JOURNAL OF CATALYSIS 51, 243–255 (1978)

Tracer Studies of Cyclopropane Reactions on Molybdena–Alumina Catalysts

E. A. LOMBARDO,[1] M. LO JACONO,[2] AND W. KEITH HALL[3]

Laboratory for Surface Studies and the Department of Chemistry, University of Wisconsin—Milwaukee, Milwaukee, Wisconsin 53201

Received July 27, 1977

The oxidation state of a molybdena–γ-Al_2O_3 (8%) catalyst was varied by reduction with either H_2 or CO under carefully controlled conditions. The decomposition of cyclopropane was studied and correlations were sought between surface chemistry and catalytic function. Temperatures between 50 and 130°C and a pulse reactor were employed. In every case propylene, ethylene, and *n*-butenes were produced in proportions depending upon the extent of reduction. When cyclopropane was reacted over a catalyst reduced with D_2, deuterated propylenes were formed in increasing percentages with higher extents of reduction. Similar results were obtained when the catalyst was first thoroughly reduced with D_2, then reoxidized and finally reduced to different extents with CO. When mixtures of cyclopropane-d_0 and -d_6 were co-isomerized, the products were readily equilibrated. Methylcyclopropane reacted much faster than cyclopropane, yielding both isomerization and metathesis products. No trace of isobutane was detected. A small portion of the first cyclopropane to contact the catalyst reacted to form ethylene and the methylene carbene. Otherwise the data were consistent with a proton-catalyzed ring opening followed by metathesis on coordinatively unsaturated Mo (IV) ions occurring through a carbene mechanism. The results are discussed in terms of current literature.

INTRODUCTION

The nature of the active sites on molybdena–alumina catalysts has become a matter of considerable interest because of the potential use of these materials as catalysts for coal hydrogenation. Recently Hall and co-workers (*1*, *2*) and Abdo *et al.* (*3*) studied the reduction process necessary for their activation. A substantial quantity of hydrogen was found to remain associated with the catalyst after reduction and evacuation at about 500°C. The hydrogen consumed in the reduction (H_c) could be divided into that irreversibly held as OH groups on the catalyst surface (H_I) and that recovered as water. The latter provided a measure of the number of anion vacancies, □, produced. These experimental quantities provide a useful index of the catalyst surface. Earlier attempts to correlate them with catalytic function (*4*, *5*) in the isomerization of cyclopropane, as well as in the hydrogenation of simple hydrocarbons, led to some uncertainties which have now been resolved.

Metal oxides are active catalysts for reactions such as alkene hydrogenation, isomerization, polymerization, and iso-

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[1] On leave from Facultad de Ingenieria Quimica, Universidad del Litoral, Santa Fe, Argentina.

[2] On leave from Centro di studio su struttura ed attivita catalitica di sistemi di ossidi, Istituto Chimica Generale, Citta Universitaria, 00100 Roma, Italia.

[3] To whom all correspondence should be addressed.

0021-9517/78/0512-0243$02.00/0

topic exchange processes (H_2–D_2, alkene–D_2, alkene–alkene). Extensive studies have been carried out on Cr_2O_3 (*6*), Co_3O_4 (*7*, *8*), and ZnO (*9*). The support used for our catalyst, alumina, is also active for most of these reactions although its activity is particularly low for hydrogenation and polymerization (*10–12*). It has been shown previously that molybdena–alumina is active for all these reactions (*4*, *5*) and, in addition, has the ability to catalyze metathesis reactions (a property which is common to very few elements of the Periodic Table). Another interesting difference between Cr_2O_3, ZnO, and Al_2O_3, on one hand, and molybdena–alumina, on the other, is that the former are not able to open the cyclopropane ring below 100°C, whereas the reaction is very facile over the latter (*4*). Moreover, the activity for this reaction increased with the extent of reduction. This suggested that Brönsted sites are developed during the reduction of these catalysts; these are able to protonate the cyclopropane ring leading to the formation of propylene (*13–15*). On this basis, molybdena–alumina resembles silica–alumina more than alumina. In a previous work (*4*) it was suggested that Mo-OH groups might be responsible for the acidic properties of these materials. It was noted, however, that adjacent OH groups held by the alumina support might have been activated (made more acidic by the adjacent CUS molybdenum ions) by the reduction and have thus become responsible for this function. Therefore, deuterium tracer experiments were carried out with catalysts reduced with either H_2 or CO. The isomerization of methylcyclopropane was also studied and the mechanism and possible sites for metathesis were explored.

EXPERIMENTAL

Catalyst. The catalyst was prepared by impregnation of γ-alumina (Ketjen CK 300) with ammonium paramolybdate solution, followed by drying at 120°C and final air calcination at 540°C for 16 hr. Surface areas and pore volumes for support and catalyst were, respectively, 192, 185 m^2/g and 0.5, 0.42 ml/g. The molybdenum content of catalyst was 8%; the chief impurities (Ca, Cr, Cu, Mg, Si) as determined by spectrographic analyses of samples were all less than 0.01%.

Catalyst pretreatment and reduction. As described earlier (*2*), 1 g of catalyst was sealed in a quartz microreactor and subjected to an overnight pretreatment in flowing dry O_2 at 500°C. It was then evacuated for 40 min at the temperature of reduction (400 to 500°C) before a known amount of H_2 or D_2 was added and circulated through the reactor. The H_2 (or D_2) consumption could be calculated from the drop in pressure. At the end of reduction, the residual H_2 was evacuated for 60 min at the same temperature. The water released by the reduction was then measured. The extent of the reduction (H_c/Mo), the amount of hydrogen irreversibly held on the catalyst (H_I/Mo), and the number of vacancies formed ($\square$/Mo) were calculated from these data (*2*). After the reduction, the catalyst was cooled to reaction temperature and contacted with flowing, purified helium.

