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(platinum)   (aluminum)

The adsorption of C$_2$H$_4$ on supported Pt model catalysts is investigated with High Resolution Electron Energy Loss Spectroscopy for the cases of Pt vapor deposited on an oxidized Al foil and a single crystal of TiO$_2$. At 160 K the HREELS spectra show evidence of the di-σ bonded ethylene species present on the supported Pt clusters, but upon warming to 325 K, only the TiO$_2$ supported model catalyst shows evidence of forming the ethylidyne species commonly seen on Pt(111) single crystals. The oxidized Al supported species begins to decompose by 250 K, and no spectra characteristic of ethylidyne has been seen. In the case of the TiO$_2$ supported model catalyst, we believe this is the first HREELS observation of ethylidyne on supported metal clusters.

(titanium dioxide)

sigma

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ABSTRACT

The adsorption of C_2H_4 on supported Pt model catalysts is investigated with High Resolution Electron Energy Loss Spectroscopy for the cases of Pt vapor deposited on an oxidized Al foil and a single crystal of TiO_2. At 160 K the HREELS spectra show evidence of the di-σ bonded ethylene species present on the supported Pt clusters, but upon warming to 325 K, only the TiO_2 supported model catalyst shows evidence of forming the ethylidyne species commonly seen on Pt(111) single crystals. The oxidized Al supported species begins to decompose by 250 K, and no spectra characteristic of ethylidyne has been seen. In the case of the TiO_2 supported model catalyst, we believe this is the first HREELS observation of ethylidyne on supported metal clusters.

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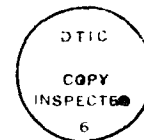Department of Physics and Materials Research Institute, Indiana University,

Bloomington, IN., 47405, USA

Introduction

Low surface area model catalysts have been a subject of great interest to surface science in recent years, serving as a bridge between well characterized single crystal surfaces and true high surface area commercial catalysts. Surface science spectroscopies such as Temperature Programmed Desorption (TPD), X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), and High Resolution Electron Energy Loss Spectroscopy (HREELS) have been applied to these systems in an attempt to better understand the unique properties of these small, supported clusters [1-5]. Systems consisting of transition metals vapor deposited onto metal oxide substrates, such as Al_2O_3 and TiO_2 have been studied by Transmission Electron Microscopy (TEM), showing that their morphologies closely resemble those of heterogeneous commercial catalysts [6]. The advantages or studying these systems lie in the ability of the experimenter to closely control the creation of these catalysts and exposure to various reactants, while allowing him to probe the catalyst with different surface science spectroscopies.

Relatively little work has employed HREELS as a probe in investigations of this type. Several studies utilizing HREELS to investigate CO adsorption on vapor deposited Ni and Pt have established the feasibility of these investigations and have pointed

out differences between such studies and HREELS work done on single crystals of these metals [1,2,4]. Our first work in this area prompted the construction of a new HREELS spectrometer equipped with a dual pass monochromator to maximize beam current to the sample. The instrument is similar to one described previously, with the addition of a rotating analyzer platform, allowing data collection as far as 30 degrees off-specular [7]. With the new instrument we have been able to investigate the adsorption of C_2H_4 on vapor deposited Pt particles, looking at low temperature spectra (160 K) and evolution of the surface as the sample is warmed to 325 K. This has been studied for Pt on a thermally oxidized aluminum foil and a single crystal of TiO_2. Both of these substrates are commonly used as catalytic supports and have been thoroughly examined with HREELS [8-10]. This work presents the first HREELS observation of ethylidyne formation on TiO_2 supported Pt model catalysts. In the case of the Pt clusters on an oxidized Al foil, no evidence of ethylidyne is observed.

Preparation and Characterization

The UHV chamber used for these studies was equipped with an RFA for LEED and AES, a quadrapole mass spectrometer for residual gas analysis, an ion gun for argon sputtering, a dual-pass monochromator HREELS spectrometer with a rotatable analyzer section for angle resolved measurements, and a thin film evaporator with a quartz crystal microbalance to measure the mass deposition. The ion-getter pumped chamber has a base pressure near 1×10^{-10} Torr and 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 a temperature above 850 K and cooled to 160 K with liquid N_2.

