DOE/ER/14289--3

Report for DOE Grant, number DE-FG02-92ER14289

by

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entitled

An Investigation of Molybdenum and Molybdenum Oxide Catalyzed Hydrocarbon Formation Reactions.*1(i) Experiments on Model Catalysts at High Pressure*

Experiments have been carried out using various model oxide catalysts at high pressure (~450 Torr) to establish their relative metathesis activities. These models fell into two classes, the first being a series of oxygen overlayers on molybdenum, and second were oxide layers formed on a molybdenum foil substrate synthesized by controlled oxidation either in the ultra-high vacuum portion of the apparatus or by using the high-pressure reactor. Metallic molybdenum (Mo), molybdenum dioxide (MoO_2) and molybdenum trioxide (MoO_3) were tested for their activity for metathesis under identical reaction conditions and were prepared using literature protocols by oxidizing metallic molybdenum under controlled conditions in the ultra-high vacuum chamber to make MoO_2 [1-12] and at higher pressures in the isolatable cell to make MoO_3 [13,14]. This strategy also allows samples to be prepared and characterized and their catalytic activity tested without any intervening exposure to air. The oxidation procedure was tested prior to high-pressure experiments by reproducing the LEED patterns assigned to MoO_2 on a Mo(100) single crystal substrate [11] and by comparing the Mo/O Auger intensities for MoO_2 and MoO_3 which corresponded well to their respective stoichiometries. However, in order to further check the nature of the oxides, they were examined using X-ray photoelectron spectroscopy and synchrotron-radiation-excited ultraviolet photoelectron spectroscopy (done at Brookhaven) [15-17]. Heating in ultra-high vacuum shows that reduction to metallic molybdenum is underway by 1220 K and further heating to 1420 K results in complete reduction to the metal. Heating the sample for 30 s in the presence of 2×10^{-7} Torr of propylene at 873 K, however, results in a significantly more rapid rate of reduction. This temperature is within the range over which metathesis was carried out on MoO_2 and where an induction period in the catalytic rate was found.

It was found that a MoO_2 film provided the most active catalyst for olefin metathesis carried out above 700 K, with metallic molybdenum being the worst catalyst and the activity of MoO_3 intermediate between the two [18,19]. This result is in accord with current views on their relative activities based on experiments on supported catalysts [20,15]. Interestingly, an induction period was found in the metathesis rate of the MoO_2 catalyst [16,17] and activities are compared for the steady-state portion of the reaction after the completion of any induction period. In view of the reduction of MoO_2 found in the presence of propylene by XPS, this effect may be due to the reduction of the oxide layer so that the active catalysts under these conditions likely consists of an oxycarbide rather than MoO_2 .

The kinetics of olefin metathesis catalyzed by metallic molybdenum (the worst catalyst) have been investigated in detail [21] and this work was extended to probe the reaction kinetics of the most

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active model MoO_2 catalyst. The temperature dependence of the reaction displays an extremely interesting behavior, having two completely different activation energies. Reaction at higher temperatures proceeded with an activation energy of ~ 60 kcal/mol whereas reaction at lower temperatures showed a considerably lower value of ~ 7 kcal/mol. There are several important points to note about this result. First, this suggests that there are two completely different reaction pathways to metathesis products; one proceeding with a high activation energy which therefore predominates at high temperature and another proceeding with a much lower activation energy that predominates at low temperature. This was a completely unexpected result. The high-temperature activation energy is very similar to that observed on metallic molybdenum *but the reaction proceeds with a higher rate*. In addition, the reaction has also been measured during this project to be first order in propylene pressure; an identical dependence as observed on metallic molybdenum [21].

The relative activities of the model oxides for reaction at 650 K (in the low-temperature regime) for both MoO_2 and MoO_3 show comparable activities and, under these conditions, molybdenum metal is essentially inactive. More importantly, the absolute reaction rates agree well with those found for supported molybdenum oxide catalysts *with high loadings* [15]. In addition, the activation energy found in this case is close to that found for supported catalysts [22] suggesting that the MoO_2 or MoO_3 formed *in situ* are good models for supported catalysts, at least, at high loadings. Note also that no induction period is observed for the low-temperature reaction.

The temperature regime in which the low activation energy was found corresponds well to that used in commercial catalysts (< 700 K). Metathesis has been proposed to proceed at these low temperatures via the so-called "carbene" mechanism [23-47] where reaction is initiated by carbene ($\text{CH}_2(\text{ads})$) formation. This further reacts with an alkene to form a metallocycle which subsequently decomposes by the reverse of this reaction to form metathesis products. In this scheme, the carbene provides the "active site" for the reaction and is generally proposed to be present on the surface in relatively small concentrations. However, surface chemistry studies of small alkenes (ethylene and propylene) on $\text{Mo}(100)$ [48,49] have revealed a significant rate of carbon-carbon bond scission consistent with this mechanism although paradoxically an apparent rapid rate of active site (carbene) formation leads to a relatively low catalytic rate since metallic molybdenum is, by no means, an active catalyst.