For CO reduction the same procedure was followed. After evacuation following reduction, the catalyst retained some CO (CO_I). The amount of CO_I was essentially zero until the average oxidation state of the Mo was lowered to 5.5. With higher reductions, CO_I was lower than H_I for the same extent of reduction. CO_I was quantitatively recovered as CO_2 when the catalyst was reoxidized. The catalyst was therefore used repeatedly after regeneration equivalent to the pretreatment in O_2.

Gases. All gases were obtained from commercial sources. The helium used as carrying gas was further purified by passage through Pyrex traps containing $CaCl_2$ and $MgClO_4$ and then a trap filled with activated charcoal thermostated at −195°C.

Propylene and cyclopropane were supplied by Union Carbide Corp., Linde Division (specialty gas product group). They were twice distilled from −78 and −195°C and were outgassed. Methylcyclopropane was an A. P. I. standard sample of better than 99.9% purity. The cyclopropane-d_6 and propylene-d_6 were prepared by repeated exchange of cyclopropane with D_2 over alumina (*11*). They were purified by a gas chromatographic preparative column of 40% dimethylsulfolane on AnaKrom C22A. The mass spectral analysis gave virtually identical isotopic distributions for the unconverted cyclopropane and the propylene by-product; it was 92% C_3D_6 and 8% C_3D_5H. The 50/50 mixture of C_3D_6/C_3H_6 cyclopropane, prepared from C_3D_6 and C_3H_6, had an isotopic distribution of 46% C_3D_6, 4% C_3D_5H, and 50% C_3H_6.

Equipment and procedures. The quartz microreactor, containing 1.00 g of sample, was connected through glass joints to a conventional vacuum system. The reactor could be surrounded by a furnace; pretreatment and reaction temperatures were maintained constant within ±0.5°C by an electronic controller above 100°C. A regulated water bath was used below 100°C.

Pulses of reactant hydrocarbon were injected into the helium carrier stream from a calibrated 1.15-ml doser and were passed over the catalyst at 1 atm of total pressure. The pulse size (amount) could be varied by using different pressures of reactant in the doser. The products emerging from the catalyst were collected in a −195°C trap for 15–40 min and then were flashed onto a 13 ft × 0.25 (o.d.) in., 40% dimethylsulfolane on AnaKrom C22A (80/100 mesh) column at 0°C for analysis. Provision was made to recover samples of products as they were eluted from the column for mass spectrometric analysis.

Mass spectrometric data. The samples of cyclopropane, propylene, and ethylene were analyzed with an MS-10 mass spectrometer, using an ionization voltage of 13 eV. The deuterium distribution was calculated after the usual correction for the presence of naturally occurring heavy carbon (^{13}C).

Aliquots of the pure compounds were used to obtain patterns for cyclopropane, cyclopropane-d_6, propylene, propylene-d_6, and ethylene. Since the various other isotopic species were not available the cracking patterns for d_1 through d_5 species were calculated utilizing the patterns for the pure d_0 and d_6 compound by a method similar to that used by Schissler *et al.* (*16*). This method gave reasonably accurate results for our system; in fact, it was found that the lowest *m/e* peaks essentially vanished when the contribution from all species had been subtracted. Furthermore, the analysis of mixtures of C_3D_6 and C_3H_6 gave isotopic distributions which agreed with those known to be present.

RESULTS

The results of a study (*4*) in which cyclopropane was reacted over molybdena–alumina (reduced to different extents) have been reported previously. The products were cyclopropane, propylene, ethylene, *n*-butenes, and polymeric material retained by the catalyst. It was found that the catalyst became more active as the extent of reduction increased. When hydrogen was present, isomerization was enhanced but hydrogenation of the resulting olefins was complete and competed favorably with both metathesis and polymerization (*4*, *5*).

Tracer Experiments with Cyclopropane

When pulses of cyclopropane were passed over a catalyst reduced with D_2, cyclopropane-d_1, propylene-d_1, and ethylene-d_1 appeared. The data are shown in Fig. 1. Multiply deuterated products were formed in only small amounts.

The deuterium distributions in the different products are reported in Table 1. The extent of deuteration of the products increased with the extent of reduction; for example, for $D_c/Mo = 0.39$, 1.1, and 1.6, the amounts of propylene-d_1 (extrapolated to zero pulse number) were about 5, 14, and 33%, respectively. Thus, the propylene-d_0 was the chief product. For the three extents of reduction referred to above, only 0.2×10^{18}, 3×10^{18}, and 2×10^{19} deuterium atoms of the 1.0×10^{20}, 2.5×10^{20}, and 2×10^{20} atoms available as D_I appeared in the products (summed over all the products).

To investigate further the origin of the deuterium incorporated into the products, the catalyst was first thoroughly reduced with D_2 (1.5 e/Mo), then reoxidized with carefully dried oxygen, and finally reduced with CO. In this way the D_I was eliminated during the reoxidation, while not affecting the OD groups terminating the residual alumina surface.

