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A Study of the Unreduced Molybdena–Alumina System

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The isomerization and metathesis of 1-butene was carried out over a series of molybdena–alumina catalysts (1.0–8.2 wt% Mo) prepared by the adsorption equilibrium method. Catalytic conversion measurements (including the effect of preadsorbed water), tracer experiments (1-butene-d_0+1-butene-d_8), pyridine adsorption followed by IR spectroscopy, and ESR studies were used as tools for the characterization of the solids. The pyridine adsorption experiments showed an increase in the number of acid sites as well as in the acid strength with increasing metal loading. The catalytic measurements showed a related increase in the rate of isomerization as the %Mo is increased. The *cis*/*trans* ratios decreased with increasing molybdenum loading, suggesting an increase in the acid strength of the remaining alumina hydroxyl groups. The results suggest a Brønsted acid mechanism for the isomerization reaction over catalysts with molybdenum loading ≥ 3.9% Mo. The 1.0% molybdena–alumina catalyst behaved totally different. The results suggest a π-allylic mechanism operative on the unperturbed alumina surface. The rate of formation of ethylene and propylene (products of metathesis) increased dramatically with increasing molybdenum loading. The catalysts evacuated at 500°C were considerably more active for the metathesis transformations than after evacuation at low temperatures. A Mo(V) signal was observed for the 6.0% Mo catalyst after evacuation at 500°C and/or after contacting the catalyst with the olefin. No Mo(V) signal was observed for the 1.0% Mo catalyst. The results suggest that the more easily reducible the catalyst is, the easier it would be to effect olefin metathesis.

INTRODUCTION

n-Butene reactions over molybdena-alumina catalysts have been the subject of detailed studies (*1–7*). Over a freshly oxidized catalyst (8% Mo–alumina), the isomerization of butenes was suggested to proceed by an acid mechanism (*2*, *3*). The metathesis activity was induced by contacting the catalyst with the hydrocarbons; the acidic-type isomerization decreased materially during the reaction, while the *cis–trans* transformation was found to proceed exclusively by metathesis. The induction of metathesis activity was accompanied by a slight reduction of the catalyst.

Hightower and Hall (*8*) showed many years ago that initial *cis*/*trans* ratios near unity are expected for *n*-butene isomerization over moderate to strong acid catalysts. This requires that there be no difference in activation energy for formation of these two isomers from 1-butene. With weaker acids, the pathway may be more nearly concerted so this may no longer be true. In an earlier examination of an 8% molybdena–alumina catalyst (*3*), it was found such was the case. These ideas are extended and confirmed herein.

During the past years a variety of molybdenum oxidation states (Mo(II) (*9*), Mo(IV) (*10*), Mo(V) (*11*), and Mo(VI) (*12*) have been suggested as active sites for the metathesis reaction. Differences in activation procedures, reaction conditions, catalyst preparation, and supports have considerably complicated the understanding of this matter.

Different reports on the possible promoters for the metathesis reaction have recently appeared in the literature. Zhang *et al.* (*13*) claimed that distorted square py-

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ramidal Mo(V) species play a decisive role in the metathesis function of a 10.2% MoO_3–silica catalyst. Mo(IV) species were suggested as being responsible for the severe dehydrogenation and coking out of the reaction olefin. Identification of these species was done by XPS and ESR techniques.

Basrur *et al.* (*14*), using ESR, temperature-programmed desorption, and IR spectroscopy, detected trace amounts of acetone and acetaldehyde during the induction period of a 20% tungsten oxide–silica catalyst treated with propylene. Lattice oxygen atoms from tungsten oxide were suggested to be involved in the formation of the oxygenated compounds.

Interesting results for the metathesis of propylene over a series of MoO_3–alumina catalysts (0.5–13 wt% MoO_3) have recently been shown by Grünert *et al.* (*15*). For catalysts activated by thermal treatment (900–1140 K) in flowing inert gas, an increase in the catalytic activity per Mo atom was observed with decreasing MoO_3 contents. According to the authors, the activity attained after thermal activation was exclusively due to sites originating from Mo(VI) species.

The present paper is concerned with the isomerization and metathesis of 1-butene over a series of unreduced molybdena–alumina catalysts with varying metal loading. The influence of the Mo content on the possible active sites is addressed. Catalytic conversion measurements, tracer experiments, adsorption of pyridine followed by IR spectroscopy, and ESR studies have been used as tools for the characterization of the catalysts.

