Catalysis Letters 21 (1993) 1–10

The activity of molybdenum and molybdenum oxide model catalysts for olefin metathesis

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Received 15 March 1993; accepted 26 May 1993

The activity of various molybdenum oxides supported on a molybdenum foil substrate for the catalysis of propylene metathesis is measured using an isolatable, high-pressure reactor incorporated in an ultra-high vacuum (UHV) chamber which allows samples to be transferred directly from vacuum into the catalytic test chamber. MoO_x samples are prepared both by oxidation of metallic molybdenum and reduction of molybdenum trioxide. The results suggest that the presence of an oxygen overlayer on the catalyst inhibits reaction and that the ranking of activity for metathesis at 870 K using 450 Torr of propylene for oxide samples is $MoO_2 > MoO_3 > Mo$ where MoO_2 is ~ 30 times more active than molybdenum metal under these conditions.

Keywords: Olefin metathesis; catalytic activity; model catalysts; molybdenum oxides; surface analysis

1. Introduction

Supported catalysts are commonly prepared by calcining a precursor salt dispersed on a high-surface-area substrate and then "activated" by reducing in hydrogen or nitrogen to produce some lower oxidation state or the metal itself. The resulting catalytic properties (e.g., activity and selectivity) often depend critically on the conditions used for activation (temperature, pressure, nature of the gas). Supported molybdenum oxides are good examples of this since they show a wide variation in catalytic behavior depending on activation conditions, catalyzing olefin metathesis [1–6], hydrogenolysis [7–10], hydrogenation [8,11] or cyclization reactions [12] to varying extents depending on the reduction temperature.

In order to establish how catalyst preparation conditions and the resulting structure relate to activity, it is advantageous to be able to transfer a model catalyst from the preparation region *directly* to a catalytic reactor. The incorporation of a high-pressure reactor in an ultra-high vacuum chamber allows this type of experi-

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ment to be implemented; the high pressure portion being used for catalyst preparation and testing, the ultra-high vacuum region being used for sample analysis, characterization and preparation. This experimental strategy has been used predominantly for measuring the activity of metallic model catalysts (often oriented single crystals) prepared and characterized in ultra-high vacuum (UHV) [13]. It, however, also opens up a range of alternative catalyst preparation strategies, so that, for example, MoO_2 can be prepared either by reduction of MoO_3 in hydrogen [15] (via a protocol that mimics conventional catalyst preparation strategies) [15] or via direct oxidation at low pressure [16–22] (using a protocol only accessible from ultra-high vacuum).

In addition to strong variations in catalytic properties of molybdenum oxides as a function of oxidation state [23,24], a significant amount of literature has evolved over the past decade documenting the oxidation and reduction properties of molybdenum and its oxides, so that the complete range of oxidation states from Mo(0) to Mo(VI) can be synthesized directly from metallic molybdenum. This system is therefore ideal for exploring changes in catalyst activity as a function of the nature of the oxide.

2. Experimental

Experiments were carried out using a stainless steel, ultra-high-vacuum (UHV) chamber incorporating an isolatable, high-pressure reactor that has been described in detail in previous publications [25]. The chamber is pumped by means of a liquid-nitrogen-trapped diffusion pump and operates at a base pressure of $\sim 1 \times 10^{-10}$ Torr following bakeout. For these experiments, a molybdenum foil (area ~ 6 cm^2, 99.97% purity, Johnson–Matthey) is attached, by means of tantalum rods, to the end of a rotatable, *XYZ* translation stage and can be resistively heated to 2000 K. It can be enclosed in a small-volume (108 cm^3), high-pressure reaction cell which has an external recirculation loop equipped with a capacitance manometer and sampling valve for diverting a portion of the reaction mixture to a gas chromatograph for analysis. Reactions were carried out at a temperature of 870 K using propylene pressure of 450 Torr and the sample temperature is held constant (± 2 K) using a temperature controller. The total pressure is made up to 760 Torr using nitrogen and the gas mixture homogenized by recirculating it for 20 min prior to reaction. Reaction rates are measured from the slope of the product accumulation curve for low ($<1\%$) conversions. Because of the small catalyst area, this corresponds to a large number (~ 1000) of turnovers. An induction period was observed in the product accumulation curves for some of the catalysts (see below). In this case, rates were calculated from the linear portion of the curve following completion of any induction period.

