of SnO$_2$ is labile and that the partially reduced state of SnO$_2$ is stable to surface rearrangement. An interesting study might be to determine how the presence of surface hydroxyl groups would affect the temperature at which evacuation of surface O or OH occurs. By comparison to the reducible oxides, the refractory oxides generally have too strong a metal-oxygen for the parent element to be found in more than one stable (metastable) oxidation state in the presence of oxygen.

Furthermore, tin has two oxides with stable oxidation states. It was shown in Chapter 1 that CO reduction of SnO$_2$ to SnO requires very little input of energy and that the re-oxidation by $O_2$ occurs spontaneously at 298K. Having two stable oxidation states which can be accessed by relatively mild condition may enable the hydroxyl groups of tin oxide to act as oxidizing agents. If this principle is important, then other such multivalent oxides ought to work when in combination with a noble metal. Several were described in Chapter 1 including a variety multivalent metal oxides in combination with gold and the oxides of iron and manganese with Pt. Each of the metal oxides possess at least two easily accessible oxidation states.

A direct route to investigating the effect of hydroxyl groups on CO-oxidation activity is presented. In this study, the Pt/SnO$_2$ catalyst was silylated to remove the OH groups and the resulting change in the CO-oxidation activity was measured. The effect of silylation on
the surface species of Pt/SnO$_2$ was also investigated using DRIFTS. Typical means for removing hydroxyl groups by drying at temperatures greater than 200°C to 300°C causes a loss of SnO$_2$ surface area making it difficult to separate the effects of OH loss and surface area loss on CO-oxidation activity. The present study provides a means for tying up hydroxyl groups without a loss of SnO$_2$ surface area.

4.2. EXPERIMENTAL

4.2.1. Water and silica gel. As stated in Chapter 1, using silica gel as a catalyst support was a means for incorporating a source and sink for water into the Pt/SnO$_2$ catalyst. Because the SnO$_2$ and the silica gel support have high surface area, what is collectively termed, “water” exists as both physically adsorbed water and chemically bound hydroxyl groups. The fraction of each cannot be distinguished in this study.

To determine the effect of water on the catalyst's activity, a known weight of deionized water was added to a known weight of catalyst. All samples came from a single batch of catalyst whose composition was 7% Pt, 42% SnO$_2$ and 51% silica gel. Several samples were prepared in this manner, incrementing the amount of water added to each additional sample until no more could be absorbed, the saturation point. Samples with lower water content were prepared by dehydrating the as-prepared catalyst in air in a convection oven either with or without a desiccant of magnesium perchlorate. Next each catalyst sample was tested for activity in the reactor system described in Figure 1.1 in Chapter 1. The amount of each catalyst sample tested was normalized to 150 mg of as-prepared catalyst (no water added or removed) so that an equal amount of catalyst on a dry basis was used for each different water content. Each sample was pretreated in situ for 1 hour at 125°C under 10 sccm of 5% CO in He. The catalyst activity was measured at 55°C for 18,000 minutes under 10 sccm of a reaction gas mixture containing 1% CO, 0.5% O$_2$, 2% Ne (internal standard), balance He.
After testing the catalyst, a known weight of the sample, nominally 100-mg, was heated in a porcelain crucible at 1000°C to constant weight. The first bake ran 60 minutes followed by at least two 30-minute bakes. The weight loss was considered to be proportional to the amount of water present in the catalyst.

4.2.2. Water vapor tests. Two tests involving the effect of water vapor on CO-oxidation activity were carried out. In one test the water vapor concentration in the reaction gas mixture was held constant while the temperature of the catalyst was increased from 25°C to 60°C. In the second test, the temperature of the catalyst was held constant at 25°C and the concentration of water vapor in the reaction gas mixture was varied.

The reactor setup is shown in Figure 4.1. For studies involving varying water vapor concentration, the reaction gas mixture was prepared by passing the zero air from the Balston air treatment system (to remove water and CO₂) over a 0.5-L bed of 1/8" diameter alumina beads which had been saturated with DI H₂O and then equilibrated in ambient air for several days. As the dry air passed over the alumina pellets, the water vapor concentration in the stream decreased from 25,000 ppm (2.5% partial pressure) down to about 4000 ppm (0.4% partial pressure) over several hours. For studies involving constant water vapor concentration, room air was used instead of the zero air passed through the hydrated alumina pellets. Next, enough CO was added to the humidified air from a tank of compressed gas containing 5.03% CO in He (Scott Specialty Gases) using a 0 to 9.99 sccm Hastings mass flow controller to give the desired concentration. Unless otherwise stated, the CO concentration was controlled at 100 ppm. The humidified test gas stream then passed through the sample cell of an EG&G Model 911 DEW-ALL dew point and relative humidity analyzer to determine the water concentration.

The reactor system is much like that described in Chapter 1 except that only one reactor, instead of four, was used. The reaction gas mixture could be passed through the bypass instead of the catalyst by switching the two, 3-way valves. Both catalyst reactor and
Figure 4.1. Schematic of catalyst reactor system used for determining the effects of water vapor on the activity of Pt/SnO₂ catalysts.

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bypass were housed in a convection oven for temperature control.

The blended gas was pulled through the plug-flow reactor bypass to the 10-m gas cell (Infrared Analysis, Inc.) at 2.00 liters per minute (Lpm) using a Neptune Dyna-Pump and controlled via a metering valve. Atmospheric pressure was maintained via venting the excess dry air to atmosphere. The system pressure was measured with a Transmetrics absolute pressure gauge attached to the gas cell. The total flow rate was measured using a 0-9.99 Lpm Hastings Mass Flowmeter. The absorbance of CO and CO₂ was determined by integrating band areas.

The gas cell was calibrated by comparing the infrared absorbance, A, of each analyte to its known concentration. The concentration of each species is directly proportional to the absorbance via the Beer-Lambert Law (A=εcl where ε is the absorptivity constant, c is the concentration, and l is the path length through the sample). In tests where the test gas stream was humidified, only the P branch of the CO absorption band (centered around 2146 cm⁻¹) was integrated to calibrate and to measure the CO concentration due to the interference of H₂O of the Q branch. The absorption band for CO₂ (centered around 2350 cm⁻¹) was unaffected by the presence of water. Although not shown in the schematic, during calibration the effluent stream from the gas cell was double-checked using a GC with a methanizer and FID detection which could easily detect concentrations of CO and CO₂ down to 1.0 ppm. The concentrations measured using the GC method were within 10% relative to that measured by FTIR. This is reasonable for such low concentrations using these methods.

4.2.3. Silylation tests. The composition of the catalyst studied was 1.2% Pt/SnO₂ on cordierite honeycomb monolith. The monolith geometry (shown in Figure 2.1) had 400 cells/in² giving each cell a 0.05-in width. Four samples consisting of 3 by 3 cells by 1.5 inches long were cut from a larger piece. Two of these samples were treated with silylating agents, isopropenoxy-trimethylsilane, IPOTMS, or trimethylsilylimidazole,
TMSIM, (from ACROS Organics), at a concentration of 0.25 g gram in 1.8 grams acetone (HPLC grade from Fisher Scientific) for about 2 hours and then rinsed three times with acetone and allowed to dry in ambient air. Another sample was treated for the same period of time in acetone without a silylating agent in order to subtract out any potential effect of the solvent. The final sample was not treated. The samples were tested simultaneously, plug-flow style, at 24±1°C under a flow of 10 sccm 1.00% CO, 0.500% O₂, 2.00% Ne, balance He (MG Industries) using the reactor system described in Chapter 1 and shown in Figure 1.1.

In addition to the activity tests, parallel samples were investigated using DRIFTS to investigate the extent of loss of hydroxyl groups. About 15 mg of sample was ground together with about 100 mg IR-grade KBr. Ground samples, rather than intact, were used to obtain DRIFTS spectra which were not a function of orientation of the sample on the sample stage. Because the silylation was not carried out in situ, spectra were recorded before, during, and after heating the silylated sample to 125°C within the DRIFTS attachment, in order to ensure that any physically adsorbed water or acetone was removed from the samples during transfer to the sample stage.

4.2.4. Rare-isotope H₂¹⁸O. Figure 4.2 shows a schematic of the set-up used to prepare and incorporate water into the reaction gas mixture. The system was designed such that the reaction gas mixture could have a background gas of “wet” or “dry” He without changing the concentrations of CO and O₂. Rare isotope H₂¹⁸O was prepared by reducing ¹⁸O₂ with a near stoichiometric amount of H₂ over a Pt on carbon catalyst, Pt/C. The Pt/C catalyst was held at 145°C to 150°C to drive the produced H₂¹⁸O off and into the reaction gas mixture. The 1% ¹⁸O₂ in He with a 2% Ne internal standard was obtained from MSD Isotopes and was 98.4 at% ¹⁸O. The concentration of water produced was controlled by the amount of ¹⁸O₂ and H₂ admitted into the Pt/C catalyst gas. In order to keep the water concentration low, the ¹⁸O₂-H₂ mixture was diluted with UHP He (MG...
Figure 4.2. Schematic of production of H$_2^{18}$O over Pt, and means for switching between “dry” and “wet” reaction gas mixtures prior to introduction to Pt/SnO$_2$ catalyst.
Industries). The total flow rate of the "wet" He gas was about 20 sccm. The concentration of water was varied from 2000 to 6000 ppm. Because some water invariably adsorbs onto the various surfaces of the reactor system, the amount quoted is an upper limit. The water stream was monitored using MS to ensure that all $^{18}$O$_2$ was converted to H$_2$,$^{18}$O; no m/e 36 signal could be observed indicating an $^{18}$O$_2$ level less than 1-2 ppm. It should also be noted that common isotope H$_2^{16}$O was also present in the system and varied similarly with changes in H$_2^{18}$O concentration. The major component was, however, the rare-isotope form, H$_2^{18}$O. The presence of common-isotope water does not affect the qualitative nature of these studies.

The CO and O$_2$ concentrations were incorporated into the reaction gas mixture by mixing 2.00 sccm of 5.00% CO and 1.00 sccm of 5.00% O$_2$ (Scott Specialty Gases) with 20.0 sccm of He to give a final flow rate of 23.0 sccm containing about 4350 ppm CO and 2170 ppm O$_2$. All flows were controlled using Hastings Mass Flow Controllers. For the tests involving interaction of common-isotope C$_{16}$O$_2$ with Pt/SnO$_2$, C$_{16}$O$_2$ was incorporated into the gas mixture by diluting from 3.033 % C$_{16}$O$_2$ in He (Scott Specialty Gases) with He using the either the O$_2$ or the CO mass flow controller as shown in Figure 4.2.

The catalyst tested was 0.234 g of 1.6 % Pt/SnO$_2$ on cordierite honeycomb (total weight = 0.9621 g). The test temperature was always near room temperature (25±2°C). Catalyst treatment prior to testing with C$_{16}$O$_2$ or C$_{16}$O + $^{16}$O$_2$ will be discussed in the results of these experiments, Section 4.3.4.

4.3. RESULTS

4.3.1. Effect of water content of catalyst-coated silica gel. The weight percent of water in the as-received silica gel was 18.2% prior to coating with Pt/SnO$_2$ and 3.73% after coating. Figure 4.3 shows the conversion efficiency in percent yield of CO$_2$ at
12,000 minutes of exposure to the reaction gas, plotted against the water content of each Pt/SnO$_2$ on silica gel sample. As a measure of the error in catalyst homogeneity, the CO conversion efficiency of three separate samples from the batch of the Pt/SnO$_2$ containing 3.73% H$_2$O was measured, and the relative standard deviation determined. The error bars for each sample in the figure represent this relative standard deviation of about 3% of the conversion efficiency. Because an analytical microbalance was used, the sample weights were known to the nearest 0.01 mg. Weight changes due to baking were on the order of mg to 10’s of mg so the percent water composition of all samples was known to the ±0.01%. Consequently each sample contained a distinctly different quantity of water and there was no overlap. The error in determining the water content was insignificant by comparison the that determined for the conversion efficiency.

The activity of the slightly dehydrated sample, 2.03% H$_2$O, showed a slightly higher...
conversion efficiency than the others. The most dehydrated sample, 1.62% H₂O, showed a slightly lower activity than the others except for the sample which was saturated with water, 23.86% H₂O. For the rest of the samples the activity remained relatively constant over the range of water content from 3.73% to 20.72%. These data demonstrate that using silica gel as a catalyst support minimizes the influence of water on the conversion efficiency over Pt/SnO₂. The depressed activity of the most dehydrated sample indicates that water is important to low-temperature CO oxidation over Pt/SnO₂. The depressed activity of the water-saturated sample indicates that the excess water can also hurt CO-oxidation. Silica gel supported Pt/SnO₂ could be advantageous for use in closed-cycle CO₂ lasers where vapor phase water significantly reduces laser power.