EXPERIMENTAL

I. Catalysts

γ-alumina (Ketjen CK-300), surface area 206 m^2/g, was used as the support. The catalysts were prepared by the adsorption equilibrium method devised by Wang and Hall (*16*). The preparation procedure was identical to that used in Ref. (*16*). The different Mo loadings (1.0–8.2 wt% Mo) were obtained by varying the initial pH of the $(NH_4)_6Mo_7O_{24}.4H_2O$ solution. Table 1 summarizes these results. The catalysts were dried for 2 h at 100°C and calcined for 5 h at 500°C. The chemical analysis was performed using atomic absorption spectroscopy. Surface areas were determined in a conventional BET system (*17*). The data are shown in Table 1.

TABLE 1

Chemical Composition, Preparation Parameters, and Surface Areas of the Molybdena–Alumina Catalysts

Mo loading (wt% Mo)	Initial pH[a]	Equilibrium pH[b]	Surface area (m^2/g)
1.0	9.2	9.0	216
3.9	5.5	6.4	221
6.0	4.0	5.7	216
8.2	2.0	3.6	220

[a] Initial and [b] equilibrium pH values involved in the preparation of the catalysts. For more details see Ref. (*16*).

II. Procedures

Reactions were carried out at 58°C in an all-glass recirculation system (*2*, *17*). Prior to the reaction the catalyst was treated with O_2 (60 cm^3 (STP)/min) at 500°C for 2 h to condition it. It was then evacuated for 1 h at 500°C or at 58°C.

The reaction products were analyzed by on-line gas chromatography, using a Varian 6000 chromatograph with a thermal conductivity detector. The separation of the product mixture was done on a 10 m × 2 mm (i.d.) column containing 20% Bis(2-methoxy ethyl adipate) on chromosorb P-AW (60–80 mesh) thermostated at 50°C. After the separation procedure the individual components were analyzed for the deuterium distribution by mass spectrometric analysis (Hewlett–Packard 5995).

The experiments involving preadsorbed water were carried out as follows: after evacuation at 500°C the catalyst was exposed to outgassed water vapor for 1 h at room temperature, followed by an evacuation period of 2 h at the given temperature. The reaction was then carried out at 58°C.

A Perkin–Elmer 621 IR spectrophotometer (resolution 2 cm^{-1}) was used to study the pyridine adsorption. The sample wafers had a thickness of 8–12 mg/cm^2. A vacuum-tight spectroscopic cell similar to that used in Ref. (*23*) was used. The cell could be attached to a conventional BET vacuum system. After oxygen pretreatment (500°C), the catalysts were evacuated ($<10^{-5}$ Torr) at the same temperature for 1 h and cooled to 70°C. The sample was then exposed to 4 Torr of pyridine vapor for 1 h at 70°C. The wafer was then evacuated for 1.5 h at different temperatures before the spectra were recorded.

The integrated intensity (absorbance) of the band near 1545 cm^{-1} was used as measure of the amount of Brønsted-bound pyridine. The data were then normalized to constant wafer thickness.

The electron spin resonance spectra were recorded on a Varian E-line X-band spectrometer at room temperature. DPPH ($g = 2.0036$) was used as a reference standard. The catalyst was placed in a glass reactor with a quartz sidearm attached above the catalyst chamber, similar to that described by Hall (*18*). The solid could then be pretreated in a similar way as for the catalytic reactions.

III. Reagents

1-Butene was Matheson C. P grade. It was purified using a freeze–pump–thaw technique described previously (*2*). The 1-C_4D_8 was Merck (97.5% isotopic purity), it showed no impurities by gas chromatography. The $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was BDH reagent grade (total impurity level <200 ppm). Pyridine (Aldrich, spectrophotometric grade) was degassed using the freeze–pump–thaw technique (*23, 25*). The oxygen (GIV) was passed over an activated molecular sieve trap to remove traces of water.

IV. Data Treatment

The initial slopes of the plots of conversion (percentage of each hydrocarbon) vs time combined with extrapolated selectivities at zero conversion provided the way of calculating initial rates of appearance of the different reaction products.