When pulses of cyclopropane were passed over the catalysts reduced to different extents, cyclopropane-d_1, propylene-d_1, and ethylene-d_1 were again the principal deuterated species (Fig. 2). Comparison of the data in Figs. 1 and 2 showed that the main character of the results was the same but that the intercepts for similar extents of reduction in Fig. 2 were, for each case, about 50% of those in Fig. 1.

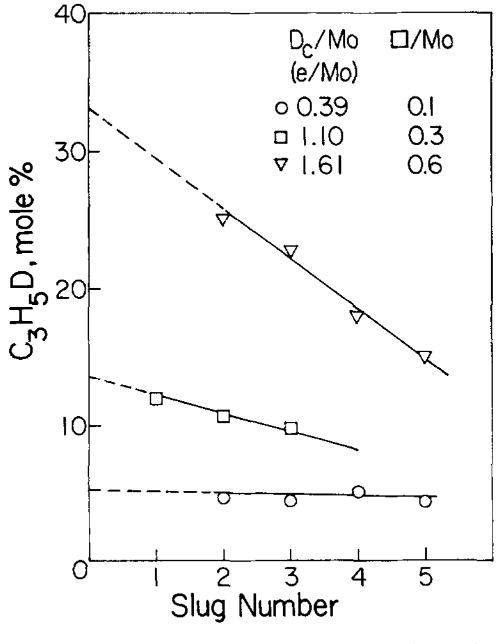


FIG. 1. Propylene deuteration during isomerization of cyclopropane over molybdena–γ-alumina reduced with D_2.

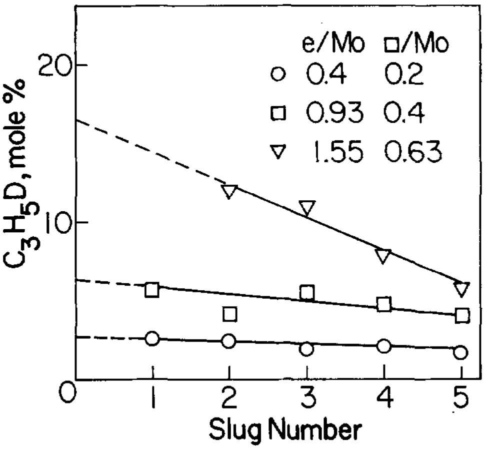


FIG. 2. Propylene deuteration during isomerization of cyclopropane over molybdena–γ-alumina pretreated as follows: reduced with D_2 to 1.5 e/Mo; reoxidized and reduced with CO to different extents as noted.

Another important observation in these experiments was that the overall activities between the H_2- and the CO-reduced catalysts at the same extents of reduction were similar. The product distributions also resembled each other.

Table 2 presents the results obtained in experiments where the first pulse of cyclopropane-d_6 was followed by pulses of cyclopropane-d_0; the catalysts had been reduced in either manner described above. The products obtained when the first pulse of cyclopropane-d_6 passed through the catalyst had essentially the same composition as the initial reactant. The products from the second and successive pulses contained a broad spectrum of multiply deuterated species in the products propylene and ethylene, while the distributions in the unreacted cyclopropane were more nearly like those obtained from the experiments of Table 1. In all these experiments a portion of the first pulse was retained by the catalyst partly as a polymeric residue and

TABLE 1

Cyclopropane Reactions on Deuterated Molybdena-Alumina Reduced to Varying Extents[a]

	Extent of reduction[b]																												
	D_e/Mo = 0.39 □/Mo = 0.1					D_e/Mo = 1.1 □/Mo = 0.3			D_e/Mo = 1.61 □/Mo = 0.6					e/Mo = 0.4 □/Mo = 0.2					e/Mo = 0.93 □/Mo = 0.4					e/Mo = 1.55 □/Mo = 0.64				
	1[c]	2	3	4	5	1	2	3	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Temperature (°C)	50	50	50	50	50	50	50	50	109	109	109	109	109	90	90	90	90	90	90	90	90	90	90	90	90	90	90	90
Ethene[d]	0.2					1.5	1.8	1.3	1.3	3.9	2.2	2.1	1.9	0.9	0.6	0.5	0.5	0.5	1.9	1.5	1.3	0.9	1.4		6.6	2.2	1.8	1.5
Propene[d]	0.5					0.8	1.7	3.0		3.8	6.1	6.3	6.3	3.7	4.2	4.2	4.2	4.0	1.1	4.0	4.0	3.0	4.3		2.6	5.9	6.2	6.0
Cyclopropane[d]	14					1.1	9.2	9.1		0.8	1.9	2.1	2.2	7.7	9.5	9.6	9.7	9.4	0.3	3.2		3.4	3.8		2.0	2.1	2.3	2.6
n-Butenes[d,e]											2.5	3.0	2.8		0.4	0.5	0.5	0.5	0.1	1.4		1.2	1.7		0.2	1.8	2.4	2.4
$(1 - \Delta/\Delta^\circ) \times 100$	5	5	5	5	5	93	36	37	100	95	87	86	85	47	35	34	33	34	98	78		76	64	100	86	86	84	82
Analysis of cyclopropane (mol%)[f]																												
d_2																									0.6	0.5		
d_1		2	1	0.6		11	4	2						1.5	1	1.7	1.1	1	4.1	2.3	2.2	2.1	1.1		9.9	4.8	3.2	2.2
d_0		98	99	96.4		89	96	98						98.5	99	98.3	98.9	99	95.9	97.7	97.8	97.9	98.9		89.5	94.7	96.8	97.8
Analysis of propylene (mol%)[f]																												
d_2						3.5	0.4	0.4		5.8	2.6	1.3	0.8						0.3	0.1	0.4	0.3	0.4		6.7	1.7	2.2	3.7
d_1		5	4.4	5	4	12	10.6	9.6		25.2	23	17.6	15	2.7	2.5	2	2.2	1.9	5.7	4.1	5.5	4.8	4.1		12.0	10.8	7.8	5.8
d_0		95	95.6	95	96	84.5	89	90		69	74.4	81	84.2	97.3	97.5	98	97.8	98.1	94	95.8	94.1	94.9	95.5		81.3	87.5	90.0	90.5

[a] Catalyst weight = 1.00 g (5.08×10^{20} Mo/g); pulse size = 0.54 ml = 14.5×10^{18} molecules; He flow rate = 65 ml/min.

