

## The Activity for the Metathesis of Propylene of $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$

ALAN BRENNER<sup>1</sup> AND ROBERT L. BURWELL, JR.

*Ipatieff Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois 60201*

Received June 20, 1977; revised November 7, 1977

The activity of  $\text{Mo}(\text{CO})_6/\gamma\text{-Al}_2\text{O}_3$  for the metathesis of propylene in a pulse reactor, mostly at 53°C, has been investigated. A number of different surface species which are the products of various pretreatments exhibit catalytic activity. The degree of dehydroxylation of the alumina is an important variable. On partially dehydroxylated alumina, the *initial* catalytic activity increases in the sequence  $\text{Mo}(\text{CO})_3\text{ads}$ ,  $\text{Mo}(\text{CO})_2\text{O}_2\text{ads}$ , " $(\sigma\text{-O}^-)_2\text{Mo}$ ," and " $(\sigma\text{-O}^-)_2\text{Mo}$ " treated with oxygen at 23°C. " $\text{Mo}(\text{CO})(\text{O}_2)_2\text{ads}$ " and  $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$  activated at 500°C are inactive. A  $\text{Mo}(\text{CO})_6$  on dehydroxylated alumina activated at 100°C is somewhat less active than that on partially dehydroxylated alumina but material activated at 500°C (average oxidation number, O.N. = 0.4) is active.  $\text{Mo}(\text{CO})_3\text{ads}$  and  $\text{Mo}(\text{CO})_2\text{O}_2\text{ads}$  on hydroxylated alumina are inactive. No more than about 1% of a pulse of propylene is retained by the various catalysts. Activity for metathesis of propylene on  $\text{Mo}(\text{CO})_3\text{ads}$  increases with pulse number and pulses of ethylene are also effective in activating  $\text{Mo}(\text{CO})_3\text{ads}$ . On most other catalysts, activity declines with pulse number, often rapidly. Selectivities in the metathesis to the primary products, ethylene and 2-butene, exceed 99%. It appears likely that only a rather small fraction of the surface molybdenum becomes catalytically active.

### INTRODUCTION

$\text{Mo}(\text{CO})_6/\gamma\text{-Al}_2\text{O}_3$  was one of the first catalysts (1) reported for the metathesis (2) of olefins. Having 18 electrons in its valence shell, molybdenum hexacarbonyl should be coordinatively saturated. Since exchange between carbonyl and  $\text{C}^{18}\text{O}$  is slow at 116°C in the gas phase (3), one would not expect that molybdenum hexacarbonyl as such could activate olefins at lower temperatures. The first study aimed at the elucidation of the surface reactions which convert  $\text{Mo}(\text{CO})_6\text{ads}$  into active catalysts was that of Davie and coworkers (4, 5). Infrared and mass spectroscopic data led them to suggest that  $\text{Mo}(\text{CO})_4\text{ads}$

or  $\text{Mo}(\text{CO})_3\text{ads}$  was the active catalytic site after activation of  $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$  at 100°C. Later, more detailed examination of the correlation of activity with the intensity of the C-O stretching band led Howe and co-workers to conclude that the active species on catalysts activated at 100°C were completely decarbonylated (6). However, Burwell and Brenner (7) established that the catalyst activated at 100°C with the rigorous exclusion of oxygen was nearly quantitatively present in the form  $\text{Mo}(\text{CO})_3\text{ads}$  and that this form probably constituted an active catalytic site or its precursor.

In the preceding paper (8), the predominant surface species present after various conditions of activation of  $\text{Mo}(\text{CO})_6/\gamma\text{-Al}_2\text{O}_3$  were determined. This paper reports a study of the metathesis of propylene to

<sup>1</sup> Present address: Department of Chemistry, Wayne State University, 247 Life Sciences Building, Detroit, Michigan 48202.

ethylene and 2-butene on the product of these activations.

### EXPERIMENTAL

The details of catalyst preparation, characterization, and measurement of catalytic activity have been described previously (7-9). Mo(CO)<sub>6</sub>/Al<sub>2</sub>O<sub>3</sub> was prepared *in situ* from 0.250 g of 60- to 80-mesh alumina and then activated. The alumina was of the standard degree of dehydroxylation [calcined at 450°C in flowing oxygen (8)] unless otherwise stated. The activity for the metathesis of propylene was measured at 53°C by passing a 0.86 cm<sup>3</sup> STP pulse of propylene through the catalyst bed in an ultrapure helium carrier at a flow rate of 1 cm<sup>3</sup>/sec. Products were collected for 3 min in a silica gel trap at -196°C and, by warming the trap, the adsorbed gas was then released as a pulse for gas chromatographic analysis. The only detectable impurity in the propylene (Phillips Research Grade) was 0.02% propane. The maximum total exposure to oxygen during 20 pulses of propylene was about  $4 \times 10^{-4}$  cm<sup>3</sup> STP or about 0.001 O<sub>2</sub>/Mo on the usual catalyst which contained 0.6% Mo by weight. The sensitivity for measurement of the conversion of propylene was 0.01%. Reproducibility in conversion between separate preparations and activations of catalysts was about 15%. Unless stated otherwise, activities are for the first pulse of propylene.

Some runs gave equilibrium conversions of propylene. Thus, runs at much lower conversions are unlikely to have involved serious concentration gradients in the catalyst pores. Further, two runs on catalysts prepared in the same fashion on 70- to 80- and 120- to 140-mesh alumina gave the same conversion, 13%, to within the usual reproducibility.

Mo(CO)<sub>6</sub>/silica was prepared using Davison Grade 62 wide-pore silica gel which had been rinsed with 0.1 M nitric

acid and washed with redistilled water. It was exposed to flowing oxygen at temperatures varying from 180 to 360°C before impregnation with Mo(CO)<sub>6</sub>.