The treatment for the tracer data was similar to that used by Hightower and Hall (*19*). In short, after C^{13} and fragmentation corrections, the data were expressed in terms of the mole fraction of each isotopic species. The number of hydrogen atoms exchanged per molecule was calculated from eq. (1), where N_i is the mole fraction of the isotopic species containing i atoms of deuterium:

$$\text{atoms exchanged/molecule} = \sum_{i=1}^{4} iN_i + \sum_{i=5}^{8} (8 - i)N_i. \quad (1)$$

The isotope effect was calculated according to

$$\text{isotope effect} = \sum_{i=0}^{3} N_i \Big/ \sum_{i=5}^{8} N_i. \quad (2)$$

RESULTS

The products of double bond shift (*cis*- and *trans*-2-butene), cross-metathesis between isomerized 2-butene + 1-butene (propylene) and productive metathesis (ethylene), obtained over the 3.9% molybdena–alumina catalyst, evacuated at 500°C, are shown in Fig. 1 as a function of time of reaction.

Table 2 summarizes the initial rates for the isomerization reaction (production of *cis*-2-butene, *trans*-2-butene, and propylene) and for the metathesis transformation (production of ethylene), after evacuation of the catalysts at 500°C. Propylene is included in the isomerization products since it is formed by the 1-butene + isomerized 2-butenes cross-metathesis reaction.

The isomerization rate is very low on the 1.0% Mo catalyst; it is very similar to the value obtained on the pure support. For

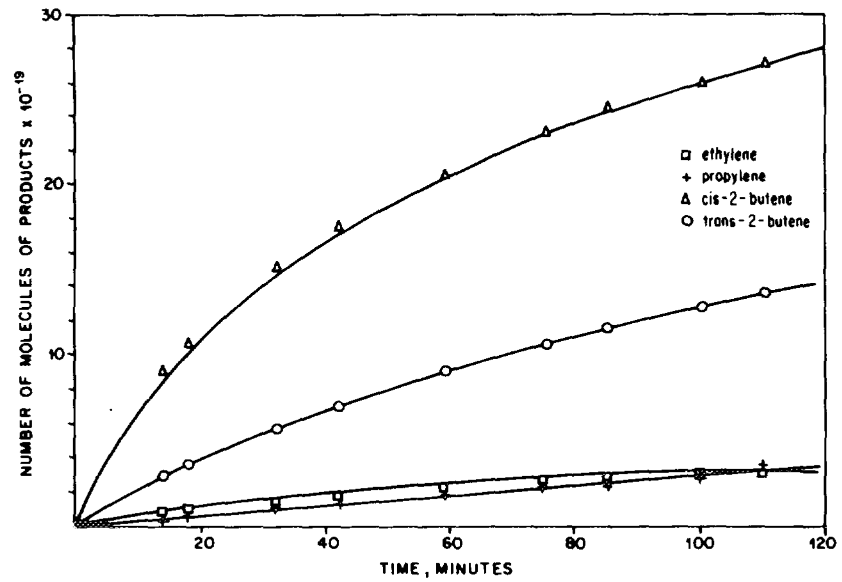

FIG. 1. Product distribution for the isomerization and metathesis of 1-butene over a 3.9% molybdena-alumina catalyst evacuated at 500°C. Reaction temperature = 58°C.

higher Mo loadings the rate markedly increases, remaining practically constant for loadings ≥ 6% Mo. The *cis/trans* ratios show a steady decrease as the molybdenum content increase, for catalysts with Mo loadings ≥ 3.9%. For the 1.0% Mo catalyst, no production of etylene or propylene was observed even after 1 h of reaction. The

TABLE 2

Product Distribution for the Isomerization and Metathesis of 1-Butene over Molybdena-Alumina Catalysts[a] (Evacuation Temperature = 500°C)

Catalyst	Initial rates of formation/(molec./g_{Mo} min) · 10^{18}				*cis/trans*	I^b	M/I^c
	C_2H_4	C_3H_6	*cis*-C_4H_8	*trans*-C_4H_8			
Alumina	—	—	5.9[d]	3.3[d]	1.8	9.2[d]	—
1.0% Mo	nd[e]	nd[e]	5.6[d]	2.9[d]	1.9	8.5[d]	—
3.9% Mo	17	12	240	80	3.0	332	0.10
6.0% Mo	31	103	238	101	2.4	442	0.14
8.2% Mo	34	92	211	108	1.9	411	0.17

[a] Initial pressure of 1-butene = 160. Torr, reaction temperature = 58°C; for other experimental details, see text.

