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ABSTRACT

A model catalyst made by Pt vapor deposition onto a thin alumina film is investigated with TEM and HREELS. The preparation techniques are fully described, then the results of TEM analysis for Pt deposits from 0.3 ML to 1.7 ML are reported, for which clusters varying from 1.0 to 1.6 nm in diameter are observed. HREELS spectra are reported for the cases of CO and C_2H_4 adsorption onto the model. For the case of CO adsorption, it is shown that the catalyst is stable when heated to 500 K. For the case of ethylene adsorption, π and di-σ species are identified for adsorption at 165 K, but on warming to 325 K, ethylidyne is only observed for the larger Pt deposits. This is the first HREELS observation of the ethylidyne species on alumina supported catalysts.

The Application of HREELS to Model Catalysts: CO and C_2H_4

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Introduction

The application of surface science spectroscopies to supported metal clusters as an attempt to model real catalyst systems has been a topic of much interest recently. Various techniques to model catalysts and characterize them with AES, XPS, HREELS, TEM, STM, and other surface science spectroscopies have been developed [1-8]. For vibrational spectroscopy, a goal has been to use the wealth of information that has been gathered on single crystal - adsorbate systems as a base with which to interpret adsorption and reactions on transition metal clusters [1,9,10]. In our previous work we have examined C_2H_4 adsorption on Pt vapor deposited onto TiO_2 and oxidized Al substrates [11]. The current work is a more complete examination of vapor deposited Pt clusters, using AES to calibrate the Pt deposition, TEM to determine the cluster size distributions as a function of metal deposition, and HREELS to study the adsorption of CO and C_2H_4 at various temperatures. Here we are able to report the first HREELS observation of ethylidyne ($\equiv C\text{-}CH_3$) on an alumina supported catalysts.

In our previous work with Pt on an oxidized aluminum foil, HREELS spectra of C_2H_4 at 165K allowed us to identify di-σ and π bonded species adsorbed on the Pt clusters, consistent with the work of Moshin et al. [12]. Upon warming to room temperature, the observed spectra was not characteristic of the expected ethylidyne which has been observed on both Pt clusters and Pt(111) single crystals. Since ethylidyne has been observed with IRAS on Pt/Al_2O_3 model catalysts made by standard chemical techniques, our previous model was judged to be different from these in a fundamental way. Our conclusion that an interaction between the Pt and the alumina, and possibly the underlying bulk Al occurs is supported by evidence of just such an interaction in the case of Pd on oxidized alumina as reported by Yates et al. [13]. Diffusion of transition metals through thin oxide layers has also been observed by Ocal et al. for the cases of Pt and Au on TiO_2/Ti, Au on Al_2O_3/Al, and by Schleich et al. for Pd on SiO_2/Si [14,15,16]. For all of these the oxide layer was thermally grown on a crystal of the bulk metal and alloying took place between the underlying bulk metal and the deposited transition metal. After concluding that this interaction was affecting the ethylene thermal decomposition, we decided that a different technique for making this model catalyst was in order. As previously discussed, a constraint on the model was that the oxide layer must be thin enough to allow a means of electron transport in order to avoid a build up of charge, since surface charging can be a severe problem for HREELS. It was decided that thin films of alumina would be grown on an Pd crystal, by reactive Al deposition in an oxygen environment. After in situ Al_2O_3 deposition the film could be examined with AES and HREELS. An additional part of this research was that alumina films and Pt overlayers were also deposited onto carbon covered TEM grids. The TEM grids could then be removed from the UHV chamber for analysis, allowing us to examine the cluster size distribution, in addition to the adsorbate HREELS spectra.