In some runs the reactor was modified by adding a column of Cr<sup>2+</sup>/SiO<sub>2</sub> immediately before the catalyst. This material removes oxygen to undetectable levels (10). The oxygen trap was bypassed during calcination of the alumina and for 1 min during the passage of each pulse of propylene.

### RESULTS

#### *Products of Metathesis*

Simple metathesis of propylene would yield equimolar amounts of ethylene and 2-butene. The equilibrium conversion is 43% at 53°C (11). No by-product hydrocarbons, C<sub>6</sub> or lower, were observed in any experiment except for traces of 1-butene. The selectivity of metathesis to ethylene and 2-butene exceeded 99.8% with respect to volatile products. The amount of ethylene in the exit pulse usually exceeded that of 2-butene but the ratio of the two tended to unity with increase in the pulse number, the temperatures of reaction, or the catalytic activity. The ratio *trans*-2-butene/*cis*-2-butene was usually greater than 2.8, the equilibrium value (11), but the ratio fell toward 2.8 as the pulse number or the catalytic activity increased. For a typical Mo(CO)<sub>3</sub>ads catalyst which gave an initial conversion of about 1%, the *trans/cis* ratio in pulse Nos. 1, 3, and 27 was 10, 3.8, and 2.9, respectively, and, for ethylene/2-butenes, 2.5, 1.3, and 1.0, respectively.

The catalytic activity for the metathesis of propylene by catalysts containing 0.56% Mo is shown in Fig. 1 as a function of the loss in carbon monoxide during activation.

#### *Activity of Mo(CO)<sub>3</sub>ads Catalysts*

In some runs a Cr<sup>2+</sup>/SiO<sub>2</sub> trap was inserted immediately before the reactor as

a test of the effect of any oxygen impurity. Two runs with this special reactor at a loading of 0.54% Mo gave the normal stoichiometry for the formation of  $\text{Mo}(\text{CO})_3\text{ads}$ , the normal activity for methathesis in the first pulse of propylene, and the normal increase in activity with pulse number.

The conversion for catalysts of three different loadings is shown in Fig. 2 as a function of pulse number, and Fig. 3 shows the activity of  $\text{Mo}(\text{CO})_3\text{ads}$  as a function of loading. These runs were accompanied by small losses of carbon monoxide from the catalyst. For the 1.0% catalyst of Fig. 2, the losses in pulse Nos. 1, 2, 9, and 20 were 0.0013, 0.00073, 0.00075, and 0.00049 CO/Mo, respectively. Exposure to propylene at higher temperatures results in a greater degree of activation as well as a substantial adsorption of propylene. A pulse of propylene (0.86 cm<sup>3</sup> STP) was trapped in the reactor for 3 min at 97°C, the reactor was then purged with helium at 53°C, and the activity was remeasured. Results are shown in Table 1. In runs at -18°C, the activity steadily declined with pulse number from pulse No. 1. Exposure of catalysts to pulses of propylene at 53°C

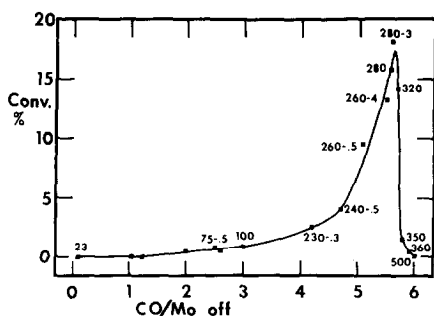


FIG. 1. Variation of the conversion of propylene with the average number of molecules of carbon monoxide lost from  $\text{Mo}(\text{CO})_6$  on 0.25 g of standard alumina (0.56% Mo) during activation in flowing helium. The number before the hyphen indicates the temperature of activation in degrees centigrade; the number after the hyphen, the period of time in hours at the indicated temperature. Where no time is shown, the period is 1 h.

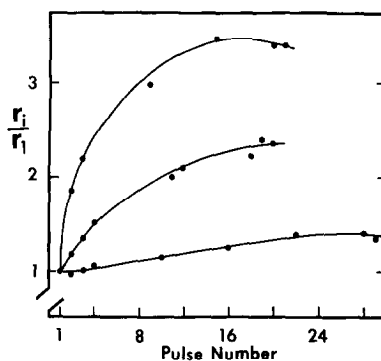


FIG. 2. Variation with pulse number in the catalytic activity of  $\text{Mo}(\text{CO})_3\text{ads}$  on 0.25 g of standard alumina at various loadings. The y axis shows the conversion at pulse  $n$  divided by the conversion at pulse 1. The loadings are: upper curve, 1.00%; middle curve, 0.34%; lowest curve, 0.14%.

did not change the weak EPR absorption of  $\text{Mo}(\text{CO})_3\text{ads}$  (8).

Catalysts can also be activated by exposure to ethylene at 53°C. Seven pulses of ethylene were passed over a fresh  $\text{Mo}(\text{CO})_3\text{ads}$  catalyst containing 0.78% Mo. The total adsorption from these pulses was  $0.1 \pm 0.1$  ethylene/Mo and less than 0.02% propylene was formed. The conversion of a pulse of propylene which was passed over the catalyst was six times that expected for fresh  $\text{Mo}(\text{CO})_3\text{ads}$ . In another run seven consecutive pulses of ethylene were

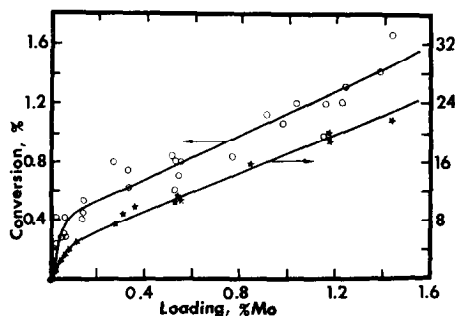


FIG. 3. The conversion in the first pulse vs loading for  $\text{Mo}(\text{CO})_3\text{ads}$  and for  $\text{Mo}(\text{CO})_2\text{O}_2\text{ads}$  on 0.25 g of standard alumina. The scale for the conversion for  $\text{Mo}(\text{CO})_3\text{ads}$  is shown at the left, and that for  $\text{Mo}(\text{CO})_2\text{O}_2\text{ads}$ , at the right.