[b] The initial rate of isomerization (*I*) was calculated as the sum of the initial rates of formation of propylene, *cis*-2- and *trans*-2-butene.

[c] The metathesis/isomerization ratio (*M/I*) was calculated as in Ref (*4*). $M/I = 2(C_2H_4)/((C_3H_6) + (2 - \text{Butenes}))$; the values in parentheses are the corresponding initial rates of formation.

[d] Values expressed in (molec./g_{cat} min) × 10^{18}.

[e] Not detected.

TABLE 3

Product Distribution for the Isomerization and Metathesis of 1-Butene over Molybdena–Alumina Catalysts[a] (Evacuation Temperature = 58°C)

Catalyst	Initial rates of formation/(molec./g_{Mo} min) · 10^{18}				cis/trans	I^b	M/I^c
	C_2H_4	C_3H_6	cis-C_4H_8	trans-C_4H_8			
Alumina	—	—	5.7[d]	3.1[d]	1.8	8.8[d]	—
1.0% Mo	nd[e]	nd[e]	5.6[d]	2.8[d]	2.0	8.4[d]	—
3.9% Mo	3.6	1.9	235	81	2.9	318	0.023
6.0% Mo	10	29	269	112	2.4	410	0.048
8.2% Mo	23	64	220	115	1.9	399	0.12

[a] Initial pressure of 1-butene = 160, Torr, reaction temperature = 58°C; for other experimental details, see text.

[b] and [c] are defined in Table 2.

[d] Values expressed in (molec./g_{cat} min) × 10^{18}.

[e] Not detected.

metathesis/isomerization ratio (*M/I*, defined in Table 2) shows an increase with increasing molybdenum loading.

The results for the catalysts evacuated at 58°C are given in Table 3. The general trends shown for the isomerization reaction are very similar to those found in Table 2. The initial production of ethylene and propylene decreases considerably compared with the data shown in Table 2. In particular, the 3.9 and 6.0% Mo catalysts were the most affected.

It is known from the literature (*20*) that the activity for Brønsted acid catalysis is enhanced with the degree of hydroxylation of the surface; the reverse is true for basic catalysts (*20*, *21*). The 1.0 and 6.0% Mo catalysts were tested in this respect for the isomerization and metathesis of 1-butene.

The initial rate of isomerization for the 6.0% Mo catalyst (Table 4) decreases with the temperature of dehydroxylation of the surface. This behavior is contrary to expectation for a hydride insertion mechanism where vacancies are required for catalytic activity, as shown for an 8% molybdena–alumina catalyst previously reduced with hydrogen at 500°C (*22*).

The production of ethylene and propylene increases sharply with the temperature of dehydroxylation of the surface. For the 1.0% Mo catalyst the highest isomerization rate obtained was for the catalyst evacuated at 500°C, as it was for the pure support.

Table 5 shows the results for the 1-butene-d_0 + 1-butene-d_8 reaction over the 1.0 and 8.2% molybdena–alumina catalysts. For the latter the number of hydrogen atoms exchanged per molecule were: 0.14 (1-butene) and 0.65 (*cis*- and *trans*-2-butene). Small isotope effects, 1.20 and 1.26, were involved in the production of *cis*- and *trans*-2-butene, respectively. The H–D exchange pattern was stepwise. These results totally agree with earlier studies done on conventional acid systems (*8*) and on an 8% molybdena–alumina catalyst (*2*, *3*). The 3.9 and 6.0% Mo catalysts showed a similar trend.

The 1.0% Mo catalyst behaved very differently. The extensive hydrogen exchange (0.76 H/D atoms exchanged per molecule of unisomerized 1-butene) indicates that multiple exchange took place besides isomerization. Large isotope effects (2.82 for the *cis*- and 3.13 for the *trans*-2-butene) were obtained. These results are very similar to those found in the literature for alumina (*19*) and ZnO (*21*).

