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CHARACTERIZATION OF THE SURFACES OF PLATINUM/TIN OXIDE BASED CATALYSTS BY FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

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INTRODUCTION

A Pt/SnO_2 catalyst has been developed at NASA Langley that is effective for the oxidation of CO at room temperature (1). A mechanism has been proposed to explain the effectiveness of this catalyst (2), but most of the species involved in this mechanism have not been observed under actual catalytic conditions. A number of these species are potentially detectable by Fourier Transform Infrared Spectroscopy (FTIR), e.g., $HOSnO_x$, $(HO)_yPtO_z$, Pt·CO, and $SnHCO_3$. Therefore a preliminary investigation was conducted to determine what might be learned about this particular catalyst by transmission FTIR.

The main advantage of FTIR for this work is that the catalyst can be examined under conditions similar to the actual catalytic conditions. This can be of critical importance since some surface species may exist only when the reaction gases are present. Another advantage of the infrared approach is that since surface vibrations are probed, subtle chemical details may be obtained.

The main disadvantage of this approach is that FTIR is not nearly as sensitive as the Ultra High Vacuum (UHV) surface analytical techniques such as Auger, Electron Spectroscopy for Chemical Analysis (ESCA), Electron Energy Loss Spectroscopy (EELS), etc. Another problem is that the assignment of the observed infrared bands may be difficult.

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EXPERIMENTAL

The "NASA 12C" catalyst (6.43% Pt, 44.35% SnO_2, 49.22% SiO_2 (dry wt.); 4% water by ignition, 80 m^2/g B.E.T. surface area), and some of its components, Davidson Silica gel (Grade 11, Mesh 28-200), SnO_2 (made in house by the dissolution of tin with nitric acid) were pressed into neat half inch diameter pellets weighing around 20-30 milligrams each. A pellet was held between 2 stainless steel washers in the middle of a specially designed infrared cell. (A detailed description has been given previously (3)). This cell was connected by a stainless steel tube to a vacuum system which enabled gases to be exchanged with the cell while it was in the sample compartment of the FTIR. The cell could also be heated and cooled without being removed from the FTIR.

The vacuum system used was an all welded bakeable stainless system which was pumped by a turbomolecular pump backed by a mechanical pump. The base pressure of the system was around 1×10^{-7} Torr. The surface was probed by transmission FTIR using a Nicolet 5PC system with 4 wavenumber resolution. All gases used were of research grade.

RESULTS AND DISCUSSION

Reference Spectra

Initially, reference spectra of "neat" pellets of the NASA 12C catalysts, SiO_2, and SnO_2 were recorded. The SiO_2 spectrum contained a broad OH stretching band between 3750 and 2800 cm^{-1}, two unknown bands at approximately 1950 cm^{-1} and 1868 cm^{-1}, the water scissor mode at 1635 cm^{-1}, and a band at 1264 cm^{-1}. Below 1264 cm^{-1} the sample was highly absorbing, probably due to various Si-O-Si modes. The unknown bands at 1950 and 1868 cm^{-1} were present in the as received material, and these are assumed to be due to some sort of contaminant picked up in the manufacturing process. The 1635 cm^{-1} band was observed to significantly decrease as the sample was exposed to dry air. However, this band could not be completely removed at room temperature, even after being purged with dry air for two and a half days. In fact, even after baking the catalyst at 125°C for one hour this band was still observed. Obviously some water is strongly held by the silica gel.

The spectrum of a neat pellet of SnO_2 was also recorded. SnO_2 fundamental and combination bands have been reported at various wavelengths between 1560 and 300 cm^{-1}(4). We also observed many absorption bands in this region. However, many bands were observed that could not be attributed to SnO_2. For example, a strong band in the OH stretching region (around 3500 cm^{-1}) was observed. Also observed was a band in the CH stretching region (around 2900 cm^{-1}, and a band in the carbonyl region at 1731 cm^{-1}).

