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Support Effects Studied on Model Supported Catalysts

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PI:

Raymond J. Gorte
Department of Chemical Engineering
University of Pennsylvania
220 S 33rd Street
Philadelphia, PA 19104

DOE Contract Specialist:

Robert L. Kladiva
US Department of Energy
Chicago Field Office
9800 South Cass Avenue
Argonne, IL 60439

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Results for 1991/92:

The composition and structure of oxide support materials can significantly change the catalytic behavior of metal and oxide catalysts. In order to better understand this support effect, we are studying model catalysts in which the active phase is deposited onto flat oxide substrates. Particular emphasis is being placed on metals catalysis for application to automotive emissions control and to acidity in supported oxides. During the last year, we have made a number of interesting discoveries in this area which are outlined below:

Particle-Size Effects

In past years, we examined the effect of metal particle size on desorption kinetics for CO and other adsorbates on Pt and Rh. The studies were carried out on model catalysts which were prepared by vapor deposition of Pt onto oxidized Al and α - $\text{Al}_2\text{O}_3(0001)$, and it was shown that there are strong changes in the CO desorption kinetics due to particle size on Pt, but not on Rh. For very small, Pt particles (<2.0 nm), we observed a single desorption state in TPD of CO at 510K, a similar desorption temperature to that reported for CO from stepped Pt crystals. As particle size increased, a second desorption state appeared at ~400K, which increased in relation to the 510-K state in a regular manner with particle size. Since the main desorption feature on Pt(111) and other crystal planes with high surface coordination also occurs at this temperature, we assigned the changes in the TPD curves with particle size as being due to changes in site geometry. In contrast to this, we observed only small changes in the TPD curves of CO from Rh as a function of particle size. Changing the crystal plane also had only a minor influence on the TPD curves for CO from Rh, which in turn supports the argument that the changes observed with particle size on Pt are due to crystallographic variations. This work had been published earlier ("A Comparison of the Desorption of CO from Pt and Rh Particles on α - $\text{Al}_2\text{O}_3(0001)$ ", E.I. Altman and R.J. Gorte, *Surface Science*, 195 (1988) 392.)

In the past year, we set out to determine how changes in desorption properties affect catalyst activity. A reaction chamber was set up to measure rates on the same samples on which TPD measurements are made. We chose to study CO oxidation because there is some controversy in the literature over whether this reaction is structure sensitive and because the reaction is inverse first order in CO due to the fact that the surface is covered with CO under typical reaction conditions. Changes in desorption properties should be reflected in the reactivity, and this is exactly what we observed. For large particles, the turnover rates, activation energies, and reaction orders were identical to results reported in the literature for single crystals. However, for very small particles for which the desorption peak temperatures are much higher, the activation energy increases from 30 to 41kcal/mol and observed rates are at least 50 times lower at typical reaction temperatures. Furthermore, these reaction results can be understood using simple rate models, inserting adsorption and desorption kinetics obtained from TPD measurements. These results demonstrate that CO

oxidation is structure sensitive on Pt and that this structure sensitivity is due to changes in the CO desorption rate with particle size. The results are also exciting because they demonstrate that one can predict reaction rates from TPD measurements undertaken in UHV. These results are in press (Reference 9).

To confirm that the elementary rate measured in TPD experiments in UHV, we are in the process of extending our rate measurements for NO reduction by CO over Rh. This reaction is of great industrial importance and earlier TPD studies have shown that there are dramatic changes in the NO desorption and decomposition with particle size in UHV ("The Adsorption of NO on Small Rh Particles on α -Al₂O₃(0001)", E.I. Altman and R.J. Gorte, *Journal of Catalysis*, **113** (1988) 185.). We expected that these changes in the rates of the elementary steps should affect the macroscopic rates at higher pressures and this is indeed what we find. Both the activation energy and absolute rates change dramatically when the particle size is decreased below $\sim 25\text{\AA}$. However, our current experimental setup does not allow us to measure N₂O formation rates. Therefore, we are setting up a collaborative effort with Dave Belton at GM to measure these rates for us. It is hoped that this work will be completed within the next year.

