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An Investigation of Model Catalyzed Hydrocarbon Formation Reactions.

1. Overall Progress

Work has focused on two areas aimed at understanding the chemistry of realistic catalytic systems:

1. The synthesis and characterization of model supported olefin metathesis catalysts.
2. Understanding the role of the carbonaceous layer present on Pd(111) single crystal model catalysts during reaction.

Synthesis and Characterization of Model Olefin Metathesis Catalysts

Experiments have been performed to examine the surface chemistry of metathesis reactants, ethylene, propylene and 2-butenes, on the most active MoO_2 model catalyst. The turnover frequencies on these oxide layers are substantially lower than for the most active supported catalysts. It was also found that the surface is extremely unreactive in ultrahigh vacuum and that alkenes merely adsorb molecularly and desorb intact without undergoing any thermal decomposition. It was, however, also found that oxygen overlayers on molybdenum affected the olefin metathesis rate where the rate of propylene metathesis increases with the addition of ~0.5 monolayer of oxygen and then decreases once again with the addition of further oxygen. These were not as active as the oxides but do provide model systems for examining the effect of catalyst oxidation. Note that it has been shown that surface metal oxidation states up to +4 can be attained by adsorbing ~1.5 monolayers of oxygen on Mo(100) [1]. This system also has the advantage that the chemistry of oxygen overlayers on Mo(100) has been studied rather extensively [2-9] and the surface coverages calibrated using the array of LEED patterns exhibited by this system. These LEED patterns have been reproduced in our laboratory and allow various oxygen coverages to be

obtained routinely.

Initial work was carried out to examine the chemistry of ethylene on oxygen-covered Mo(100). The major discovery in this case was that, at appropriate oxygen coverages, methane was formed from the reaction of ethylene on oxygen-covered molybdenum surfaces [10]. This result is important in view of the reaction pathway proposed for olefin metathesis which postulates the initial formation of a carbene active site. The carbene is proposed, according to this mechanism, to further react with an alkene forming a metallacycle. This can thermally decompose *via* the reverse of this reaction to form metathesis products [11-24]. The C₁ formation found in these experiments corresponds to the first step in this pathway. As a baseline for studying these systems, we have also examined the chemistry of methylene iodide on various oxygen-covered Mo(100) surfaces [25] and find that methane is formed, and experiments using deuterium reveal that adsorbed methylene species react with adsorbed, surface hydrogen. This chemistry has also been studied on Mo(110) by others where facile hydrogenation of reactively formed carbenes to methane was also found [26]. We have also studied methyl groups on clean Mo(100) by adsorbing methyl iodide and the results reveal that hydrogenation of adsorbed methyl species to methane is the rate-limiting step in methane formation from adsorbed CH₂ species [27].

Species	Frequencies/cm ⁻¹	Temperature range/K	Decomposition activation energy/kJ/mol
Mo(CO) ₅	2033, 2012, 1964, 1700	80-150 K	-
Mo(CO) ₃	2021, 2000, 1955, 1701	160-180	-
Oxalate species	1720, 1290, 1130	205 to 275 K	76
Bidentate carbonate species	1660-1580, 1020	300 to 560 K	141
MoO ₂ (CO) _x	~1920 on HA ~2000 on PDA XPS peaks at 231.3 and 234.5 eV BE	205 to 560 K	-

Table 1: Properties of surface species identified on alumina following adsorption of molybdenum hexacarbonyl.

These studies indicate that ethylene can adsorb dissociatively on oxygen-modified Mo(100) to form carbene species which can hydrogenate to methane. No recombination reactions were detected. A similar chemistry is found for propylene where significantly more methane is found

than when ethylene is adsorbed on the surface [28]. In addition, while clean Mo(100) yields no methane following ethylene adsorption, significant amounts of methane are formed from propylene adsorbed on clean Mo(100) [28]. Such chemistry has never been observed before in ultrahigh vacuum.

