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The Isomerization of Cyclopropane over Reduced Molybdena–Alumina Catalysts

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The isomerization and metathesis of cyclopropane were carried out over a series of reduced molybdena–alumina catalysts (1.7–13 wt% Mo). The distribution of Mo oxidation states was determined by XPS. The average Mo oxidation state estimated from XPS agreed with that obtained by measuring the O_2 consumption on reoxidation for a given catalyst. A good correlation was found between the catalytic activity for the isomerization reaction and the relative intensity of the XPS peak attributed to paired double-bonded Mo (IV) species (as in MoO_2). The results indicate a direct relationship between these Mo (IV) species and the coordinative unsaturated sites involved in the formation of metallocyclobutane. The latter is reportedly the intermediate required for the isomerization reaction to take place. © 1997 Academic Press

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INTRODUCTION

The isomerization of cyclopropane has been the subject of detailed research for over 50 years (1–7). The homogeneous gas phase reaction (1–3) has been shown to be unimolecular and extremely slow at temperatures below 425°C. Acids have long been known to catalyze the opening of the cyclopropane ring (4–7), the reaction being quite facile. For example, the isomerization can be carried out over solid Brønsted acids, such as silica–alumina at near room temperature (5).

Over molybdena–alumina catalysts the reaction has been thoroughly investigated by W. K. Hall and co-workers (8–11). Early work showed that the activity for the isomerization reaction increased with the extent of reduction of the catalyst (8 wt% Mo/Al_2O_3) (8). The reaction was poisoned by the adsorption of water, and the activity was restored by evacuation of the catalyst at 500°C. These results were contrary to the findings over acid catalysts, e.g., silica–alumina (5). Further work (10) showed clear evidence for the presence of Brønsted acidity for the oxidic catalyst but not for the reduced system. These results cast serious doubts on the isomerization of cyclopropane being acid-catalyzed over reduced molybdena–alumina catalysts.

More recent work (11) suggested that the ring opening was carried out through metallocyclobutane intermediates (MCB) by direct insertion of the coordinatively unsaturated transition metal ion into the cyclopropane ring, in agreement with models presented in the literature (12). Other data supported the necessity for the formation of the MCB intermediate for the isomerization reaction to take place (13, 14).

The preceding results highlight the importance of MCB as a key intermediate in the isomerization of cyclopropane over reduced molybdena–alumina catalysts. Interestingly, coordinatively unsaturated sites (CUS) are essential for the formation of this intermediate. Different authors (8, 9, 15–20) have suggested Mo (IV) species as having adequate unsaturation to promote the direct insertion reaction, and, thus, the formation of the MCB intermediate, crucial for the ring opening of cyclopropane.

From the previous discussion it follows that while a correlation between the catalytic activity for the isomerization reaction and the extent of reduction has been established (8), no attempts have been made to investigate a possible quantitative relationship between catalytic activity and the abundance of discrete Mo oxidation states. These studies are important since they may shed light on the nature of the active species responsible for the isomerization reaction. The lack of these studies was the driving force for the present paper. The main purpose was to study the possible correlations between the activity for the isomerization of cyclopropane and the relative abundances of different oxidation states of Mo species. The latter were obtained from the analysis of X-ray photoelectron spectra (XPS) of a series of reduced molybdena–alumina catalysts.

EXPERIMENTAL

γ-Alumina (Ketjen CK-300), surface area 210 m^2/g, was used as the support. The catalysts were prepared by

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impregnating with $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (BDH, reagent grade) to incipient wetness. The solids were dried for 2 h at 100°C and calcined for 5 h at 500°C. The Mo loading was determined by atomic absorption spectroscopy.

Reactions were carried out at 25°C in an all-glass recirculation system (15). The initial amount of cyclopropane used was 50 cc (NTP). The reaction products were analyzed by on-line gas chromatography. The analytical procedures are fully described elsewhere (9, 11). The initial slopes of the plots of conversion (percentage of each hydrocarbon) vs time provided the way of calculating initial rates of appearance of the different reaction products. Prior to the reaction, the catalyst was treated with pure O_2 (60 cm^3/min) at 500°C for 8 h to condition it. The catalysts were reduced with pure H_2 at 500°C for 2 h and then evacuated at this temperature (absence of H_R) or at 25°C (presence of H_R) for 1 h. The average Mo oxidation state (AOS) was determined by measuring the O_2 consumption (at 500°C) required for complete reoxidation, after the reduction procedure. Volumetric techniques (21–23) were used.