Investigation of the water vapor pressure over uncoated silica gel provides an explanation for the relative insensitivity of the activity to water content. Table 4.1 shows the vapor pressure of water over silica gel at 40°C as a function of the percent water content. These data show that the water vapor remains low, a partial pressure of about 0.3%, even when the water content is as high as 20% of the total weight. Incorporating silica gel into the catalyst then would provide a source and sink for water and would tend to even out the activity over a broad range of water content.

Table 4.1. Vapor Pressure of Water over Silica Gel as a Function of Water Content

<table>
<thead>
<tr>
<th>% H₂O</th>
<th>Vapor pres., mm Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>0.0076</td>
</tr>
<tr>
<td>1.00</td>
<td>0.013</td>
</tr>
<tr>
<td>1.20</td>
<td>0.05</td>
</tr>
<tr>
<td>3.00</td>
<td>0.175</td>
</tr>
<tr>
<td>6.00</td>
<td>0.505</td>
</tr>
<tr>
<td>12.00</td>
<td>1.5</td>
</tr>
<tr>
<td>20.00</td>
<td>2.5</td>
</tr>
</tbody>
</table>

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**4.3.2. Water vapor tests.** The following two experiments were conducted to investigate the extent to which vapor phase H₂O aids or hinders the CO-oxidation activity. The catalyst tested was a 3-in long core measuring 0.29 inches in diameter of 2.2% Pt/SnO₂ on cordierite honeycomb monolith (400 cells/in²). The CO concentration in the reaction gas mixture was 100 ppm and the flow rate was 2.00 L/min (linear flow rate of 2 ft/s).

**Varying humidity at constant temperature.** As indicated in the Experimental section, the humidity was varied by passing zero air over a bed of hydrated alumina pellets. Then enough CO was added via a flow controller to give the reaction gas mixture a constant concentration of 100 ppm. At the beginning of the test the pellets held the greatest amount of water and the H₂O concentration was at its highest, about 1.6% (16,000 ppm). As the zero air continued to deplete water from the pellet bed over the first 1200 minutes of the test, the concentration of water in the reaction gas mixture dropped from 1.6% to 0.26%. From 1200 minutes to the end of the test, 1600 minutes, the water concentration remained constant at 0.26% probably due to desorption from the surfaces of the reactor system. The concentration of water in the reaction gas mixture at any given time during the test is shown by the black curve in Figure 4.4 with values indicated on the right-hand axis.

Also shown in Figure 4.4 is the time dependence of the CO and CO₂ concentration in the effluent stream from the catalyst, as well as the mass balance (red line); values are on the left-hand axis. The sum of CO and CO₂ in the effluent stream at any given time should equal 100 ppm. During the first 120 minutes, the CO concentration decreased from 100 to 90 ppm and then began increasing again until none was removed from the reactant gas stream at around 600 minutes. Because the catalyst had reactive, preadsorbed oxygen in some form (O, O₂, or OH), the decrease in concentration corresponds to a titration of this oxygen. During this same period, however, no CO₂ was detected in the effluent stream. Once the water vapor concentration dropped below 0.75%, small amounts of CO₂ appeared.
in the effluent stream, about 7.4 ppm, with a concurrent loss of CO, but the mass balance between CO and CO\(_2\) was significantly below the expected value of 100 ppm.

The behavior of the catalyst under high H\(_2\)O concentration suggests that physically adsorbed H\(_2\)O either competes for active sites with CO or O\(_2\), or holds-up intermediates in the oxidation pathway on the catalyst surface or both. Platinum’s high affinity for CO suggests that no competition is likely. Because O\(_2\) can adsorb on partially reduced SnO\(_2\), however, competition with water for dissociative adsorption of O\(_2\) is possible. Also, it has been suggested that carbonate- and bicarbonate-like species have been observed on SnO\(_2\) and Pt/SnO\(_2\) using DRIFTS.\(^1\) It is reasonable that such a species might be present on the surface since CO\(_2\) and H\(_2\)O readily form an equilibrium with carbonic acid, H\(_2\)CO\(_3\) as occurs in the atmosphere. Atmospheric CO\(_2\) accounts for some degree of acidity on rain (about a pH of 5). If the quantity of water on the surface of the catalyst were reduced, the hold up of carbonate might decrease.
Once the water vapor concentration dropped below 0.4%, the concentration of CO\textsubscript{2} in the effluent stream increased rapidly from 7.4 ppm to near 50 ppm, and the mass balance approached the expected value of 100 ppm. Upon falling to about 0.26%, the water vapor concentration appeared to level off although the absorption band for water in the IR spectra indicated that there were further decreases in the water vapor concentration in the reaction gas mixture during this time. During this "drying-out" period, the amount of CO oxidized increased from 48 to 57 ppm and the mass balance was very near 100 ppm. Although not shown, under "dry" reaction gas flow ([H\textsubscript{2}O] < 0.001%), 78±2 ppm CO was oxidized to CO\textsubscript{2}. It is possible that the difference between the activities under 0.26% H\textsubscript{2}O and dry (H\textsubscript{2}O less than 10 ppm) conditions was due to adsorbed water on the catalyst surface. It is also likely that some portion of the difference was due to decay of catalyst activity over the total time that the tests were performed.

The scatter in the mass balance during the time the water vapor concentration levelled off at 0.26% was used as an estimate of the error in measuring the CO and CO\textsubscript{2} concentrations. This is a reasonable point at which to determine the error since changes in catalyst behavior due to water concentration are minimal. The estimate of error here is about ±3 ppm or 3% relative error and equal to that discussed earlier due to fluctuation in the pressure in the gas cell. Considering this error to be an upper limit for the measurement of the CO and CO\textsubscript{2} concentrations, the initial dip in the concentration is real suggesting that the adsorption of CO (probably chemisorption) does occur. The absence of CO\textsubscript{2} in the effluent stream is confirmed from the detection limit of CO\textsubscript{2} which could be detected in amounts as low as 0.6 ppm in this study.

It is interesting to note that the lower limit in water vapor concentration was not reached for maximum activity. The results presented here are in contrast to those presented by Boulahouache, at. al. who reached no upper limit to the activity enhancement over 1% Pt/SnO\textsubscript{2} on cordierite even at a water vapor partial pressure of 18.2 mbar (about 1.8%).\textsuperscript{13}
Differences in the methodology of testing were likely the reason. In Boulahouache’s study, the water vapor concentration was increased rather than decreased as it was here. Under this condition of dynamic water vapor concentration, the catalyst would likely exhibit a hysteresis effect. Running the water concentration from high to low would give higher surface concentration of water than if it were run from low to high. A possible reason that Boulahouache did not observe a maximum enhancement to the activity was that his catalyst did not reach a static equilibrium with the water vapor in their reaction gas mixture. Similarly, the minimum water vapor concentration at which activity was enhanced was not reached in this study.

It is interesting to note that Boulahouache prepared their catalyst via a sol-gel technique which may have had some impact on the differences in the behavior under water vapor although this is unlikely. The wide gap between the reported values for enhancement of activity indicate that more work is required to determine optimum values of water vapor concentration under which Pt/SnO₂.

**Constant humidity with varying temperature.** The purpose of this experiment was to determine the effect of temperature on the activity of Pt/SnO₂ with a near constant H₂O concentration in the reaction gas mixture. A small amount of heat might be able to alleviate the inhibition in CO oxidation activity by water.

The experimental set-up shown in Figure 4.1 was used here except that, instead of hydrating zero air over hydrated alumina pellets, ambient, room air was used. The dew point temperature was monitored real-time with a strip chart recorder connected to the Dew-All Humidity Analyzer. Due to the high concentration of CO₂ in ambient air (300 ppm), only the CO concentration could be monitored with FTIR. The pressure in the gas cell varied from 14.51 to 15.01 psia during the course of the experiment. Consequently, there was a 3% relative variation in the number of gas molecules in the gas cell and, therefore, a 3% relative error in determining the concentrations of both CO and CO₂.
Figure 4.5 shows the percent CO converted in the catalyst effluent stream at each temperature analyzed. The water concentration in the ambient air used in making up the reaction gas mixture varied from 6300 ppm to 9500 ppm during the course of the test. The concentration was determined from dew point measurements, and corresponds to a relative humidity of about 45% to 55% at 25°C.25

As mentioned above, the same catalyst under flow of dry reaction gas mixture converted 78 ppm CO to CO₂ at a temperature of 19.8±0.5°C. By comparison, only about 2% is converted at 23.5°C. As the temperature was increased the catalyst converted more CO to CO₂. Upon reaching a temperature of 60.8°C the catalyst was oxidizing about 35 ppm CO out of a 100 ppm CO in the test gas stream, less than one-half of the rate from the “dry” sample. Also note that the rate of conversion with temperature is not linear but rather increases with increasing temperature. Using the rule of thumb that the reaction rate
doubles for every 10°C temperature increase suggests that the curvature actually lags behind the expected level. That this rule of thumb does not hold is not surprising considering the effects of the adsorbed water and the flow effects resulting from a plug-flow reactor rather than a recirculating or continuously-stirred reactor. For a plug flow reactor, the intrinsic kinetics are generally only valid when conversions across the catalyst bed are less than 10%. As such, a calculated activation energy from these data would only be an observed, rather than the intrinsic value for this particular reactor system with this particular configuration. However, even with these limitations, results from an Arrhenius plot yield an activation energy, $E_{act}$, of 60 kJ/mol and a pre-exponential factor of $10^{11}$. This value compares with previously determined values for the oxidation of CO under dry conditions in a continuously-stirred reactor of 24 kJ/mol and 1690 by Miller.\textsuperscript{26} As expected, the $E_{act}$ is lower for the latter conditions as a portion of the $E_{act}$ would include the energy required to desorb molecular water from the surface of the catalyst.

For catalyst applications where water might be present in the analyte gas passing over the catalyst, it is possible that a small amount of heating could alleviate the problem of water adsorption on the catalyst.

4.3.3. Silylation tests. Figure 4.6 shows the CO-oxidation activities over time of the IPOTMS-, TMSIM-, and acetone-treated catalyst samples, as well as the untreated sample at 24±1°C. Each catalyst showed some initial activity followed by a rapid decline. This was likely due to titration by CO of active, preadsorbed oxygen. During the first 1200 minutes, only the unsilylated catalyst showed significant conversion of CO to CO$_2$, 30% to 35%. The acetone- and IPOTMS-treated samples showed a conversion of about 1% to 2%, and the TMSIM-treated sample showed no activity.

At about 1200 minutes, the catalysts temperatures were raised to 125°C for 30 minutes under the flowing test gas stream to drive off any residual acetone that might have been adsorbed on the catalyst surface. This temperature was used because DRIFTS spectra
of the silylated catalysts (to be discussed in the next section) indicated that acetone desorbed from the catalyst surface by heating to 125°C. Immediately after heating, each catalyst showed some activity. This may have been due to oxidation on Pt alone which should be unhindered by silylation. Very rapidly, however, the silylated catalysts resumed their original paths of decay which indicated that any residually adsorbed acetone could not be responsible for the decreased CO conversion activity.

Only the untreated (non-silylated) sample showed any significant activity for CO oxidation. It should be noted that the fluctuation in the activity of the untreated catalyst sample was due to a malfunctioning flow controller. The backup flow meter indicated a fluctuation of 10±0.6 sccm; the scatter in % yield CO\textsubscript{2} represents the same relative error.

It is interesting to note that the activity of the acetone-treated sample showed a reduced activity even though it desorbs readily from the catalyst by a temperature of 125°C. Because acetone has a strong affinity for water, it is possible that a chemically-induced condensation...
of surface hydroxyl groups of SnO₂ occurred. As occurs during heating hydrous SnO₂ to temperatures greater than 200 to 300°C, adjacent surface hydroxyl groups condense to form water and a surface bridging Sn–O–Sn bond.²⁷ Such chemically induced condensation occurs also with carbohydrates. Carbohydrates (i.e. sugar or cotton) can be reduced to carbon using either heat or concentrated sulfuric acid. The affinity of the sulfuric acid for water is so great that it will actually break the C–OH and C–H bonds to rob the hydrocarbon of water leaving behind carbon. This condensation of hydroxyls is consistent with DRIFTS spectra of untreated versus acetone-treated catalyst samples and will be discussed in the next section.

In conclusion, the parallel activity of the acetone- and IPOTMS-treated catalyst samples indicates that the reduced activity may have been due solely to the acetone solvent used to dilute the silylating agent. Although the DRIFTS spectra of the IPOTMS-treated sample indicated the presence of trimethylsilyl groups as will be discussed briefly. Similarly for the TMSIM-treated sample, the complete loss of activity may have been due to the solvent. The possibility remains that the loss of activity was due to silylation of the hydroxyl groups which prevented dissociative adsorption of O₂.