Support Effects on ZnO and Zirconia

We have also studied the effect of support composition by examining the growth of Pt films on ZnO(0001)Zn and ZnO(0001)O. Samples were again prepared by vapor deposition of Pt onto flat substrates in ultra high vacuum. On both ZnO surfaces, AES and TEM indicated that Pt grew as a 2-D film at 300K, in contrast to results for Pt on α -Al₂O₃(0001) where 3-D particles are formed under these conditions. Furthermore, transmission electron diffraction (TED) showed that the Pt grew as an ordered overlayer on the ZnO crystals. Heating the Pt/ZnO surfaces resulted in the formation of Pt particles starting at $\sim 650\text{K}$, but the Pt particles were still oriented with the ZnO. On both ZnO surfaces, TPD curves for CO from high Pt coverages ($>$ one monolayer) and from large Pt particles formed by heating thinner films were identical to TPD curves for CO from Pt on α -Al₂O₃(0001). The main desorption features were observed at 400 and 510K, which are interpreted as arising from different site geometries on the Pt by comparison to results from Pt single crystals. However, for Pt at submonolayer coverages prior to particle formation, the TPD curves for CO from Pt on ZnO(0001)Zn were shifted down in temperature by $\sim 60\text{K}$ compared to results for Pt on ZnO(0001)O. These results are interpreted as indicating a chemical interaction between Pt and the Zn⁺² ions which are in direct contact on the Zn-polar surface but not on the O-polar surface. This suggests that the support can affect adsorption properties but that the interactions are very local and are due to direct contact between the metal atoms and the oxide cations.

For Pt films on ZrO₂(100), there are again indications of Pt interacting with the Zr⁺⁴ cations when there is direct contact between Pt and the oxide. Both TEM and

AES provided evidence for relatively strong interactions between the particles and the substrate. Growth of the film is 2-D at room temperature and TED indicated that the films and particles (formed by heating the 2-D films or exposing them to air) were again oriented with respect to the underlying ZrO_2 lattice. TPD of CO from relatively high Pt coverages ($>1 \times 10^{15} \text{Pt/cm}^2$) and from Pt following particle formation showed desorption features which were essentially identical to those found on Pt single crystals. For submonolayer quantities of Pt prior to annealing, adsorption of CO does appear to be affected by the presence of Zr^{+4} desorbing at $\sim 50\text{K}$ lower temperatures than are observed on noninteracting supports. This tends to confirm the conclusions reached for ZnO that direct contact between the catalytic metal and the cations on the surface are responsible for strong support effects.

We also examined Rh on $\text{ZrO}_2(100)$ to determine whether similar effects could be observed here. The AES and TEM results were almost identical to that found with Pt. Growth of the film is again 2-D at room temperature with particles forming at higher temperatures. The films are oriented with respect to the surface. However, the desorption properties for CO and NO, while being found to vary with particle size, did not seem to be strongly affected by the presence of the support. The TPD results were very similar to those observed for Rh on $\alpha\text{-Al}_2\text{O}_3(0001)$ and followed similar trends with particle size. Since adsorption properties for Rh do not appear to be affected by the presence of zirconia and are also not strongly affected by particle size, these results might suggest that the changes observed with Pt are actually due to structural changes due to the presence of the support rather than chemical interactions. However, the results for ceria suggest that this is not the case and that interactions between the support and the metal are very specific.

Support Effects on Ceria

The results for Pt on ceria were essentially identical to that for Pt on oxidized Al. Desorption properties for NO, CO, and H_2 were all found to vary with particle size but the results were identical to that observed for Pt on alumina. No evidence for strong interactions between Pt and ceria were observed. This is in contrast to what we found with Rh. For Rh, the desorption features for both NO and CO are very different on Rh/ceria compared to Rh/alumina. This appears to be primarily due to migration of oxygen from the support onto the Rh at very low temperatures. During TPD measurements for CO, we found that substantial amounts of CO_2 desorbed from the surface. By doing multiple TPD measurements while avoiding high temperatures, we found that we could deplete the amount of CO_2 which formed; however, when the sample was annealed to 900K, significant amounts of oxygen would reappear. The presence of adsorbed oxygen was also apparent from the TPD curves following NO adsorption. These curves were found to be skewed in a similar manner to that expected following adsorption of oxygen.