Preparation

All of the model catalyst preparation, AES, and HREELS were done in an ion-pumped stainless steel UHV chamber with a base pressure of 1×10^{-10} Torr. It is equipped with a Varian ion gun for sputtering, a UTI 100C mass spectrometer for residual gas analysis, a Varian RFA for LEED and AES, a dual source evaporator for thin film deposition, and a dual pass monochromator HREELS spectrometer with a rotatable analyzer section for angle resolved measurements. A detailed description of the HREELS spectrometer has been published previously [17]. The UHV chamber also has an auxiliary turbomolecular pump on a load-lock system, allowing samples to be changed in less than an hour. The sample could be heated to 850 K and cooled to 160 K with liquid nitrogen. The HREELS experiments were performed on a Pd(111) single crystal which had been polished to a final grit size of 1 μm following standard metallographic techniques. Initial cleaning of the Pd crystal was accomplished by cycles of 0.5 KeV Ar^+ sputtering at 800 K followed by annealing for 30 minutes at 800 K, until no surface impurities could be detected by AES.

Reactive evaporation of alumina has been studied and is known to produce amorphous Al_2O_3 with the correct stoichiometry [18,19]. The alumina was deposited by evaporation of Al from a resistively heated multi-strand tungsten filament in an oxygen pressure of 3×10^{-6} Torr and with a sample temperature of 750 K. In AES spectra of these films, no 68 eV Al peak characteristic of elemental Al^0 was detected, but a very strong 55 eV peak attributed to an oxidized Al^{+3} species was observed. With an Al evaporation rate of about 0.01 nm/s and the oxygen partial pressure stated previously, the ratio of oxygen to aluminum impingment is between 10 and 20, which is a range shown to produce Al_2O_3 with the correct stoichiometry [19]. After the sample cooled to room temperature, Pt deposition was accomplished by evaporation of Pt wire from a tungsten filament, during which the chamber pressure stayed at or below 2×10^{-9} Torr. The evaporation rate was held constant as much as possible for all thicknesses to

insure uniform and repeatable depositions, since nucleation and growth of metallic clusters is very dependent on the rate of deposition [20]. An important step in the catalyst preparation was the calibration of the evaporation thickness monitors, using AES. The thickness monitor was based on a crystal oscillator circuit with a quartz crystal mounted on the evaporator, at the same distance away from the filament as the sample was located. The design is similar to those reviewed by Chopra [20]. The frequency of the oscillator was recorded, and then an amount of Pt was deposited directly onto the Pd(111) substrate. An AES scan in the range of 100 to 600 eV was done, and the new oscillator frequency was recorded. This process was then repeated until several layers of Pt had built up on the Pd substrate, and the results are shown in Fig. 1. The attenuation of the Pd 330 eV Auger peak as a function of the crystal oscillator frequency clearly shows breaks, which are interpreted as due to the completion of Pt monolayers growing in a layer by layer manner on the Pd surface [21]. With a lattice mismatch between Pt and Pd of less than 1%, it not surprising to observe this layered growth. Layer by layer growth, also referred to as the Frank - van der Merwe growth mechanism has also been observed by Beauvais et $al.$ for Pt on the (100) face of Pd, for thicknesses up to three ML [22]. Our HREELS experiments with CO and C_2H_4 adsorbed on this surface indicate that for Pt amounts greater than 1 ML, only Pt - adsorbate peaks are detected, further supporting the layered growth mechanism. It should be noted here that throughout this paper, the Pt depositions are described in units of monolayers (ML). This is meant as the mass equivalent of that amount of Pt, if it were deposited on this Pd(111) surface. Although on the Al_2O_3 surface the Pt is observed as clusters, we feel that using this convention describes the amount of the deposition in an clear and concise way.

