JOURNAL OF CATALYSIS 64, 150–162 (1980)

Catalysis and Surface Chemistry

II. Reactions of Propylene over Reduced Molybdena–Alumina Catalysts[1]

E. A. LOMBARDO,[2] M. LO JACONO,[3] AND W. KEITH HALL[4]

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

Received January 1, 1980

When cyclopropane was isomerized using a microcatalytic pulse technique over a reduced molybdena–γ-alumina catalyst (0.3 to 1.5 e/Mo), the resulting propene underwent secondary reactions including polymerization, metathesis to ethene and butenes, and hydrogenation (in H_2 carrying gas) to propane, ethane, and butane. Isotope exchange also occurred when D_2 or cyclopropane-d_6 was used. Complementary tracer studies were also made with propene-d_0 and D_2 using a static recirculation system. The kinds of sites required for the several reactions were classified and estimates made of their concentrations using strongly adsorbed (poison) molecules as probes. Small amounts of CO and NO were effective poisons for hydrogenation and exchange, but not for isomerization or metathesis in these experiments, but some poisoning of isomerization by CO was observed in pulse experiments. H_2O, pyridine, and NH_3 were less selective, but all of the reactions tested were poisoned. CO_2 and N_2O were ineffective and O_2 appeared to selectively reoxidize the active hydrogenation sites. From the data obtained, it could be estimated that the site concentrations utilized for these reactions were much lower than the measurable parameters such as anion vacancies, Mo^{4+} or Mo^{5+} centers, etc; they amounted to no more than a few percent of the Mo present and may have corresponded to multiplet vacancies. The chemisorption of NO and of CO correlated with both the extent of reduction and the vacancy concentration as did hydrogenation and exchange, and these same molecules, when chemisorbed, effectively poisoned these reactions.

INTRODUCTION

Molybdena–alumina catalysts are of considerable current interest because of the possibility that they may be used for the hydrogenation of coal to synthetic crude oil. During the past several years, work in our laboratory has been directed toward defining the surface chemistry of these materials (*1–3*) and relating this to catalytic function (*4–6*).

The reduction process was studied (*1*, *2*) and the changing surface composition characterized in terms of the anion vacancies (□) produced as H_2O is removed from the epitaxial monolayer and the hydrogen retained on the catalyst surface (H_I) as a result of reduction. During the early stages of reduction, approximately half the hydrogen consumed was used in each process. Thus, when the overall extent of reduction corresponded to an *average* valence of Mo^{5+}, then e/Mo = 1.0, H_IMo = 0.5, and □/Mo = 0.25, where e/Mo is the *average number* of electrons the Mo^{6+} has been reduced (in this case to Mo^{5+}). The data were further interpreted, however, to mean that at this point about 50% of the Mo was Mo^{5+}, about 25% Mo^{4+}, and 25% remained Mo^{6+}. On further reduction, H_I/Mo remained about constant and then decreased while □/Mo increased monotonically as e/Mo approached 2.0; the catalyst studied

---

[1] Presented at the 52nd Colloid and Surface Science Symposium, Knoxville, Tenn. June, 1978.

[2] On leave from Universidad Nacional del Litoral, Facultad de Ingenieria Quimica, Santiago del Estero 2829, Santa Fe, Argentina.

[3] On leave from Centro di Studio su Struttura ed Attivita Catalitica di Sistemi di Ossidi, Istituto Chimica Generale, Citta Universitaria, Piazzale Delle Scienze, Rome, Italy.

[4] To whom all correspondence should be addressed. Department of Chemistry, University of Wisconsin, Milwaukee, Wisc. 53201.

0021-9517/80/070150-13$02.00/0

(8% Mo) was not reduced much beyond Mo^{4+} with H_2 below 600°C, although somewhat higher values of e/Mo could be obtained using CO as the reducing agent. These characteristics enabled us to make subsequent catalytic studies (*4–6*) where the reactions were selected to test for particular catalyst functions.