The molybdenum foil sample is cleaned using a standard protocol and adjudged clean when no contaminants (e.g., carbon) are detected using Auger spectroscopy. The stoichiometry of the oxides was also measured using Auger spectroscopy (from the O/Mo Auger ratio; see below) where spectra were, in this case, collected using a hemispherical analyzer. Spectra were accumulated by electron counting and the resulting *n*(*E*) spectrum differentiated using conventional Savitzky–Golay methods [26]. The spectrometer was operated in fixed-retard-ratio (FRR) mode using a retard ratio of 10. This allowed data to be accumulated using an incident beam current of 0.1 μA to minimize possible electron beam damage of the oxide surface.

Ultra-high purity oxygen, hydrogen and nitrogen were used for these experiments and CP grade propylene was further purified by several bulb-to-bulb distillations prior to use.

3. Results

A full range of molybdenum oxidation states are accessible by either oxidation of molybdenum at low pressures in an ultra-high vacuum chamber (for oxidation states up to +4) or at high pressures (in the reaction cell) for higher oxidation states. MoO_2 growth by the oxidation of metallic molybdenum has been studied very extensively [16–22] and this oxide is formed on the molybdenum foil using an oxygen exposure of 2000 L (using a pressure of 3×10^{-5} Torr for 67 s) at a sample temperature of 1050 K and, in some cases, subsequently allowing the sample to cool in oxygen. A MoO_3 film can be grown on molybdenum foils using a procedure that consists of heating in 150 Torr of oxygen at 560 K for 60 min [14]. The peak-to-peak Auger intensity ratio for the O KLL transition (520 eV kinetic energy) to the Mo MNN transition (at 221 eV kinetic energy) was 2.1 ± 0.1 for MoO_2 and 3.4 ± 0.1 for MoO_3 grown using the methods described above. These ratios were obtained using normal incidence for the exciting electron beam and the ratio of these values (1.6 ± 0.1) agrees well with the relative stoichiometric ratios (1.5). Lower oxidation states ($< +4$) are accessed using various oxygen overlayer coverages [27,28] and the oxidation state of the surface molybdenum has been measured for various oxygen coverages using X-ray photoelectron spectroscopy [29,30]. Coverages were calibrated in this work using a Mo(100) single crystal using the array of ordered LEED structures displayed by these surfaces [27,28]. The diffraction patterns obtained in our work were in very good agreement with previous results and allowed a protocol for synthesizing lower oxidation state surfaces to be established.

Reactions were carried out using polycrystalline substrates for several reasons. First, reasonably high surface area foil samples can be obtained more conveniently than single crystals. Second, any surface damage caused by repeated oxidation/reduction is less serious on a foil than on a single crystal and finally, any possible structure sensitivity in the oxide catalyst is less likely to pose serious problems using a polycrystalline substrate. The activity of the model catalysts is measured using

450 Torr of propylene at a sample temperature of 870 K. Metathesis products (ethylene and 2-butene) were detected as well as small amount of methane due to hydrogenolysis.

The resulting plot of propylene metathesis activity for a range of oxides formed by molybdenum oxidation, displayed in histogram form and normalized to the rate when catalyzed by metallic molybdenum, is shown in fig. 1. Note that in this case Mo(+4) can be made either by oxidation in the vacuum chamber as described above (leading to a film of MoO_2) [16–22] or from an oxygen overlayer at a coverage of 1.4 [29,30]. Both oxidation procedures gave essentially identical reaction rates. The addition of a small amount of oxygen to produce a metal oxidation state of ~ 1 (corresponding to an oxygen coverage of approximately 0.5) results in a seven-fold increase in the metathesis activity. Addition of an electron withdrawing adsorbate to the surface clearly enhances the activity. However, the addition of further oxygen results in a severe diminution in the effectiveness of the model catalyst. Oxidation states of +2 and above correspond to oxygen coverages >1.0 [29,30] so that the lower activity of the higher oxidation state samples may be attributed to the effect of site blocking by oxygen.