XPS spectra of the reduced catalysts were obtained with a modified AEI ES200 spectrometer equipped with an aluminum anode (Al $K\alpha = 1486.6$ eV) at a power of 240 W (12 KV and 20 mA). The catalysts were pressed as pellets at 2000 kg/cm^2 and mounted on a sealable probe which permitted transfer of the pretreatred catalyst from an external reaction chamber to the spectrometer without exposure to air. The spectrometer was interfaced to an IBM PC compatible for data collection. The subsequent data analysis was also carried out in the PC environment under DOS, using programs (GOOGLY software) written in-house (24). A damped nonlinear least-squares fitting (NLLSF) routine was used to curve fit the Mo 3*d* envelopes. The binding energy (BE) values were referenced to the Al 2*p* line (74.5 eV). The methodology used for curve fitting the Mo 3*d* envelope and the assumptions made for quantitative analysis of Mo oxidation states, in molybdena–alumina catalysts, is similar to those used in different papers (25, 26) by D. M. Hercules and co-workers.

RESULTS AND DISCUSSION

Figure 1 shows typical Mo 3*d* curve-fitted spectra for the reduced 1.7% Mo and 8.8% Mo catalysts. As shown, only three sets of Mo 3*d* doublets were necessary to satisfactorily curve fit the data. The doublets are identified by their oxidation state assignment (Table 1).

Table 1 shows the XPS parameters, BEs, and full widths at half maximum (fwhm's), obtained for the series of reduced molybdena–catalysts. The BE and fwhm values for the Mo (VI) 3*d* doublet were obtained from the XPS spectra of the oxidic catalyst. A good agreement with other values reported in the literature is observed (25–29). The XPS parameters found for the Mo (V) and Mo (IV) were a result of the curve fit procedure. The Mo 3*d* binding energies for Mo (VI), Mo (V), and Mo (IV), for the 8.8% Mo catalyst, agree within 0.2 eV with earlier results obtained on the same instrument, for an 8 wt% molybdena–alumina catalyst (25), reduced at 500°C. It should be noted however that two binding energy values were reported for Mo (IV) (29–32): a high binding energy value (Mo $3d_{5/2}$ 231.5–232 eV) attributed to ionic "isolated" Mo (IV) and a low binding energy value (Mo $3d_{5/2}$ ca. 230 eV) typically associated with Mo (IV) as in MoO_2 and ascribed to paired double-bonded Mo (IV).