Cyclopropane was selected as a test reactant primarily because (although it is thermally stable to 450°C) its isomerization to propene is facile in the presence of a strong Brönsted acid, and it was suspected that H_I might be such an acid. Indeed, a correlation between isomerization activity at 109°C and H_I was reported (*4*), but it was shown later (*5*) that CO-reduced catalysts possessed about the same activity as those reduced with H_2 and tracer results indicated that the surface concentration of active Brönsted sites was nearly two orders of magnitude less than that for H_I. It was also found in microcatalytic pulse experiments that the isomerization activity was appreciably higher in H_2 carrying gas than in He.

Cyclopropane turned out to be a happy choice of test reactant for another reason. The propene formed by isomerization was completely hydrogenated to propane at room temperature, thus illustrating the great activity of this catalyst for this function. Moreover, the disproportionation of a portion of the propene to ethene and butene was also catalyzed and the corresponding paraffins appeared when H_2 was present. Both hydrogenation and metathesis correlated with anion vacancy concentration (*4*). A portion of the first pulse of cyclopropane reacted with the surface to form the methylene carbene, the intermediate for metathesis, freeing an equal quantity of ethene (*5*). The extent of this process also correlated with □/Mo, but the slope of the plot indicated that carbene was formed on only about 2% of these coordinatively unsaturated sites (CUS).

A tracer study (*6*) was made of the hydrogenation of ethene as a function of surface chemistry. The principal product was always ethane-d_2 (from C_2H_4 + D_2), but multiple deuteration occurred as the CUS was increased. The characteristic multiple exchange patterns in the ethane product could be explained by the participation of a carbene intermediate formed as a side reaction from the alkyl intermediate required for hydrogenation. Polymerization could be fit into the same scheme and evidence was advanced that this process also correlated with the CUS concentration. Thus, olefin hydrogenation, disproportionation, and polymerization, as well as carbene formation, may all utilize a common set of sites and the concentration of these may be much less than measured by □/Mo. In the work reported herein, the effects of "selective poisons" on the several reactions have been studied and estimates made of the maximum concentrations of the active sites. tracer results for propene are compared and contrasted with the earlier ones for ethene (*6*) and for cyclopropane (*5*).

EXPERIMENTAL

Catalyst and pretreatment procedures. The same molybdena–alumina catalyst (8% Mo) and activation procedures used previously (*2–6*) were adopted for the present work. Before each run, the catalyst was calcined in flowing dry O_2 overnight at 500°C. After evacuation for 40 min at this temperature, it was reduced with a known amount of H_2 or CO and the extent of reduction measured from the amount of gas consumed (after correction for adsorption) (*1, 2*). When the desired extent of reduction was reached, the catalyst was evacuated for 90 min. The data were calculated as the *average* extent of reduction (below Mo^{6+}) measured as H_c/Mo (atoms/atom) or as the average number of electrons (e/Mo) the catalyst was reduced. On evacuation at 500°C after reduction, weakly adsorbed hydrogen (H_R) was pumped off the surface while strongly held hydrogen (H_I) or carbon monoxide (CO_I) remained on the surface (*3, 6*). By using graphs obtained in earlier studies (*2, 3*), the amounts of H_I, CO_I, and oxygen vacancies □/Mo could be estimated for a given extent of reduction.

Reaction procedures. One type of experiment was carried out in the same all-glass circulation system used earlier (*6*). The gases were pumped over the catalyst at room temperature and into a mixing chamber which contained about 95% of the total system volume (~300 cm^3). The exit stream from this could be sampled for glc analysis, before passing once again over the catalyst. Less than 1% of the circulating gas was removed for each analysis.

The reactant mixtures were prepared volumetrically (in an attached BET system) by introducing a measured amount of propene first into the circulation system, where it was frozen and outgassed before H_2 or D_2 was admitted in the desired amounts. The gases were thoughly mixed before contacting the catalyst.

A second type of experiment was made with a microcatalytic pulse system, using the same reactors and glc system as in the static experiments. Pulses [1.15 cm^3 (NTP)] of cyclopropane or propene were injected into the H_2 or He carrier gas stream and passed over the catalyst at 1 atm total pressure. The products emerging from the catalyst were collected in a −195°C trap for 20 min before flashing into the chromatographic column.