The preparation of the aluminum sample has been previously described, but, briefly, a 99.999% pure polycrystalline foil was mechanically polished to a final grit size of 1 micron [1]. This sample was then mounted in the UHV chamber, and, initially, several cycles of ion sputtering with 1.5 keV Ar^+ ions and annealing to 720 K were required to remove the carbon and oxygen impurities present on the aluminum foil. Subsequent daily cleaning consisted of twenty minutes of sputtering, followed by thirty minutes of annealing. As previously described, a thin oxide layer could be formed on this foil by exposing it to 240 L of O_2 and heating it to 720 K. We have estimated that this procedure renders a 0.5 to 1.0 nm thick oxide layer, which has similar properties to those of bulk Al_2O_3, yet is thin enough to allow electron spectroscopies to probe the surface without a buildup of charge.

A single crystal of TiO_2 was cut in the (100) direction and mechanically polished to a final grit size of 1 micron, following standard metallographic techniques. The crystal was then mounted in the UHV chamber and cleaned by several cycles of ion sputtering with 1.5 keV Ar^+ ions for twenty minutes and annealing at 650 K for thirty minutes. Subsequent daily cleaning consisted of 20 minutes of sputtering followed by thirty minutes of annealing at 650 K. Following the work of Mohamed, et al., the

sample was cooled to room temperature in 1×10^{-6} Torr of O_2. This procedure was necessary because it is known that sputtering and vacuum annealing will create defects on a TiO_2 surface, producing oxygen vacancies [11]. We found that ignoring this step led to unpredictable results.

The Pt deposition, previously described in detail, was carried out by resistively heating 0.1 mm diameter Pt wire on a filament made of two strands of 0.25 mm diameter tungsten, until evaporation occurred. The deposition was monitored by a quartz crystal oscillator mounted opposite the sample, equidistant from the filament. The mass deposition has been calibrated by AES and TEM as reported previously [1]. The vapor deposition of the mass equivalent of 1 to 3 monolayers of Pt was done with the substrate temperature at 300 K, then the sample was cooled down to 160 K and exposed to a saturation dosage of C_2H_4 (2 to 3 L). HREELS data were recorded before deposition, after deposition, after dosing with ethylene at 160 K and after warming the sample to 325 K. As previously reported, the Pt deposit grew as clusters on the oxidized Al foil, averaging 1.0 to 2.0 nm in diameter. Platinum has been observed as clusters on TiO_2 in studies similar to this one [12]. The HREELS data further support the growth as clusters rather than a continuous overlayer.

Results and Discussion

The HREELS data shown in Fig. 1 are those of the oxidized Al foil, and the same foil with a 1 to 2 monolayer mass equivalent covering of Pt clusters. The partial screening of the strong Fuchs-Kliewer phonons at 425 cm^{-1}, 640 cm^{-1}, and 860 cm^{-1} has been addressed in previous work by us and others [1,13]. As shown in the upper curve in Fig. 1, a small amount of CO contamination on the Pt clusters was often present, giving rise to a loss peak at 2040 cm^{-1}, but we also note that no peak characteristic of a bridging CO species was ever observed. Upon exposure to 2 L of C$_2$H$_4$ at 160 K, we observe several new loss peaks in the HREELS spectra, as shown in Fig. 2. Three strong hydrocarbon peaks are seen in this spectra, from which we tentatively identify the di-σ bonded ethylene species, which has been observed by IRAS on high surface area Pt/Al$_2$O$_3$ catalysts and on Pt(111) by HREELS [14-16]. The 3000 cm^{-1} peak is quite broad and is probably due to both the symmetric and asymmetric v-CH stretching modes of the di-σ bonded species. These losses have been observed at 2920 cm^{-1} and 3000 cm^{-1}, respectively, on Pt(111). The presence of a π bonded species could also give rise to a loss around 3040 cm^{-1} and cannot be ruled out as a possible reason for the broad width of this loss. The 1445 cm^{-1} mode matches up well with the symmetric CH$_2$ scissor mode seen in the spectra from Pt(111) (ca. 1430 cm^{-1}). Again, some amount of a π bonded species present would cause a loss in this region due to the CC stretch and cannot be ruled out. The π bonded species has been observed on highly dispersed Pt/Al$_2$O$_3$ catalysts by IRAS [14,15]. The third strong mode, which appears at 1200 cm^{-1} has not been clearly identified in published reports of ethylene on Pt(111); however, several reports show a weak mode at 1220 cm^{-1} in their off-specular spectra [16,17]. We argue that this is the same loss peak, with impact scattering, as opposed to dipole scattering, as the dominant scattering mechanism in our spectra. With the surface roughened by the Pt clusters, the surface reflectivity falls off, as evidenced by the drop off in the elastic scattering intensity, typ-