Since the SnO_2 was produced by the reaction of tin with nitric acid, it was expected that some nitrates might be detected. Indeed, strong bands were observed at 1600, 1506, and 1240 cm^{-1}, which could possibly be due to the presence of nitrates. In the preparation of this material the final product is baked only to several hundred degrees Centigrade to avoid sintering and loss of surface area. However, it is apparent that some contaminants are not removed under these conditions. It is not known at this time what role, if any, these contaminants play in the catalytic mechanism.

The transmission spectrum of a neat pellet of the NASA 12C catalyst was also analyzed. The platinum was added to this catalyst by way of a platinum ammonia complex which was then reduced with formic acid. Therefore, we were concerned that some additional contamination might be present from this procedure. However, the bands observed were essentially identical to those observed in the silica gel and/or the SnO_2. i.e., no bands due to the platinum incorporation procedure were observed.

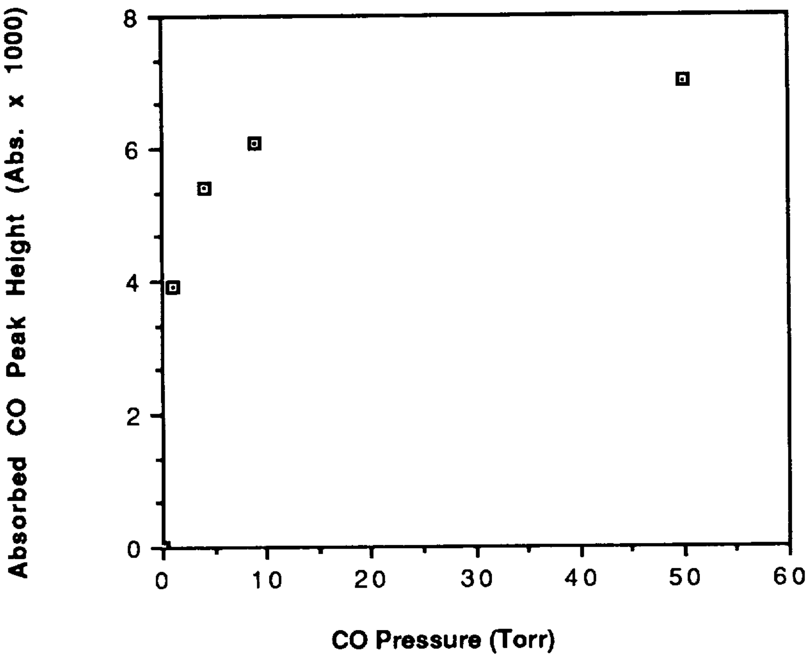
Effect of Pretreatment

The effect of the pretreatment on the NASA 12C catalyst was investigated as follows. First, the catalyst was heated under vacuum. The temperature was slowly brought up to 125°C and then held at that temperature for 1 hour. No significant changes in the infrared spectrum were observed as a result of this treatment. At this point 50 Torr of CO was allowed into the cell. Spectra were recorded after 10 minutes and 35 minutes. The new features observed were due to gas phase CO_2 (doublet between 2300 and 2400 cm^{-1}), gas phase CO (doublet between 2100 and 2230 cm^{-1}) and chemisorbed CO (2070 cm^{-1}). The location of the chemisorbed CO peak is consistent with the linear or "atop" Pt-CO species. The bridge bonded Pt_2CO species which normally absorbs in the vicinity of 1840 cm^{-1} was not observed. It is interesting to note that the intensity of the Pt·CO peak observed was only 0.01 Absorbance units. This value is dramatically smaller than the intensity that is normally observed for CO chemisorption on supported platinum. Bastein et. al. observed that a 50/50 Pt/Sn alloy supported on alumina had a 5 fold reduction in the intensity of the chemisorbed CO peak compared to unalloyed platinum (5). Given this size of pellet and platinum loading in our experiments the reduction of the chemisorbed CO peak is somewhere between a factor of 20 and 100! In other words, the presence of the tin oxide has significantly altered the nature of the platinum, probably due to the formation of some kind of alloy.

Compared to the spectrum taken after 10 minutes the 35 minute exposure produced more CO_2 but there was no significant change in the chemisorbed CO peak. This indicates that the steady state concentration of chemisorbed CO was reached in 10 minutes or less. The cell was then cooled to 38°C and evacuated for 10 minutes. This resulted in the removal of gas phase CO and CO_2 but caused no significant change in the chemisorbed CO peak; however, after an overnight evacuation virtually all of the chemisorbed CO was removed.