Figures 2a and 2b show the IR spectra for pyridine adsorption over the 8.2 and 3.9% molybdena–alumina catalysts, evacuated

TABLE 4

Influence of Preadsorbed Water on the Isomerization and Metathesis of 1-Butene over Molybdena-Alumina Catalysts[a]

Catalyst	Evacuation temperature (°C)	Initial rates of formation/ (molec./g_{Mo} min) 10^{18}				I[b]	M/I[c]
		C_2H_4	C_3H_6	*cis*-C_4H_8	*trans*-C_4H_8		
	300	—	—	0.39[d]	0.24[d]	0.63[d]	—
Alumina	400	—	—	0.80[d]	0.40[d]	1.2 [d]	—
	500	—	—	5.7 [d]	3.2 [d]	8.9 [d]	—
	300	—	—	0.45[d]	0.24[d]	0.69[d]	—
1.0% Mo	400	—	—	0.60[d]	0.31[d]	0.91[d]	—
	450	—	—	1.2 [d]	0.59[d]	1.8 [d]	—
	500	—	—	4.9 [d]	2.4 [d]	7.3 [d]	—
	250	—	—	420	217	637	—
6.0% Mo	300	—	25	380	220	625	
	400	12	55	308	134	497	0.048
	500	34	98	236	104	438	0.16

[a] For experimental details, see text.

[b] and [c] are defined in Table 2.

[d] Values expressed in (molec./g_{cat} min) × 10^{18}.

at different temperatures. These spectra were obtained by substracting the contribution from the sample before the adsorption of pyridine. The bands at about 1450, 1495, 1579, and 1621 cm^{-1} correspond, respectively, to the 19*b*, 19*a*, 8*b*, and 8*a* breathing vibrations of the Lewis-bound pyridine (*23*, *25*). The small bands at ca. 1543 cm^{-1} (19*b*) and 1638 cm^{-1} (8*a*) can be assigned to pyridine adsorbed on Brønsted acid sites (*23*, *25*, *31*).

For the 8.2% Mo catalyst the integrated intensity for the band at ca. 1543 cm^{-1} decreases with increasing evacuation temper-

TABLE 5

Isotopic Distribution for the Isomerization of 1-Butene-d_0 + 1-Butene-d_8 on Molybdena-Alumina Catalysts[a]

Catalyst	% Conversion	Butene isomers	Isotope distribution (%)									H/D exchange[b]	Isotope effect[c]
			d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8		
		1-but[d]	50.0							2.1	47.9		
		1-but.	42.3	4.1	1.0					7.7	44.9	0.14	0.90
8.2% Mo	12.5	*cis*	26.5	23.2	4.8				5.8	20.1	19.6	0.65	1.20
		trans	26.9	24.1	4.7				5.4	20.3	18.6	0.65	1.26
		1-but[d]	50.0							2.0	48.0		
		1-but	20.1	17.2	7.9	0.8		0.6	8.3	22.0	23.1	0.76	0.85
1.0% Mo	15.2	*cis*	34.0	29.5	8.1	2.2		1.1	4.0	12.0	9.1	0.76	2.82
		trans	36.1	30.2	7.5	2.0		0.9	3.8	10.1	9.4	0.72	3.13

[a] Total amount of gas = 0.72 mmol, T = 58°C, evacuation temperature = 500°C.

[b] and [c] were calculated according to the equations used by Hightower and Hall (*19*), see text.

[d] Initial mixture.