**DRIFTS study of silylated catalyst samples.** To aid in determining whether or not the catalyst samples were successfully dehydroxylated and/or silylated DRIFTS spectra were taken of samples parallel to those tested for CO-oxidation activity. All of the spectra are divided into two regions from 3800 to 1300 cm⁻¹ and from 1300 to 400 cm⁻¹ which will be called the “OH-stretch” and “fingerprint” regions, respectively. The OH-stretch region was so named for the strong O–H stretch band running from 2000 to 3700 cm⁻¹ and should not be construed as the O–H stretch band, itself. The reason for this division was to permit separate scaling of the regions and thereby prevent the strong absorption bands of the oxides of cordierite, SiO₂ in particular, from masking the weaker absorption bands in the OH-stretch region. The difference in the scaling will be apparent from the dependent
axes which are in Kubelka-Munk units. Also note that in most figures in this section, two spectra and the subtraction result of the spectra are presented. The main spectrum is in black, the spectrum being subtracted is in blue, and the subtraction result is in red. Particular emphasis is given to those absorption bands associated with hydroxyl groups.

It should also be noted that differences existing in the exact sample size and in the degree of grinding of the samples might lead to differences in the quantities of the various surface species among samples and hence differences in the intensities of the associated adsorption bands. When subtraction spectra of different samples (i.e. silylated minus untreated catalyst) were prepared, the spectrum of the silylated sample was scaled relative to that of the untreated sample so as to minimize the major absorption bands present in both. Because different molecular species have different absorption sensitivities, this method of scaling spectra for subtraction may show some inaccuracy. Consequently, interpretation of slight differences in the subtraction spectra are somewhat speculative and perhaps only qualitative. This will be mentioned where appropriate. Some differences found in the subtraction spectra are large and can be interpreted with relative certainty.

Table 4.2 lists the band assignments the surface hydroxyl groups of SnO$_2$ as determined from Harrison and Guest's IR study of the dehydration of SnO$_2$ gels between ambient and 400°C. Surface hydroxyl groups of SiO$_2$ and Al$_2$O$_3$ come from Kiselev and Lygin. Also included are the general band assignments for surface hydroxyl groups on the Pt/SnO$_2$ catalyst coating as suggested by DRIFTS spectra taken before and after silylation.

Figures 4.7a and b show the DRIFTS spectra of the 1.2% Pt/SnO$_2$ catalyst coating on cordierite, cordierite without catalyst coating, and the subtraction result which leaves bands associated with the catalyst coating. These spectra were taken after baking the samples at 125°C and cooling to room temperature. The broad absorption between
Table 4.2. Band Assignments for Hydroxyl Groups of SnO₂, SiO₂, and Al₂O₃

<table>
<thead>
<tr>
<th>Function</th>
<th>Wavenumber, cm⁻¹</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>isolated O–H stretch, SnO₂</td>
<td>3640</td>
<td>38</td>
</tr>
<tr>
<td>isolated O–H bend, SnO₂</td>
<td>1245, 1175</td>
<td>38</td>
</tr>
<tr>
<td>H-bonded O–H stretch, SnO₂</td>
<td>3700 to 2000</td>
<td>38</td>
</tr>
<tr>
<td>H-bonded O–H bend, SnO₂</td>
<td>broad 1250-800 and 870, 940</td>
<td>38</td>
</tr>
<tr>
<td>isolated O–H stretch, SiO₂</td>
<td>3750</td>
<td>39</td>
</tr>
<tr>
<td>isolated O–H stretch, Al₂O₃</td>
<td>3800, 3780, 3744, 3733, 3700</td>
<td>39</td>
</tr>
<tr>
<td>general O–H, Pt/SnO₂ on cordierite</td>
<td>3750-2000, 1225, 1125, 1086, 925, 810</td>
<td>this study</td>
</tr>
</tbody>
</table>

3750 cm⁻¹ and 2000 cm⁻¹ is characteristic of the O–H stretch of hydrogen-bonded, surface hydroxyl groups. By comparison to the spectrum of the Pt/SnO₂ catalyst coating, it can be seen that the cordierite contributes very little to the total concentration of surface hydroxyl groups. Of particular interest are the sharp absorption band in the cordierite spectrum and the sharp edge in the catalyst spectrum around 3750 cm⁻¹. Several absorption bands in the region from about 3650 to 3850 cm⁻¹ have been assigned to the O–H stretch of isolated surface hydroxyl groups of SnO₂, Al₂O₃, and SiO₂. Also present in the cordierite spectrum are bands from 2800-3000 cm⁻¹ and 2200-2375 cm⁻¹ which are indicative of adsorbed hydrocarbon and CO₂, respectively.

From the fingerprint region shown in Figure 4.7b, there are several absorption bands evident in the subtraction spectrum which are indicative of surface bound hydroxyl groups. The region assigned to O–H bend of various types of surface hydroxyl groups of SnO₂ appears to run from about 770 to 1400 cm⁻¹ with bands at 1225, 1086, 925, and 810 cm⁻¹ and a shoulder on the high frequency end of the strong 1086-cm⁻¹ band at about 1150 cm⁻¹. All of the bands except the very strong band at 1086 cm⁻¹ show good agreement with those reported by Harrison in this region. It is interesting that there appears to be a shift to
Figure 4.7a. DRIFTS spectra of 1.2% Pt/SnO$_2$ on cordierite, uncoated cordierite, and the subtraction result: OH stretch region.

Figure 4.7b. DRIFTS spectra of 1.2% Pt/SnO$_2$ on cordierite, uncoated cordierite, and the subtraction result: fingerprint region.

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lower energy of about 15 to 25 wavenumbers. The differences in the strength of various absorption bands may be due to different quantities of the various types of surface bound hydroxyl groups as was suggested by Harrison for SnO₂. It is also possible that the band at 1086 cm⁻¹ which was unassigned by Harrison is due to Pt-bound hydroxyl groups. This is consistent with the findings of Gardner and Hoflund of increased hydroxyl group concentration associated with Pt, or Pt(OH)₂, resulting from a 125°C, CO reduction of Pt/SnO₂ as reported in Section 1.3.2.

The band in the region 400 to 770 cm⁻¹ is a composite of many absorptions which might be due to Sn–O–Sn or Sn–O–Si, –Al, –Mg, or –Pt symmetric and antisymmetric stretches. It is interesting to note that these bands appear to be completely absent from the SnO₂ films prepared from thermal decomposition of SnEH on Al metal presented in Chapter 2. It is possible then that these absorption bands are due specifically the interactions of Pt with SnO₂, but more work is necessary to elucidate the nature of such interactions. Harrison speculated that absorption bands at 770 and 710 cm⁻¹ were due to the symmetric and antisymmetric stretches of surface bridge-bonded oxygen in Sn–O–Sn resulting from the condensation of adjacent OH groups.²⁵

Now that the absorption bands associated with hydroxyl groups of the catalyst have been discussed, it is important to determine the extent to which physically adsorbed water affects the spectra. Figures 4.8a and b show the DRIFTS spectra of the same catalyst of Figures 4.7a and b before and after baking at 125°C. Note that the catalyst was baked until there was no change in intensity of the OH region which generally took less than 15 minutes. Examining the OH-stretch region of the spectra reveals a significant reduction in both the O–H stretching and bending bands and can be attributed to a loss of physically adsorbed water. Additionally, the region around 3700 cm⁻¹ shows an increase in the intensity of the band attributed to isolated hydroxyl groups. The band at 3750 cm⁻¹ shows a decrease in intensity perhaps suggesting a loss of SiO₂-associated hydroxyl groups.
Figure 4.8a. DRIFTS spectra of 1.2% Pt/SnO₂ on cordierite before and after baking at 125°C; OH-stretch region.

Figure 4.8b. DRIFTS spectra of 1.2% Pt/SnO₂ on cordierite before and after baking at 125°C; fingerprint region.
The fingerprint region of the spectra reveals little difference in the absorption bands before and after baking. Consequently the subtraction result was multiplied by a factor of 10. Baking resulted in a slight increase in the band at 1086 cm\(^{-1}\) with concomitant slight decreases in the bands on either side, centered around 1125 cm\(^{-1}\) and 925 cm\(^{-1}\). It is interesting to note that these correspond to absorption bands assigned by Harrison to surface hydroxyl groups, the 1125 cm\(^{-1}\) to an isolated OH which remains stable to 300°C and the 925 cm\(^{-1}\) which remains until 250°C during heating.\(^{27}\) If these bands were assigned correctly by Harrison, then it is possible that the presence of Pt makes them labile to condensation at a lower temperature. The bands at 1250 cm\(^{-1}\) appears to remain unchanged while that at 810 cm\(^{-1}\) is buried in too much noise for changes to be discernable.

Figures 4.9a and b show the spectra of the acetone-treated catalyst sample and untreated catalyst sample of the previous two figures after baking at 125°C, along with the subtraction result. The OH-stretch region reveals a further decrease in intensity of the O–H stretch band indicating further loss of hydroxyl groups. In the region of 3600 cm\(^{-1}\) to 3750 cm\(^{-1}\), the general shape of the spectra of the acetone-treated and untreated catalyst samples are the same indicating preservation of the isolated OH groups. It is possible that acetone removed more physically adsorbed water than was possible by baking at 125°C. The decrease in the edge at 3750 cm\(^{-1}\) in the subtraction spectrum, however, suggests that there might be a slight decrease in one form of isolated hydroxyl group. This slight decrease may or may not be an artifact resulting from positioning of samples in the DRIFTS apparatus.

If the spectral differences are significant, the fingerprint region reveals interesting information. The band at 925 cm\(^{-1}\) shows a possible slight decrease in intensity due to treatment in acetone. Those at 1225 and 810 cm\(^{-1}\), again, show no significant difference. The reduction in the band at 1086 cm\(^{-1}\) due to acetone, showing increased intensity after baking, may provide insight into the loss of CO-oxidation activity discussed previously. Baking at 125°C did not harm the catalyst's level of activity, but treatment with acetone
Figure 4.9a. DRIFTS spectra of acetone-treated and untreated 1.2% Pt/SnO$_2$ on cordierite; OH-stretch region.

Figure 4.9b. DRIFTS spectra of acetone-treated and untreated 1.2% Pt/SnO$_2$ on cordierite; fingerprint region.

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nearly destroyed it. Although not shown, the spectra of the acetone treated sample prior to baking at 125°C showed a small absorption band at 1700 cm\(^{-1}\) indicative of the C=O stretch of residual acetone which was absent after baking. This indicates that residual acetone was not the cause of the significantly reduced CO-oxidation activity of Pt/SnO\(_2\). Although speculative at this point, determining the identity of the species giving the strong absorption at 1086 cm\(^{-1}\) may provide a valuable key to the ambient temperature activity of Pt/SnO\(_2\).

Figures 4.10a and b show the spectra of the IPOTMS-treated and the untreated catalyst after baking at 125°C, along with the subtraction result. In the spectrum of the IPOTMS-treated sample, the presence of the strong O–H stretch band indicates that the catalyst sample was perhaps only slightly silylated. The presence of the band near 3000 cm\(^{-1}\), however, is due to the C–H stretch of the methyl groups of the trimethylsilyloxy groups and indicates that some degree of silylation was achieved. Further evidence for the presence of trimethylsilyloxy groups comes from the absorptions bands at 1270, 850, and 756 cm\(^{-1}\) which are assigned to the rocking vibrations between the hydrogen atoms and the carbon atom of the methyl groups of the trimethylsilyl group, (CH\(_3\))\(_3\)Si–. These assignments came from Connely.\(^{29}\)

Also of interest in the OH stretch region is the shift in the location of the O–H stretch maximum from 3360 cm\(^{-1}\) in the untreated catalyst sample to 3435 cm\(^{-1}\) in the IPOTMS-treated sample. This shows up in the subtraction result as a loss of OH intensity on the low-frequency side of the band with a concurrent increase in the intensity of the high-frequency side. These changes can be attributed to a loss of H-bonding and are consistent with the effects of silylation of surface hydroxyl groups. As the degree of silylation increases the concentration of H-bonding correspondingly decreases. In addition, the decrease in intensity of the sharp edge around 3750 cm\(^{-1}\) of the IPOTMS-treated sample relative to that of the untreated sample is consistent with a loss of isolated hydroxyl groups which would be expected during silylation. Further evidence of a loss of isolated hydroxyl
Figure 4.10a. DRIFTS spectra of IPOTMS-treated and untreated 1.2% Pt/SnO₂ on cordierite; OH-stretch region.