Thin films of both MoO_2 and MoO_3 mimic the activity of alumina-supported molybdena when the loadings are high. It has been demonstrated that the activity of olefin metathesis catalysts formed by decomposing metal carbonyls on the surface initially increases with loading, but then subsequently decreases as the loading increases further [11]. This has been ascribed to the formation of a continuous oxide layer at high loadings. This result is in accord with the relatively low catalytic activities of oxide films described above. In order to synthesize model catalysts which more closely simulate the active, low-loading catalysts, we have studied the adsorption of Mo(CO)_6 on thin films of alumina grown on a Mo(100) substrate using a combination of temperature-programmed desorption and X-ray, Auger and reflection-absorption infrared spectroscopies. Alumina films are grown by evaporating aluminum onto a Mo(100) substrate and then oxidizing it with water or oxygen. The degree of hydroxylation of the films can be controlled either by growing them using oxygen (to form a dehydroxylated sample) or with water (so that the surface is hydroxylated). The surface chemistry of the alumina films was compared with that of high-surface-area alumina using ammonia and trimethyl aluminum where the agreement between the chemistry found in both regimes is excellent [29]. We then investigated the chemistry of molybdenum hexacarbonyl on thin alumina films [30,31]. Mo(CO)_6 adsorption was studied at 80 K on hydroxylated alumina where the majority (98%) desorbs molecularly at ~200 K. A small portion decarbonylates and the resulting CO desorbs at ~310 and 560 K where equimolar amounts desorb in each state. This observation has previously led to the suggestion that Mo(CO)_6 adsorption results in the formation of a stable Mo(CO)_3 intermediate on the surface [12]. Comparison of the total desorption yield due to decarbonylation with the yield of CO from the Mo(100) substrates reveals that only ~2% of the initially adsorbed Mo(CO)_6 decarbonylates, a conclusion that is confirmed by X-ray photoelectron spectroscopic analyses of the surface to measure the molybdenum coverage. These experiments also show that the molybdenum deposited on the surface is in a ~+4 oxidation state. It was also demonstrated that decarbonylation does not take place on special sites on the alumina by adsorbing Mo(CO)_6 onto the surface a second time. This results in an identical desorption spectrum and the deposition of an additional 2% of a monolayer of molybdenum. This process can be repeated thus allowing the molybdenum loading to be precisely controlled. Reflection-absorption infrared spectra of the carbonyl-covered surface reveals the formation of intermediate Mo(CO)_5 and Mo(CO)_3 species that form on heating to ~200 K. The molybdenum appears to completely decarbonylate on heating to ~205 K where an adsorbed oxalate species is identified from its infrared fingerprint [31]. This thermally decomposes at ~300 K to desorb CO and form a bidentate carbonate species:

This is a completely new interpretation of the chemistry of $\text{Mo}(\text{CO})_6$ on alumina and also elegantly explains the equimolar amount of CO desorbing in each state. The surface species and their properties are summarized in Table 1.

We have also recently studied the adsorption of $\text{Mo}(\text{CO})_6$ on alumina to 300 K. The features in the infrared spectra collected, in this case, are identical to those found by adsorbing at 80 K and annealing to 300 K.

We have carried out preliminary experiments to examine the surface chemistry of propylene on $\text{Mo}(\text{CO})_6$ /hydroxylated alumina model catalysts. These were prepared by adsorbing molybdenum hexacarbonyl at 300 K at a relatively low molybdenum coverage of $\sim 3\%$ of a monolayer (approximately $0.3 \text{ Mo atoms/nm}^2$).

Figure 1: Infrared spectra collected for a model catalyst formed by reacting $\text{Mo}(\text{CO})_6$ with an alumina film at 300 K and annealing to various temperatures (marked adjacent to the corresponding spectrum), then reacting with 5 Torr propylene at 400 K

Figure 1 shows the effect of pre-heating the sample, prepared by adsorbing $\text{Mo}(\text{CO})_6$ at 300 K, to various temperatures in ultrahigh vacuum. These were then subsequently reacted in 5 Torr of propylene at 400 K for a period of 60 minutes. These spectra were collected in a slightly unusual way. After evacuating the propylene to a background pressure of $\sim 1 \times 10^{-9}$ Torr following reaction, a background spectrum was collected of the reacted sample. This was then heated to 750 K and the spectrum was recorded. In this case, removal of species from the surface are indicated by *negative* excursions in the spectrum. This procedure was followed for two reasons. First, it minimized the delay between background and data collection, yielding much better spectral data. Second, it allows direct correlations to be made between infrared and temperature-programmed desorption data. These spectra reveal a strong variation in intensity with catalyst annealing temperature, with the greatest intensity found after heating to $\sim 450 \text{ K}$. Interestingly, this coincides with the greatest metathesis activity found on the high-surface-area catalyst [12]. This correlation should be treated with