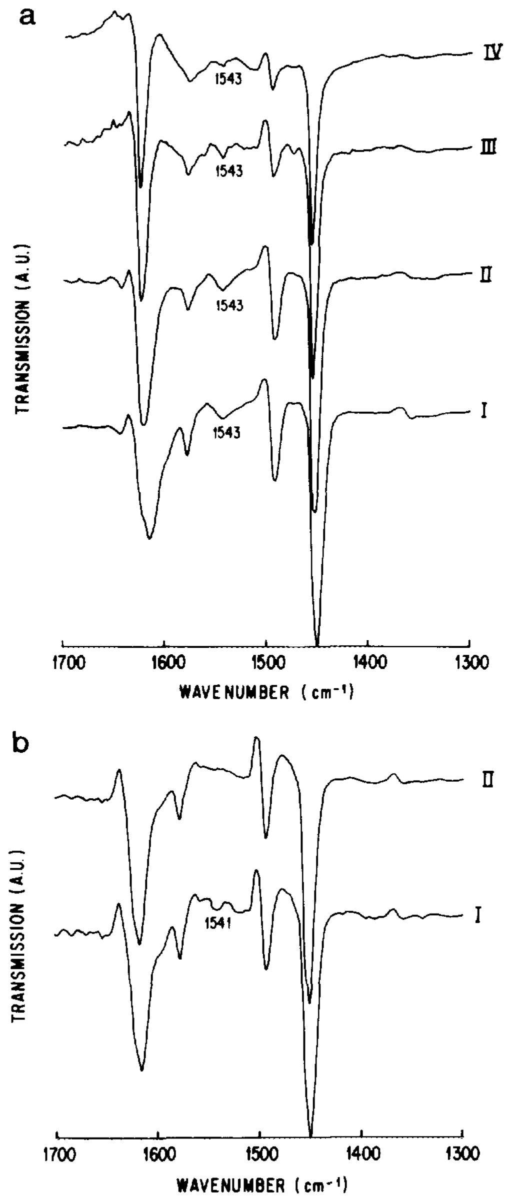

FIG. 2. (a) Infrared spectra of pyridine adsorbed on the 8.2% molybdena-alumina catalyst following evacuations at: (I) 70°C, (II) 170°C, (III) 270°C, and (IV) 370°C. (b) Infrared spectra of pyridine adsorbed on the 3.9% molybdena-alumina catalyst following evacuations at: (I) 70°C and (II) 120°C.

ature, as shown in Table 6. It should be noted, however, that the band was still present after evacuation at 370°C.

TABLE 6

Integrated Intensity for the Band near 1543 cm^{-1} after Evacuation of Pyridine at Different Temperatures

Catalyst	Evacuation temperature (°C)	Integrated intensity[a]
8.2% Mo	70	207
	170	198
	270	143
	370	51
3.9% Mo	70	71
	120	[b]
1.0% Mo	70	[b]

[a] Integrated intensity normalized to unit wafer thickness (mg/cm^2) and given in arbitrary units per gram of total catalyst.

[b] Not detected.

Figure 2b shows the data obtained for the 3.9% molybdena-alumina catalyst. After evacuation at 70°C, the integrated intensity of the band near 1543 cm^{-1} is smaller (Table 6) than that observed for the 8.2% Mo catalyst. In this case, however, the band was totally removed after evacuation at 120°C. The 1.0% Mo catalyst showed no Brønsted acidity even after evacuation at 70°C.

The ESR data for the 6.0% Mo catalyst as a function of the temperature of evacuation is shown in Fig. 3. In all cases the $g_\perp$ value was 1.948 ± 0.001. This signal has previously been attributed to Mo(V) species in a square pyramidal molybdenyl con-

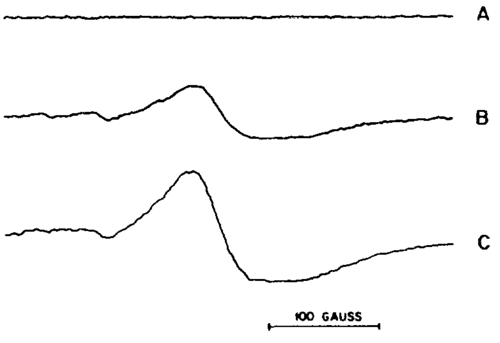

FIG. 3. ESR spectra of the 6.0% molybdena-alumina catalyst evacuated at: (A) 25°C, (B) 250°C, and (C) 500°C.

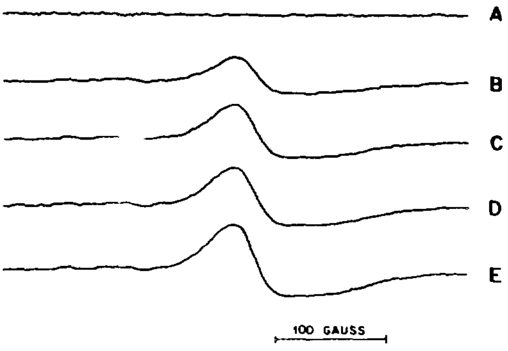

FIG. 4. ESR spectra of the 6.0% molybdena–alumina catalyst, evacuated at 25°C, in contact with 160 Torr of 1-butene for: (A) 0 min, (B) 8 min, (C) 35 min, (D) 60 min, and (E) 120 min.

figuration (C_{4v}) (*18*). No Mo(V) was present after evacuation at 25°C. For higher evacuation temperatures, the intensity of the signal increased correspondingly. The 1.0% Mo catalyst showed no Mo(V) signal even after evacuation at 500°C.

Figure 4 shows the ESR data for the 6.0% Mo catalyst, evacuated at room temperature, in contact with 160 Torr of 1-butene as a function of time. An increase in the intensity of the signal with time was observed. The same experiment carried out on the 1.0 Mo% catalyst showed no Mo(V) species even after 1 h.