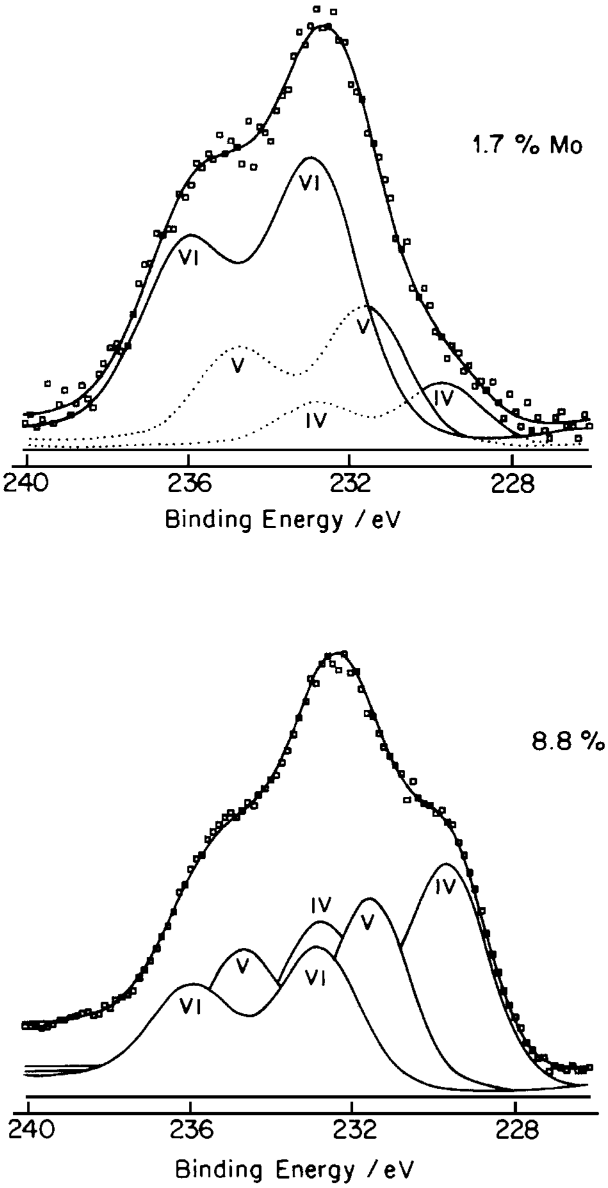

FIG. 1. Mo 3*d* curve-fitted spectra for reduced 1.7% Mo and 8.8% Mo catalysts. The Mo $3d_{5/2}$–$3d_{3/2}$ doublets are designated by their assigned oxidation states. Mo (V) (Mo $3d_{5/2}$ BE 231.5 ± 0.1 eV) refers to Mo (V) and ionic Mo (IV), whereas Mo (IV) (Mo $3d_{5/2}$, BE 229.7 ± 0.1 eV) designates paired double-bonded Mo (IV). See text for details.

TABLE 1

XPS Parameters Derived for the Series of Reduced Molybdena–Alumina Catalysts

	Binding energies, eV[a]			fwhm, eV[c]		
Catalysts	Mo (VI) $3d_{5/2}$	Mo (V) $3d_{5/2}$[b]	Mo (IV) $3d_{5/2}$	Mo (VI) $3d_{5/2}$	Mo (V) $3d_{5/2}$	Mo (IV) $3d_{5/2}$
1.7% Mo	232.9	231.6	229.7	2.5	2.3	2.3
3.8% Mo	232.9	231.5	229.6	2.4	2.2	2.2
5.5% Mo	232.9	231.5	229.7	2.3	2.2	2.1
8.8% Mo	232.8	231.6	229.7	2.3	2.1	2.2
13.0% Mo	232.9	231.6	229.7	2.2	2.2	2.0

[a] The difference between the binding energy values of Mo $3d_{3/2}$ and Mo $3d_{5/2}$ was kept constant (3.1 eV) for all oxidation states. For more details see Ref. (25).

[b] Mo (V) (Mo $3d_{5/2}$, BE 231.5 ± 0.1 eV) refers to Mo (V) and ionic "isolated" Mo (IV), whereas Mo (IV) (Mo $3d_{5/2}$, BE 229.7 ± 0.1 eV) designates paired double-bonded Mo (IV). For more details see text.

[c] Identical Mo $3d_{3/2}$ and Mo $3d_{5/2}$ fwhm values were used. For more details see Ref. (25).

Since the high binding energy value is comparable to that typically used for Mo (V), one cannot rule out that the Mo 3*d* doublet attributed to Mo (V) is in fact a convolution of the contributions from Mo (V) and ionic Mo (IV). Thus, in this manuscript, for the sake of simplicity, Mo (V) (Mo $3d_{5/2}$, BE 231.5–231.6 eV) will refer to Mo (V) and ionic Mo (IV) whereas Mo (IV) (Mo $3d_{5/2}$, BE 229.7 eV) will designate paired double-bonded Mo (IV).

No significant shift in the binding energy of the different Mo oxidation states was observed as the Mo loading was increased. The fwhm's for the different oxidation states, for any particular catalyst, were within 0.2 eV.