TEM Experiments

TEM analysis of vapor deposited films has been established as a good technique to examine the nucleation of metallic clusters [23]. Carbon coated copper mesh TEM grids, purchased from SPI, Inc., were mounted on the sample stub and transferred into the UHV chamber, one at a time. After an alumina overlayer of 3 to 5 ML was grown on the surface, some amount of Pt from the mass equivalent of 0.1 to 2.0 ML were vapor deposited onto each grid. The grid was then removed from the vacuum chambe and mounted in the TEM. Micrographs of the Pt clusters on the Al_2O_3 covered grids were then taken. TEM micrographs of a grid with just the Al_2O_3 overlayer were also taken, and no evidence for clustering of the alumina was seen. An example of these micrographs is shown in Fig. 2a. After enlargements of these micrographs were made, the particles in each photo were traced out and measured. A histogram of the cluster size distribution for a 1.7 ML deposition is shown in Fig. 2b. After all of the distributions were measured, average cluster size, density, and coverage were computed and are shown in Fig. 3. The measurements show that up to about 0.4 ML, the average particle size stays roughly constant, at about 1.0 nm, but beyond this point the average cluster size begins to increase. Since particles smaller than 1.0 nm were very difficult to identify from the background, we think it likely that the depositions less than 0.4 ML are dominated by clusters smaller than 1.0 nm. For depositions greater than the 1.7 ML shown, the clusters began to coalesce into larger, oddly shaped structures which made analysis much more difficult. For this reason no attempt was made to include depositions greater than 1.7 ML in this study. At 1.7 ML the average cluster size had increased to 1.6 nm, with many clusters larger than 2.0 nm present.

The solid curve in Fig. 3a is the result of a calculation which uses an average of the measured cluster density and the calculated volume of one monolayer of Pt to predict the average cluster diameter as a function of the Pt deposition. Fig. 3b shows the measured and calculated area covered. The calculation is simply the average clus-

ter density multiplied by the calculated cluster areas. These calculations assume bulk densities and hemispherical growth for the Pt clusters. Although neither assumption can be fully justified, it is clear that the TEM analysis gives a consistent view of the cluster growth, and that the amount of Pt deposited as measured by the AES calibrated thickness monitor is roughly the same as that observed in the TEM pictures.

HREELS Experiments

After the TEM experiments provided the structural data on this model system, HREELS experiments were used to examine the catalysts during preparation and after adsorption with CO and C_2H_4. First it was necessary to characterize the Al_2O_3 surface. The HREELS data shown in Fig. 4 are typical of the spectra taken after deposition of 2 to 4 ML of Al_2O_3 onto the Pd(111) surface. The main features in this spectra are the Fuchs-Kliewer phonons at 605 and 880 cm^{-1}, which have been discussed previously [24,25,10]. Also seen are the combination modes in the range of 1200 to 1800 cm^{-1} due to an electron exciting more than one of the surface phonons. This background of combination losses never proved to be a problem in the interpretation of adsorbate peaks as can be seen in the HREELS spectra shown in Figures 4-8. A necessary task was to determine if this amount of Al_2O_3 was sufficient to completely cover the underlying Pd(111) substrate. In order to demonstrate this, HREELS spectra were taken after exposing this surface to as much as 50 L (1 L = 10^{-6} Torr-sec) of C_2H_4 at room temperature. If the alumina clustered on the Pd(111) substrate, then clean or O_2 precovered patches of the Pd surface should readily adsorb the C_2H_4 and be easily detected in the HREELS spectra [26]. It is clear from the observed HREELS data shown in Fig. 4b that this did not occur, and no C_2H_4 peaks were ever detected on the Al_2O_3 surface.

After Pt deposition, the usual procedure was to take a HREELS spectrum to observe how the Pt affected the intensity and width of the elastic peak. Typically, the count rate was reduced by a factor of 5, but the resolution stayed constant at about 7 meV. Often a small CO peak was detected at 2050 cm^{-1}. To examine the thermal stability of this model, CO was used as the test adsorbate, since CO thermal desorption from Pt(111) has been studied and is known to take place at 400 K, leaving the substrate clean [27]. In Fig. 5a, we show a HREELS spectra of Pt/Al_2O_3 sample after exposure to 5 L of CO at room temperature. We note the strong ν C-O stretching