[b] First three experiments reduced with H_2, last three experiments thoroughly reduced with D_2. Oxidized and reduced with CO.

[c] Pulse No.

[d] Number of molecules $\times 10^{-18}$.

[e] *n*-Butene mixture approximately at equilibrium.

[f] No deuterated product containing more than two deuteriums was detected.

TABLE 2

Tracer Experiments Showing Intermolecular Hydrogen Exchange between First and Successive Pulses during Isomerization of Cyclopropane[a]

	Extent of reduction														
	D_c/Mo = 1.02 □/Mo = 0.25				e/Mo = 0.93 □/Mo = 0.4					e/Mo = 1.52 □/Mo = 0.62					
	Deuterium				D_2, reoxidation, CO					D_2, reoxidation, CO					
	1[b]	2	3	4	1	2	3	4	5	1	2	3	4	5
Reactant	d_6-	d_0-	d_0-	d_0-P	d_6-	d_0-	d_0-	d_0-	d_0-	d_6-	d_0-	d_0-	d_0-	d_0-
Temperture (°C)	50	50	50	50	90	90	90	90	90	90	90	90	90	90
$(1 - \Delta/\Delta^\circ) \times 100$	76	27	25	34	92	87	87	79	75	100	87	91	84	83
Analysis of cyclopropane (mol%)														
d_6	91.8			—[c]										
d_5	8.2			—[c]										
d_4				—[c]		0.6					0.8	0.7		
d_3		1.4	0.7	—[c]		2.5	0.4				3.7	3.8	0.5	0.1
d_2		4.3	2.5	—[c]		11.0	4.3	0.9	0.5		12.9	17.1	6.9	2.3
d_1		19.0	14.3	—[c]		33.0	22.6	9.9	5.3		34.7	37.2	27.1	19.2
d_0		75.3	82.5	—[c]		52.9	72.7	89.2	94.2		47.8	41.2	65.5	78.4
Analysis of propylene (mol%)														
d_6	90	17	1.3		86.3	2.8					0.1			
d_5	10	22	8.1		13.7	9.5	0.3				2.5			
d_4		24	19.6	0.9		22.7	2.3				10.4			
d_3		18	28.6	4.5		19.2	8.7	1.3			24.2	15.4	5.9	1.2
d_2		11	24.2	16.6		18.3	23.4	8.8	2.5		31.5	16.2	21.6	8.5
d_1		3	14.2	35.0		16.7	35.1	30.1	18.4		20.6	49.4	39.7	33.4
d_0		5	4.0	44.0		10.8	30.0	59.8	79.1		10.7	19.0	32.8	56.9

[a] Catalyst weight = 1.0 g (5.08×10^{20} Mo/g); pulse size = 0.54 ml = 1.45×10^{19} molecules.

[b] Pulse No.

[c] Propylene slug.

partly as strongly adsorbed propylene. The results indicate that a fast exchange occurs between the products retained on the surface from a given pulse and the molecules from the subsequent ones.

In the first experiment of Table 2 only the first pulse showed a mass loss while in the other experiments this mass loss was still detectable after several pulses. Therefore, the first experiment is best suited to show the consistency of the data presented. Of the first 1.45×10^{19} molecules passed over the catalyst, 0.94×10^{19} were unaccounted for. If the molecules retained during the first pulse underwent exchange with the propylene product of the second the following calculation can be made: 0.94×10^{19} molecules adsorbed from the first pulse (90% d_6, 10% d_5) will exchange with 0.45×10^{19} propylene molecules formed from the second (90% d_0, 10% d_1; from the second experiment in Table 1) giving a theoretical D/H ratio of 2.03 in the propylene compared to an experimental value of 1.81. The discrepancy between these two numbers disappears if one considers that the degree of deuteration of cyclopropane is now larger than in the first pulse of the second experiment in Table 1. Taking this difference into account the theoretical value of D/H for propylene becomes 1.81 as compared with the experimentally determined 1.81.