The variation of the extent of reduction of the Mo phase as a function of Mo loading is shown in Table 2. A reasonable agreement is found between the values obtained from reoxidation experiments and those estimated from the XPS data. The latter were calculated based on the assumption that only Mo (V) contributes to the Mo 3*d* doublet (BE, Mo $3d_{5/2}$, 231.5 ± 0.1 eV; Mo $3d_{3/2}$, 234.6 ± 0.1 eV). These results are consistent with the implied assumption in the present study that the distribution of Mo oxidation states in the sample prior to the catalytic run is similar to that of the catalyst subjected to the same pretreatment conditions and analyzed by XPS. As the Mo loading is increased the average oxidation state of the Mo phase decreases from 5.4 (1.7% Mo) to 4.2 (13.0% Mo). This can be understood in terms of the higher reducibility of the high loading Mo catalysts compared to the low loading solids. The latter reportedly contain predominantly difficult to reduce monomeric Mo species, while a large proportion of easier to reduce polymolybdate species are found in the high-loading Mo catalysts (22).

TABLE 2

Average Mo Oxidation State (AOS) in Mo Catalysts Estimated from O_2 Consumption and XPS Experiments[a]

Catalyst	$(AOS)_{O_2}$	$(AOS)_{XPS}$
1.7% Mo	5.4	5.4
3.8% Mo	5.0	5.1
5.5% Mo	4.8	4.9
8.8% Mo	4.4	4.7
13.0% Mo	4.2	4.6

[a] The average Mo oxidation state (AOS) was determined by measuring the O_2 consumption (at 500°C) required for complete reoxidation, after the reduction procedure.

Figure 2 shows the distribution of Mo oxidation states vs metal loading. The relative abundance of each Mo oxidation state was calculated by dividing the Mo 3*d* area for a given oxidation state by the total area of the Mo 3*d* envelope (25). It can be seen that the percentage of Mo (VI) decreases with increasing metal loading. The relative abundance of Mo (V) shows an increase, with Mo loading, up to the 3.8% Mo catalyst. For higher loading, the variation is small, although showing some random behavior. The percentage of Mo (IV) shows a steady increase with increasing Mo loading up to 5.5% Mo. For higher Mo loading, the percentages of the Mo phase present as Mo (IV) are very similar.

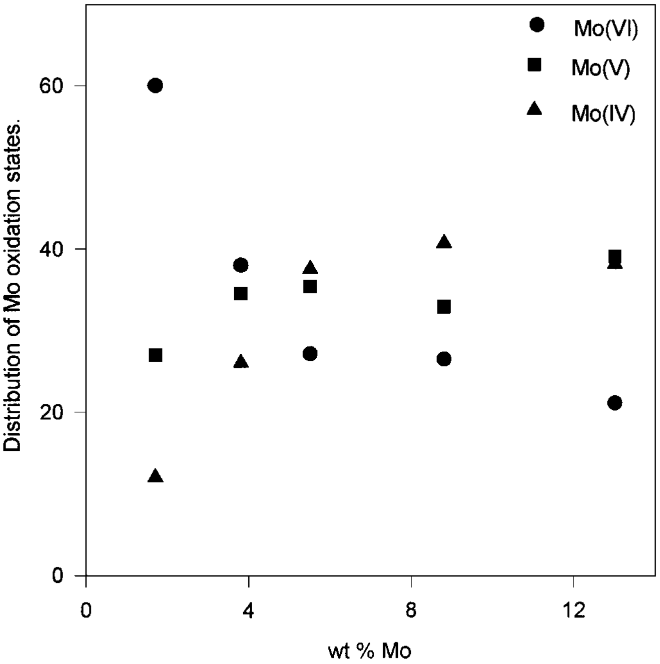

FIG. 2. Distribution of Mo oxidation states vs weight percentage of Mo. The percent of each Mo oxidation state was calculated by dividing the Mo 3*d* area for a given oxidation state by the total area of the Mo 3*d* envelope. Mo (V) (Mo $3d_{5/2}$, BE 231.5 ± 0.1 eV) refers to Mo (V) and ionic Mo (IV), whereas Mo (IV) (Mo $3d_{5/2}$, BE 229.7 ± 0.1 eV) designates paired double-bonded Mo (IV). See text for details.