An induction period in catalytic activity was evident in all of the oxide catalysts but *not* for metallic molybdenum. As noted above, the rates displayed in fig. 1

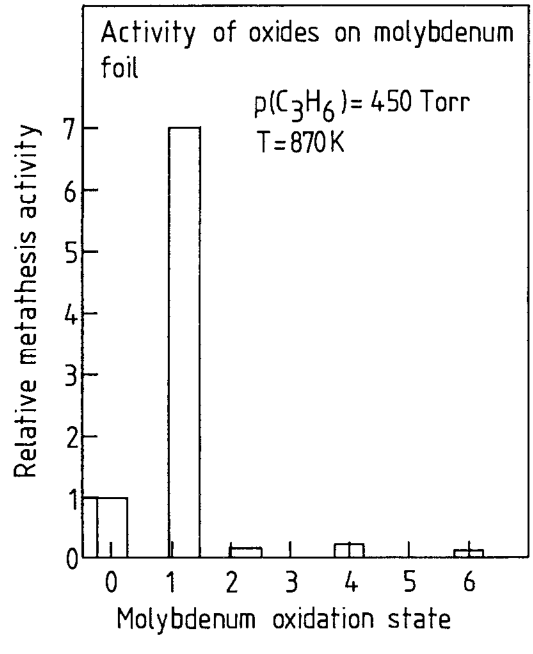

Fig. 1. Histogram showing the activity of various oxidation states of molybdenum compared with the activity of metallic molybdenum metal where oxides are formed by the oxidation of molybdenum.

(and in subsequent figures) are for a steady-state reaction measured after completion of any induction period.

It is also possible to synthesize model metathesis catalysts following the methods used for supported catalysts [15]; i.e., by calcining to form MoO_3 (as described above) and then by reducing in hydrogen (760 Torr, 790 K, 1 h) [14]. It has been shown, using both X-ray photoelectron and Raman spectroscopies that such a protocol leads to the formation of MoO_2 [14]. The resulting relative metathesis activity for MoO_2 and MoO_3 formed in this way, but without any subsequent annealing in vacuo, again compared to the activity of metallic molybdenum, is represented by the dark histograms in fig. 2. These rates were similarly measured using 450 Torr of propylene at a reaction temperature of 870 K. The MoO_2 sample (made by hydrogen reduction of MoO_3) shows a similar activity to that of metallic molybdenum whereas the activity of MoO_3 is substantially lower. It is usual, however, in preparing supported, reduced molybdena catalysts, to outgas the sample at ~ 800 K in vacuo prior to use. Annealing MoO_2 formed by MoO_3 reduction at 800 K in ultra-high vacuum (with a background pressure of $\sim 1 \times 10^{-9}$ Torr) for 20 s significantly enhances the activity (fig. 2; open histogram) since the sample is now ~ 5 times more active than metallic molybdenum. A similar vacuum annealing procedure for MoO_3 (fig. 2; open histogram) also significantly increases the