TABLE 1  
Effect of Exposure to Propylene at 97°C upon the Activity of Mo(CO)<sub>3</sub>ads  
for Metathesis at 53°C<sup>a</sup>

	Pulse number										
	1	2	3	— <sup>b</sup>	4	— <sup>b</sup>	5	— <sup>b</sup>	6	— <sup>b</sup>	7
Conversion (%)	1.2	3.8	4.8	—	14.6	—	15.6	—	13.6	—	13.6
CO loss/Mo (× 10 <sup>3</sup> )	1.2	0.7	0.6	0.7	0.6	1.5	0.4	1.0	0.4	1.1	0.8
C <sub>3</sub> H <sub>6</sub> uptake	—	—	—	1.2	—	1.3	—	1.3	—	0.16	—

<sup>a</sup> Catalyst weight, 0.125 g; loading, 2.16% Mo.

<sup>b</sup> A 0.86 cm<sup>3</sup> pulse of propylene was trapped in the reactor for 3 min at 97°C. Had no adsorption occurred, the pressure of propylene would have been 89 Torr. The uptake of propylene is expressed as the ratio, propylene/Mo, although the fraction of propylene retained by the support is unknown.

passed over Mo(CO)<sub>3</sub>ads which previously had been used to disproportionate propylene. The amounts of propylene produced were 0.62, 0.33, 0.21, 0.24, 0.17, 0.15, and 0.11 mole%, respectively. Similar results were obtained by pulses of ethylene at 100°C after metathesis of propylene at this temperature.

Since Mo(CO)<sub>3</sub>ads is formed reversibly from Mo(CO)<sub>6</sub> (8), it was of interest to check if the active site on this type of catalyst is also reversibly formed. Mo(CO)<sub>3</sub>ads was first exposed to sufficient pulses of propylene until the activity had stabilized at its maximum value and then it was exposed to flowing CO at 100°C. After 15 h, 92% of the Mo was recovered as Mo(CO)<sub>6</sub> and the activity dropped by 91%. In another run a flow of CO for 5 h at 100°C led to the recovery of 88% of the Mo(CO)<sub>6</sub> and reduced the activity by 83%.

Exposing Mo(CO)<sub>6</sub>/γ-alumina which had been activated at 100°C *in vacuo* to trichloroethylene (C<sub>2</sub>HCl<sub>3</sub>) at room temperature led to a large increase in metathesis activity (12). Although we also observed large activation by exposure at 23°C, at this temperature an entire pulse of C<sub>2</sub>HCl<sub>3</sub> can be adsorbed by the support rendering it impossible to measure the reaction with Mo(CO)<sub>3</sub>ads. We therefore investigated the reaction between 0.082 cm<sup>3</sup> pulses of

C<sub>2</sub>HCl<sub>3</sub> and Mo(CO)<sub>3</sub>ads at 100°C. After passing six pulses of C<sub>2</sub>HCl<sub>3</sub> over Mo(CO)<sub>3</sub>ads at 100°C, a total of 1.2 CO/Mo had been evolved and this value was only slowly increasing with pulse number. The ratio, (CO evolved)/(C<sub>2</sub>HCl<sub>3</sub> adsorbed, corrected for background adsorption on the alumina) was 2.5. For catalysts of loading less than 0.14% Mo, a single pulse of C<sub>2</sub>HCl<sub>3</sub> increased the activity 90-fold. Catalysts of higher loading all gave equilibrium metathesis of the propylene after exposure to C<sub>2</sub>HCl<sub>3</sub>.

Pulses of nitrogen, CO, and CO<sub>2</sub> at 23°C had no effect on the activity of Mo(CO)<sub>3</sub>ads. Exposure to flowing hydrogen for 10 min at 23 or 100°C also had no effect.

#### Activity of Mo(CO)<sub>4</sub>ads and Mo(CO)<sub>5</sub>ads

Since these materials are unstable at 53°C in flowing helium, their catalytic activities were measured at lower temperatures and the results are presented as the ratio of their activities to that of Mo(CO)<sub>3</sub>ads of the same loading measured at the same temperature. Mo(CO)<sub>5</sub>ads is of zero or very low activity. The relative activity of Mo(CO)<sub>4</sub>ads at -18°C was 0.56 ± 0.11. Similar results were obtained in preparations from fresh Mo(CO)<sub>3</sub>ads

and from  $\text{Mo}(\text{CO})_3\text{ads}$  which had been exposed to propylene. The activity of  $\text{Mo}(\text{CO})_4\text{ads}$  quickly drops to about two-thirds of its value in pulse No. 1.

*Activity of Catalysts Activated above 100°C and Effect of Exposure to Oxygen*

Catalysts activated at about 280°C are initially much more active than  $\text{Mo}(\text{CO})_3\text{ads}$  (Fig. 1). However, the activity drops rapidly with pulse number. The relative activities in the first four pulses on such catalysts are about (1.00), 0.85, 0.76, 0.70. After letting the activity stabilize, an equimolar mixture of CO and hydrogen was allowed to flow for 3 h at 100°C over a catalyst which had been activated for 3 h at 280°C. This treatment had negligible effect on the activity. Such treatment does not reverse the formation of species formed by the decomposition of  $\text{Mo}(\text{CO})_3\text{ads}$  (8).