vibration at 2050 cm^{-1}, in addition to the alumina phonon modes. This sample was then heated to 500 K, then allowed to cool to room temperature. At this point an additional HREELS spectrum was taken and is shown in Fig. 5b. It is clear that most of the CO is no longer present. After this scan the surface was again exposed to 5 L of CO and another HREELS spectra was taken. As shown in Fig. 5c, the CO peak again was observed at the same frequency, with about the same intensity. From this we conclude that this model catalyst is stable to 500 K, and that no diffusion of Pt through the oxide layer occurs when the catalyst is heated. AES spectra corroborated this finding, showing little or no change in the intensities of the peaks associated with Pt. We also note that similar HREELS experiments in which the catalyst was heated to 700 K for 30 to 60 minutes and then cooled showed similar stability. CO could still be adsorbed after this treatment; however, this longer heating led to a doubling of the elastic peak intensity and a decrease in the CO peak intensity. We argue that this increase in the surface reflectivity is due to sintering of the Pt clusters, leaving more of the bare Al$_2$O$_3$ exposed and decreasing the total Pt surface area. Chu and Ruckenstein have examined the sintering process for Pt on alumina for various treatments and have published results which support our observations [28].

For the case of ethylene adsorption, a freshly prepared Pt/Al$_2$O$_3$ sample was cooled down to 165 K and exposed to 3 L of C$_2$H$_4$. At this point HREELS spectra were recorded for this system. As shown in Fig. 6b, the new peaks due to the ethylene appeared at 1200, 1420 with a shoulder at 1490, 2950, and 3050 cm^{-1}. This spectrum is very similar to one reported previously for a Pt/TiO$_2$ model catalyst, and has been identified as due to di-σ and π bonded ethylene species. Comparing this spectrum with those published by Moshin et al., it is clear that the 1200 cm^{-1} peak is due to the C=C stretch, the 1490 cm^{-1} is due to the C-H bending mode, and the broad mode at 3000 cm^{-1} is due to the symmetric and asymmetric C-H modes, all for the π-bonded species. The peak at 1420 cm^{-1} is due to the CH$_2$ scissor mode of the di-σ

species, and some of the intensity at 3000 cm^{-1} is also due to this species [12]. We also note a peak near 1020 cm^{-1}, observed as a shoulder on the Al$_2$O$_3$ phonon at 880 cm^{-1}, which by comparison to ethylene on Pt(111) is identified as due to the C-C stretch of the di-σ species. This peak was not observed by Moshin et $al.$ because at this frequency the Al$_2$O$_3$ phonons dominate the infrared absorption spectra. Upon warming this sample to 325 K, HREELS data like those shown in Fig. 6c are observed, in which the main hydrocarbon peaks are observed at 440, 1130, 1335, 1400, and 2920 cm^{-1}. We identify this spectra as due to ethylidyne on the Pt. The 2920 cm^{-1} peak is due to the ν CH mode, the 1335 and 1400 cm^{-1} peaks are due to the symmetric and asymmetric δ CH$_3$ modes, and the 1130 cm^{-1} is identified as due to the ν CC mode. The 440 cm^{-1} is identified as the carbon metal stretch, and the shoulder at 920 cm^{-1} is due to a CH$_3$ rocking mode. Similar to the 1020 cm^{-1} shoulder discussed previously, these two peaks have not been observed by infrared techniques, for which the Al$_2$O$_3$ substrate dominates the low frequency absorption. This species has been observed on many single crystal surfaces including Pt(111), and also on Pt/TiO$_2$ and Pt/Al$_2$O$_3$ model systems previously [29,11,12]. As shown in Fig. 7, HREELS spectra for a range of Pt coverages from 0.3 ML up to 1.3 ML showed little change in the ethylene spectra as a function of the Pt coverage, only the strength of the observed peaks changed. In contrast to this, the spectra recorded after the sample was warmed to room temperature showed a dependence on the amount of Pt deposited, as shown in Fig. 8. For coverages up to about 0.6 ML, the peaks identified as ethylidyne peaks are not present or too weak to be detected. As the Pt coverage grows, the ethylidyne peaks become easily recognizable.