To our knowledge, this is the first direct evidence for oxygen migration between

a support and a metal at low temperatures. Although workers had speculated that ceria might act as an oxygen storage component on Pt/ceria catalysts for automotive emissions, a conclusion which would require migration, we find no evidence for this kind of effect on Pt, while the effect is clearly evident for Rh. This very interesting property suggests a number of applications which will not be discussed here.

Supported Oxides

A number of interesting results have been obtained in our studies of high-surface-area, supported oxides. First, we examined a series of silica-alumina catalysts, including commercial FCC materials, using TPD-TGA measurements of isopropylamine. In previous work on zeolites, we had showed that isopropylamine decomposes to propene and ammonia between 575 and 650K on Brønsted-acid sites. On high-silica zeolites like H-ZSM-5, we find that there is one Brønsted site for each framework Al (T.J. Gricus Kofke, R.J. Gorte, G.T. Kokotailo, and W.E. Farneth, *Journal of Catalysis*, 115 (1989) 265). On a series of steam-deactivated, FCC catalysts which are much more difficult to characterize using standard methods, we find a linear relationship between the number of sites measured using isopropylamine decomposition and both the x-ray lattice parameter and MAT activities (A.I. Biaglow, C. Gittleman, R.J. Gorte, and R.J. Madon, *Journal of Catalysis*, 129 (1991) 88.) These results suggested that similar observations might be observed for amorphous catalysts as well. This is exactly what we found. On pure silica and pure alumina, isopropylamine does not decompose in TPD-TGA, indicating that there are no strong Brønsted sites. On silica-aluminas, however, a clear decomposition feature is observed between 575 and 650K. Furthermore, hexane cracking measurements show a strong correlation between activity and the number of sites measured in TPD-TGA. This work has been extremely well received and a number of industrial firms have asked us to examine samples for them. At least one major catalyst manufacturer has adopted our isopropylamine, TPD technique for characterization of their materials.

Next we examined the adsorption properties of a series of titania silicates in collaboration with Prof A. Datye (University of New Mexico). While these systems are not strongly acidic, they are very important for use as supports in SCR catalysts. The goal of including silica is to obtain a high surface area for the titania component. However, it is difficult to determine this surface area in the presence of silica so that different preparations can be tested. Using TPD-TGA of isopropanol, we found that the alcohol could be evacuated from silica at room temperature, but not from titania. Furthermore, by looking at a series of well-characterized titania silicates for which the titania surface area could be measured by other techniques, we were able to show that the alcohol coverage on all of the titanias was $\sim 2 \times 10^{18}$ molecules/m². This suggests that 2-propanol adsorption can be used to determine the titania surface area of unknown materials.

Finally, we attempted to prepare model, low-surface-area, niobia-alumina and silica-alumina catalysts in order to better understand the nature of acid sites generated in mixed oxides. Our first studies were of niobia deposition on oxidized Al films and on

an α - $\text{Al}_2\text{O}_3(0001)$ crystal. Vapor deposition of niobia resulted in amorphous, 2-D films which were stable upon heating up to at least 900K in vacuum. However, the presence of niobia had no measureable effect on the acidity of the samples. TPD of 2-propanol and isopropylamine occurred from sharp desorption features at 185K and 140K respectively on all surfaces examined, indicating that no acid sites were present on any of samples. An alternate approach to deposition of niobia using $\text{Nb}(\text{C}_2\text{H}_5\text{O})_5$ resulted in significant carbon contamination. Studies of silica-aluminas were similarly unsuccessful. We attempted to make these materials by 1) reacting oxidized silica with aluminum alkoxides and several other forms of alumina and 2) by studying silica-aluminas like mica. However, we were unable to observe acid sites on any of the materials, even after various ion-exchange processes were attempted.

While we believe it should be possible to form good, model acid catalysts, our work has suggested that it will be nontrivial to do this. Given that a number of other areas of greater interest to us have opened up, we do not plan to pursue this area of research.

Low Energy Ion Scattering

At the beginning of last year, we began a collaboration with Dr. Tom Buck (formerly of Bell Labs) who is a leading expert in the area of ion scattering. He developed an angle-resolved, time-of-flight instrument which enables one to determine surface structure and composition. In our initial study with him, we examined the neutralization of Ne ions scattered off a Cu-Au alloy surface and became proficient in using this technique. We are now planning to apply this technique to the study of oxides and metal overlayers on oxides. This work is just beginning and we do not have any results on this at the present time.