Figure 2: Plot of infrared spectra collected for a $\text{Mo(CO)}_6/\text{Al}_2\text{O}_3/\text{Mo(100)}$ model catalyst annealed at 500 K *in vacuo* and reacted with propylene at 500 K for various times.

caution since the activity of our planar model catalyst has yet to be measured, but it does illustrate the relationships that can be obtained between the catalytic activity and the nature of the surface species that are formed.

A similar set of experiments are displayed in Fig. 2, now for a sample that had been "activated" by heating *in vacuo* at 500 K, but by reacting for various times in propylene (5 Torr) at 450 K. These reveal an initial rapid increase in signal for the first 60 minutes of reaction and a subsequent slower increase. Again, it should be emphasized that these spectra represent the difference caused by heating to 750 K and can therefore be directly correlated with products found in temperature-programmed desorption. These yield modes at 2963, 2926 and 2858 cm^{-1} in the C-H stretching region. Other features are noted between ~ 1430 and 1610 cm^{-1} . Modes between 1400 and 1500 cm^{-1} are likely due to C-H bending modes and features at higher frequencies may be due to C=C stretches.

It is well known that propylene reacts with alumina [31,32]. The infrared spectrum of propylene reacting with alumina alone at 450 K for 60 minutes is compared in Fig. 3 with the corresponding spectrum for a molybdenum-covered sample. Alumina exhibits features at 1570, 1495 and 1438 cm^{-1} in good agreement with literature values [31,32]. It should also be mentioned that oxalate species, which are formed on the surface by annealing at 450 K *in vacuo*, has a characteristic frequency at $\sim 1438 \text{ cm}^{-1}$, so that the negative excursion found after heating to 750 K (which causes the oxalate species to decompose to yield CO), may include contributions from this species. The alumina features are present in the manifold of peaks present in the data shown in Fig. 2 and are more prominent at longer reaction times. This suggests that the slow growth in spectral intensity as a function of time (Fig. 2) is primarily due to reaction with the oxide support and that propylene reacts relatively rapidly with molybdenum centers. The spectral changes associated with just the molybdenum can be obtained by subtracting the features due to reaction on the alumina and the results are also displayed in Fig. 3. This yields features at 1607 and 1465 cm^{-1} . The 1607- cm^{-1} feature is likely due to a C=C stretching mode and the 1495- cm^{-1} mode due to C-H stretches [33].

The reaction of molybdenum hexacarbonyl has been studied at higher temperatures ($\sim 600 \text{ K}$) [34]. In this case, reaction of Mo(CO)_6 with alumina leads to the formation of molybdenum carbide (MoC) as evidenced by both Auger and X-ray photoelectron spectroscopies. This is reduced to the metal on heating to $\sim 1200 \text{ K}$ by reaction with the oxygen of the alumina to desorb CO. Here the origin of the oxygen was demonstrated by growing an alumina layer using isotopically labeled oxygen (^{18}O). The carbide could be reformed by heating the sample in ethylene and once again reduced by annealing at 1200 K to evolve CO.

Role of Carbonaceous Layers in Hydrocarbon Catalysis

Figure 3: Comparison of the infrared collected for $\text{Mo(CO)}_6/\text{Al}_2\text{O}_3$ (annealed *in vacuo* at 500 K) compared with the spectra on alumina alone. Shown also is the difference between the two.