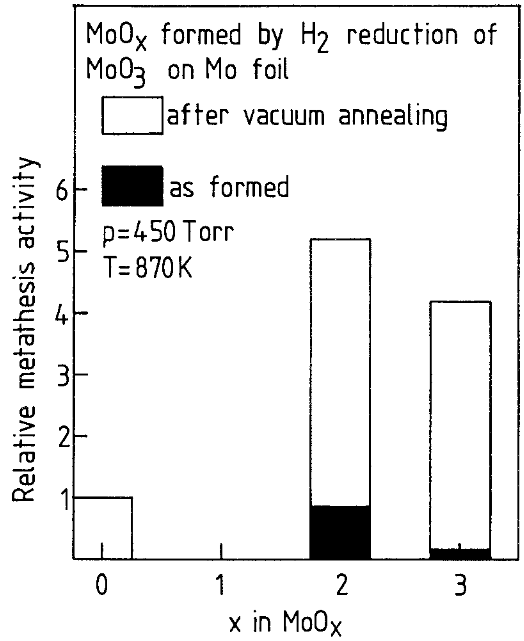

Fig. 2. Histogram showing the relative activity of molybdenum oxides formed by oxidation and reduction of molybdenum compared to metallic molybdenum. (■) without annealing in vacuo and (□) after annealing in vacuo.

activity for this catalyst for olefin metathesis. In order to understand this enhancement in activity, the O/Mo ratio was measured for MoO_3 using Auger spectroscopy (using a glancing incidence (10°) electron gun to enhance the surface sensitivity) as a function of annealing temperature. The initial O/Mo stoichiometric ratio is taken to be 3 for the freshly prepared oxide (corresponding to the formation of MoO_3) and the results of this experiment are displayed in fig. 3. A decrease in the O/Mo ratio is evident on annealing the surface to ~ 700 K. The average surface stoichiometry at this annealing temperature corresponds to $MoO_{\sim 2.5}$. The O/Mo ratio again increases on heating to ~ 1000 K and subsequently decreases rapidly at higher annealing temperatures. Such a decrease in O/Mo ratio on annealing MoO_3 to ~ 700 K has been ascribed to the removal of oxygen from the outermost layer of the molybdenum oxide to expose the underlying molybdenum ions [31]. These results suggest that forming MoO_3 by metal oxidation leads to an oxide with a surface layer consisting of oxygen. Desorption of this outer oxygen layer by heating to ~ 800 K exposes the underlying molybdenum ions which may provide the "active sites" for the initiation of catalysis. It should be noted that other effects such as structural changes in the oxide following annealing could also affect the activity of the oxide catalyst.

As analogous strategy was tried for molybdenum dioxide synthesized by direct oxidation. This is also likely to lead to an oxygen-terminated surface when the

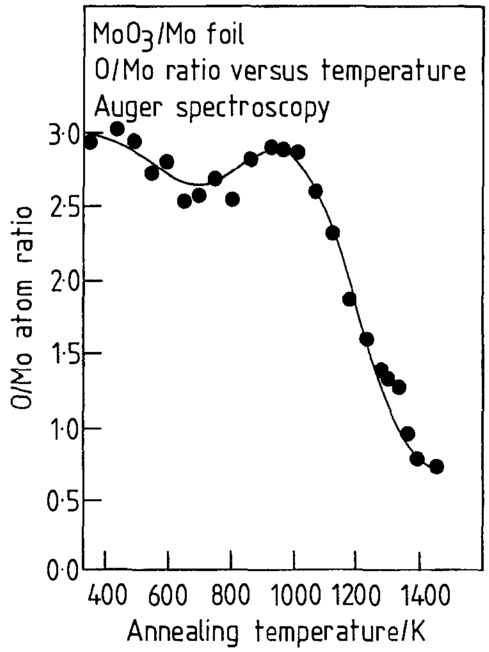

Fig. 3. Plot showing the O/Mo stoichiometry for MoO_3 as a function of annealing temperature measured using Auger spectroscopy obtained using a glancing incidence electron gun.