Figure 4.10b. DRIFTS spectra of IPOTMS-treated and untreated 1.2% Pt/SnO₂ on cordierite; fingerprint region.
groups comes from the decrease in the absorption intensity at 1225 cm$^{-1}$.

Figures 4.1a and b show the DRIFTS spectra of the TMSIM-treated catalyst sample and the untreated sample after baking at 125°C along with the subtraction result. As with the IPOTMS-treated sample the presence of the strong O–H stretch band indicates only slight silylation was achieved. The same bands for the trimethylsilyloxy groups present in the IPOTMS-treated sample spectrum are present in the TMSIM-treated sample spectrum albeit more intense. This may indicate that TMSIM provided a more thorough silylation of the catalyst sample and is consistent with the higher suppression in CO-oxidation activity. Also present are an additional band around 3150 cm$^{-1}$ (N–H stretch) and several bands between 1300 and 1700 cm$^{-1}$ which are indicative of imidazole, one of the breakdown products of TMSIM. Imidazole has a boiling point of 257°C, but is soluble in acetone. Considering the affinity of Pt for C=C double bonds, it is reasonable for the surface to remain slightly contaminated with imidazole even after rinsing with acetone and baking at 125°C. This also indicates that the loss of activity may have been due to tying up Pt sites as well as hydroxyl groups.

In the OH stretch region, although there is no shift in the absorption maximum of the O–H stretching band as seen in the IPOTMS-treated sample spectrum, there is a similar decrease in the sharp edge associated with isolated hydroxyl groups. It also appears that the high-frequency side of the OH band is more reduced in the TMSIM-treated sample than in the IPOTMS treated sample. These observations suggest a greater loss of isolated hydroxyl groups and are consistent with the more severely reduced CO-oxidation activity of the TMSIM sample.

It is reasonable that full silylation of all hydroxyl groups did not occur due to steric effects created the microporous texture of the catalyst coating. Nonetheless, the loss of CO activity is indicative that some impact was achieved via silylation. Due to the potential steric hinderance effects of the trimethylsilyloxy groups, themselves, in the normal operation of
Figure 4.11a. DRIFTS spectra of IPOTMS-treated and untreated 1.2% Pt/SnO₂ on cordierite; OH-stretch region.

Figure 4.11b. DRIFTS spectra of IPOTMS-treated and untreated 1.2% Pt/SnO₂ on cordierite; fingerprint region.

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the catalyst, the observations presented in this section do not constitute positive proof that hydroxyl groups are involved in the ambient temperature oxidation of CO over Pt/SnO₂. That silylation occurred with a consequent loss in the amount of H-bonding and the quantity of isolated hydroxyl groups was confirmed. These losses correlate with a severe decrease in CO-oxidation activity. Together this data provides further support of a model incorporating hydroxyl groups in the process of ambient-temperature oxidation of CO over Pt/SnO₂.

Using silylation or other means of removing hydroxyl groups may prove to be a useful means of investigating the purpose of hydroxyl groups in the reaction pathway. In addition, this process may facilitate the assignment of adsorption bands in various spectral methods of surface analysis. Further work in this area should prove to be both interesting and informative.

4.3.4. Rare isotope H₂¹⁸O. Harrison, et. al. used thermogravimetric analysis in conjunction with transmission IR spectroscopy to identify two forms of physisorbed H₂O on SnO₂ gels: a loosely held form which can be removed by evacuation at room temperature or by heating to about 75°C and a more tightly bound form, hydrogen-bonded to surface OH groups which can be removed by evacuation between 100°C and 150°C. Above 200°C, OH groups condense to form bridging Sn–O–Sn bonds and H₂O. In the reverse process, water dissociates on dry or dehydroxylated SnO₂ to form hydroxyl groups, both lattice and surface adsorbed. Consequently, the Pt/SnO₂ catalyst can be labeled with rare-isotope, ¹⁸OH groups by drying at temperatures greater than 200°C followed by treating with rare-isotope H₂¹⁸O vapor. The excess molecular water can then be removed by heating the catalyst to between 150°C and 200°C without condensing the surface OH groups. This process enables distinction between OH and H₂O related processes on the catalyst.

The 1.6% Pt/SnO₂ on cordierite catalyst described in Section 4.2.4 was labeled with
$^{18}$OH in the manner described above by first drying in a flowing He stream at 273°C for 5.5 hours followed by flowing a 2000 ppm $H_2^{18}$O He stream over the catalyst overnight (about 18 hours) at about 25°C. It should be noted that because the catalyst could not be completely dehydroxylated, there still existed common-isotope $^{16}$OH on the catalyst surface. Then catalyst was dried again at 176°C under a stream of dry He while monitoring the effluent stream with the mass spectrometer until all of the molecular water was down to background levels, about 3.5 hours. Both rare- and common-isotope water was removed from the catalyst; the majority was rare-isotope $H_2^{18}$O. This was done to ensure that any molecular water was removed from the catalyst leaving behind only groups. The catalyst was cooled to room temperature (25±2°C) and then a stoichiometric mixture of common-isotope $C^{16}$O and $^{16}O_2$ in dry He was passed over the catalyst for the first 58 minutes, then 2000 ppm $H_2^{18}$O was added. Figure 4.12 shows the conversion efficiency in % yield of $CO_2$ (right-hand axis) and concentration (left-hand axis) of each kind of carbon dioxide as

![Figure 4.12](image-url)
well as the total. While dry reaction gas mixture was passed over the $^{18}$OH-labeled catalyst, there was an initial spike in activity and all three forms of carbon dioxide are present: unscrambled $^{16}$O$_2$ and scrambled $^{16}$O$^{18}$O and $^{18}$O$_2$. The total conversion efficiency leveled off at about 50% and the scrambled forms continues to decrease indicating a depletion of surface $^{18}$OH. The presence $^{16}$O$^{18}$O and $^{18}$O$_2$ indicates that the oxygen of surface hydroxyl groups is active. Because the surface also possessed $^{16}$OH, at least a fraction of the common-isotope $^{16}$O$_2$ must have resulted from interaction with these hydroxyl groups.

When the dry He was switched to the “wet” He (containing 2000 ppm H$_2^{18}$O), the total activity increased to 100% conversion with increases in the concentration of each form of CO$_2$. This indicates that molecular water both catalyzes CO oxidation and that it interacts with either the reactants or products to produce the scrambled-isotope $^{16}$O$^{18}$O and $^{18}$O$_2$.

To determine whether water vapor interacts with reactants or products, the same catalyst was labeled with $^{18}$OH, as before, and a stream containing 1000-ppm CO$_2$ in dry He was passed over the Pt/SnO$_2$ catalyst at 23 sccm. The catalyst temperature was 25±2°C. Figure 4.13a shows the isotopic forms of CO$_2$ over time; the green line shows the concentration of CO$_2$ being fed to the catalyst gas stream. There appears to be a delay in the build-up of CO$_2$ which may be due to adsorption on the catalyst surface. It is not clear what the form of CO$_2$ is since tin carbonates are unstable and decompose into SnO$_2$ and CO$_2$. Evidence for surface carbonates and bicarbonates on SnO$_2$ gels and Pt/SnO$_2$ has been found using transmission IR and DRIFTS studies suggesting that these are the likely, surface-adsorbed forms of CO$_2$.

The presence of $^{16}$O$^{18}$O indicates that surface hydroxyl groups, as opposed to molecular water, can interact with carbon dioxide. Note that the $^{18}$O$_2$ remained below detectable levels.

Figure 4.13b is a continuation of the data 4.13a and shows the impact of (1) removing CO$_2$ while continuing dry He flow and (2) then switching the flowing stream to
Figure 4.13a. Scrambling of $^{16}\text{O}_2$ by adsorption on $^{18}$OH-labeled Pt/SnO$_2$.

Figure 4.13b. The effect of $\text{H}_2^{18}$O on the outgassing of CO$_2$ from Pt/SnO$_2$. 

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He with 2000 ppm H$_2^{18}$O. The green line shows the mass spectrometric signal at 44 m/e (C$^{16}$O$_2$) from an empty reactor tube before and after removing the CO$_2$. This data shows the length of time that is required for the all of the gas-phase CO$_2$ to be flushed from the reactor bed at the given flow rate (20.0 sccm). By comparison, when the Pt/SnO$_2$ catalyst is in the reactor tube, both C$^{16}$O$_2$ and the C$^{16}$O$^{18}$O signals take longer to decay than the empty reactor. This indicates that gas phase CO$_2$ is retained on the catalyst surface, but decomposes slowly. When H$_2^{18}$O is added to the He stream, there are initial increases in both C$^{16}$O$_2$ and C$^{16}$O$^{18}$O. This demonstrates that water catalyzes the breakdown of surface adsorbed carbon dioxide. The presence of C$^{16}$O$^{18}$O also suggests that water may operate by reacting with adsorbed CO$_2$, although it may have just been displacing adsorbed C$^{16}$O$^{18}$O. These associated steps in the mechanism will be discussed further in Chapter 5 on the oxidation mechanisms of Pt/SnO$_2$.

Finally, the following observations are also important to note. First, the rare-isotope was stream (2000 ppm H$_2^{18}$O in He) was monitored to ensure that there was complete conversion of $^{18}$O$_2$ to water; no signal was observed at m/e 36 indicating a level lower than 1 to 2 ppm. Second, no detectable scrambling between C$^{16}$O$_2$ and H$_2^{18}$O was observed in the empty reactor tube indicating that all scrambling was the result of the catalyst—not the system plumbing. Third, H$_2^{18}$O neither increased nor decreased the CO-oxidation rate over Pt on cordierite, but scrambling was observed with the small amount that was produced (about 40-50 ppm out of a possible 4300 ppm). Forth, scrambling was observed when C$^{16}$O$_2$ + H$_2^{18}$O was passed over SnO$_2$ on cordierite, but no detectable reaction was observed when C$^{16}$O + $^{16}$O$_2$ + H$_2^{18}$O reaction was passed over it. This is expected since water resists the adsorption of both CO$_2$ and mixtures of CO+O$_2$. This will be discussed more in Chapter 5.
4.4. SUMMARY

This chapter has discussed the effect of water on the CO-oxidation activity on Pt/SnO₂ catalyst coatings on cordierite monolith. It has been shown that, although essential to the reaction, water is required only in small amounts. In small amounts the water is present on the catalyst in both as hydroxyl groups and as molecular water. At least some of these hydroxyl groups are located on the SnO₂. Platinum may hold some hydroxyl groups as well, but this is unlikely in the presence of CO.

There are two possible ways in which the hydroxyl groups might catalyze the oxidation reaction between CO and O₂: aiding in the dissociative adsorption of O₂ or oxidizing the CO itself. Conceivably, hydroxyl groups serve both of these functions. Interfering with the hydroxyl groups via silylation has been shown to significantly reduce or even eliminate the ambient temperature oxidation of CO to CO₂ over Pt/SnO₂. As mentioned in the introduction, elimination of hydroxyl groups from Al₂O₃ eliminates dissociative adsorption of O₂.¹⁷

Excess molecularly adsorbed water reduces the CO-oxidation activity of Pt/SnO₂, possibly by interfering with the dissociative adsorption of O₂ on SnO₂. More about this will be discussed in Chapter 5. In the correct amounts, however, water optimizes the activity of Pt/SnO₂ for CO oxidation.

The interaction of CO₂ with Pt/SnO₂ might be explained in terms of the acid-base chemistry of CO₂ and SnO₂. The Lux-Flood definition would be appropriate here.³¹ According to this definition, the SnO₂ is the base and CO₂ the acid which react to produce a carbonate salt of tin(IV).

\[ \text{SnO}_2 + \text{CO}_2 \rightarrow \text{SnO(CO}_3) \]

Addition of H₂O to dry SnO₂ forms α- and β-stannic acids, SnO₂•xH₂O, increasing the
acidity and the likelihood of breakdown of the carbonate explaining the observed rate increase upon addition of water to dry Pt/SnO₂.

The results presented above provide a partial, or perhaps even complete, explanation for the question as to the role for water in the CO oxidation mechanism on Pt/SnO₂. Specifically, water helps remove CO₂ from the surface of Pt/SnO₂. The experiments involving molecular water—particularly, the rare-isotope experiments—cannot support or disprove the potential roles of surface hydroxyl groups in the dissociative adsorption of O₂ or in the oxidation of CO to CO₂. Since the absence of water or hydroxyl groups aids in the retention of CO₂, and adding water reverses the process by stimulating breakdown of adsorbed CO₂, it is reasonable to assume that CO₂ retention may be a rate-limiting step in the oxidation of CO over Pt/SnO₂. Consequently, it is important to know the state of “hydration” of the catalyst in order to accurately compare reaction rates among different Pt/SnO₂ catalyst samples.
CHAPTER 5
MECHANISTIC CONSIDERATIONS

5.1. INTRODUCTION

Whether in the gas phase or on a catalyst, in order for CO to react with O$_2$ to form CO$_2$, two things must happen: an O=O double bond must break and a C=O double bond must form. It might be possible for one species to adsorb on a catalyst and then react with the other from the gas phase. This is known as an Eley-Rideal mechanism. It has been largely dismissed on noble metals at temperatures above 25°C due to kinetic data suggesting that both CO and O must be adsorbed in order to react.\(^1\) The reaction between adsorbed species can be described by Langmuir-Hinshelwood kinetics.