A better understanding of the isotopic mixing in the reaction products can be achieved through experiments where 50/50 mixtures of cyclopropane-d_6 and -d_0 are co-isomerized over the catalyst. Some results from such an experiment are shown in Fig. 3. Five pulses of the mixture were sent over the catalyst (D_c/Mo = 1.00) at 50°C. For the first pulse, the deuterium

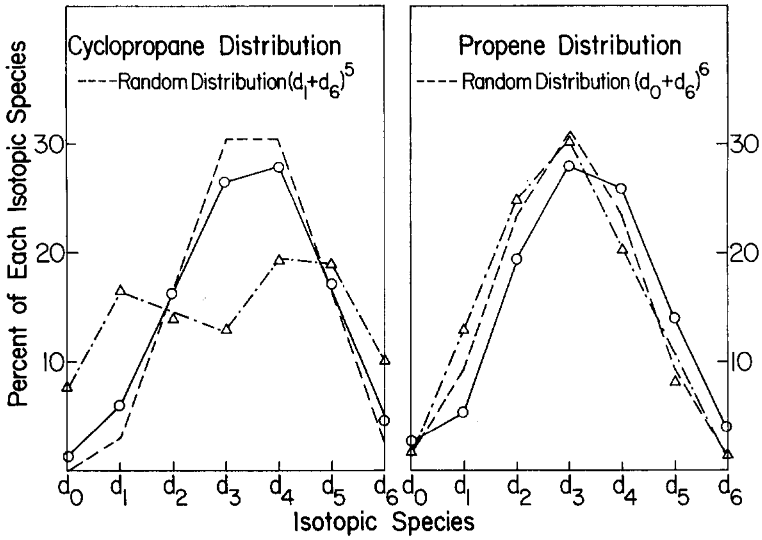


FIG. 3. Co-isomerization of an equimolecular mixture of d_0-, d_6-cyclopropane over molybdena–γ-alumina. $D_c/Mo = 1.00$, reaction temperature = 50°C. (○), first pulse, (△) fifth pulse.

distribution in the recovered cyclopropane and propylene was an isotopic equilibrium between C_3D_6 and C_3H_5D. Going from the first through the fifth pulse changes were noted, i.e.: (a) deuterium distribution in the cyclopropane shifted from random; the mole fractions of d_6, d_5, d_1, and d_0 rose while the mole fractions of d_4 and d_3 decreased; (b) by contrast, the isotopic distribution in propylene changed to an equilibrium between C_3D_6 and C_3H_6 by the fifth pulse.

In the experiment shown in Figs. 4 and 5, the catalyst was reduced again to the same extent (1.01 D_c/Mo). The 50/50 mixtures of cyclopropane-d_6 and -d_0 were

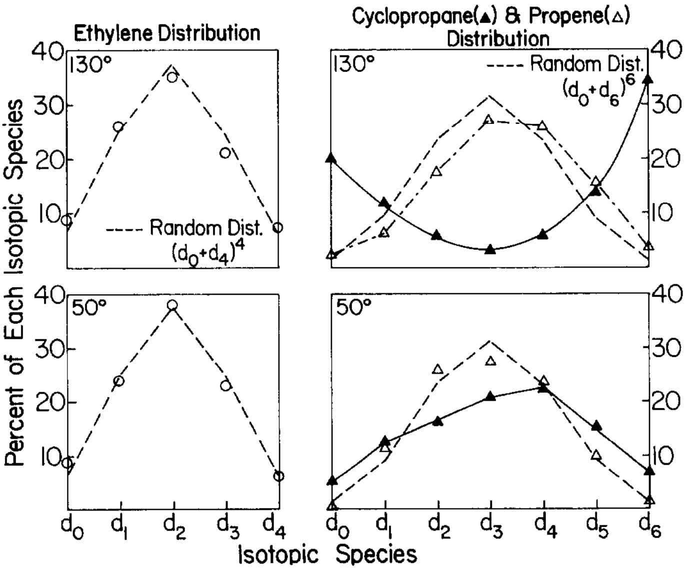


FIG. 4. Co-isomerization of an equimolecular mixture of d_0-, d_6-cyclopropane on molybdena–γ-alumina at different temperatures; $D_c/Mo = 1.01$.

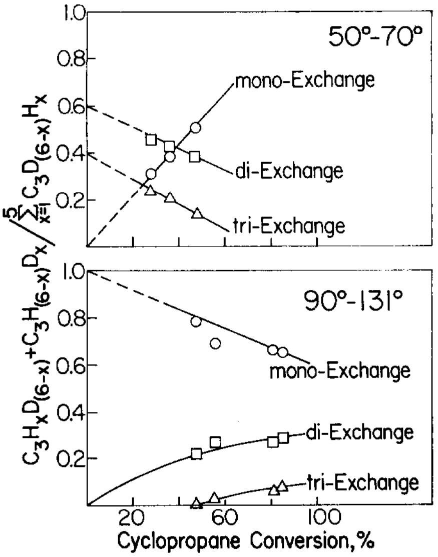


FIG. 5. Isotope mixing of cyclopropane. Conversion was varied by changing temperature.

co-isomerized over the catalyst at increasing reaction temperatures (50, 70, 90, and 130°C). In Fig. 4 it is shown that the deuterium distribution in cyclopropane shifted from near equilibrium at 50°C to stepwise exchange at 130°C, while the distribution in propylene and ethylene remained isotopically equilibrated at all temperatures.

This is further demonstrated in Fig. 5 where it is shown that at low temperatures (50–70°C) the monoexchanged species extrapolated to zero at zero conversion, while diexchanged and triexchanged species extrapolated to about 0.6 and 0.4, respectively. At higher temperatures, 90 and 131°C, cyclopropane-d_1 extrapolated to unity, while the d_2 and d_3 species extrapolated to zero. (These experiments showed that the isotopic equilibrium distribution in the propylene was independent of the deuterium distribution in cyclopropane.)