Exposing catalysts which had been activated at 200–300°C to a pulse of oxygen at 23°C increases the initial activity, probably beyond that resulting from the conversion of residual  $\text{Mo}(\text{CO})_3\text{ads}$  to  $\text{Mo}(\text{CO})_2\text{O}_2\text{ads}$ . For example, a catalyst of loading 0.56% Mo gives a conversion of 10% after activation at 260°C. This material, which had lost 5.1 CO/Mo, adsorbed 0.60  $\text{O}_2/\text{Mo}$  and then gave a conversion in the first pulse of propylene of 28%. An equivalent catalyst, activated at 100°C and quantitatively converted to  $\text{Mo}(\text{CO})_2\text{O}_2\text{ads}$  (8), gave a conversion of 12% (Fig. 3). Exposing a catalyst which had been heated to 500°C for 25 min (3.3 H/Mo evolved) to several pulses of oxygen at 53°C increased the conversion from 0.01 to 2%.

$\text{Mo}(\text{CO})_2\text{O}_2\text{ads}$  (7, 8) is initially much more active than  $\text{Mo}(\text{CO})_3\text{ads}$  (Fig. 3), but the activity declined during the first five pulses relatively from (1.00) to 0.55, 0.45, 0.39, and 0.34. At 53°C in flowing

helium the losses of carbon monoxide in successive intervals of 3 min were 0.07, 0.03, 0.02, and 0.01 CO/Mo. During the first three pulses of propylene, the losses were 0.10, 0.03, and 0.01 CO/Mo. Heating  $\text{Mo}(\text{CO})_2\text{O}_2\text{ads}$  to 200°C in flowing helium led to the evolution of 0.9 CO/Mo and a decrease in activity of 75%. Heating to 500°C resulted in a further loss of 0.8 CO/Mo (the cumulative loss was now 5.7 CO/Mo) and zero activity. Three runs in which  $79 \pm 5\%$  of the  $\text{Mo}(\text{CO})_2\text{O}_2\text{ads}$  was converted to " $\text{Mo}(\text{CO})(\text{O}_2)_2\text{ads}$ " (8) led to losses in activity of  $71 \pm 4\%$ .

$\text{Mo}(\text{CO})_6\text{ads}$  reacts slowly with oxygen at 23°C, probably to form  $\text{Mo}(\text{CO})_2\text{O}_2\text{ads}$  (8). A catalyst which had adsorbed 0.07  $\text{O}_2/\text{Mo}$  gave a conversion of 3.5%, 22% of the activity expected from complete conversion to  $\text{Mo}(\text{CO})_2\text{O}_2\text{ads}$ . (However, note that the plot in Fig. 3 is nonlinear.)  $\text{Mo}(\text{CO})_5\text{ads}$  behaved similarly.

*Activity of Catalysts Made from Highly Hydroxylated and Dehydroxylated Aluminas*

A catalyst containing 1.28% Mo was made by impregnating alumina which had been dehydroxylated at 950°C. After activation at 100°C in flowing helium for 1.5 h it gave a conversion of 0.52% [38% of the conversion of  $\text{Mo}(\text{CO})_3\text{ads}$ ]. The conversion increased to 0.62% (15% of  $\text{Mo}(\text{CO})_3\text{ads}$ ) after five pulses. Heating the catalyst to 500°C increased the conversion to 2.9%, roughly 100 times the activity of standard catalysts heated to 500°C. The oxidation state of the Mo in this material was 0.4. Exposure of the catalyst to several pulses of oxygen at 23°C increased the conversion to 8.8% and the oxidation number to 1.7. Exposure to oxygen at 500°C for 10 min reduced the conversion to 0.09%, and exposure for 30 min reduced it to zero. Flowing hydrogen at 600°C for 30 min reduced the oxidation state to 4.2 and increased the initial con-

version to 0.7%. The conversion plateaued at 2% after four pulses. The oxidation-reduction cycle could be repeated with similar results.

Mo(CO)<sub>3</sub>ads and Mo(CO)<sub>2</sub>O<sub>2</sub>ads made on fully hydroxylated alumina were completely inactive. Passing helium containing 21 Torr of water vapor over active Mo(CO)<sub>3</sub>ads (standard alumina) at 23°C until water vapor broke through the catalyst bed also led to an inactive catalyst. This material, exposed to 1 atm of carbon monoxide at -16°C for 50 min, adsorbed 0.50 CO/Mo, compared to an adsorption of 1.0 CO/Mo in about 0.5 min for standard Mo(CO)<sub>3</sub>ads (8). The net adsorption (corrected for adsorption on the alumina) of 1.2 NH<sub>3</sub>/Mo on standard Mo(CO)<sub>3</sub>ads also reduced the conversion to zero.

#### Catalysts Derived from Mo(CO)<sub>6</sub>/Silica Gel

Catalysts prepared from silica gel had loadings of only roughly 0.03% due to the large amount of Mo(CO)<sub>3</sub> which evaporated during activation at 100°C (9). The evolution of CO after 1 h was 3.2 ± 0.4 CO/Mo. The turnover frequency<sup>2</sup> for these catalysts was 1.2 ± 0.3 sec<sup>-1</sup>, 15-fold larger than for Mo(CO)<sub>3</sub>ads on alumina at similar loadings. The conversions fell slowly with pulse number. Upon exposure to a pulse of oxygen at 23°C two of these catalysts adsorbed oxygen and lost carbon monoxide in a ratio of 1.0 ± 0.2. However, the adsorption of oxygen was only 0.3 ± 0.1 O<sub>2</sub>/Mo. The exposure to oxygen had little effect upon activity. Heating to 500°C resulted in the cumulative liberation of 5.1 CO/Mo and a decline in conversion to 0.03%.