ically from 3×10^5 to 3×10^3 Hz. This causes the HREELS spectra to be dominated by the impact scattering mechanism. Typical dipole loss intensities are a factor of 1 to 5×10^{-3} less than the elastic peak intensities, and with the roughened surface, our elastic peak intensity is only 1 to 5×10^3 Hz [18]. This will imply dipole loss intensities less than 5 Hz, and the observed impact losses with intensities of 20 to 100 Hz will surely be the dominant losses. Thus, we argue that the strong mode observed at 1200 cm^{-1} is the same as that which has been seen as a weak mode on Pt(111) where the dipole scattering mechanism is dominant under specular scattering conditions.

HREELS work on single crystal TiO_2 has been previously published and is possible on this surface because it is a partially ionic semiconductor, which prevents charge from building up [8]. Fig. 3 shows a HREELS spectra of the TiO_2 crystal prepared as stated previously and cooled in 10^{-6} Torr of O_2. The TiO_2 vibrational peaks at 370 cm^{-1} and 750 cm^{-1} are due to the emission of Fuchs-Kliewer phonons, and have been discussed for the case of the (100) face previously [8]. Deposition of the mass equivalent of 2 monolayers of Pt changes the HREELS spectra as shown in Fig 3. The elastic scattering intensity falls by a factor of 2 to 4, to a level similar to that of the the intensity of the Pt covered oxidized Al. The intensity of the clean TiO_2 was a factor of 20 to 40 less than that of the clean oxidized Al foil. The phonon peaks are partially screened, depending on the amount of Pt deposited. Just as in the case of the oxidized Al foil, a small amount of CO contamination often gave rise to a loss peak at 2040 cm^{-1}. It is interesting to note that if the Pt deposit grew as a continuous overlayer, this amount should be enough to screen out the phonon peaks from the substrate [13]. After exposure to 2 L of C_2H_4 at 160 K, the HREELS spectra (Fig. 4) looks similar to the 160 K $C_2H_4/Pt/Al_2O_3$ /Al spectra of Fig. 2, although the peaks are more clearly defined. We identify the peaks at 2950, 1400, and 1190 cm^{-1} as due to the di-σ bonded ethylene species, these frequencies being very similar to those of the di-σ species observed on Pt(111). We also identify the peak at 3010 cm^{-1} as due to the

asymmetric mode of the di-σ bonded species. This asymmetric loss is due to a dipole forbidden mode and has been observed as a weak shoulder in the work on Pt(111); in the current work where impact scattering is dominant, the intensity of this loss is expected to be as strong as that from the symmetric losses. As in the case of the oxidized Al supported species, the presence of a π bonded species cannot be ruled out and could contribute to the broad peaks around 1450 cm^{-1} and 3000 cm^{-1}. Additionally, we observe a shoulder on the 750 cm^{-1} TiO$_2$ phonon at 940 cm^{-1}, similar to that seen on Pt(111). Thus, we identify this spectra as due to di-σ bonded ethylene and possibly some amount of π-bonded ethylene [14-16].