Reactions with Methylcyclopropane

In order to substantiate further the protonic nature of the isomerization mechanism, methylcyclopropane was reacted on catalysts reduced to different extents. The data are presented in Table 3. Four observations are significant: (a) MCP reacted faster than CP; (b) no trace of isobutene was detected; (c) the *n*-butenes were at equilibrium; and (d) at higher extents of reduction, substantial amounts of C_2H_4 appeared that are hard to understand on the basis of simple metathesis as this would have to stem from reaction of 1-butene

TABLE 3

Cyclopropane and Methylcyclopropane Reaction Products[a]

	Extent of Reduction							
	1.38 e/Mo		1.52 e/Mo		0.95 e/Mo		0.93 e/Mo	
Reactant	MCP		CP		MCP		CP	
Pulse No.	1	4	1	4	1	4	1	4
Total conversion	100	100	100	84	100	100	98	74
Product analysis (% of reactant)								
C_2H_4	8.9	2.0	4.9	12.6	—	—	13.2	9.4
C_3H_6	10.4	26.5	—	43.1	2.9	5.2	7.7	29.8
$\triangle$	—	—	—	16.2	—	—	1.8	26.0
n-C_4H_8[b]	5.6	45.8	—	17.1	12.1	82.1	0.5	11.5
cis + *trans*-2-C_5H_{10}	—	7.5	—	—	—	7.5	—	—
Mass loss	75.1	18.2	95.1	11.0	85.0	5.2	76.8	23.3

[a] Catalyst weight = 1.00 g; reaction temperature = 90°C; pulse size = 1.45×10^{19} molecules; He = carrying gas.

[b] No isobutene detected. *n*-Butene mixture at equilibrium.

with itself. Note that a and b are fully consistent with a protonic mechanism.

Excess C_2H_4 Formed during CP Reactions

As reported earlier (*4*), the first two pulses in each experiment yielded ethylene in excess over the butene formed by metathesis. The data obtained by different experimenters with different samples of catalyst at different reaction temperatures and after reduction with either H_2 or CO all fell on the same straight line when the excess C_2H_4 was plotted vs □/Mo (Fig. 6). The possibility that *n*-butenes are much more strongly adsorbed than ethylene was eliminated by substituting propylene for cyclopropane as the reactant. Now, the C_2H_4/C_4H_8 ratio was essentially unity, i.e., the *excess* ethylene was found to be nil.

Kinetics and Acid Sites

The microcatalytic pulse technique is not well suited for kinetic studies. Only when the reaction is strictly first order is it possible to obtain reliable kinetic data (*17*). In this case the following equation applies:

$$kK = (F^\circ/273RW)\ln[100/(100 - X)], \tag{1}$$

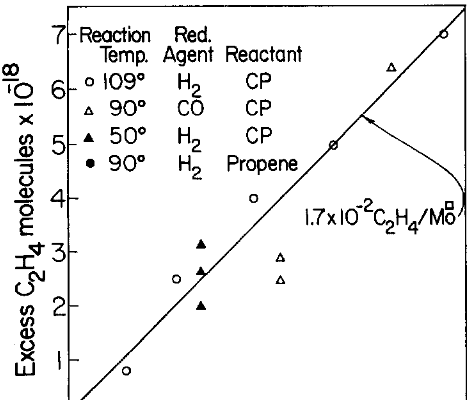


FIG. 6. Excess ethylene formed in first pulses when cyclopropane was reacted on molybdena-γ-alumina.

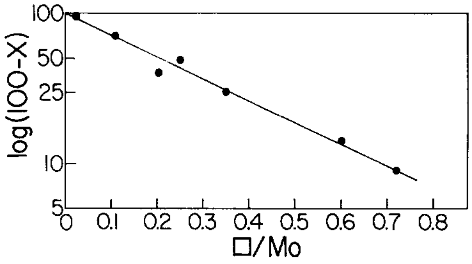


FIG. 7. Correlationship between first-order rate constants for cyclopropane conversion and molybdenum vacancies (□/Mo).

where k is the reaction rate constant, K is an adsorption equilibrium constant, F° is the helium carrier flow rate, R is the gas constant, and W the weight of the catalyst. An attempt was made to ascertain the reaction order using data obtained in the present work. A plot of log $[100/(100 - X)]$ vs $1/F^\circ$ was made for various pressures of cyclopropane in the doser. Although straight lines were obtained, the reaction was found to be less than first order; but that is all that can be said. Nevertheless, the data previously reported by Lo Jacono and Hall (*4*) have been reprocessed assuming first-order kinetics (Fig. 7). This plot demonstrates that the catalytic activity definitely increases with vacancy concentration. Evidently, Brönsted sites are alumina OH groups in close proximity to these anion vacancies.

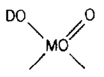
DISCUSSION

Isomerization Mechanism and Active Centers

Lo Jacono and Hall (*4*) found that the fractional conversion of a pulse of cyclopropane (using He carrying gas) was best correlated with the (H_I + □)/Mo ratio. H_I, they suggested, is a measure of the concentration of Brönsted acid sites on the surface (extensive factor of the acidity) and the vacancies (□) affect their acid strength (intensive factor). Since the isomerization is thought to proceed via the Baird and Aboderin mechanism (*18, 19*) in which a nonclassical protonated cyclopropane ion is formed (*13, 15*), a substantial fraction of the cyclopropane and propylene formed by the isomerization over a deuterated catalyst should be monodeuterated. In the first three experiments of Table 1, 1.45×10^{19} molecules of cyclopropane were passed over 1.00 g of molybdena–alumina the D_I contents of which were 9.9×10^{19}, 25.4×10^{19}, and 19.8×10^{19}/g, respectively. Thus, the number of D_I available was about 10-fold greater than the number of reacting molecules. The data of Figs. 1 and 2 for the first pulses suggest that only a small fraction (say 2–5%) of the catalyst D_I is present at the active Brönsted sites. The fraction of propylene-d_1 in the products from subsequent pulses should be a smaller fraction of the total than it was for the first, i.e., the propylene-d_1 vs pulse number plot should extrapolate to unity at zero pulse number, and its slope should depend upon the ratio of the number of cyclopropane molecules being reacted to the number of deuterated Brönsted sites. Thus, if 10% of the product from the first pulse is propylene-d_1, no more than 1% of the product from the second pulse should become deuterated, etc. Figures 1 and 2 show that this behavior was not followed; the propylene curves cannot be extrapolated to unity. One reason for this may be that the D atoms on active sites mix with those on inactive ones by proton hopping during the time frame of the experiment. However, another important contribution is treated below.