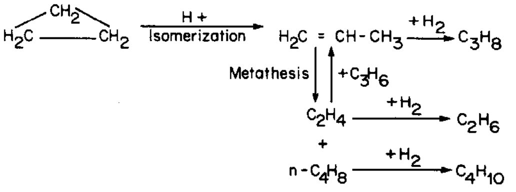
Mass spectrometric analysis. Provisions were made to trap and recover the individual products at the exit of the glc column for mass spectrometric analysis. Blank tests showed that no detectable isotopic mixing occurred on the column. The different compounds were analyzed at low ionization voltage, 13 eV; more details are given elsewhere (*5*, *6*).

Gases and purification procedures. H_2 and He were used as carrier gases in the microcatalytic pulse experiments; they were passed over anhydrous $CaCl_2$ and $MgClO_4$ and given a final cleanup with activated charcoal thermostated at −195°C. Ethene, propene, and cyclopropane were research grade, but were outgassed using a freeze–pump–thaw technique. Cyclopropane-d_6 and C_2D_4 were prepared by repeated exchange of these hydrocarbons with D_2 over a highly pure alumina (*7*). CO_2, N_2O, and O_2 (all research grade) were distilled between dry ice and liquid nitrogen temperatures to eliminate possible traces of water; NO was also distilled between these temperatures to eliminate both H_2O and NO_2; NH_3 (research grade) was used as received.

RESULTS

Reactions Studied

The three types of reactions shown in Scheme 1 were studied. Hydrocarbons were reacted with D_2 and deuterated hydrocarbons with H_2 (as well as different combinations of these). The catalyst was reduced with H_2, CO, or D_2, as required.



SCHEME 1

Thus isomerization, metathesis, and hydrogenation could be assayed simultaneously and additional information obtained by employing tracers. Still another reaction, olefin polymerization, was always present; it was repressed by hydrogen, but enhanced by further reduction. The reactions of propene with H_2 were studied in the recirculation system at 21°C. Because of the complexities introduced into the kinetics by the metathesis reaction (*8–12*), initial reaction rates were used for purposes of correlation.

A series of experiments were made in which 22 cm^3 (NTP) of propene and 110 cm^3 (NTP) of H_2 were reacted over the catalyst reduced to different extents (0.3 to 1.5 *e*/Mo). These data are summarized in Fig. 1 and show that hydrogenation was greatly enhanced by increasing the extent of reduc-

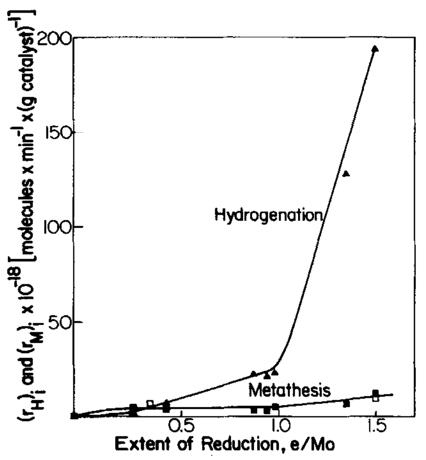


FIG. 1. Effect of catalyst reduction on initial rates of hydrogenation of propene, ▲ $(r_H)_i$, and of its metathesis, ■ $(r_M)_i$; a static recirculation system was used; reaction temperature was 21°C; reactants were 22 cm^3 (NTP) C_3H_6, 110 cm^3 H_2; amount of catalyst was 1.0 g up to 1.0 e/Mo and 0.1 g at higher extents of reduction. Empty squares correspond to runs without H_2 but with 22 cc C_3H_6.

tion while the metathesis activity was only slightly affected. This was further confirmed in two runs where the metathesis reaction was studied in the absence of H_2. The empty squares in Fig. 1, which represent the initial rates for the latter experiments, fitted well with the data obtained in presence of H_2. Evidently the rate of metathesis is not limited by hydrogenation as might be expected if both reactions took place on the same sites. A blank experiment was made over an oxidized catalyst. As shown in Fig. 1, this catalyst had no activity for hydrogenation.