Publications Citing DOE Support for 1991-92:

1. "A Study of Pt Films on $ZrO_2(100)$ ", S.I. Roberts and R.J. Gorte, *Journal of Physical Chemistry*, **95** (1991) 5600.
2. "Adsorption of CO and NO on $Rh/ZrO_2(100)$ ", G. Zafiris and R.J. Gorte, *Journal of Catalysis*, **132** (1991) 275.
3. "A Study of Niobia Deposition on $\alpha-Al_2O_3(0001)$ and Oxidized Al", S.I. Roberts and R.J. Gorte, *Applied Surface Science*, **55** (1992) 135.
4. "A Study of NO Adsorption on Model Pt and Rh Catalysts", G. Zafiris, S. Roberts and R.J. Gorte, *ACS Symposium Series*, **495** (1992) 73.
5. "A Method for Measuring the Titania Surface Area on Mixed Oxides of Titania and Silica", A.I. Biaglow, R.J. Gorte, S. Srinivasan, and A.K. Datye, *Catalysis Letters*, **13** (1992) 313.
6. "Characterization of CO, NO, and H_2 Adsorption on Model Pt/CeO₂ Catalysts, G.S. Zafiris and R.J. Gorte, *Surface Science*, **276** (1992) 86.
7. "Isopropylamine Adsorption for the Characterization of the Acid Sites in Amorphous Silica-Aluminas", J. Tittensor, R.J. Gorte, and D. Chapman, *Journal of Catalysis*, **138** (1992) 714.
8. "Evidence for Low-Temperature Migration of Oxygen from Ceria to Rh", G.S. Zafiris and R.J. Gorte, *Journal of Catalysis*, **139** (1993) xxx.
9. "CO Oxidation on Pt/ $\alpha-Al_2O_3(0001)$: Evidence for Structure Sensitivity", G.S. Zafiris and R.J. Gorte, *Journal of Catalysis*, **140** (1993) xxx.
10. "Differences in the Neutralization of 2.4 to 10 keV Ne^+ Scattered from the Cu and Au Atoms of an Alloy Surface", T.M. Buck, W.E. Wallace, R.A. Baragiola, G.H. Wheatley, J.B. Rothman, R.J. Gorte, and J.G. Tittensor, submitted.

Plans for 1991/92:

Our efforts in the next year will be in three specific areas: 1) Reaction rate measurements, 2) TPD studies with other oxide systems, and 3) Ion-scattering studies. In reaction rate studies, we plan to finish our NO reduction story on Rh/alumina. However, most of the time will be spent studying CO oxidation on Rh/ceria. Our TPD results in UHV have suggested that there may be a second reaction mechanism on this surface involving oxygen from the ceria. There is also some indication of this in the literature. Se Oh and C. Eickel (S. Oh and C. Eickel, J.Catal., 112, 543 (1988) have also seen evidence for this in earlier reaction studies. They found that the reaction, which is normally inverse-first-order in CO, became zeroth order at very high CO pressures (near 100 torr). Presumably, this was due to a second reaction becoming dominant at these conditions. Our preliminary data has reproduced these results on our model catalysts.

In the area of TPD studies, we plan to examine Pd and other rare earths. Currently, Ford is incorporating Pd and La_2O_3 in their catalyst formulations and other rare earths are also being examined for possible use in automotive catalytic converters. We believe that our previous work has shown that TPD studies can be utilized effectively to predict the kinds of properties one will expect to see in these systems.

Our initial ion-scattering studies will concentrate on $\text{ZnO}(0001)$, both Zn and O faces. We initially just hope to show that ion scattering can be used to distinguish these surfaces and to examine the bond angles at the surface. If this is successful, we will examine the nature of Pt layers deposited on these surfaces.

Finally, we have recently found a vender who will supply us with a CeO_2 single crystal. Our plan is to examine Pt and Rh overlayers on this crystal using TEM in a manner similar to that used in our Pt/ZnO studies to determine whether the interface regions are different for these two metals and to see if we can understand the differences between ceria-supported Pt and Rh from the interfaces.

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