<sup>2</sup> Turnover frequency (or number) is calculated by dividing molecules of propylene converted by the number of atoms of molybdenum on the catalyst and by the estimated half-width of the pulse at the middle of the catalyst bed, 1.6 sec at 53°C.

#### DISCUSSION

The relative activities of the various catalysts are summarized in Table 2.

Metathesis of propylene over all of the catalysts in this paper gave >99% selectivity to ethylene and 2-butenes. In the early pulses of propylene and especially for the less active catalysts the ratio of ethylene/2-butene exceeded 1.0 and the ratio of *trans*-2-butene/*cis*-2-butene exceeded the equilibrium value of 2.8, but both ratios approached the ideal values with increases in pulse number, temperature of reaction, or catalytic activity. All or part of the deviations might well be due to the stronger adsorption on the alumina of butenes compared to ethylene and of *cis*-2-butene compared to *trans*-2-butene. A conversion of 1% produces only 0.0043 cm<sup>3</sup> STP each of ethylene and 2-butene, so a very small adsorption could greatly alter the observed product distribution, particularly with species of lesser activity.

TABLE 2  
Activity of Catalysts for Metathesis in the First Pulse of Propylene<sup>a</sup>

Nature of catalyst	Relative activity
Mo(CO) <sub>3</sub> ads	0.0
Mo(CO) <sub>2</sub> ads	≤ .02
Mo(CO) <sub>4</sub> ads	<0.6
Mo(CO) <sub>3</sub> ads	1.00
Mo(CO) <sub>3</sub> ads + H <sub>2</sub> O (g)	0.0
Mo(CO) <sub>2</sub> ads + C <sub>2</sub> HCl <sub>3</sub>	90
Mo(CO) <sub>2</sub> O <sub>2</sub> ads	14
Mo(CO) <sub>2</sub> O <sub>2</sub> ads + H <sub>2</sub> O (g)	0.0
"Mo(CO)(O <sub>2</sub> ) <sub>2</sub> ads"	~0.0
"(σ-O <sup>-</sup> ) <sub>2</sub> Mo"	23
"(σ-O <sup>-</sup> ) <sub>2</sub> Mo" + O <sub>2</sub> at 23°C	36
Mo(VI)	~0.01
Mo(CO) <sub>3</sub> /dehydroxylated alumina (activated at 100°C)	0.4
Mo(0)/dehydroxylated alumina (activated at 500°C)	2.1
Mo(0)/dehydroxylated alumina (activated at 500°C) + O <sub>2</sub> at 23°C	6.5
Mo(0)/dehydroxylated alumina (activated at 500°C) + O <sub>2</sub> at 500°C	0.0
Mo(CO) <sub>6</sub> /silica (activated at 100°C)	15
Mo(CO) <sub>6</sub> /silica (activated at 500°C)	~0.04

<sup>a</sup> The support is alumina of the standard degree of dehydroxylation unless noted otherwise. It must be emphasized that these are initial activities and the ordering of steady-state activities would be radically different. Generally, most catalysts deactivate, whereas Mo(CO)<sub>3</sub>ads increases in activity. The loading is 0.6% Mo.

*Catalysts Derived from Standard Alumina*

Although the loss of carbon monoxide at 100°C corresponded very reproducibly to the formation of  $\text{Mo}(\text{CO})_3\text{ads}$ , more than one species of this formula must have been present. In the graph of conversion in the first pulse of propylene vs loading, conversion rises rapidly to about 0.06% Mo and then slows rather abruptly (Fig. 3). From 0.12 to 1.44% Mo the graph is linear with a slope corresponding to a turnover frequency of  $0.007 \text{ sec}^{-1}$ . In the first region the turnover number is about ten times greater.  $\text{Mo}(\text{CO})_2\text{O}_2\text{ads}$  exhibits similar behavior, although the activities are higher (Fig. 3). The linear sections of the plots might be taken to indicate that  $\text{Mo}(\text{CO})_3\text{ads}$  is of a uniform nature from 0.12 to 1.44% Mo. However, the extent of activation of  $\text{Mo}(\text{CO})_3\text{ads}$  by pulses of propylene varies with loading in this region (Fig. 2). It appears, then, that although the species formed by activation at 100°C have all lost 3 CO they must exhibit substantial nonuniformity which results from variation in the geometry of the three surface ligands and in the ratio of  $\sigma\text{-O}^-/\sigma\text{-OH}$  (8).

Since the initial activity of catalysts formulated as  $\text{Mo}(\text{CO})_3\text{ads}$  is rather small, one must consider whether the activity arises in fact from species other than  $\text{Mo}(\text{CO})_3\text{ads}$ .  $\text{Mo}(\text{CO})_6\text{ads}$  and  $\text{Mo}(\text{CO})_5\text{ads}$  are too inactive to contribute significantly. The activity, if any, of  $\text{Mo}(\text{CO})_4\text{ads}$  is clearly less than that of  $\text{Mo}(\text{CO})_3\text{ads}$ . At least in part, the activity of  $\text{Mo}(\text{CO})_4\text{ads}$  catalysts may result from the presence of a few percent of  $\text{Mo}(\text{CO})_3\text{ads}$  which has a high turnover number at low loadings (Fig. 3).