We have also studied the enhancement in activity due to various oxygen overlayers on molybdenum. Oxygen adsorption on molybdenum has been studied very extensively [50-54] and various surface overlayers can be characterized using LEED and are obtained by pre-covering the surface with oxygen and annealing the sample to various temperatures to desorb oxygen to form lower overlayer coverages. It is indeed found that addition of sub-monolayer coverages of oxygen increases the metathesis activity [18,19]. The catalytic activity, however, decreases for higher oxygen coverages, an effect that is preliminarily ascribed to site blocking by oxygen. This effect will be explored using surface science experiments as outlined below. Note that these experiments were carried out using a molybdenum foil and therefore must be repeated using single crystal model catalysts.

1 (ii) Reaction Studies on Metallic Molybdenum

In order to further scrutinize the pathway for olefin metathesis on metallic molybdenum at high temperatures, we have investigated the reaction of ethylene catalyzed by molybdenum [55]. In this case, metathesis is degenerate in the sense that ethylene merely yields ethylene. However, we find the formation of methane and higher hydrocarbons up to C_6 . These higher hydrocarbons are proposed to form by C_1 polymerization [55,56]. This reaction is analogous to the hydrocarbon

formation step in CO hydrogenation and it has been shown that a Mo(100) single crystal can catalyze this reaction [5770]. This idea is confirmed since a Schulz-Flory plot for the hydrocarbons detected from the reaction of *ethylene* catalyzed by molybdenum and yields a good straight line indicating that these higher hydrocarbons are formed by C_1 polymerization.

These results suggest an alternative possible reaction pathway for olefin metathesis at higher temperatures. In this case, rather than reacting with a hydrocarbon to form a metallocycle to yield the final metathesis products, surface carbenes recombine to form the metathesis products. Thus, propylene dissociatively adsorbs forming $CH_{2(ads)}$ and $CH(CH_3)_{(ads)}$. This chemistry has been shown to be facile on Mo(100) [48,49]. These can again recombine forming propylene or alternatively two $CH_{2(ads)}$'s can react to form ethylene or two $CH(CH_3)_{(ads)}$ species can react to yield 2-butene. Assuming that there is no surface activation barrier to such a dimerization reaction, and theoretical calculations suggest that there is none [71], a simple calculation yields an approximate value for the heat of adsorption of the carbene on the molybdenum surface of ~ 115 kcal/mol. We also find significant stereoselectivity for olefin metathesis carried out on a flat, well-ordered Mo(100) single crystal surface where the cis-2-butene/trans-2-butene ratio exceeds that expected thermodynamically [72]. Such a stereoselectivity has been observed in alkene formation from the decomposition of carbene-containing organometallic complexes and so that this stereoselectivity is consistent with the proposed associative mechanism. Note that in this reaction pathway, the C_1 species formed on the surface no longer forms an *active site* as it does in the carbene-metallocycle mechanism but is a reactant, thus reconciling the apparent conflict between the catalytic and surface science results alluded to above.

It has also been found that olefin metathesis proceeds in the presence of a relatively thick carbonaceous layer [56, 73,74]. This appears to be a common phenomenon in transition metal catalyzed reactions of hydrocarbons [56, 73-76]. For example, the presence of a hydrocarbon layer is implicated in another project to investigate palladium-catalyzed reactions of acetylene [75,76]. Here acetylene reacts to form benzene both in ultra-high vacuum (i.e., in temperature-programmed desorption) and also at high pressures [154,155]. In this case, in spite of apparently facile benzene formation in TPD (where approximately 30% of the adsorbed acetylene converts to benzene [77-79]), the activity of the sample for benzene formation under catalytic conditions at higher pressures (i.e., ~ 20 Torr) is rather insipid showing turnover frequencies of $\sim 10^{-2}$ reactions/site/s [80]. Catalytic experiments on high-surface-area, supported palladium catalysts by Lambert *et al* have shown that the *initial* rate of benzene formation from acetylene is high and then decays to a low, steady-state rate [81]. They have further shown that addition of hydrogen to the reaction mixture resulted in an increase in the rate of benzene formation; a rather surprising result since hydrogen is not a reactant in the formation of benzene from acetylene. We therefore decided to try such high-pressure reactions using a model palladium catalyst in order to see if we could see a similar phenomenon on an unsupported palladium catalyst. We were indeed able to detect a significant enhancement in the benzene formation rate to the extent that we were able to obtain benzene formation rates of $\sim 4 \times 10^{-2}$ reactions/site/s at *room temperature* by the addition of 600 Torr of hydrogen to 100 Torr of acetylene. We also detected significant amounts of ethylene in accord with palladium's well-known activity as an acetylene hydrogenation catalyst [82-847]. Surprisingly, however, we also found substantial amounts of C_4 hydrocarbons. This observation, however, is consistent with conclusions from surface-science studies which indicate that benzene is formed by reaction of acetylene with an adsorbed C_4H_4 species which has been identified spectroscopically by our group in collaboration with other workers [85]. This result prompted us to attempt similar strategies in the case of molybdenum-metal catalyzed olefin metathesis. There are several similarities between the two reactions. First, they are hydrocarbon conversion reactions that do not directly involve hydrogen so that it was of interest to see if a similar enhancement in