freshly prepared oxide sample is cooled in oxygen. However, samples prepared by exposure to 2000 L of oxygen but where the oxygen is pumped from the chamber prior to cooling show a significant enhancement in metathesis activity (by a factor of ~ 25) compared to metallic molybdenum. The relative reaction rates for propylene metathesis for the best MoO_2 and MoO_3 catalysts (both formed by direct oxidation followed by annealing in vacuo) compared to metallic molybdenum are shown in fig. 4. In this case, reaction rates are plotted as turnover frequencies (reactions/(site s)) again using 450 Torr of propylene at a reaction temperature of 870 K. The turnover frequency for olefin metathesis measured for a metallic molybdenum foil under these circumstances is ~ 0.5 reactions/(site s) where the site density is taken to be equal to that on a Mo(100) surface (with 1.0×10^{15} exposed molybdenum atoms/cm^2). This value is in very good agreement with that obtained by extrapolating kinetic data for metathesis catalyzed by a Mo(100) single crystal [32] where the turnover frequency r_m is given by

$$r_m = 8.0 \times 10^{12} p(C_3H_6) \exp(-65000/RT),$$

where the propylene pressure is measured in Torr and so has a first-order pressure dependence and proceeds with an activation energy of 65 kcal/mol. This yields a rate of ~ 0.2 reactions/(site s), in good agreement with the experimental value, suggesting that olefin metathesis catalyzed by metallic molybdenum is not strongly

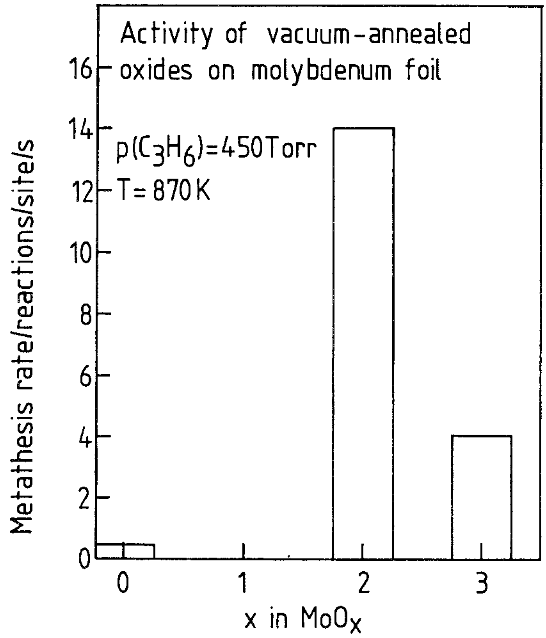

Fig. 4. Plot of reaction rate measured in reactions/(site s) for MoO_3, MoO_2 and Mo where the oxides are made by direct oxidation followed by annealing in vacuo.

structure sensitive. The surface molybdenum ion densities in the oxides can be estimated compared to metallic molybdenum using Auger spectroscopy which gives values of 0.7 ± 0.1 for MoO_2 and 0.6 ± 0.1 for MoO_3. The data were obtained by comparing the molybdenum Auger intensity of the oxide to that of the metal after heating the samples to ~ 1800 K to remove surface oxygen and where the spectra of the oxide and metal were taken using identical experimental conditions. Metallic molybdenum contains 0.065 Mo atoms/$Å^3$, MoO_2 has 0.031 Mo ions/$Å^3$ and MoO_3, 0.02 ions/$Å^3$. The area ratio of molybdenum ions in MoO_2 and MoO_3 compared to metallic molybdenum can be calculated from these values and yields 0.61 and 0.45 respectively. These are in reasonable agreement with the Auger ratios measured above and are used to estimate the molybdenum ion site densities to calculate turnover frequencies measured in reactions/(site s) for MoO_2 and MoO_3 in fig. 4. This assumes that all potential surface atoms *are* indeed available for catalysis and that an "active site" contains a single surface molybdenum atom. This suggests that the optimum oxide catalyst is MoO_2 and that the propylene metathesis rate is ~ 14 reactions/(site s) under these experimental conditions.

A cis-2-butene to trans-2-butene ratio larger than predicted thermodynamically for these experimental conditions (0.92 [33]) is observed in the metathesis products catalyzed by all the model oxide catalysts. The ratio was also found to decrease as the reaction proceeds.