Since catalysts activated at 270°C are initially 20 times as active as  $\text{Mo}(\text{CO})_3\text{ads}$  (Fig. 1), one might suspect that a low concentration of the active sites characteristic of higher temperatures of activation are responsible for the activity of  $\text{Mo}(\text{CO})_3\text{ads}$ . The following observations indi-

cate that such sites are absent and that the activity is in fact due to  $\text{Mo}(\text{CO})_3\text{ads}$ .

(i) Flowing CO over  $\text{Mo}(\text{CO})_3\text{ads}$  lowers the activity in direct proportion to the amount of  $\text{Mo}(\text{CO})_3\text{ads}$  removed as  $\text{Mo}(\text{CO})_6$ . However, a flow of CO and hydrogen has no effect on the activity of catalysts activated at 280°C. Thus, the sites responsible for the activity of  $\text{Mo}(\text{CO})_3\text{ads}$  are reversibly formed whereas the active sites on the high-temperature catalyst are not.

(ii) The activity of  $\text{Mo}(\text{CO})_3\text{ads}$  rises with successive pulses of propylene but that of the high-temperature catalyst falls.

(iii) Decomposition beyond  $\text{Mo}(\text{CO})_3\text{ads}$  is accompanied by the oxidation of Mo and the evolution of hydrogen (8). The hydrogen evolution necessary to generate the activity observed for the high-temperature catalyst does not occur at 100°C.

Since  $\text{Mo}(\text{CO})_2\text{O}_2\text{ads}$  is about 15 times as active as  $\text{Mo}(\text{CO})_3\text{ads}$ , one might also suspect that the activity of  $\text{Mo}(\text{CO})_3\text{ads}$  results from small amounts of oxygen in the carrier gas reacting to convert  $\text{Mo}(\text{CO})_3\text{ads}$  to  $\text{Mo}(\text{CO})_2\text{O}_2$ . However, from the measured impurity in oxygen, it can be calculated that the cumulative quantity of oxygen reaching the catalyst by the tenth pulse could convert only 0.5% of the  $\text{Mo}(\text{CO})_3\text{ads}$  at a loading of 0.56% Mo and thereby increase the activity by merely 7%. Runs at this loading with an oxygen trap immediately before the reactor gave normal conversions. At a loading of 0.04% Mo, the oxygen could convert 7% of the  $\text{Mo}(\text{CO})_3\text{ads}$  and double the activity. Thus, the high turnover numbers of  $\text{Mo}(\text{CO})_3\text{ads}$  at low loadings are not primarily caused by oxygen although oxygen probably contributed to the scatter of the data at the lowest loadings.

We conclude, therefore, that some form of  $\text{Mo}(\text{CO})_3\text{ads}$  is active. Since this species appears to be *molecularly* dispersed (8), the

metathesis reaction probably occurs at a single atom of molybdenum.

Mild oxidation of Mo(CO)<sub>3</sub>ads to form Mo(CO)<sub>2</sub>O<sub>2</sub>ads results in a 15-fold increase in the initial activity. Further oxidation to "Mo(CO)(O<sub>2</sub>)<sub>2</sub>ads" destroys the activity. The rapid decline in the activity of Mo(CO)<sub>2</sub>O<sub>2</sub>ads may be related to the loss of CO which occurs mostly during the early pulses of propylene. It is clear that an intermediate oxidation state of the Mo is responsible for high activity and that more oxidized Mo is inactive. It has previously been reported that oxygen can either activate (5) or deactivate (6) catalysts made by heating Mo(CO)<sub>6</sub>/alumina at 100°C. It would appear that the catalyst had been exposed to less oxygen in the first reference so that the activation reaction was dominant, but to more in the second reference so that deactivation dominated.

Figure 1 shows that the maximum initial activity occurs at activation temperatures near 270°C. At this temperature Mo(CO)<sub>3</sub>ads is being oxidized and the main product is probably "(σ-O<sup>-</sup>)<sub>2</sub>Mo" (2 H/Mo are evolved) (8). Thus, the species most likely responsible for the high activity near 270°C is "(σ-O<sup>-</sup>)<sub>2</sub>Mo," particularly since more oxidized species are inactive.

From the peak to the high-temperature foot of Fig. 1 there is only a small change in loss of CO, but a 1000-fold drop in activity and further oxidation of "(σ-O<sup>-</sup>)<sub>2</sub>Mo" by σ-OH. After heating to 500°C a total of 4 H/Mo (plus 0.2 CH<sub>4</sub>/Mo) have been evolved and the oxidation number of the Mo is 5.6. Since oxidation to Mo(VI) destroys activity, the residual activity after heating to 500°C is due to a small amount of Mo in an oxidation state less than 6.

O'Neill and Rooney (13) have reported that Mo(CO)<sub>6</sub>/Al<sub>2</sub>O<sub>3</sub> activated *in vacuo* for 2 h at 90°C converts ethylene into propylene in a static reactor, but only when the catalyst has been previously exposed to propylene. Further they report that ex-

posure of the catalyst to ethylene poisons the subsequent metathesis of propylene. On the contrary, we find that pretreatment with ethylene promotes the metathesis of propylene. Passage of pulses of ethylene over catalysts previously exposed to propylene leads to the appearance of propylene but some of this may be adsorbed propylene displaced by ethylene. However, at both 53 and 100°C, there is probably a residual conversion of ethylene, about 0.1% of each pulse. Thus we find much less propylene is formed from ethylene than found by O'Neill and Rooney (13), but we agree in observing that ethylene produces very little propylene on a fresh catalyst. It may be noted that they prepared their Mo(CO)<sub>6</sub>/Al<sub>2</sub>O<sub>3</sub> in air. Our experience suggests that they may have made some Mo(CO)<sub>2</sub>O<sub>2</sub>ads in this process (8).