adsorb onto the surface in the presence of the carbonaceous layer at sufficiently high pressures. Measuring the temperature variations in the adsorption isotherm reveals a heat of adsorption of CO on vinylidene-saturated Pd(111) of 8 ± 1 kcal/mol compared with 35 kcal/mol on clean Pd(111) [36,37]. We have also probed the adsorption of CO on the thicker carbonaceous layer formed on Mo(100) and find adsorption on this surface at high CO pressures [38], again confirming that adsorption can occur on the surface in the presence of a carbonaceous layer at sufficiently high pressures. Similar results have been found by others using sum-frequency generation [39]. It was therefore suggested that acetylene could adsorb onto the vinylidene-covered surface. Furthermore, results from the organometallic literature suggest that an acetylene and a vinylidene can react to form a C_4H_4 intermediate [40-42]. This implies that an analogous reaction between acetylene and vinylidene might take place on a palladium catalyst to ultimately form benzene. This notion was tested by forming a ^{13}C -labeled vinylidene layer on alumina-supported palladium and by using nuclear-magnetic resonance spectroscopy to gauge the vinylidene coverage. This technique was selected since it is inherently sensitive to ^{13}C nuclei while being insensitive to ^{12}C . The presence of vinylidene was confirmed using infrared

hydrocarbon species during reaction. The nature of these species depends on the catalyst and reactant so that ethynylidyne species are present during ethylene hydrogenation and vinylidenes during acetylene cyclotrimerization. Our goal is to determine the role of these species in the catalytic reaction. It has been demonstrated that benzene is synthesized from acetylene on Pd(111) and ultrahigh vacuum studies have revealed that it forms by an initial reaction between two adsorbed acetylene molecules to yield a metallocyclic C_4H_4 intermediate which reacts with a third acetylene to yield benzene [35]. This reaction pathway is suppressed under high acetylene pressures since the Pd(111) model catalyst is covered by vinylidene species, although benzene is still formed catalytically. The presence of the vinylidene overlayer completely prevents subsequent adsorption in ultrahigh vacuum. However, we have demonstrated, using infrared spectroscopy, that CO can adsorb reversibly onto a vinylidene-saturated Pd(111) surface when the CO pressure is sufficiently high and the resulting isotherm is shown in figure 4. The CO coverage was calibrated, in this case, from the change in absorbance in the infrared spectrum of CO on clean Pd(111) as a function of coverage, for low coverages.

The data in figure 4 clearly show that molecules can

spectroscopy. It was shown that the rate at which vinylidene species were removed from the surface was equal to the rate at which benzene is formed catalytically [43]. Moreover, it was found using mass spectroscopy that two ^{13}C atoms are incorporated into the benzene that is formed during the reaction. This result indicates that the benzene formation pathway under catalytic conditions differs to that found from ultrahigh vacuum studies, where now acetylene and vinylidene react to form a C_4H_4 intermediate which is proposed to react to form benzene as follows:

Thus, the reaction pathway is modified under catalytic conditions by the presence of the vinylidene layer which becomes a reactant. This reaction proceeds more slowly than that on clean Pd(111).

Figure 4: Adsorption isotherm for CO on a vinylidene-saturated surface collected at a sample temperature of 300 K. The saturation coverage calculated from the integrated absorbance of CO on the clean surface is estimated to be ~32% of that which can be accommodated on clean Pd(111). The line plotted through the data is a Langmuir isotherm.

It has been found previously that these carbonaceous layers can be removed in hydrogen pressures of a few Torr and the removal of vinylidene and ethylidyne on Pd(111) by hydrogen has been measured using infrared spectroscopy. Since infrared radiation is not absorbed by hydrogen, experiments to interrogate the surface using infrared spectroscopy in the presence of a high pressure of gas is straightforward. It was shown that ethylidyne species react with high pressures of hydrogen and that the rate of removal is first order in hydrogen pressure. It is proposed therefore that the role of hydrogen in hydrogenation reactions is two-fold. First, as a reactant, and second, to remove the carbonaceous layer during reaction so that the ethylidyne coverage is a function of hydrogen pressure. This notion has been used to successfully rationalize the catalytic hydrogen pressure dependences during hydrogenation [44].