In the second experiment in Table 1, 67% of the first pulse (9.7×10^{18} molecules) disappeared from the mass balance. This material remained on the catalyst as polymeric residues and/or chemisorbed propylene. The data of Table 2 show that this adsorbed propylene undergoes displacement, mixing, and isotopic exchange with that produced from the second pulse. Taking this into account the following rough calculation demonstrates that the amount of propylene-d_1 in the second pulse cannot be less than 1% as predicted for the ideal system, i.e., the propylene produced in the second pulse could contain $9.7 \times 10^{18} \times 0.12 = 1.16 \times 10^{18}$ molecules of propylene-d_1 from the residue left from the first pulse, mixed with 36% of $14.5 \times 10^{18} \times 0.01 = 0.05 \times 10^{18}$ molecules from the second pulse, making a total of 1.21×10^{18} molecules of propylene-d_1 in a total of 14.9×10^{18} propylene molecules. Thus, up to 8% propylene-d_1 could be present. This value is close to the experimental value of 10.7%. Moreover, if propylene-d_2 is also considered, the theoretical value differs from the experimental one even less, i.e., 12.3% theoretical vs 11.5% experimental. Thus, the number of D_I acting in the isomerization reaction can be estimated from the data from the first pulse as $14.5 \times 10^{18} \times 0.12 = 1.7 \times 10^{18}$ sites/g. This is only about 0.7% of the D_I present. Moreover, the intercepts in Fig. 1 measure approximately the number of sites which are active at different temperatures and extents of reduction. Note that the first two experiments were carried out at 50°C, and the third, at 109°C.

The second set of three experiments (Table 1) was designed to provide information concerning the active sites. Since the exchange of alumina OH groups with D_2 is facile above 300°C, reduction with D_2, followed by reoxidation and then reduction with CO should eliminate deuteroxyls directly bonded to Mo, e.g.,

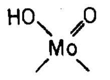


but should not eliminate those bonded to the alumina surface. The Mo concentration (8%) is sufficient to eliminate about 50% of the alumina OH. Fransen *et al.* (*20*) have shown recently that upon reduction a molybdena–alumina catalyst similar to ours developed ir bands in the OD region at almost the same frequencies as for the parent alumina. We have confirmed this with our catalyst (*21*). The present experiments demonstrate that it is the acidity of these hydroxyls which is enhanced by the molybdena layer by an amount which increases with the extent of reduction. Kiviat and Petrakis (*22*) demonstrated by ir studies of adsorbed pyridine that Brönsted acidity appeared when the molybdena monolayer was formed on the alumina surface. They did not, however, characterize an increased acidity on reduction.

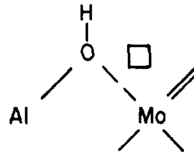
The experiments with CO-reduced and H_2-reduced catalysts yielded essentially the same product distribution, although the activity was somewhat higher for the former when compared at the same extent of reduction. The tracer experiments showed consistently lower deuterium contents in the isomerized propylene and unreacted cyclopropane, but otherwise the distribution of deuterium and the slopes of the curves in Fig. 2 were very similar to those in Fig. 1. Moreover, these results and those in Table 1 resemble data obtained in similar experiments reported for silica–alumina (*14*). The conclusion is unambiguous; only a small fraction ($\sim 1\%$) of the available hydroxyl groups function as Brönsted sites at reaction temperatures up to 109°C, and these are bound to alumina.

The products of co-isomerization of mixtures of cyclopropane and cyclopropane-d_6 were all close to isotopic equilibrium (Figs. 3 and 4). (In this connection, the data resembled more closely those expected for alumina catalysts than for silica–alumina.) Consequently, they did not provide much insight into the mechanisms of the reactions occurring. They did, however, contribute a couple of interesting points. Figure 3 shows that at 50°C, the isotopic distributions in both the cyclopropane and propylene products from the first pulse resembled the equilibrium distribution for mixtures of d_6 and d_1 compounds more closely than that for the d_6 and d_0 compounds. Data for the fifth pulse, on the other hand, conformed closely to the latter. This could be explained by assuming that 7.2×10^{18} molecules of cyclopropane-d_0 underwent exchange with the $2–4 \times 10^{18}$ *active* Brönsted OD sites initially present on the catalyst (possibly replenished by secondary exchange of the OH produced with cyclopropane-d_6), prior to isomerization. That only this small fraction of the total OH was involved suggests that the exchange occurs via the Baird and Aboderin nonclassical ion (*18*, *19*), but that the highest barrier along the reaction coordinate lies between this ion and the product propylene. This was substantiated by the second interesting observation that when the temperature was increased to 130°C, the isotopic distribution for the cyclopropane shifted to that expected for a stepwise process far from equilibrium (Figs. 4 and 5), while the propylene formed remained at isotopic equilibrium. Methylcyclopropane was found to react faster than cyclopropane at a given temperature and extent of reduction (Table 3). This is as expected for the proton-catalyzed ring opening and is a well-established principle of organic chemistry. Moreover, methylcyclopropane yielded exclusively *n*-butenes as isomerization products (Table 3). This observation was also consistent with the acid-catalyzed ring opening and differs from the results found for metals like Pt, Ni, and Pd, which tend to form preferentially isobutanes (*23–25*) on hydrogenolysis; W metal, a close neighbor to Mo, yielded a similar amount of both normal and isobutanes (*23*).