DISCUSSION

The results shown in this work strongly suggest an acid mechanism for the isomerization of 1-butene over molybdena–alumina catalysts with %Mo ≥ 3.9%. A very interesting feature is the decrease in the cis/trans ratio observed (3.0 for the 3.9% Mo, −1.9 for the 8.2% Mo catalyst), with increasing Mo loading.

Goldwasser *et al.* (*3*) proposed a 2-butyl carbonium ion common intermediate to explain the results obtained for the isomerization of *n*-butenes over an 8% molybdena-alumina catalyst. In particular, it was shown that *cis*/*trans* ratios very different than unity were possible in acid-catalyzed reactions. The authors suggested that when the carbonium ion was free on a surface of high acidity, the energy barriers between the intermediate and the product 2-butene molecules were about equal, in accordance with the results obtained by Hightower and Hall (*8*) over silica–alumina (*cis*/*trans* ratio ~1). If the intermediate was not a free ion (lower surface acidity) *cis*/*trans* ratios larger than one could be obtained.

Our results, for Mo loadings ≥ 3.9% Mo, can be interpreted in terms of the above model, by considering an increase in the acid strength of the catalyst protons as the molybdenum loading is increased. This conclusion is supported by the pyridine adsorption experiments. As shown in Fig. 2b and Table 6, for the 3.9% Mo catalyst, a lower evacuation temperature (120°C) was needed to totally eliminate the band at ca. 1543 cm^{-1}. For the 8.2% Mo catalyst (Fig. 2a and Table 6), a temperature above 370°C was necessary to totally eliminate the mentioned band. Since the more weakly bound pyridine will desorb at the lower temperature, while the more strongly bound will require higher temperatures to desorb, these data strongly suggest an increase in the strength of the acid sites as the metal loading is increased.

Brønsted acidity has been observed on molybdena–alumina catalysts in the past (*23, 25, 31–33*). Segawa and Hall (*23*) measured the Brønsted and Lewis acidity of a series of molybdena–alumina catalysts, prepared by the adsorption equilibrium method, using pyridine chemisorption and IR spectroscopy. An increase in the Brønsted acidity (measured by the integrated intensity of the 1545 cm^{-1} band) was observed with increasing Mo loading. Exposure to water increased the Brønsted acidity of the 8.0% Mo catalyst. The results obtained in this work show a similar trend concerning the number of acid sites.

Different interpretations concerning the nature of the Brønsted acidity on high-loading molybdena–alumina catalysts have appeared in the literature. Some authors have suggested that Brønsted acid sites are part of the supported metal oxide (*23*, *34*) or part of a possible metal oxide–support complex (*35*). Others claim that alumina hydroxyl groups, activated by the supported transition metal oxide, are responsible for the Brønsted acidity (*25*). The latter explanation is preferred in this work, *vide infra*.

The results obtained for the 1.0% Mo catalyst were totally different. An increase in the isomerization rate was obtained by increasing the temperature of dehydroxylation of the surface. Multiple exchange and primary isotope effects were observed in the 1-butene-d_0+1-butene-d_8 reaction. These results are very similar to those obtained on the pure support (*19*, *21*), which has been shown to isomerize olefins via the π-allylic intramolecular mechanism. Seemingly, the isomerization reaction on the 1.0% Mo catalyst occurs on "unperturbed" free alumina surface of the catalyst. No Brønsted acidity was observed for this preparation (Table 6).

In our view, the majority of the data shown in this work can be understood in terms of the surface model presented by Hall (*18*, *24*) and the work of Suarez *et al.* (*25*).

Hall (*18*, *24*) has shown that low-loading molybdena–alumina catalysts, prepared at high pH, contained predominantly tetrahedrally coordinated monomeric species. These, difficult to reduce, monomers are well dispersed on the support. For higher loadings, pH of preparation <7, patches of polymolybdate species two layers thick are found, in addition to minor amounts of tetrahedral entities. The polymeric molybdena species are more easily reducible than the monomeric entities. IR spectra showed a decrease in the alumina hydroxyl groups as the catalyst was loaded with increasing amounts of molybdenum, suggesting a replacement of the surface hydroxyl groups by molybdate species, in accordance with other studies (*28*, *29*). This model has been widely accepted in the literature (*6*, *7*, *25*, *30*).