TABLE 3

Initial Rates/(molecules/g_{Mo} · min) × 10^{18} for the Formation of C_3H_6 (Isomerization) and C_2H_4 (Metathesis)[a]

	Evac. temp. = 500°C			Evac. temp. = 25°C		
% Mo	C_2H_4	C_3H_6	(TOF/10^{-4})[b]	C_2H_4	C_3H_6	(TOF/10^{-4})[b]
1.7	—	13	(2.9)	—	6.1	(1.3)
3.8	2.1	28	(2.9)	—	15.0	(1.5)
5.5	6.1	42	(3.0)	1.1	18.2	(1.3)
8.8	32	50	(3.3)	1.5	20.6	(1.3)
13.0	29	48	(3.4)	1.9	20.4	(1.4)

[a] Reaction temperature = 25°C. Initial cyclopropane pressure = 150 Torr. Weight of catalyst = 0.3–0.6 g.

[b] The numbers in parentheses are the turnover frequencies for the formation of propylene, expressed in molecules of C_3H_6 per Mo (IV) per second.

Table 3 shows the initial rates for the formation of propylene (isomerization) and ethylene (metathesis) obtained over the series of reduced Mo-alumina catalysts. An equivalent amount of 2-butenes (compared to C_2H_4) was also formed in the metathesis reaction. Two sets of data, in the presence and in the absence of H_R, are presented. As shown in Table 3 and Fig. 3 there is an increase in the rate of ethylene and propylene formation with Mo loading. For catalysts evacuated at 500°C, the activity for the formation of both products was higher compared to that obtained over catalysts evacuated at room temperature (presence of H_R), in agreement with previous results (13). The turnover frequencies (TOF) for the formation of propylene, expressed as molecules of C_3H_6 per Mo (IV) per second, are also shown in Table 3. It can be seen that the TOF remain essentially constant for the series of catalysts, for a given evacuation temperature. These results strongly suggest that a linear correlation must exist between the initial rate of formation of propylene and the abundance of Mo (IV). This is clearly illustrated in Fig. 4. Two straight lines (correlation coefficients of 0.99 and 0.98, with and without H_R, respectively) were obtained. The latter underlines the direct relationship between paired double-bonded Mo (IV) species and the rate for cyclopropane isomerization.

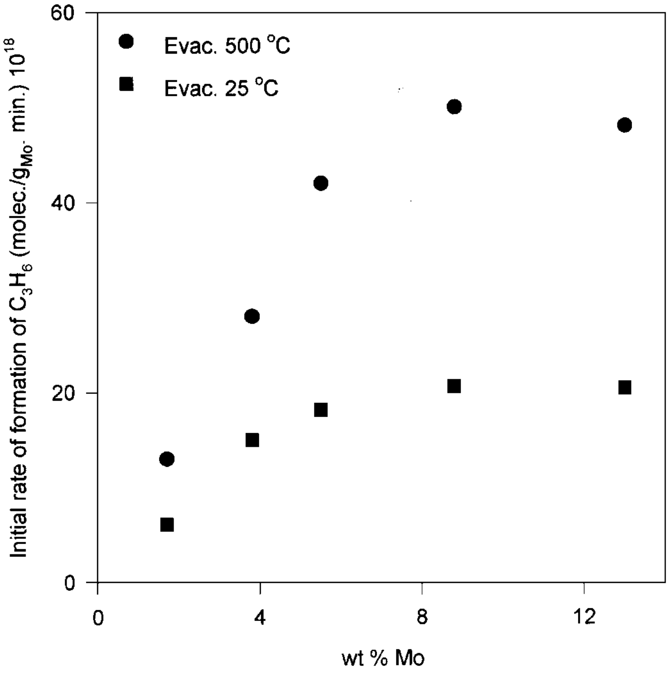

FIG. 3. Initial rate of formation of C_3H_6 vs weight percentage of Mo.