reaction rate could also be obtained. Second, it was intriguing to see whether the addition of hydrogen to the reaction mixture would yield gas-phase reaction products that reflected the nature of the hydrocarbon species present on the surface as was found for palladium. Finally, as mentioned above, a common feature of many hydrocarbon reactions including olefin metathesis is that they appear to proceed in the presence of a strongly-bound hydrocarbon layer where this effect was first discovered by Somorjai *et al* [76] who showed that platinum-catalyzed ethylene hydrogenation proceeded in the presence of a carbonaceous layer which, in that case, consisted of ethylidyne [86,87] and an analogous strongly bound hydrocarbon is found to form following acetylene adsorption on palladium which has been demonstrated to consist of a vinylidene species [88].

A similar hydrogen effect was found for the metathesis of propylene where a significant enhancement in metathesis rate is evident when hydrogen is added to the reaction mixture. Moreover, the rate of formation of higher hydrocarbons also increases with addition of hydrogen. This is exactly what would be expected if strongly bound hydrocarbon species were reacting with hydrogen.

1(iii) Surface Chemistry Experiments

Surface chemistry experiments have carried out in the following areas:

- (a) Studies on metallic surfaces in ultra-high vacuum
- (b) Investigation of Mo(CO)_6 adsorption on alumina.

1 (iii) (a) Studies on metallic surfaces in ultra-high vacuum

We have studied the surface chemistry of the reactants for olefin metathesis (ethylene and propylene) on Mo(100) pre-covered by various amounts of oxygen and some of our results will be discussed briefly in this section. Note that alkenes adsorbed onto clean Mo(100) predominantly decompose [48,49] whereas covering the surface with about 1.5 monolayers of oxygen results in significant molecular desorption of propylene. Here, a molecular peak is found at ~260 K for low propylene exposures shifting to 220 K as the exposure increases. A low temperature (~130 K peak) is due to desorption of a condensed layer of propylene. Similar results are found for a (2x2) overlayer (where the oxygen coverage is ~1.2 monolayers). Photoelectron spectra, in particular, of the C 2s region confirm the presence of intact C_3 species on the surface. In contrast, however, significantly less propylene desorbs for a $\sqrt{5}\times\sqrt{5}$ surface where now more reactive, four-fold hollow sites are exposed. This gives rise only to a single peak centered at ~250 K. The corresponding hydrogen desorption spectra show a concomitant increase in the amount of hydrogen desorbing from the Mo(100) surface as the oxygen coverage decreases.

1 (iii) (b) Investigation of Mo(CO)_6 adsorption on alumina.

In view of the results described above which show that metathesis catalyzed by oxides at low temperatures mimics the kinetics of supported metathesis catalysts when the molybdenum oxide is present at high loadings, we will attempt to synthesize molybdenum oxides supported on alumina in the coverage range $0 < \Theta(\text{MoO}_x) < 1$. We have already grown an *amorphous* alumina layer on a tantalum foil substrate to model the alumina support in the new vacuum chamber by evaporating aluminum in the presence of oxygen to form the oxide. We have carried out preliminary

experiments to show that $\text{Mo}(\text{CO})_6$ adsorbs onto this layer. Note that this method is similar to that used extensively by Burwell *et al* [89] for synthesizing active metathesis catalysts and deposit $\text{Mo}(\text{CO})_6$ onto the oxide surface.

1 (iv) Theoretical Calculations

We have collaborated with Professor Dilano Saldin of the Department of Physics, as originally proposed, to develop theoretical strategies for identifying surface species. We have previously used near-edge X-ray adsorption fine structure (NEXAFS) spectroscopy to identify relatively complex surface species formed on palladium [88,85]. In analyzing these data, it was found that it was crucial to include exchange corrections in the calculations to obtain good agreement with experiment. This was initially done rather crudely by adding the correction after the scattering calculation had been performed. This work was pivotal, however, in emphasizing the importance of exchange and correlation effects. We found, however, that the *a priori* inclusion of various exchange and correlation potentials resulted in a spacial variation of the chemical potential which is physically unrealistic. We have therefore developed a method for including the exchange and correlation potential that simultaneously maintains a constant chemical potential within the system [90]. Comparison of the positions of the experimental gas-phase NEXAFS peaks of acetylene with results of a calculation which includes Slater exchange corrections yields both the σ and π resonances but with peak profiles and positions that are rather different from the experiment. When the exchange and correlation energy is included through self-energy corrections, the NEXAFS profile resembles the experimental result more closely and the σ - π spacing is also very close to the experimental value. We are further refining the model to attempt to improve the agreement and this should allow us to use NEXAFS in a quantitative way.

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