On warming these two surfaces up to 325 K, a temperature at which ethylidyne has been identified as the only stable species on Pt(111), we observe quite different behavior from these two surfaces. The HREELS spectra from the Pt/TiO$_2$ sample shown in Fig. 4 has three strong peaks, all of which correspond to Pt(111) ethylidyne HREELS peaks. We observe the v-CH$_3$ at 2920 cm^{-1}, the δ-CH$_3$ at 1335 cm^{-1} with a shoulder at 1400 cm^{-1}, and the v-CC stretch at 1115 cm^{-1}. Again, the relative intensities differ from those of ethylidyne on Pt(111), but we interpret this as the same surface species, with impact scattering as the dominant mechanism. In this case the evidence strongly supports the recent XPED work of Tamura, et al., who have observed a preferential ordering of Pt on the (100) and (110) faces of TiO$_2$ after annealing to 823 K, such that the Pt clusters grew with the (111) face parallel to the surface. Such clusters would contain the 3-fold sites necessary for the formation of ethylidyne [19].

A similar spectra is not observed in the case of warming the Pt/Al$_2$O$_3$/Al to 325 K. In fact, by 250 K the spectra from this surface changes to that shown in Fig. 2. Here, only two hydrocarbon peaks are seen, a v-CH stretching mode at 2930 cm^{-1}, and a mode at 1415 cm^{-1}, which is likely to be a CH deformation mode. We note the similarity of this spectra with those of ethylene on oxygen precovered Pt(111), published by Steininger, et al., but we do have enough evidence to identify this spectra at

this time [16].

Since ethylidyne has been shown to exist on Pt/Al_2O_3 catalysts with IRAS, we do not know the reason why an ethylidyne spectra is not observed for this model catalyst [14,15]. The cause of this could be Pt cluster size effects, the lack of 3-fold sites, or interactions with the oxidized Al support. Evidence of cluster size influence on the bonding of CO on supported Pt has been seen by Gorte, et al., but can be ruled out in this case because the observed behaviour has been seen for varying amounts of Pt from 0.25 monolayer equivalent up to the mass equivalent of up 4 monolayers [5]. We expect that cluster size effects would appear in this regime, as this range is similar to that studied by Gorte, et al. For clusters on the large end of the scale, threefold sites are likely to be present, as they are in the case of the Pt/TiO_2 surface. TPD studies have shown CO desorption indicative of (111) sites on alumina supported Pt clusters for clusters with an average diameter of 4 nm by Gorte, et al [5]. Finally, this leaves the possibility of interactions between the Pt and alumina, and possibily the bulk Al, as a reason for the lack of ethylidyne production on this model catalyst. The work of Yates, et al. [20], has shown that a deposited metal can diffuse through a thermal oxide to the metal- oxide interface, and it is conceivable that such a situation could strongly affect the Pt bonding characteristics. With this in mind we are currently examining alternate methods of Al_2O_3 preparation.

Summary

The HREELS spectra of C_2H_4 on model catalysts of Pt on oxidized Al foil and TiO_2 at 160 K and 325 K have been presented. In the case of the Pt/TiO_2 system, both spectra compare well with what has been observed on Pt(111), but in the case of the oxidized Al support, no evidence for ethylidyne is observed. This is the first HREELS observation of ethylidyne on supported clusters.

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Figure Captions

Fig. 1.   Lower curve : HREELS spectra of the oxidized Al foil.

Upper curve : HREELS spectra of the oxidized Al foil with 1-2 monolayer equivalent covering of Pt clusters.

Fig. 2.   Lower curve : HREELS spectra of $Pt/Al_2O_3/Al$ model catalyst after an exposure to 2L of C_2H_4 at 160 K.

Upper curve : HREELS spectra of the same surface after warming to 325 K.

Fig. 3.   Lower curve : HREELS spectra of a single crystal of TiO_2.

Upper curve : HREELS spectra of TiO_2 crystal with 1-2 monolayer equivalent covering of Pt clusters.

Fig. 4.   Lower curve : HREELS spectra of Pt/TiO_2 model catalyst after an exposure to 2L of C_2H_4 at 160 K.

Upper curve : HREELS spectra of the same surface after warming to 325 K.

Note Added in Proof

More recent HREELS experiments of platinum on vapor deposited Al_2O_3 by the authors have produced spectra in which ethylidyne has been clearly identified. This supports the idea that alumina preparation is a key step in making these model catalysts, and that an interaction between the Pt and the Al foil could be affecting the ethylene decomposition in the present work.

Pt/Oxidized Al

Ethylene/Pt/Oxidized Al

Pt/Titanium Dioxide

Ethylene/Pt/Titanium Dioxide