Davie *et al.* have reported that exposing Mo(CO)<sub>6</sub>/alumina which has been activated at 100°C *in vacuo* to C<sub>2</sub>HCl<sub>3</sub> at room temperature increases the activity for the metathesis of propylene 155-fold (there may be a fivefold variation in this number due to irreproducibility of the value for the normal activity) (12). We find that exposing Mo(CO)<sub>3</sub>ads to C<sub>2</sub>HCl<sub>3</sub> at 100°C increases the activity by 90-fold. The activation process probably involves the evolution of 2 CO, leaving a monocarbonyl species. This species has a turnover frequency of about 5 sec<sup>-1</sup>, the highest for any of the catalysts in the present investigation.

#### *Hydroxylated Alumina*

On this support Mo(CO)<sub>3</sub>ads and Mo(CO)<sub>2</sub>O<sub>2</sub>ads do not catalyze the metathesis of propylene. Further, on Mo(CO)<sub>3</sub>ads on standard alumina, metathesis is poisoned by water vapor at 23°C and the poisoned catalyst is much less reactive in adsorbing carbon monoxide at -16°C than is the unpoisoned catalyst. The effect of water suggests that (σ-OH)<sub>3</sub>Mo(CO)<sub>3</sub>, which is necessarily the form on hydroxylated



alumina, is less active than a species like  $(\sigma\text{-OH})_2(\sigma\text{-O}^-)\text{Mo}(\text{CO})_3$  which is likely to be present on partially hydroxylated alumina (8).

### Dehydroxylated Alumina

Activation of  $\text{Mo}(\text{CO})_6$ /(dehydroxylated alumina) permits preparation of molybdenum species on dehydroxylated alumina difficult to prepare in other ways. After activation at  $100^\circ\text{C}$ , the material is about one-fourth as active catalytically as  $\text{Mo}(\text{CO})_3$ ads on standard alumina. However, after activation at  $500^\circ\text{C}$ , it is about 100 times as active as material of the same loading on standard alumina. Because of the absence of surface alanol groups ( $\sigma\text{-OH}$ ), the main oxidation state of Mo on dehydroxylated alumina is  $\text{Mo}(0)$ , whereas on standard alumina it is  $\text{Mo}(\text{VI})$ . In parallel with  $\text{Mo}(\text{CO})_3$ ads on standard alumina, mild oxidation of  $\text{Mo}(0)$  on dehydroxylated alumina leads to a large increase in activity but further oxidation destroys the activity. Thus, on dehydroxylated alumina, the following oxidation numbers and the corresponding conversions (%) were: 0.4, 2.9%; 1.7, 8.8%; 4.2, 2%; and 6, 0%.

It appears, then, that on both aluminas  $\text{Mo}(\text{VI})$  is inactive but that a wide range of lower oxidation states may be active. Activity for metathesis is also exhibited by homogeneous catalysts over a wide range of oxidation numbers (2).

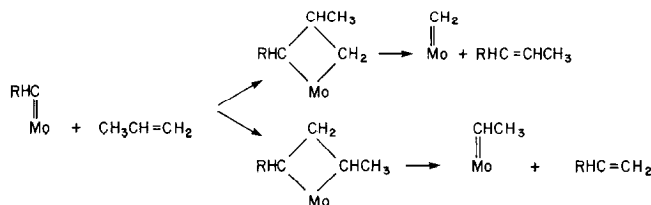
### Activity of $\text{Mo}(\text{CO})_6$ Supported on Silica

$\text{Mo}(\text{CO})_6$ /silica gel activated at  $100^\circ\text{C}$  has a turnover number about 15 times greater than that of  $\text{Mo}(\text{CO})_3$ ads (on

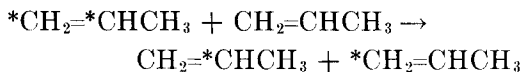
standard alumina). Howe and co-workers (6) reported that activation at  $100^\circ\text{C}$  *in vacuo* of the silica-based catalyst produced an activity sixfold greater than that of the alumina-based catalyst. Since the activation of  $\text{Mo}(\text{CO})_6/\text{SiO}_2$  resulted in the complete disappearance of the infrared bands due to carbonyl ligands, they concluded that the material had lost all carbonyl ligands. Our measurements show that roughly 3  $\text{CO}/\text{Mo}$  are evolved from  $\text{Mo}(\text{CO})_6$ /silica by activation at  $100^\circ\text{C}$  (but we have no evidence to determine if any stable subcarbonyl species are formed) and that further decarbonylation at  $500^\circ\text{C}$  greatly lowers the activity. Since we found that activation of  $\text{Mo}(\text{CO})_6$ /silica at the loadings attempted by Whan results in over 95% of the  $\text{Mo}(\text{CO})_6$  evaporating from the silica (9), the catalysts examined by his group may have been extremely low in Mo and difficult to examine by infrared spectroscopy.