Suarez *et al.* (*25*) using pyridine adsorption followed by IR spectroscopy, observed an increase in the number of Brønsted acid sites as the catalyst (7.49% molybdena–alumina) underwent a slight reduction (average oxidation state of +5.6). On the basis of simple electronegativity concepts, the authors suggested that alumina hydroxyl groups close to the small molybdena clusters were made more acidic by inductive effects. A slight reduction increased the number of these hydroxyl groups, in accordance with other studies (*18*).

In view of the above discussion and the results shown in this work, we suggest an increase in the acid strength of the alumina hydroxyl groups located close to the molybdena clusters, as well as an increase in the number of such OH groups, as the molybdenum loading is increased. These acid hydroxyl groups should not be confused with the total amount of hydroxyl groups left in the support. The latter are known to decrease with increasing metal loading (*18*). The increased acidity of the 8.2% Mo catalyst compared to that of the 3.9% Mo catalyst is related to the increase in catalytic activity shown in Tables 2 and 3. The decrease in the initial rate for the 3.9% Mo catalyst can be understood in terms of a higher contribution (compared to the 6.0 and 8.2% Mo solids) of monomeric species, which have been shown to have a negligible effect on the surrounding hydroxyl groups (1.0% Mo catalyst).

The above results may be contrasted with those for the metathesis transformations which were quite different. The main observations were: (i) The evacuation temperature of the oxygen (Tables 2 and 3) had a profound effect on the rate of formation of ethylene and propylene, particularly for the 3.9 and 6.0% Mo catalysts. (ii) A strong increase in the activity was observed with increasing Mo loading. (iii) The production of ethylene and propylene increased sharply with the extent of dehydroxilation of the surface. (iv) Qualitative ESR results showed a Mo(V) signal $g_\perp = 1.948 \pm 0.001$), which increased with the oxygen evacuation temperature for the 6.0% Mo catalyst. No such signal was observed for the 1.0% molybdena-alumina catalyst.

The main reason for carrying out the ESR experiments was to gain some insight on which catalysts were reduced during the evacuation at 500°C and/or during the induction period (contact with the olefin at 58°C). These results should be taken as a qualitative assay for catalyst reducibility, and not as a quantitative correlation between Mo(V) ESR signal and metathesis activity.

Goldwasser *et al.* (*2*) reported an extent of reduction of electrons/Mo(e/Mo) ~0.3 for an 8% molybdena–alumina catalyst after the butene induction period. This value was an upper limit and was estimated from the amount of butene adsorbed irreversibly, assuming each such molecule provided two electrons by dehydrogenation, i.e., one water molecule. In this work we have made a similar assumption and the values obtained were: 0.27 for the 8.2% Mo catalyst, 0.23 for the 6.0% Mo catalyst, 0.12 for the 3.9% Mo catalyst, and 0.03 for the 1.0% molybdena–alumina catalyst. These values were obtained after 60 min of reaction, using an evacuation temperature of 500°C and a reaction temperature of 58°C.

From the above discussion it follows that the more easily reducible the catalyst is, the easier it would be to effect olefin metathesis. Thus, the low-loading catalyst, which is known (*18*) to contain predominantly difficult to reduce monomeric species, showed neither metathesis activity nor any sign of reduction at 58°C. Other authors, working on related systems, have shown an increase in the metathesis activity with increasing metal loading (*26*, *27*).

Recently, Grünert *et al.* (*15*) have shown a decrease in the catalytic activity for the metathesis of propylene with increasing Mo loading, for a series of molybdena–alumina catalysts activated by thermal treatment (900–1140 K) in flowing inert gas. The results in the present work are not in conflict with these data, since an increase in the catalytic activity with increasing Mo loading, was observed for catalysts activated at 820 and 900 K (*15*). Only after being treated under temperatures above 1000 K do the low-loading catalysts reach their full metathesis activity (*15*); here, solid-state reactions may occur.

CONCLUSIONS

1. The results suggest a Brønsted acid mechanism for the isomerization reaction over catalysts with Mo loading ≥3.9%. An increase in the acid strength with increasing Mo loading is suggested.
2. A π-allylic mechanism (similar to that over alumina) is proposed for the isomerization reaction over the 1.0% Mo catalyst.
3. The more easily reducible the catalyst is, the easier it would be to effect olefin metathesis.

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