On a catalyst, CO must adsorb, and O$_2$ must adsorb and dissociate in order for reaction to occur. O$_2$ can dissociatively adsorb on Pt and other clean metal surfaces at temperatures as low as 150 K,\(^2,3\) but the adsorption probability, or “sticking coefficient,” of CO is about 10 times greater than that of O$_2$.\(^4\) In addition, O$_2$ has a more rigid site requirement because adjacent open sites are required for adsorption and dissociation to occur, whereas CO requires only one open site.\(^4,5\) As a result, the reaction between CO and O$_2$ is negligible on Pt, except at very low ratios of CO/O$_2$ or at elevated temperature (>450 K), because the surface rapidly becomes saturated with CO.

On a one-component catalyst, CO and O$_2$ must compete for the same active sites. Theoretical evidence exists for the need to eliminate competition. Ziff, et al. performed a Monte Carlo simulation of the reaction between CO and O$_2$ on a hypothetical one-component catalyst surface, much like might be found on a real single crystal plane of a noble metal.\(^6\) By making the adsorption probabilities (sticking coefficient) equal, the influence of site requirements for CO and O$_2$ could be observed. When the partial pressure
ratio of CO to O₂ was greater than 0.525 CO poisoned the Pt catalyst.⁶ This suggests that even with equal adsorption probabilities, favorable site requirements for the reactive species is required. CO has a adsorption probabilities about 10 times greater than O₂ which would only shift the partial pressure ratio at which poisoning occurs to lower values. By comparison, consider the reaction between H₂ and O₂ on a noble metal. Both are diatomic molecules and require adjacent open sites for adsorption and dissociation. Adsorption probabilities aside, their equal site requirements alone eliminate competition, and the reaction would be predicted to occur at low temperature, consistent with observation.

Adding a second component capable of dissociatively adsorbing O₂ might eliminate the competition between CO and O₂. Theoretical evidence comes from Monte Carlo studies carried out by Herz, et.al. for the reaction between CO and O₂ on a hypothetical, two-component catalyst.⁷ The restrictions were imposed that CO could adsorb on only one component and O₂ could adsorb on both catalyst components, much like might occur over an NMRO catalyst. The results suggested that a sustained activity of 10 orders of magnitude could be obtained by the addition of just 1% of a component capable of dissociatively adsorbing O₂ without competition from CO.⁷

Consequently, one means by which Pt/SnO₂ may provide the synergistic activity for CO oxidation is via elimination of competition for active sites: Pt adsorbing CO, and SnO₂ dissociatively adsorbing O₂. At the molecular level, the catalyst appears as small islands of Pt on a SnO₂ surface. By creating a periphery of contact between Pt and SnO₂, CO can be brought into contact with atomic oxygen. Empirical evidence for the elimination of competition comes from kinetic studies which indicate that the reaction is not inhibited by CO as it is over Pt.⁸,⁹ In addition, Grass and Lintz found the reaction on Pt/SnO₂ to be zero order in both CO and O₂ at CO concentrations that would normally eliminate the reaction on Pt alone.¹⁰ They also proposed a mechanism involving CO adsorption on Pt and O₂ dissociative adsorption on SnO₂, with a possible rate-limiting step of surface...
diffusion of atomic oxygen to the periphery.\textsuperscript{10} A similar mechanism was proposed by Schryer, et al. with separate functions for each component and an active site consisting of a hydroxylated platinum-tin alloy forming at the periphery of the Pt and SnO\textsubscript{2} during a reductive treatment at elevated temperature.\textsuperscript{11} The alloy was identified in a collaborative effort with Hoflund at the University of Florida using Auger, XPS, and ISS surface studies of various Pt/SnO\textsubscript{2} catalysts before and after reductive CO treatment.\textsuperscript{12}

The Pt-Sn alloy could also serve to eliminate competition between CO and O\textsubscript{2} by breaking up the Pt into smaller islands within the Sn. CO adsorbs readily on Pt but not on Sn. O\textsubscript{2} adsorbs on both Pt and Sn. Intermingling Pt and Sn at the atomic level might facilitate O\textsubscript{2} adsorption on Pt while eliminating the CO domination. This is somewhat similar to tin’s function in Pt-Sn hydrocarbon reforming catalysts. Tin is inactive in the hydrocarbon transformations but presumably divides the Pt into small clusters and thereby prevents unacceptable side reactions.\textsuperscript{13} Modifying the adsorption properties of Pt changed the nature of the possible reactions. A similar mechanism for low-temperature, CO oxidation has been proposed for Pt-Ag\textsuperscript{14}, Pt-Rh\textsuperscript{15} and Pd-Sn\textsuperscript{16} alloys.

Rather than alloying with the noble metal, the support metal oxide itself might modify the normal characteristics of the noble metal. The process by which a support oxide-metal interface shows synergistic activity has been given the name “strong metal-support interaction” or SMSI.\textsuperscript{17} SMSI requires intimate contact between the noble metal and support oxide such as might be obtained during harsh reduction followed by re-oxidation. During a high-temperature reductive treatment of a metal-metal oxide system, the parent metal of a support oxide can be reduced to its zero valence and migrate through the supported metal to the surface. Upon exposure to oxygen, the relocated parent metal can then be re-oxidized creating a surface with metal oxide islands on the supported metal. The presence of the normally inert metal oxide as islands on the supported metal can modify the adsorption character, selectivity, and reactivity normally observed for the

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supported metal. This has been observed for the Ni on TiO$_2$ systems for the reaction between CO and H$_2$ to form CH$_4$ and O$_2$.\textsuperscript{18} Levin, et al. have also simulated the effects of high temperature reduction by vapor depositing TiO$_2$ partial layers on clean Rh surfaces.\textsuperscript{19} The resulting surface showed a 14-fold increase in the reaction rate for the reaction between CO$_2$ and H$_2$.

The oxidation of CO by oxygen over single metal oxides has not been observed at normal room temperature.\textsuperscript{20} As stated in Chapter 1, several of the transition metal oxides can catalytically oxidize CO in the presence of O$_2$ between 100°C to 200°C. Although $\Delta G^\circ_{\text{rxn}}$ for CO reduction of many transition metal oxides is negative, the re-oxidation by O$_2$ is positive because not enough energy is available to break the oxygen double bond. This suggests that sustained activity would not be thermodynamically favorable at 298 K. It is, however, generally believed that lack of ambient temperature catalysis is due to the strong parent metal-oxygen bonds.\textsuperscript{17} It is possible that adding a noble metal to the metal oxide reduces the strength of metal-oxygen bonds of metal oxides. This has been reported for several NMRO systems including Ru-catalyzed reduction of iron oxide;\textsuperscript{21} Rh-catalyzed reduction of TiO$_2$;\textsuperscript{22} and Pt-catalyzed reduction of several other metal oxides.\textsuperscript{23} For Pd/SnO$_2$, it has been proposed that the presence of the Pd both catalyzes the reduction and re-oxidation of the SnO$_2$.\textsuperscript{24}

For a given NMRO catalyst, the noble metal might modify the nature of the reducible oxide or vice versa. Alloys might form during preparation yielding unique sites upon which new catalytic activity might be observed. Or the synergistic level of activity might simply be the result of elimination of competition for adsorption between reactive species. Some or all of these observations may—in part—explain the synergistic level of activity for the reaction between CO and O$_2$ on Pt/SnO$_2$. None of the preceding discussion addresses the activity enhancing effect of water for the oxidation of CO on a Pt/SnO$_2$ catalyst. Water adds an essential ingredient to the reaction mixture; that is hydrogen.
possibly as hydroxyl groups. An essential part of the explanation is undoubtedly H or OH. This is the topic will be discussed in Section 5.2.2.

5.2. CO OXIDATION

This section discusses the data presented in the preceding chapters as they contribute to an understanding of the reaction mechanism between CO and O_2 on Pt/SnO_2. Specific attention is placed on the discovered role of water and the possible roles of hydroxyl groups.

5.2.1. Separate roles for Pt and SnO_2. Bond, Fuller, and Molloy explained the mechanism of oxidation on the basis of CO spillover onto SnO_2, but CO does not adsorb appreciably on SnO_2 and would readily react with any preadsorbed atomic oxygen at low temperature making spillover unnecessary. Boulahouache, Lintz, Kons, and Shulz suggested a similar mechanism involving reverse spillover of atomic oxygen onto the Pt to react with adsorbed CO. Since the Pt would be saturated with CO, however, when atomic oxygen reached the periphery, the reaction would be instantaneous. Invoking a spillover mechanism would only serve to delay the reaction. Later, Gras and Lintz suggested that the reaction occurred at the periphery of Pt and SnO_2 but stated that no distinction could be made between this and reverse spillover.

In Chapter 2, it was shown that the activity was related to the surface areas of both Pt and SnO_2. Increasing the SnO_2 surface area provides a means for increasing adsorption of not only O_2, but also CO by increasing the surface area of the Pt. Predictable increases in CO-oxidation activity for Pt/SnO_2 catalysts were observed that were related to the surface areas of both Pt and SnO_2. In Section 2.3.2 a model was developed which related the CO-oxidation activity to the SnO_2 surface area (R ∝ A^{4/3}_{SnO_2}). Whether the surface area was increased by elevating SnO_2 loading or by etching the SnO_2-coated cordierite, the resulting activity demonstrated reasonably good agreement with the model. In Section
2.3.3 It was shown that the activity normalized to the Pt loading increased as the Pt loading decreased indicating better dispersion at lower Pt loadings. These data were shown to fit the same model.

Consider by comparison the reaction between CO and O\textsubscript{2} over a one-component catalyst (i.e. either SnO\textsubscript{2} or Pt alone). Langmuir-Hinshelwood kinetics indicate that the reaction rate, or activity, is proportional to the quantity of each adsorbed analyte. Increasing the surface area of the catalyst should increase the number of adsorption sites and thereby increase its activity. For a single component catalyst then, the reaction is a function of the surface area of that component. The derivation presented in Section 2.3.2 indicated that the CO oxidation rate, $R_{obs}$, was directly proportional to the surface areas of both Pt and SnO\textsubscript{2}. If Pt alone were responsible for the oxidation of CO, then $R_{obs}$ would have been expected to be related to only $A_{Pt}$ which was shown to increase as $A_{SnO2}^{1/3}$. But this was not observed. If only SnO\textsubscript{2} were responsible for CO oxidation, then $R_{obs}$ would have been expected a linear function of $A_{SnO2}$. But that was not observed either. Instead $R_{obs}$ was related to $A_{SnO2}^{4/3}$, the product of the adsorption sites. The accuracy of this model in fitting the observed changes in activity related to changing $A_{SnO2}$ provides convincing evidence that both components have separate non-competing roles: Pt adsorbs CO and SnO\textsubscript{2} dissociatively adsorbs O\textsubscript{2}. This is also consistent with the results of Gras and Lintz who presented kinetic data indicating these same roles for Pt and SnO\textsubscript{2}.\textsuperscript{10}

Further evidence of the independent roles comes indirectly from data presented in Section 3.3.1 on the oxidation of formaldehyde. Recall the data presented in Table 3.1. When enough CO was added to the reaction gas mixture to prevent its total conversion to CO\textsubscript{2}, the oxidation of CH\textsubscript{2}O and eventually CO ceased. The cessation of activity was inferred to result from the following chain of events: CO saturated the Pt surface preventing adsorption and oxidation of CH\textsubscript{2}O. The CH\textsubscript{2}O in turn saturated the SnO\textsubscript{2} eventually stopping the reaction between CO and O\textsubscript{2}. Similar results were obtained for reaction gas...
mixtures containing CO and methanol. Because both formaldehyde and methanol adsorb on SnO₂ and can block the reaction between CO and O₂, it is reasonable to hypothesize that O₂ dissociatively adsorbs on SnO₂ rather than Pt.

5.2.2. Role of hydroxyl groups. In light of our data and that in the literature, there are at least two possible ways in which hydroxyl groups might increase the reaction rate between CO and O₂: either by aiding in the dissociative adsorption of O₂ or by oxidizing the CO itself. Conceivably, hydroxyl groups could serve both functions.