### Mechanism

There is little definite evidence as to the mechanism of heterogeneous catalytic metathesis. The experiments which support the mechanism of Chauvin and Herisson in homogeneous catalytic metathesis (14) would be difficult to extend directly to vapor-phase, heterogeneous systems at lower temperatures. Even though there is still some question about the validity of this mechanism (18), if one assumes tentatively that it applies to the metathesis of propylene on the catalysts used in this paper, some  $\text{RHC}=\text{Mo}$  must be formed in an initial step. This species can now react as follows:



Further reaction sequences of propylene with Mo=CH<sub>2</sub> and Mo=CHCH<sub>3</sub> will generate CH=CH<sub>2</sub> and CH<sub>3</sub>CH=CHCH<sub>3</sub>, although the degenerate reaction



is likely to be much faster (15). It is also possible that some of the changes in activity of a given catalyst could be due to a change in the ratio of (degenerate/productive) rate constants and not turnover numbers.<sup>3</sup>

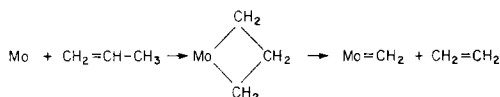
As in homogeneous catalytic metathesis, a key problem is how the initial Mo=alkylidene is formed. If the initial alkylidene is Mo=CHCH<sub>2</sub>CH<sub>3</sub> formed from propylene (14), perhaps via a MoH complex (16, 17), then reaction with propylene will give CH<sub>2</sub>=CHCH<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>CH=CHCH<sub>2</sub>CH<sub>3</sub> equal in sum to the number of catalytic sites generated. In runs at 53°C in the present work, traces of 1-butene were observed in initial pulses but no 2-pentene was detected (however, the sensitivity for detecting 1-butene is higher because it elutes earlier). Our technique should be rather sensitive for measuring anomalous products since the pulse of propylene contained an amount of olefin which was usually comparable in magnitude to that of the surface molybdenum, for example, at a loading of 0.6% Mo, C<sub>3</sub>H<sub>6</sub>/Mo was 2.5. On the assumptions given above, less than 1% of surface molybdenum atoms became converted to active catalytic sites. At this level of generation, formation of Mo=CHR might be accompanied by evolution of carbon monoxide since extra quantities of carbon monoxide of this order of magnitude were liberated during the passage of initial pulses of olefin. However, there is no correlation between the amounts of activation and CO evolution which occur during a pulse of propylene. Much larger

<sup>3</sup> Suggested by a referee. However, we have no experimental data on this point.

quantities of CO were liberated during activation by CHCl=CCl<sub>2</sub> which produced a very active catalyst.

Rapid deactivation of most catalysts which started with “(σ-O<sup>-</sup>)<sub>2</sub>Mo” or Mo-(CO)<sub>2</sub>O<sub>2</sub>ads is also consistent with conversion of only a small fraction of molybdenum to catalytically active sites since the accompanying loss in propylene is very small.

The following reaction would avoid the formation of 1-butene or 2-pentene.



This reaction would substitute excess ethylene for 1-butene or 2-pentene. The ratio, ethylene/2-butene was indeed observed initially to exceed unity but this might have resulted from retention of 2-butene. Ethylene activates Mo(CO)<sub>3</sub>ads better than does propylene. Since the fragmentation process given above is impossible, formation of Mo=CHCH<sub>3</sub> is about the only possibility if one rejects formation of CH<sub>2</sub>=Mo=CH<sub>2</sub>. However, Mo=CHCH<sub>3</sub> should react with further CH<sub>2</sub>=CH<sub>2</sub> to form Mo=CH<sub>2</sub> + CH<sub>2</sub>=CHCH<sub>3</sub>. Small amounts of propylene were indeed observed but in amounts which would again restrict formation of catalytically active sites to less than 1% of surface molybdenum.

In sum, with the exception of the catalyst formed by treatment with trichloroethylene, the techniques in this paper probably involved conversion of less than 1% of surface molybdenum to catalytically active sites in runs at 53°C if a carbene complex must be initially formed. If so, some of the turnover frequencies per true catalytic site must have been very large.

#### REFERENCES

1. Banks, R. L., and Bailey, G. C., *Ind. Eng. Chem. Prod. Res. Develop.* **3**, 170 (1964).
2. Mol, J. C., and Moulijn, J. A., *Advan. Catal.* **24**, 131 (1974).

3. Basolo, F., and Pearson, R. G., "Mechanisms of Inorganic Reactions," 2nd ed. Wiley, New York, 1967.
4. Davie, E. S., Whan, D. A., and Kemball, C., *Chem. Commun.*, 1430 (1969).
5. Davie, E. S., Whan, D. A., and Kemball, C., *J. Catal.* **24**, 272 (1972).
6. Howe, R. F., Davidson, D. E., and Whan, D. A., *J. Chem. Soc. Faraday Trans. I* **68**, 2266 (1972); Smith, J., Howe, R. F., and Whan, D. A., *J. Catal.* **34**, 191 (1974).
7. Burwell, R. L., Jr., and Brenner, A., "Catalysis Heterogeneous and Homogeneous" (B. Delmon and G. Jannes, Eds.), p. 157. Elsevier Scientific, Amsterdam, 1975; *J. Mol. Catal.* **1**, 77 (1976).
8. Brenner, A., and Burwell, R. L., Jr., *J. Catal.* **52**, 353 (1977).
9. Brenner, A., Doctoral Dissertation, Northwestern University, Evanston, Ill., 1975.
10. Schmidt, H., Private communication.
11. "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, 1952.
12. Davie, E. S., Whan, D. A., and Kemball, C., *Chem. Commun.*, 1202 (1971).
13. O'Neill, P. P., and Rooney, J. J., *J. Amer. Chem. Soc.* **94**, 4383 (1972).
14. Calderon, N., Ofstead, E. A., and Judy, W. A., *Angew. Chem. Int. Ed. Engl.* **15**, 401 (1976).
15. Casey, C. P., Tuinstra, H. E., and Saeman, M. C., *J. Amer. Chem. Soc.* **98**, 608 (1976).
16. Laverty, D. T., Rooney, J. J., and Stewart, A., *J. Catal.* **45**, 110 (1976).
17. Motz, V. W., and Farona, M. F., *Inorg. Chem.* **16**, 2545 (1977).
18. Mango, F. D., *J. Amer. Chem. Soc.* **99**, 6117 (1977).