Discussion

In order to more fully understand this model, it is necessary to briefly review other efforts to examine model catalysts of this nature. Our previous work with Pt deposited onto a thermally oxidized aluminum foil produced similar HREELS spectra for room temperature CO adsorption, and 165 K C_2H_4, although those spectra were of poorer quality. Heating the model catalyst with adsorbed CO led to loss of the CO peaks in the HREELS spectra and subsequent exposure to CO showed no evidence of further CO adsorption. AES spectra showed greatly diminished Pt peaks at this point. For the case of the adsorbed C_2H_4 on the Pt/oxidized Al foil system, by 230 K the HREELS spectra resembled those of the CCH species to which ethylene decomposes above 500 K on single crystal Pt(111) [11,30]. Work by Yates *et al.* of CO on a model catalyst of Pd vapor deposited onto an oxidized Al(111) crystal produced similar results, in which HREELS spectra of adsorbed CO as a function of temperature show that the CO peaks disappeared as the sample was heated. From a careful analysis of the HREELS and AES spectra, they concluded that alloying of the Pd and the underlying bulk Al occurred at elevated temperatures, and that the oxide layer did not act as a diffusion barrier [9,13]. As previously mentioned, similar results have been reported by Ocal *et al.* for Au and Pt on TiO_2/Ti and Au on Al_2O_3/Al and by Schleich *et al.* for Pd on SiO_2/Si. Both of these authors conclude that the transition metals diffuse slowly through the oxide by occupying cationic vacancies in the layer, even at temperatures as low as 80 K. Heating these layered systems cause rapid diffusion of the metal through the oxide layer, and an alloy layer build up at the bulk-oxide interface [14,15,16]. Our previous work with Pt on the oxidized Al foil suggests a similar finding. It should be noted that unlike the alumina film in this study, that oxidized Al foil always had a residual substantial 68 eV Al^0 peak as well as the 55 eV Al^{+3} peak in AES spectra.

In direct contrast to these results, in this work we report on a model catalyst sys-

tem in which the Pt remains active after cycling from room temperature to 700 K and back. The oxidation procedure used in this work leads to an oxide layer with fewer cationic vacancies, and as a result, diffusion of the Pt is not observed. We argue that with no unoxidized Al present, there is no possibility for a Pt-Al alloy to form, and this is the reason for the different chemical properties of the two models. Extended annealing of this sample leads to sintering of the clusters, and in fact, based on the work of Chu and Ruckenstein, it is expected that this should allow manipulations of the size distributions [28]. Further evidence for the validity of this model is demonstrated by the observation of ethylidyne at room temperature, which has also been observed by IRAS on catalysts made by standard chemical techniques. We do note, however, that the HREELS spectra obtained for this model show no evidence of a stable π bonded ethylene at room temperature, in contrast to the results reported by Moshin *et al.* Since our catalyst was never exposed to oxygen after the Pt deposition, we suggest that this difference in preparation techniques may lead to this discrepancy between our spectra and those of Moshin *et al.* [12].

Having established the validity of this model, we now discuss the finer details of these results. The spectra shown in Fig. 8 indicate that ethylidyne formation is not detected until the Pt coverage is greater than about 0.7 ML. From the TEM analysis it can be roughly estimated that the average cluster size at this deposition is about 1.4 nm. The most plausible explanation for this is that there are not sufficient sites with threefold symmetry available to the ethylene until the clusters approach this size. Although there was little change in the CO spectra after the sample was heated to 700 K, one change was that the HREELS elastic peak became larger after the annealing treatment. As stated in our previous papers on this subject, the elastic peak falls between one and two orders of magnitude after the clusters are deposited. This has been attributed to the roughening of the surface, reducing the specular reflectivity of the surface. After annealing this surface, an increase in the elastic peak intensity could

be interpreted as due to sintering of the Pt clusters, leaving more of the smoother underlying substrate exposed. A plot of the HREELS peak intensities verses the Pt coverage for the 165 K C_2H_4 spectra (Fig. 9) supports our previous conclusion that the scattering from these adsorbate covered clusters is dominated by the impact mechanism, This is shown by the nearly constant intensities of the hydrocarbon peaks, although the elastic peak drops by a factor of three. The alumina phonon mode, on the other hand, drops in intensity as the surface reflectivity decreases, as is the case for dipole-dominated scattering.