Before considering these possibilities, it is important to consider the proposed dissociative adsorption of O₂ in the absence of hydroxyl groups. Henrich and Cox suggest that O₂ adsorbs on stoichiometric SnO₂, an n-type semiconductor, by accepting an electron

\[ e^- + O_2 + SnO_2 \rightarrow O_2^- \cdot SnO_2 \]  

with dissociation being initiated by O-vacancy defects, represented as Sn²⁺, and occurring in a step wise fashion.²⁸

\[ e^- + 2 \text{Sn}^{2+} + O_2^- \cdot SnO_2 \rightarrow 2 O^- \cdot Sn + SnO_2 \]  

\[ e^- + O^- \cdot Sn \rightarrow O^2^- \cdot Sn \]  

Oxygen-vacancy defects might be described here as partially reduced SnO₂ where some of the surface tin atoms are the +2 oxidation state. In this manner, Sn²⁺ is reducing the adsorbed O₂. Cavicchi, et al. found that the number of defect sites could be increased via reduction (Sn⁴⁺ → Sn²⁺) and remain stable in the presence of oxygen up to 700K (427°C).²⁶ It is interesting that this temperature is about the same (475°C) as that Cox and Fryberger found was necessary to evacuate surface bridging O, as discussed in Section 4.1.²⁷ Considering the low processing temperatures used during catalyst preparation of
Chapters 1 and 2, which likely leave the tin oxide in a polymorphous or polycrystalline state, there will always be surface exposed tin atoms which could behave as O-vacancy defects. Drawdy et al. found evidence for the presence of both SnO and SnO₂ using ISS, AES, ESCA, and EDS to study polycrystalline SnO₂ before and after reduction in 40 torr of CO at 100°C and 175°C. Considering the improvement in CO-oxidation activity over mildly reduced Pt/SnO₂, the participation of O-vacancy defect sites in the dissociative adsorption of O₂ is reasonable.

In the presence of hydroxyl groups, there are a few means by which the dissociative adsorption of O₂ could be aided. The presence of the hydrogen may serve to stabilize the negative charge or unpaired electrons shown in reaction at any stage of the reaction sequence (1a) to (1c). Protons could become available by interaction of an OH group with an O-vacancy.

\[
\begin{align*}
\text{H} & \quad \text{O}^+ \quad \boxed{\text{Sn}} \\
\text{Sn} & \quad \text{Sn} \quad \Rightarrow \quad \text{Sn} \quad \Rightarrow \quad \text{Sn} \quad \Rightarrow \quad \text{Sn} + \text{H}^+
\end{align*}
\]

With protons available, the reaction sequence (1a) through (1c) can be written as

\[
\begin{align*}
e^- + \text{O}_2 + \text{SnO}_2 + \text{H}^+ & \rightarrow \text{HO}_2^*\text{SnO}_2 \\
e^- + 2 \text{ Sn}^0 + \text{HO}_2^*\text{SnO}_2 & \rightarrow 2 \text{ HO}^*\text{Sn} + \text{O}^*\text{Sn} + \text{SnO}_2 \\
e^- + \text{O}^*\text{Sn} + \text{H}^+ & \rightarrow \text{HO}^*\text{Sn}
\end{align*}
\]

The HO₂ species has been found hypothesized as a source of OH radicals in combustion of hydrocarbon-O₂ and H₂-O₂ flames. This species might then decompose into OH and O radicals by interaction with O-vacancies without requiring extra electrons. By stabilizing the negative charge on the O atoms, the dissociative adsorption of O₂ is more likely to occur in the presence of water or H⁺ than in its absence.
Another possible explanation for hydroxyl group-aided $O_2$ dissociation is presented in Figure 5.1. The presence of oxygen deficient sites is not required nor is it necessary to invoke reduction of $O_2$ by surface Sn$^{2+}$. Instead, hydroxyl groups serve as the site on which $O_2$ can dissociatively adsorb. This process is more easily visualized in three dimensions. In part (a) the gas phase $O_2$ (large white spheres) is shown adsorbing on the $\text{SnO}_2$ portion of the catalyst surface via hydrogen bonding to a group of hydrogen atoms (small white spheres) of surface hydroxyl groups of $\text{SnO}_2$. As a result of the hydrogen bonding, the adsorbed $O_2$ has a weakened double bond (depicted with dashed lines) and might perhaps dissociate to produce two hydronium-like species. Evidence for $H_3O^+$ on Pt/$\text{SnO}_2$ has been found using DRIFTS$^{29}$ and on $\text{SnO}_2$ using ESD.$^{12}$

Parts (b) and (c) of Figure 5.1 show the possible reactions between the $O_2$ adsorbed on $\text{SnO}_2$ and CO adsorbed on Pt. Note that the $O_2$ never requires direct interaction with the tin atoms of $\text{SnO}_2$. In part (b), the $\text{CO}_2$ is formed directly leaving another $O$ atom for reaction with CO. If a single CO molecule reacts with both oxygen atoms simultaneously, as in part (c), a carbonate- or bicarbonate-like species would form which would then decompose to form $\text{CO}_2$.

Another means by which hydroxyl groups might catalyze the reaction between CO and $O_2$ is by acting as the oxidizing agent itself. Schryer, et al. have suggested that the hydroxyl groups of Pt/$\text{SnO}_2$ oxidize adsorbed CO to $\text{CO}_2$ either directly or through formate, carbonate, or bicarbonate intermediates.$^{11}$ The presence of the H may labilize the bond between the Sn and $O$, making it easier to oxidize CO adsorbed on Pt. The composite reaction is written in (2) below.

$$\text{HO}^*\text{Sn} + \text{CO}^*\text{Pt} \rightarrow \text{CO}_2 (g) + \text{Sn}^0 + \text{Pt} + \text{H} \quad (2)$$

The form of the hydrogen is not known but could be either a radical or a proton could form OH directly with surface oxygen.
Figure 5.1. (a) Oxygen adsorption on surface hydroxyl groups of tin oxide, (b) reaction of adsorbed carbon monoxide with adsorbed O$_2$, and (c) carbonate formation and decomposition.
CO adsorbed on Pt could react with one or two hydroxyl groups to form formate, bicarbonate, or carbonate species. A formate species would form by the reaction of CO with a single hydroxyl group as shown in reaction (3).

![Chemical reaction diagram](image)

Loss of a hydrogen to a Sn-bound oxygen atom would lead to the formation of CO₂ possibly with reduction of surface Sn⁴⁺ to Sn²⁺. The Sn²⁺ would then be re-oxidized to Sn⁴⁺ by incoming O₂, although the oxidation state of Sn has not be characterized.

A bicarbonate or carbonate would form from the reaction of CO with two OH groups. This reaction would be similar to the one shown in Figure 5.1, part (c) except that the carbonate or bicarbonate could be coordinated either in a bidentate or unidentate manner with tin atoms and eventually would decompose to form CO₂. Brown and Duarte, found evidence for adsorbed carbonate, bicarbonate, and formate on Pt/SnO₂ during the reaction of CO and O₂ using DRIFTS.³⁰ The reaction sequence in (4) shows this possible pathway.

![Chemical reaction diagram](image)

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5.2.3. Role of molecular water. From the data presented in Chapter 4, there exists an optimum amount of molecular water that enhances the observed reaction rate between CO and O₂ on Pt/SnO₂. This amount is likely greater than that required for the formation of a completely hydroxylated surface. If too little water is present—even on an hydroxylated Pt/SnO₂ catalyst—CO₂ is retained for longer periods of time. Addition of small amounts of water catalyze the release of CO₂. This suggests that breakdown of surface adsorbed CO₂ is a rate-limiting step when the catalyst surface is covered with less than the optimum quantity of molecular water. The presence of too much water, on the other hand, can stop the reaction between CO and O₂.

As demonstrated in Section 4.2.4, at least part of the activity enhancement occurring by addition of molecular water to Pt/SnO₂ is the release of surface bound CO₂, consistent with the acid-base properties of SnO₂ and CO₂. This may happen by displacing bidentate carbonate to become unidentate carbonate which can then more easily desorb as CO₂ as shown below on a hypothetical surface Sn site.

\[
\text{C} = \text{O} \text{OH} \quad \text{HO} \quad \text{Sn} ^ \rightarrow \quad \text{Sn} \quad \text{Sn} \quad \text{Sn}
\]

(6)

Water may also function by reacting directly with the bound form of carbonate, effectively removing it from the surface. This would explain the presence of the scrambled-isotopic form of carbon dioxide by introducing small amounts of molecular H₂¹⁸O to the flowing dry C¹⁶O₂ reaction gas stream.

\[
\quad \text{Sn} \quad \text{Sn} \quad \text{Sn}
\]

(7)
It is interesting that the catalytic breakdown of carbonate via water is consistent with Harrison and Maunder's findings that water vapor inhibits the adsorption of CO\textsubscript{2} on SnO\textsubscript{2}.

Harrison, et al. identified two forms of physisorbed H\textsubscript{2}O on SnO\textsubscript{2}: a loosely held form that can be removed by evacuation at room temperature or by heating to about 75°C and a more tightly bound form, hydrogen-bonded to surface OH groups which can be removed by evacuation between 100°C and 150°C.\textsuperscript{31,32} The ability to identify these forms suggests that a means may exist to investigate the kind of water that is most beneficial to CO oxidation on Pt/SnO\textsubscript{2}: the loosely physisorbed form or that form hydrogen-bonded to surface hydroxyl groups of SnO\textsubscript{2}. A combination of both forms may also be optimum. Based on the enhanced CO-oxidation activity obtained by adding molecular water to an already-hydroxylated Pt/SnO\textsubscript{2} catalyst, it is reasonable to assume that the water hydrogen-bonded to surface OH is one form. Because excess water reduces activity, it is reasonable to hypothesize that this loosely physisorbed form, perhaps forming multilayers of water, inhibits adsorption or dissociative adsorption of O\textsubscript{2}. This is consistent with the loss in CO oxidation activity observed when high formaldehyde and methanol concentrations were present in mixtures also containing CO. As discussed in Sections 3.3.1 and 3.3.2, adsorption of formaldehyde and methanol on SnO\textsubscript{2} blocked out O\textsubscript{2} adsorption and oxidation of CO ceased.

5.3. VOLATILE ORGANIC COMPOUNDS

Whereas SnO\textsubscript{2} is an essential component in Pt/SnO\textsubscript{2} for the ambient temperature oxidation of CO, it was shown in Sections 3.3.1 and 3.3.2 that it is not required for the oxidation of formaldehyde, or methanol. The combination of Pt and SnO\textsubscript{2} does, however, appear to modify the concentrations of the products species in the conversion of methanol and ethanol by comparison to Pt alone. This suggests differences in the reaction pathways.
Such differences provide further evidence that SnO₂ provides dissociatively adsorbed O₂ in the conversion of the alcohols, as well as in the oxidation of CO.

Hydroxyl groups are involved in the combustion pathway of several volatile organic compounds and hydrocarbons in the gas phase. The surface of the catalyst with adsorbed reactive species may be envisioned as a 2-dimensional gas and similar mechanisms emerge. These mechanisms will show why surface OH on SnO₂ may not be necessary for the oxidation of volatile organic compounds but may nonetheless participate and actually reduce the temperature at which oxidation normally occurs on Pt alone—in particular, for the saturated hydrocarbons.

5.3.1. Formaldehyde. Recall from Table 3.1 that CH₂O adsorbs readily onto SnO₂ at room temperature but does not oxidize. Since SnO₂ can dissociatively adsorb oxygen, then it might be expected that the oxidation of CH₂O would occur on SnO₂ alone. There would be an ample supply of oxygen atoms to form CO₂ and H₂O; yet, no oxidation over SnO₂ was observed. It follows that the Pt is necessary to weaken or break the C–H bonds in CH₂O at normal room temperature. At elevated temperatures, SnO₂ might catalyze the oxidation of CH₂O with O₂.

Recall that formaldehyde decomposes on Pt in vacuum at 78 K into CO and H atoms which combine to form H₂. Also recall that O₂ can adsorb on Pt at temperatures as low as 150 K. As shown in Table 3.1, the oxidation of CH₂O occurs quite readily at room temperature over Pt alone to CO₂ and H₂O—no CO or H₂ being detected. Assuming that CH₂O decomposes at 298 K as it does at 78 K into CO and H, the dissociative adsorption of O₂ cannot be hindered by the presence of this CO because CO₂ and H₂O are produced. Considering the site requirements for the adsorption and dissociation of CH₂O and O₂, this is reasonable. Although CO requires only one adsorption site on Pt, CH₂O would require at least two sites in order to decompose. As such, CH₂O could not effectively prevent dissociative adsorption of O₂ as CO does, and the oxidation of CH₂O...
on Pt surface at ambient temperatures would be allowed.