Room Temperature Absorption of CO

The room temperature uptake of CO on NASA 12C was also investigated. Following the reductive pretreatment described above the catalyst was exposed to various concentrations of CO gas in a static cell at room temperature. Exposures of 1, 4, 9, and 50 Torr of CO were used. A graph of the chemisorbed peak height as a function of the CO gas pressure is given on the next page.



The shape of the above graph is apparently logarithmic. This is not surprising since there are a finite number of sites which become filled as the CO pressure is increased and then regardless of further increases in the pressure no more CO will chemisorb. This would mean that full coverage for this particular sample (19 mgs) is around 7 milliabsorbance units. When the sample was heated to 125°C and exposed to 50 Torr CO then the peak height was 10 milliabsorbance units. The fact that this is higher than the room temperature exposure could be due to the precision of the measurement or it could mean that some sites have a higher activation energy barrier than others. This latter view is supported by the fact that the CO which chemisorbed at room temperature was more easily pumped off than the CO chemisorbed at 125°C. In fact approximately 4 times as much CO was present after 10 minutes of evacuation for the case in which CO was absorbed at 125°C, versus CO absorption at room temperature.

It is interesting to note that as the CO coverage was increased, the CO absorption maximum decreased. For example, when the CO pressure was 1 Torr the absorption maximum was 2088 cm^{-1}, but when the CO pressure was 50 Torr it had shifted to 2070 cm^{-1}. These kinds of shifts are generally attributed to dipole-dipole coupling of neighboring CO's and normally the absorption maximum increases with CO coverage (5).

Effect of Catalyst Reduction in Hydrogen

The catalyst was exposed to 400 Torr of H_2 and heated. Spectra were taken at the following invervals: a) 15 minutes at 35°C; b) 30 minutes at 50°C; c) 35 minutes at 100°C; d) 30 minutes at 150°C; e) cooled to room temp and evacuated for 2 and 1/2 days. In the initial spectrum (a), two strong and sharp bands were observed at 1159 and 1100 cm^{-1}. These bands were gone when spectrum (b) was recorded. Most likely these are OH bending modes due to the presence of SnOH and/or SiOH. This treatment also caused a steady decrease in most of the "impurity bands" described earlier in the section entitled Reference Spectra.

After the above treatment was completed the catalyst suprisingly would not chemisorb CO at either room temperature or elevated temperatures (140°C). All attempts to restore the catalyst's ability to chemisorb CO were unsuccessful. These included baking the catalyst in oxygen and water vapor (to 200°C). Ultra High Vacuum studies on this catalyst have shown that a high temperature reduction in hydrogen causes an irreversible migration of impurities such as silicon to the surface*. These impurities are apparently responsible for the supressed CO chemisorption we have observed.

Presence of Bicarbonates

Surface hydroxyl groups have sometimes been observed to react with CO_2 to form bicarbonates. The proposed mechanism for the degradation of this catalyst involves a tin bicarbonate species. Since FTIR has been used to observe surface bicarbonates in other systems (3) it was hoped that a bicarbonate species might be observed in these experiments. Yet, no bicarbonates or carbonates were observed under any of the conditions tested, including an experiment in which the catalyst was exposed to 10

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Torr of CO_2 and heated 2 hours at 50°C. However, the degradation of the catalyst occurs very slowly over a period of months under conditions in which the catalyst is constantly exposed to CO and O_2. The FTIR experiments conducted to date do not even remotely approach these conditions.

CONCLUSIONS

This preliminary FTIR study of the NASA Pt/SnO_2 CO oxidation catalyst has shown the following:

1. The catalyst contains suprisingly high levels of impurities which are detectable by FTIR.
2. The chemisorption of CO on platinum is dramatically reduced by the presence of the tin oxide, probably due to alloy formation.
3. The reduction of this catalyst in hydrogen at 150°C causes total and irreversible loss of CO chemisorption.
4. No carbonate or bicarbonate species were observed under the conditions tested.

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