Conclusions

TEM micrographs have been presented which show Pt cluster distributions on an alumina substrate. Based on these and HREELS experiments in which the vibrational spectra of adsorb CO and C_2H_4 was analyzed, it can be concluded that this catalyst system is a stable model of a Pt/Al_2O_3 catalyst. Evidence for ethylidyne formation on these clusters has been shown, for the case of Pt distributions with an average cluster size larger than about 1.4 nm. It is expected that this general purpose fabrication technique can be extended to study other transition metal catalysts and other size distributions.

Acknowledgments

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Figure Captions

Fig. 1.   Calibration of the Pt deposition source. AES intensity of the Pd 330 eV peak, as a function of the Pt deposition measured by the quartz crystal microbalance. Least squares fit lines show breaks indicating layered growth for the Pt/Pd(111) system.

Fig. 2.   a) TEM micrograph of Pt clusters on Al_2O_3. b) Histogram of cluster sizes for a 1.7 ML Pt deposit.

Fig. 3.   a) Average Pt cluster size as a function of Pt deposition. b) Pt cluster density as a function of deposition. c) Percent of area covered by clusters as a function of deposition.

Fig. 4.   HREELS spectra of Al_2O_3 film on Pd(111). The labeled peaks are due to Fuchs-Kliewer phonon modes, and combination losses are seen in the 1400-1800 cm^{-1} range. The upper spectra was taken after exposure to 50 L of C_2H_4.

Fig. 5.   HREELS of CO/Pt/Al_2O_3/Pd(111) a) Exposure to 5 L of CO at room temperature. b) After warming to 500 K to desorb the CO. c) After another exposure to 5 L of CO at room temperature.

Fig. 6.   HREELS of Ethylene on Pt/Al_2O_3/Pd(111) a) Clean b) Ethylene at 165 K. c) Ethylidyne at 325 K.

Fig. 7.   HREELS of ethylene on various coverages of Pt, at 165 K.

Fig. 8.   HREELS of ethylene on various coverages of Pt, after warming to 325 K. Ethylidyne peaks are too weak to detect for Pt coverages less than 0.6 ML.

Fig. 9.   HREELS peak intensities as a function of Pt coverages, clearly showing dipole scattering for Al_2O_3 modes, and impact scattering for adsorbate modes.

Pt/Pd(111)

18.

10 nm

(b)

1.7 ML Pt/Al$_2$O$_3$

Size [nm]

Density [10^{12} clusters/cm^2]

(a) Cluster Size — Average Diameter [nm] vs Pt [ML]

(b) Cluster Density — Density [10¹² clusters/cm²] vs Pt [ML]

(c) Area Covered — Area Covered [%] vs Pt [ML]

Al$_2$O$_3$/Pd(111)

880

605

Energy [1/cm]

Intensity [arb]

0

1000

2000

3000

0

10000

20000

CO/Pt/Al₂O₃

C_2H_4 and C_2H_3 on Pt/Al_2O_3

C_2H_4/Pt/Al_2O_3 at 165 K

$CCH_3/Pt/Al_2O_3$ at 325 K

1.3 ML Pt

1.1 ML Pt

0.8 ML Pt

0.7 ML Pt

0.6 ML Pt

0.4 ML Pt

0.3 ML Pt

Energy [1/cm]

Intensity [arb]

Peak Intensity vs. Pt deposition