As stated in the previous section, O and H do not likely exist on Pt but rather form OH. It is also possible that CH₂O decomposes directly into CO and OH on Pt in the presence of adsorbed O. The surface of Pt would possess a large quantity of OH groups which may then oxidize CO to CO₂ and H. The H would then form more OH or H₂O. A mechanism consistent with the foregoing information might proceed as follow:

\[
\begin{align*}
O_2 (g) + Pt \rightarrow& \rightarrow O_2 \cdot Pt \\
CH_2O (g) + 3 Pt \rightarrow& \rightarrow CO \cdot Pt + 2 H \cdot Pt \\
H \cdot Pt + O_2 \cdot Pt \rightarrow& \rightarrow HO \cdot Pt + O \cdot Pt \\
CO \cdot Pt + O \cdot Pt \rightarrow& \rightarrow CO_2 (g) + 2 Pt \\
CO \cdot Pt + HO \cdot Pt \rightarrow& \rightarrow CO_2 (g) + Pt + H \cdot Pt \\
HO \cdot Pt + H \cdot Pt \rightarrow& \rightarrow H_2O (g) + 2 Pt \\
O \cdot Pt + H \cdot Pt \rightarrow& \rightarrow HO \cdot Pt
\end{align*}
\]

Although the presence of SnO₂ is not required for the oxidation of CH₂O, it may still participate in the reaction by dissociatively adsorbing O₂ as shown earlier for the oxidation of CO. As with Pt, the form of oxygen on the surface of Pt/SnO₂ responsible for oxidation may be either O or OH. Because O₂ dissociative adsorption can occur on either Pt or SnO₂ as long as CO is not present in the reaction gas mixture, the species providing O or OH is unknown and could merely be designated as "S" to indicate an active site for O₂ dissociative adsorption. O₂ adsorption proceeds as follows:

\[
O_2 (g) + 2 S \rightarrow 2 O \cdot S
\]

Rather than rewrite the reactions (7a) to (7h), any reaction involving O•Pt or HO•Pt could

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be replaced with O•S or HO•S.

5.3.2. Methanol. Similar results were obtained for the oxidation of methanol on Pt/SnO₂ and Pt as was obtained for formaldehyde. Methanol adsorbed on, but was not oxidized on, SnO₂ alone. Methanol could be completely converted to CO₂ and H₂O at 25°C, on Pt and Pt/SnO₂, but there was a small amount of methyl formate produced which was not found during formaldehyde oxidation. Adding CO to the reaction gas mixture always inhibited the oxidation of methanol on Pt. On Pt/SnO₂, CO inhibition occurred only if enough methanol was in the reaction gas mixture to saturate the SnO₂. Differences existed between Pt and Pt/SnO₂, however, in the time required to reach a steady-state activity and concentrations of products for both methanol and methanol-CO mixtures. These differences suggest possible mechanistic differences.

Methanol chemisorbs on most clean, oxygen-free metal surfaces at very low temperatures via cleavage of the O–H bond to form adsorbed H and methoxy groups, OCH₃.³⁵,³⁶ On Pt, Pd, W, Ru, and Ni the adsorbed OCH₃ then decomposes to CO and H₂.³⁵ On Ag, Cu, and Fe, on the other hand, formaldehyde is favored over CO and H₂.³⁵,³⁷,³⁸ All of these studies found that preadsorbed oxygen atoms stabilized chemisorbed methoxy from further decomposition until slightly higher temperatures were reached. On Fe, the degree of stabilization was proportional to the quantity of preadsorbed oxygen.³⁸ On clean Pt (111), methanol decomposed at 140 K to form CO and H₂.³⁵ If preadsorbed oxygen atoms were present, then methanol decomposed to methoxy, OCH₃, and H₂O. The OCH₃ was stable up to 170 K at which point it decomposed to form CO and H₂. In other words, when oxygen was present, formation of OCH₃ and water was favored over decomposition to CO and H₂.

It is interesting that excess adsorbed O stabilized rather than accelerated the decomposition of OCH₃. It might be expected that more available O would reduce rather than increase the decomposition temperature. This also suggests that O does not attack the

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C's or H's of OCH₃. This may be because the reaction between O and OCH₃ is unallowed by spin conservation rules in the gas phase which may also apply on the surface of Pt.

It is also interesting that the decomposition of CH₃OH occurs at only slightly higher temperatures than for CH₂O and the products are the same, CO and H₂. The slightly higher temperature may be related to the change in hybridization of the C and O orbitals that must occur for CH₃OH to convert to CO, C from sp³ to sp and O from sp² to sp. With the decomposition occurring at such a low temperature to produce CO and H₂, the mechanism for the oxidation of CH₃OH to CO₂ and H₂O is very likely equal to that of CH₂O for most steps. The apparent exception is the dissociation to H and OCH₃.

\[
\begin{align*}
\text{CH}_3\text{OH (g)} + 2 \text{Pt} & \rightarrow \text{CH}_3\text{O•Pt} + \text{H•Pt} \quad (8a) \\
\text{CH}_3\text{O•Pt} + \text{Pt} & \rightarrow \text{CH}_2\text{O•Pt} + \text{H•Pt} \quad (8b) \\
\text{CH}_2\text{O•Pt} + 2 \text{Pt} & \rightarrow \text{CO•Pt} + 2 \text{H•Pt} \quad (8c)
\end{align*}
\]

The adsorbed H and CO would then follow the same series of reactions as presented in (7c) through (7g).

Because methyl formate, CH₃OOCH is a by-product over both Pt and Pt/SnO₂, formate, OOCH must be present on the surface as well as OCH₃. Formate may form from the reaction between CO and OH as shown in oxidation of CO, reaction (4). It is also possible that OOCH arises from the step wise oxidation of OCH₃. Since O or OH may be provided by Pt or SnO₂, it will be designated as in (7h). With both OCH₃ and OOCH present in sufficient quantity, their reaction would produce CH₃OOCH. The mechanism may proceed as follows:

\[
\begin{align*}
\text{CH}_3\text{O•Pt} + \text{HO•S} & \rightarrow \text{CH}_2\text{O•Pt} + \text{H}_2\text{O•S} \quad (8d) \\
\text{CH}_2\text{O•Pt} + \text{HO•S} & \rightarrow \text{CHO•Pt} + \text{H}_2\text{O•S} \quad (8e)
\end{align*}
\]
Each instance where HO•S occurs could be replaced by O•S in which case the product would have been OH rather than H₂O. Spin conservation suggests that this may be a less probable route, however.

It was shown in Section 3.3.2 that CH₃OH adsorbs onto SnO₂, but does not oxidize. The adsorbed form may be either molecular or dissociated into methoxy and surface OH. Neither proposed form, OCH₃ or CH₃OH, was found to be reactive at room temperature. For this reason, adsorption on SnO₂ is not included in the mechanism. Spillover of OCH₃ or CH₂OH onto the Pt is possible and may also be a source of methyl groups in the formation of methyl formate.

There is no compelling reason to invoke SnO₂ as a necessary component for the oxidation of methanol at ambient temperature. As shown in Section 3.3.2, however, the effluent streams from Pt and Pt/SnO₂ contained different quantities of product as a function of time, and a few observations are worth noting. There was a lag time of 200 minutes in the conversion of CH₃OH to CH₃OOCH and CO₂ over Pt. Because decomposition of CH₃OH on Pt occurs at 140 K, this might not be the rate-limiting step for the reaction at room temperature and higher. Instead this suggests that dissociative adsorption of O₂ is the rate-limiting step. Since dissociative adsorption of O₂ does not occur on the metal oxides of cordierite in the temperature range investigated, it must occur on the Pt. The lag time, then, suggests that competition may exist between O₂ and CH₃OH for active sites on Pt and may have been responsible for the delay in the onset of the reaction on Pt.
Over Pt/SnO$_2$, on the other hand, the oxidation products, CO$_2$ and CH$_3$OOCH, appeared immediately indicating that O$_2$ was more readily available. As with oxidation of CO over Pt/SnO$_2$, SnO$_2$ provides a separate site for the dissociative adsorption of O$_2$ that Pt cannot provide at ambient temperature. Although SnO$_2$ is not required for conversion of CH$_3$OH, the conversion occurs more readily over Pt/SnO$_2$ than over Pt alone. Consequently, the lag time was not observed and the reaction reached a steady-state much faster.

5.3.3. Ethanol. Sexton, et al. found that ethanol decomposes on Pt surfaces in vacuum in a similar manner to methanol on Pt and at similarly low temperature. On clean Pt(111) surfaces, ethanol decomposes to form CO, H, and C. With preadsorbed O on the Pt, adsorbed ethoxy groups, CH$_3$CH$_2$CO, and OH formed instead. The CH$_3$CH$_2$CO decomposed into CO and C and H atoms at slightly higher temperature. In these studies on Pt and Pt/SnO$_2$ performed at atmospheric pressure and normal room temperature, CO$_2$, H$_2$O, CH$_3$CHO (ethanal), and CH$_4$ were produced. With a continuous supply of O$_2$, it is reasonable that CO$_2$ and H$_2$O formed rather than CO and H$_2$. The presence or absence of C on Pt or Pt/SnO$_2$ cannot be addressed here. Adsorption of ethanol likely proceeds as for methanol

\[
\text{CH}_3\text{CH}_2\text{OH} (g) + 2 \text{Pt} \rightarrow \text{CH}_3\text{CH}_2\text{O}\text{Pt} + \text{H}\text{Pt}
\]  

(9a)

with the adsorbed H forming OH with adsorbed O$_2$ or forming H$_2$O with OH, as before.

The adsorbed CH$_3$CH$_2$O only needs to lose an H atom to form CH$_3$CHO. Because sufficient O$_2$ is in the reaction gas mixture, adsorbed O or OH may aid in this process. As shown in Section 3.3.3, both CO$_2$ and CH$_3$CHO appeared at a lower temperature in the effluent stream from Pt/SnO$_2$ than from Pt suggesting that SnO$_2$ may have been providing oxygen in some form, atomic or hydroxyl. The presence of O or OH adsorbed on SnO$_2$
would enable the oxidation to occur at a lower temperature than over Pt alone. Because O
or OH can be provided by either Pt or SnO₂, however, no distinction is made in the
mechanism. Production of ethanal may also occur by loss of another H.

\[ \text{CH}_3\text{CH}_2\text{O}^*\text{Pt} + \text{HO}^*\text{S} \longrightarrow \text{CH}_3\text{CHO} \text{ (g)} + \text{H}_2\text{O} \text{ (g)} \text{ Pt} + \text{S} \]  
(9b)

\[ \text{CH}_3\text{CH}_2\text{O}^*\text{Pt} + \text{Pt} \longrightarrow \text{CH}_3\text{CHO} \text{ (g)} + \text{H}^*\text{Pt} \]  
(9c)

The CH₃CH₂O may decompose rather than form ethanal by breaking into methyl groups,
CH₃, and formaldehyde. This reaction has been suggested in combustion processes.³³

\[ \text{CH}_3\text{CH}_2\text{O}^*\text{Pt} + \text{Pt} \longrightarrow \text{CH}_3^*\text{Pt} + \text{CH}_2\text{O}^*\text{Pt} \]  
(9d)

The formaldehyde would decompose as per (7a) through (7g) and the methyl group, CH₃,
would have various fates. One fate would be the recombination with adsorbed H to form
methane.

\[ \text{CH}_3^*\text{Pt} + \text{H}^*\text{Pt} \longrightarrow \text{CH}_4 \text{ (g)} + 2 \text{ Pt} \]  
(9e)

Another fate might be reaction with OH or O to form CH₃OH or CH₃O. If so, then
methanol or methyl formate might have appeared in the product mixture but was absent.
Instead the reaction with O₂ to form formaldehyde and OH has been observed in
combustion reactions of methane and may occur on Pt and Pt/SnO₂.³³

\[ \text{CH}_3^*\text{Pt} + \text{O}_2^*\text{S} \longrightarrow \text{CH}_2\text{O}^*\text{Pt} + \text{HO}^*\text{S} \]  
(9f)

Both CH₂O and OH would have the same fate as presented in reactions (7a) through (7g).
5.3.4. 1-Propanol and 2-propanol. The higher alcohols present a different situation from the alcohols containing only 1 or 2 carbons. In vacuum on the Pt(111) face, 1-propanol absorbs in a manner similar to methanol and ethanol forming the propoxy group and which continues decomposing to CO, H and ethylidyne, CH$_3$C.$^{35}$ A possible reaction scheme follows:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \ (g) + 2 \text{Pt} & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{O}^{*}\text{Pt} + \text{H}^{*}\text{Pt} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{O}^{*}\text{Pt} + \text{Pt} & \rightarrow \text{CH}_3\text{CH}_2\text{Pt} + \text{CH}_2\text{O}^{*}\text{Pt} \\
\text{CH}_3\text{CH}_2\text{Pt} + 2 \text{Pt} & \rightarrow \text{CH}_3\text{C}^{*}\text{Pt} + 2 \text{H}^{*}\text{Pt}
\end{align*}
\] (10a, 10b, 10c)

In the presence of sufficient O$_2$, the CH$_2$O produced in (10b) would again follow the oxidation path in (7a) through (7g) rather than form CO and H as observed for the vacuum decomposition. Rather than forming CH$_3$C, the CH$_3$CH$_2$ could recombine with H to form ethane as was observed in the product mixture in the oxidation over Pt/SnO$_2$.

\[
\text{CH}_3\text{CH}_2^{*}\text{Pt} + \text{H}^{*}\text{Pt} \rightarrow \text{CH}_3\text{CH}_3 \ (g) + 2 \text{Pt} \] (10d)

The ethyl fragment could also react with O$_2$ or some form of adsorbed O, as the methyl fragment in reaction (9f), to form ethoxy and OH.

\[
\text{CH}_3\text{CH}_2^{*}\text{Pt} + \text{O}_2^{*}\text{S} \rightarrow \text{CH}_3\text{CH}_2\text{O}^{*}\text{Pt} + \text{HO}^{*}\text{S} \] (10e)

The adsorbed CH$_3$CH$_2$O would then decompose as before, reactions (9d) and 9(f). It might be expected then to see ethanal. But this would not necessarily be observed because the temperature required for complete

A similar fate was found for 1-butanol forming CO, H, and propylidyne,
and a trend becomes apparent. The higher alcohols adsorb by loss of an H, then lose the terminal CH₂O, leaving a hydrocarbon fragment with one carbon less. This fragment then reacts with some form of adsorbed oxygen forming an alkoxy which then splits of another CH₂O group. The formaldehyde is readily oxidized and the process repeats until the alcohol is completely oxidized.