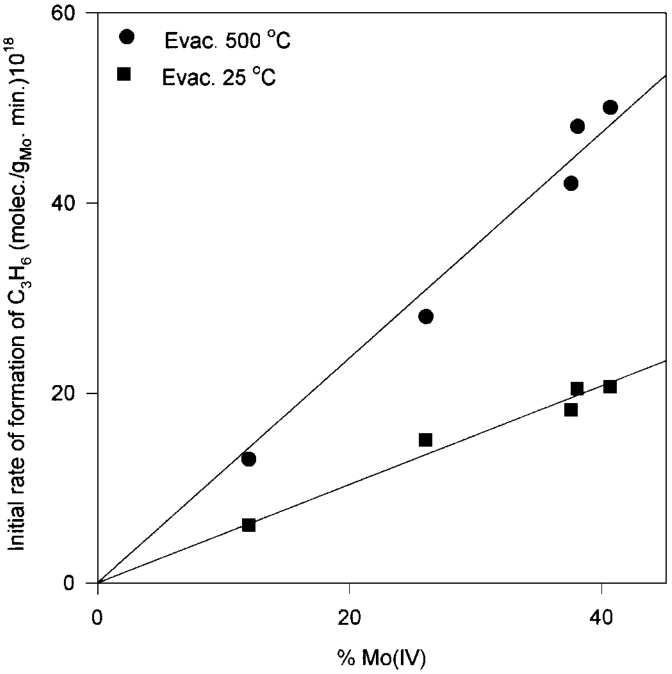

FIG. 4. Initial rate of formation of C_3H_6 vs relative abundance of Mo (IV). Mo (IV) (Mo $3d_{5/2}$, BE 229.7 ± 0.1 eV) designates paired double-bonded Mo (IV). See text for details.

In order to investigate possible correlations with other Mo species or oxidation states, an attempt was made to correlate the abundance of Mo (V) species with the catalytic activity for the isomerization reaction. The data are shown in Fig. 5. No linear correlation was found for the series of catalysts used in the present study. Although this result is consistent with the idea of Mo (IV) being directly related to the CUS involved in the formation of the MCB intermediate, it remains inconclusive because of the fact noted above that both Mo (V) and "ionic" Mo (IV) may contribute to the Mo 3*d* doublet typically attributed to Mo (V).

CONCLUSIONS

A good correlation between the relative intensity of the XPS peak attributed to paired double-bonded Mo (IV) species (as in MoO_2) and the activity for cyclopropane

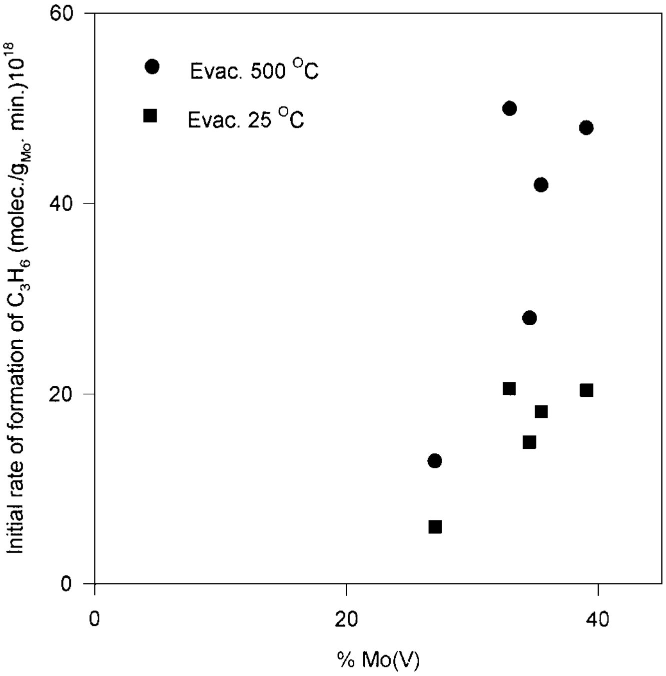

FIG. 5. Initial rate of formation of C_3H_6 vs relative abundance of Mo (V). Mo (V) (Mo $3d_{5/2}$, BE 231.5 ± 0.1 eV) refers to Mo (V) and ionic Mo (IV). See the text for details.

isomerization was found for a series of reduced molybdena–alumina catalysts (1.7–13 wt% Mo). The results indicate a direct relationship between these Mo (IV) species and the coordinative unsaturated sites involved in the formation of metallocyclobutane. The latter is reportedly the intermediate required for the isomerization reaction to take place.

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