The almost identical results obtained with H_2- or CO-reduced catalysts make it highly unlikely that



groups are the active sites for isomerization, as suggested earlier (*4*). Moreover, the data in Fig. 7 show that the anion vacancies produced as water is removed during reduction are important for isomerization. Molybdena–alumina has been shown to be a good catalyst for $H_2 - D_2$ exchange even at very low temperatures (*5*), but the H_I does not exchange with D_2 at temperatures below 250°C. It has been suggested (*5*) that H_2 is activated on these same vacancy sites. Perhaps the simplest model consistent with all these results involves an acid-catalyzed ring opening occurring on active centers formed by interaction of Al-OH groups with a neighboring Mo(CUS) (thus making them more acidic) in the way suggested by Rooney *et al.* (*26*), i.e.,

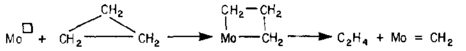


IV

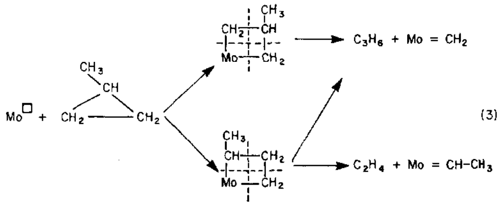
The ir data reported by Fransen *et al.* (*20*), which show that OD bands essentially identical to those found on the alumina developed on reduction, may not be inconsistent with this picture, although why the frequencies of these bands are not shifted by such an interaction is not clear.[4] Similarly, this model is also consistent with the finding of Kiviat and Petrakis (*22*) that molybdena–alumina has both Brönsted and Lewis acidity while alumina has only the latter.

Metathesis Mechanism and Sites

The older mechanism, involving two olefin molecules complexed into a four-membered ring, cannot explain the formation of excess ethylene when cyclopropane is reacted on molybdena–alumina. On the other hand, the carbene mechanism (*27–33*), which has been postulated recently for metathesis (over organometallic complexes usually containing Mo or W) does give a reasonable interpretation. In particular, the results of Gassman and Johnson (*33*) are pertinent to our system. When they reacted cyclopropane dissolved in chlorobenzene with the soluble complex formed from phenyltungsten trichloride and aluminum trichloride (1:1) at −78°C, the cyclopropane reacted "explosively" and an immediate evolution of ethylene occurred. No trace of propylene was detected. Similarly, when they reacted other alkyl-substituted cyclopropanes they found no trace of the isomeric olefin; the only products were mixtures of ethylene and olefins containing one carbon less than the starting cyclopropane. They interpreted their results as explained below for the first pulses of cyclopropane and methylcyclopropane.



(2)



(3)

Our reduced molybdena–alumina catalysts behaved similarly. From the first couple of pulses the carbene chain carrier for metathesis was formed on CUS Mo^{+n} ions; *n* is thought to be 4 because Fig. 6 demonstrates a clear relationship between carbene sites and the anion vacancies. The latter have been associated with Mo^{+4} (*2*). This would fit the requirement for the transition metal to supply two electrons to the carbene bond.

Previous work (*4, 5*) revealed that the activity for hydrogenation of olefins increased with the extent of reduction (□/Mo). Moreover, hydrogenation was so much faster than metathesis that the latter was greatly suppressed by H_2. Evidently, these reactions occur on the same sites. Figure 6 suggests that stable carbene formed on only about 1.7% of the $Mo^{\square}$. Possibly higher levels are present in the steady state, but it seems likely that not all the Mo^{+4} ions are equally active. Perhaps the Mo^{+4} must be in a special symmetry configuration, or possibly a few sites of lower oxidation state (Mo^{III} or Mo^{II}) function catalytically.

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[4] Possibly the concentration of these sites is too small to detect among the remaining OH present.

Curiously enough a plot of product-d_1 vs $\square$/Mo using the data of the first three experiments in Table 1 indicates that the active sites for isomerization are also $\sim$1.2% of Mo$^{\square}$. These numbers, although rough estimates, are consistent in that the actual number of *active* sites is much smaller than the number of Mo$^{\square}$.

In summary, molybdena–alumina catalysts are essentially bifunctional with the acidic function of alumina being enhanced by the interaction of OH groups with Mo$^{\square}$. In addition, the molybdena phase seems to behave essentially in the same way as do the other metal oxides, but has the unique ability to catalyze metathesis reactions. The activity in oxides has been frequently attributed to vacancies (CUS) formed during pretreatment at high temperatures. The ability of Mo to change its valence state rather easily seems to provide a more efficient way to produce these vacancies through reduction.

ACKNOWLEDGMENT

This research was supported by a grant from the National Science Foundation (No. CHE74-11539). We also wish to thank the Mobil Research and Development Corporation for a gift used to purchase some of the equipment used to carry out this research.

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