Although the unknown by-product in the oxidation of 1-propanol over Pt/SnO₂ was not identified as propanal, it is possible that this was its identity. 1-Propanal could easily form in a manner similar to that in which ethanal was formed from ethanol by loss of an H or by attack of O or OH. Similar reactions for the formation of 1-propanol might be:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{O}\cdot\text{Pt} + \text{Pt} & \longrightarrow \text{CH}_3\text{CH}_2\text{CHO} (g) + \text{H}\cdot\text{Pt} + \text{Pt} \quad (10f) \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{O}\cdot\text{Pt} + \text{HO}\cdot\text{S} & \longrightarrow \text{CH}_3\text{CH}_2\text{CHO} (g) + \text{Pt} + \text{H}_2\text{O}\cdot\text{S} \quad (10g)
\end{align*}
\]

2-Propanol presents a somewhat different situation from 1-propanol. Sexton found that 2-propanol decomposes in a manner similar to methanol and ethanol forming only CO, H, and C. Because it does not have a terminal OH group, this might be expected.

\[
\begin{align*}
\text{(CH}_3)_2\text{CHOH} (g) + \text{Pt} & \longrightarrow \text{(CH}_3)_2\text{CHO}\cdot\text{Pt} + \text{H}\cdot\text{Pt} \quad (11a) \\
\text{(CH}_3)_2\text{CHO}\cdot\text{Pt} + 2 \text{Pt} & \longrightarrow 2 \text{H}_3\text{C}\cdot\text{Pt} + \text{CO}\cdot\text{Pt} + \text{H}\cdot\text{Pt} \quad (11b) \\
\text{CH}_3\cdot\text{Pt} + 6 \text{Pt} & \longrightarrow \text{C}\cdot\text{Pt} + 6 \text{H}\cdot\text{Pt} \quad (11c)
\end{align*}
\]

For the normal atmospheric pressure reaction over Pt/SnO₂, it might be expected to see methane, but none was observed. No by-products were observed either, only CO₂ and H₂O. It is possible that the temperature was too high once the reaction started (100°C versus 30°C) for the CH₃ groups to combine with H. The CH₃ groups oxidize to CH₂O according to reaction (9f).
Conversion of the $C_4$ to $C_4$ alcohols on Pt-Rh has also been investigated at atmospheric pressure, rather than in vacuum, by Bart, et al. Each alcohol showed the same $T_{10}$ of 200°C when a stoichiometric amount of $O_2$ was present in the reaction gas mixture. The temperature-activity profiles reported showed essentially 100% conversion of methanol, 1-propanol, and 1-butanol at about 200°C. Ethanol required a temperature of around 500°C for essentially complete conversion and 2-propanol required about 400°C. The higher required temperature for complete conversion may have been the formation of saturated hydrocarbon by-products which have higher $T_{10}$. Methane was found in the conversion of ethanol on both Pt and Pt/SnO$_2$ and has a reported $T_{10}$ over Pt of about 550°C. By contrast, no by-products were observed in the conversion of 2-propanol on Pt/SnO$_2$.

It is also interesting to note that the $T_{10}$ for each alcohol over Pt/SnO$_2$ is significantly lower than 200°C found by Bart, et al., below 20°C for methanol and below 100°C for ethanol, 1-propanol, and 2-propanol. The differences may be due to several reasons including catalyst composition and oxygen concentration.

5.3.5. Hydrocarbons. Comparing the temperature-activity profiles of the hydrocarbons to those of the alcohols indicates that the former are more difficult to oxidize, as a group. This also indicates that the C–O bond plays an essential role in initiating the conversion over Pt and Pt/SnO$_2$ at lower temperatures. For the hydrocarbons, the reaction must be initiated by cleaving a C–H or a C–C bond, and this apparently requires a higher temperature. The proposed mechanism of dissociative adsorption of CH$_4$ over noble metals is believed to occur by homolytic cleavage of either one or two C–H bonds to form a methyl radical, •CH$_3$, or methylene radical, •CH$_2$ and •H. These radicals then react with adsorbed O to form CH$_2$O, CO, CO$_2$, and H$_2$O. The $T_{10}$ for CH$_4$ over Pt is about 550°C in excess $O_2$, with oxidation beginning near 300°C. Because the $T_{10}$ over Pt/SnO$_2$ is significantly lower, 220°C, it is possible that such radicals are not formed. Instead, the
oxidation may be initiated by the direct reaction of O or OH formed by the dissociative adsorption of \( \text{O}_2 \) on SnO\(_2\) as discussed in reactions (2a') to (2c') or in Figure 5.1.

\[
\begin{align*}
\text{CH}_4 (g) + \text{Pt} & \rightarrow \text{CH}_4 \cdot \text{Pt} \\
\text{O} \cdot \text{Sn} + \text{CH}_4 \cdot \text{Pt} & \rightarrow \text{HO} \cdot \text{Sn} + \text{CH}_3 \cdot \text{Pt} \\
\text{HO} \cdot \text{Sn} + \text{CH}_4 \cdot \text{Pt} & \rightarrow \text{H}_2 \text{O} \cdot \text{Sn} + \text{CH}_3 \cdot \text{Pt}
\end{align*}
\]

(12a)  
(12b)  
(12c)  

Once the reaction starts, the adsorbed methyl groups would react according to reaction (9f).

The higher alkanes would begin being oxidized in a similar manner by adsorbing on Pt followed by abstraction of an H at some point along the molecule by O or OH leaving an alkyl group as in reaction (12b) or (12c).

\[
\begin{align*}
\text{O} \cdot \text{Sn} + \text{RH} \cdot \text{Pt} & \rightarrow \text{HO} \cdot \text{Sn} + \text{R} \cdot \text{Pt} \\
\text{HO} \cdot \text{Sn} + \text{RH} \cdot \text{Pt} & \rightarrow \text{H}_2 \text{O} \cdot \text{Sn} + \text{R} \cdot \text{Pt}
\end{align*}
\]

(13a)  
(13b)  

Once removed, the other H atoms on the same carbon would be similarly easily removed forming OH groups or water. Once removed the carbon could react with surface O giving an alkoxy group.

\[
\begin{align*}
\text{O}_2 \cdot \text{S} + \text{R} \cdot \text{Pt} & \rightarrow \text{RO} \cdot \text{Pt} + \text{HO} \cdot \text{S}
\end{align*}
\]

(13c)  

The alkoxy group would then follow the oxidation path of the related alcohol. Because the temperature would be significantly higher than that required to completely oxidize a given alcohol, only \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) would be formed and no by-products would be observed.
5.4. SUMMARY

The sustained oxidation of CO occurs at lower temperatures over Pt/SnO$_2$ than Pt or SnO$_2$ alone. Each constituent of the catalyst serves an independent function. Pt adsorbs CO, and SnO$_2$ dissociatively adsorbs O$_2$ at low temperature. A synergy is created in the combination of the two components. The means by which SnO$_2$ dissociatively adsorbs O$_2$ may involve hydrogen which is likely present on SnO$_2$ in the form of OH groups. Additionally, the OH groups may be the oxidizing agent for CO producing formate, carbonate or bicarbonate intermediates which then decompose to CO$_2$. By example from combustion mechanisms in flames, the OH group is potentially involved in the oxidation of all of the VOCs investigated in this study. More work needs to be done to elucidate the degree of involvement of OH and H$_2$O groups of SnO$_2$. One role of water has been discovered: the breakdown of surface adsorbed CO$_2$.

The mechanisms for VOCs oxidation are speculative but reasonable and explain the appearance of the by-products. The oxidation of VOC-O$_2$ mixtures may occur on Pt at low temperature due to the presence of hydrogen which may activate diatomic oxygen. By contrast, CO requires some form of H to enable its oxidation at low temperature. The activation energy for the oxidation over Pt may be, in part, that required to break an H atom from a given molecule.

The studies presented here provide a starting point for further investigation of the conversion of VOCs over Pt/SnO$_2$ systems. The presence of SnO$_2$ was shown to have some impact on the oxidation of methanol and ethanol as well as the saturated hydrocarbons. These changes are consistent with a reduction in the competition for and the furnishing of oxygen to the reaction at temperatures lower than possible in the absence of SnO$_2$. Further studies are necessary to elucidate the nature of adsorbed species on Pt, SnO$_2$, and Pt/SnO$_2$.

In general, the class of NMRO catalysts has been shown to provide lower
temperature oxidation of CO than possible on either noble metal or metal oxide alone. Part of the reason for the reduced oxidation temperature is undoubtedly the elimination of competition for adsorption. Another reason may be the presence of hydroxyl groups. Further investigation of this class of catalysts may provide lower temperature means for the conversion of a variety of VOCs.
REFERENCES TO CHAPTER 1


REFERENCES TO CHAPTER 2


REFERENCES TO CHAPTER 3


REFERENCES TO CHAPTER 4


REFERENCES TO CHAPTER 5


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VITA

Erik Joshua Kielin

Born in Zanesville, Ohio on 12 November 1963 to Sara Mae Davis and Robert Eugene Brown. Graduated from Western Branch High School in Chesapeake, Virginia in June 1982. Received B.S. and M.S. degrees in Chemistry from Old Dominion University with an emphasis in Physical Chemistry. Completed Ph.D. requirements for the Applied Science program at the College of William and Mary in November of 98.

As an undergraduate his research interests included the isolation and identification of natural products, the kinetics of degradation of pharmaceutical agents, and the brain chemistry involved in memory. His Master's research, carried out at NASA's Langley Research Center in Hampton, Virginia, involved the development of a mass spectrometric method for qualitatively and quantitatively evaluating the components of a gaseous boundary layer. The system was to be carried on NASA's tethered satellite. His Ph.D. research focused on development of catalysts for low-temperature oxidation of carbon monoxide, hydrocarbons, and volatile organic compounds for the purification of indoor air.

For the past ten years Kielin has been working as part of Langley's Catalyst Research Team. His present research focuses on the development of low-temperature oxidation catalysts. Such catalysts have application in reduction of toxic automobile emissions during cold start-up, purification of breathing air in enclosed spaces such as homes, automobiles, and airplanes, purification of compressed air and other oxygen-containing gases, personal safety masks, and selective chemical sensors.

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Kielin's specific research interests include formulation and optimization of catalyst compositions, development of catalyst coating technology, characterization of bulk and surface properties of catalytic materials, and evaluation of their capacity for a variety of low temperature oxidations, conversions, and decompositions.

Kielin has been co-inventor on three of five patents already received and four more patent applications presently under evaluation. He has been author and co-author of several publications relating to the catalyst research effort and has received several NASA awards including several Certificates of Recognition, the first ever Paul F. Holloway Award for Excellence in Technology Transfer, and the Federal Laboratory Consortium's Award for Excellence in Technology Transfer. He is presently an employee of the Old Dominion University Research Foundation and working under contract at NASA's Langley Research Center for the Catalyst Research Team.