The situation with vinylidene is rather more complex. In this case, pressurizing a vinylidene-covered surface with hydrogen results in

Figure 5: Plot of ethylidyne coverage versus time from reaction of a vinylidene-covered Pd(111) surface with hydrogen

dissociatively on vinylidene-covered Pd(111) indicates that the hydrogen coverage should be proportional to $\sqrt{P(\text{H}_2)}$ where $P(\text{H}_2)$ is the hydrogen pressure. This implies that the vinylidene-to-ethylidyne conversion rate should have a half-order pressure dependence rather than the measured first-order dependence. It is also interesting to note that the rate constant for ethylidyne removal ($k_1 = 3.1 \pm 0.3 \times 10^{-3} \text{ Torr}^{-1} \text{ s}^{-1}$) is in very good agreement with that for vinylidene to ethylidyne conversion ($k_2 = 3.2 \pm 0.5 \times 10^{-3} \text{ Torr}^{-1} \text{ s}^{-1}$). Since the vinylidene saturation coverage ($\Theta_{\text{sat}}(\text{vinylidene}) = 1.0$ [46]) is larger than that of ethylidyne ($\Theta_{\text{sat}}(\text{ethylidyne}) = 0.25$ [47,48]), this suggests that the picture is rather complicated since several vinylidene species must be removed from the surface (presumably *via* an ethylidyne) to make room for an ethylidyne. This idea may rationalize the observed kinetics since the rate at which vinylidene can convert to ethylidyne is limited by the rate at which ethylidyne is removed by hydrogen.

The adsorption of CO on an ethylidyne-covered surface has also been studied. Since the saturation ethylidyne coverage is substantially lower than that of a vinylidene-covered Pd(111) surface, it is anticipated that CO should adsorb more easily on this open surface and this is indeed found to be the case [49]. A schematic model for the adsorption of CO on ethylidyne-covered Pd(111) where it shows that 2 CO molecules can adsorb per surface ethylidyne. The first strongly chemisorbs while the second is more loosely bound [49].

This more open structure for ethylidyne is also reflected in the adsorption of other molecules such as acetylene [50]. It is found that acetylene chemisorbs on ethylidyne-covered Pd(111) is displayed in Fig. 6 and forms benzene in temperature-programmed desorption. However, rather than desorbing in two features, only one low-temperature desorption peak is

the formation of ethylidyne, which is then removed by hydrogen. The time course of the ethylidyne coverage when pressurizing a surface initially saturated by vinylidene is shown in figure 5. This reveals an initial increase in ethylidyne coverage and a subsequent decrease. This variation can be modeled as a simple step-wise reaction with two rate constants, k_1 , the rate of vinylidene conversion into ethylidyne, and k_2 , the rate of ethylidyne removal. Note that k_2 is known independently from measurements of the rate of ethylidyne removal so that the solid line shown in figure 2 is the result of a fit to a single parameter. These experiment have been carried out as a function of hydrogen pressure and it is found that the vinylidene-to-ethylidyne conversion rate is first order in hydrogen pressure. This is a rather curious result. It is likely that the reaction of vinylidene with hydrogen proceeds *via* a vinyl intermediate. The chemistry of vinyl species on Pd(111) has been investigated by adsorbing vinyl iodide and it is found that this rapidly thermally decomposes to form ethylidyne in accord with the chemistry observed at high pressures [45]. Assuming that hydrogen adsorbs

Figure 6: Proposed surface structures for CO on ethylidyne-covered Pd(111).

detected. This feature has been previously assigned to the desorption of tilted benzene from a crowded surface while the high-temperature feature is due to the desorption of flat-lying benzene [35]. Clearly, the presence of co-adsorbed ethylidyne species crowds the surface so that only tilted benzene is present. As described above, the presence of hydrogen causes vinylidene species to convert into ethylidyne. This has been monitored *in situ* using infrared spectroscopy in the presence of gas-phase acetylene and hydrogen [50]. It is found that the ethylidyne coverage does increase with increasing hydrogen pressure as anticipated. In addition, the

amount of CO that could be accommodated onto the surface following reaction also increased with increasing hydrogen pressure, and therefore with the increasing amount of ethylidyne species on the surface. It was also found that the rate of benzene formation also increased with hydrogen pressure. This effect scaled well with the additional amount of CO that could be accommodated following reaction and was therefore suggested to be due to the more open, partially ethylidyne-covered surface formed by reaction with hydrogen. Similar effects also presumably influence the alkene hydrogenation rate and this effect is currently under investigation.

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3. Financial Statement

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