4. Discussion

The data of figs. 1 and 3 show that there is a considerable change in metathesis activity as a function of molybdenum oxide stoichiometry with samples formed by molybdenum oxidation being less active than those formed by MoO_3 reduction. Apparently an oxidation state of ~ +4 shows the largest activity.

The origin of the difference in activity between catalysts formed by oxidation and reduction may be ascribed to the nature of the outermost layer of the catalyst as indicated by the data of fig. 1 that shows that higher oxygen coverages lead to a substantial diminution in the metathesis rate. In addition, annealing MoO_3 to ~ 800 K, where the results of fig. 3 show a loss of surface oxygen, leads to a substantial increase in the rate of metathesis. This notion is given further credence by the results of fig. 4 which show that the metathesis rate catalyzed by MoO_2 formed by oxidation, but where the oxygen is evacuated from the chamber prior to cooling the sample, increases substantially. The increase in O/Mo ratio on annealing MoO_3 at higher temperatures in fig. 3 implies that the surface is being replenished by oxygen diffusion from the bulk of the MoO_3. Other effects such as structural changes in the oxide might also be responsible for the enhancement in activity. The resulting order in effectiveness of the catalysts for olefin metathesis is $MoO_2 > MoO_3 > Mo$ (fig. 4). This result is in general agreement with previous observations for supported catalysts [23,24]. Note, however, that the formal oxidation state of metal ions where the catalytic act is underway must be lower than +4 for MoO_2 and lower than +6 for MoO_3 since the oxygen co-ordination number for these ions at the surface is less than for corresponding bulk ions.

Metallic molybdenum is generally considered to be inactive as a catalyst for olefin metathesis [4,34]. It should be emphasized that any oxygen is stringently excluded from the reaction system in all experiments, particularly when metallic molybdenum is used, since the cell is evacuated to $\sim 5 \times 10^{-10}$ Torr prior to reaction. Auger analysis of a Mo(100) single crystal model catalyst reveals *no* surface oxygen (although substantial amounts of carbon are detected) nor is any CO or CO_2 detected in thermal desorption by reaction of oxygen with remaining surface carbon following reaction [32]. Reactivity comparisons are usually made at lower temperatures than the conditions under which these experiments were performed and since the activation energy for metathesis catalyzed by metallic molybdenum is $\sim$ 65 kcal/mol, the reaction rate will decrease very rapidly as the temperature is decreased.

As noted above, an induction period in the activity is found for all catalysts as a function of "time-on-stream". Such induction periods have been noted previously in olefin metathesis catalysis [35,36]. Since the induction period is present for both annealed and unannealed catalysts, the induction period cannot be ascribed reduction of the outermost layer of the oxide to reveal bare metal sites. In the context of the carbene mechanism [37], the induction period might be ascribed to the slow formation of carbene "active" sites on these catalysts. This suggestion remains to be verified but implies, however, that merely counting the number of exposed molybdenum ions on the surface will lead to a severe overestimate of the "active site" density so that the reaction turnover frequencies calculated on this basis (fig. 4) constitute a lower limit. It has been suggested that the active site density on a heterogeneous metathesis catalyst is very low [38].

5. Conclusions

The activity of model oxides for the catalysis of propylene metathesis to form ethylene and 2-butene increases in the order Mo, MoO_3, MoO_2. The metathesis rate catalyzed by a polycrystalline molybdenum foil is in good agreement with results for a Mo(100) single crystal implying that the reaction is not strongly structure sensitive on metallic molybdenum.

Termination of the catalyst by an oxygen layer results in a severe diminution in the catalytic activity suggesting that metathesis is catalyzed by molybdenum ions. Both oxygen-terminated and molybdenum-ion-terminated catalysts show an induction period excluding the possibility that reduction of the surface is responsible for this phenomenon.

Acknowledgement

We gratefully acknowledge support of this work by the US Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences under grant number FG02-92ER14289.

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