Poisoning Experiments

Eight different poison molecules were tested to establish the nature and concentration of active sites for the different reactions. These are listed in Table 1, together

TABLE 1

Effect of Different Poisons on the Catalytic Activity of Molybdena–Alumina for Various Reactions[a]

Poison	Amount adsorbed (cm^3/g)	T^b (°C)	Extent of reduction (e/Mo)	Isom. of cyclopropane at 90°C[c]	Exchange at 25 and 90°C[c]	Metathesis of C_3H_6 at 25°C and 90°C	Hydrogenation of olefins at 25°C	Polymerization at 90°C[d]
H_2O	Sat.	25	0.9	CP	(CP)	CP	(CP)	CP
			1.43	CP	(CP)	CP		CP
CO_2	0.28	25	0.9	NP	NP[f,g]	NP	NP	NP
NH_3	19.9	25	0.9	CP	NT	CP	(CP)	CP
	6.1	300	0.9	CP	NT	CP	(CP)	CP
	0.3	25[e]	0.9	30% P	NT	NP	NT	30% P
	0.6	25[e]	0.9	90% P	NT	NP	NT	55% P
	0.8	25[e]	0.9	95% P	NT	35% P	NT	75% P
Pyridine	4.7	400	1.5	CP	NT	CP	NT	CP
N_2O	0.2	25	0.9	NP	(NP)	NP	NP	NP
CO	0.18	25	0.9	25% P	PP[f,h]	NP	75% P	(NP)
NO	1.15	25	0.9	NP	CP[f]	NP	CP	NP
	2.5	25	1.35	NP	(CP)	NP	CP	NP
O_2	0.35	25	0.9	Partial Reoxidation at 90°C	NT	NP	CP	Partial reoxidation at 90°C

[a] Reaction network shown in reaction Scheme 1. Poisoning is represented by P, complete poisoning by CP, not poisoned by NP, not tried by NT, and partial poisoning by PP. When poison effect is given in parentheses, the most probable result expected from related observations is indicated (but as yet untested). Data for metathesis and hydrogenation were for propene in circulating system; the remainder, except as otherwise indicated, are for cyclopropane in microcatalytic system.

[b] Desorption temperature. Adsorption temperature was 25°C in all cases; 1 cm^3(NTP) = 2.69×10^{19} molecules = 5.38×10^{-2} molecules/Mo.

[c] Pulse technique.

[d] Polymerization is the estimated mass loss in pulse experiments and the data may include strongly adsorbed olefins and dehydrogenated residue as well as polymer.

[e] Small successive additions of NH_3.

[f] Olefin $-D_2$ exchange.

[g] Hydrocarbon –D catalyst exchange.

[h] Intermolecular exchange.

with information concerning their effects. Data for hydrogenation and metathesis were taken from experiments in which propene and hydrogen, or propene and helium, respectively, were circulated over the catalyst; the remainder were derived from cyclopropane pulse experiments. For convenience the data for the different poisons will be discussed separately below.

H_2O. Catalysts reduced to 0.9 and 1.43 *e*/Mo were exposed to water at its vapor pressure at room temperature for 3 min before reacting cyclopropane at 90°C using the pulse technique with He carrier. The isomerization activity almost completely disappeared. Moreover, no activity was observed for any of the reactions when propene was substituted for cyclopropane. When a poisoned catalyst was evacuated for 30 min at 110°C, a conversion of about 5% of the cyclopropane was observed. As shown previously (*4*), the conversion level was further increased after evacuation at 210 and 300°C and the original activity was almost completely restored after evacuation at 500°C. The large amount of water adsorbed and the nonselectivity of the poisoning did not justify further studies.

CO_2. In contrast with the alumina base (*13, 14*), CO_2 was not irreversibly adsorbed on the oxidized catalyst at room temperature, even after pretreatment and evacuation at 550°C. Evidently the molybdena layer covers the alumina sites which are active for olefin $-D_2$ exchange. Chemisorption did occur on reduced catalysts, however, in amounts which increased almost linearly with extent of reduction, but CO_2 was not an effective poison (Table 1). At 1.5 *e*/Mo, 1.1 cm^3 (NTP)/g was chemisorbed, but a portion of this could be displaced by olefin; three pulses reduced the amount left on the catalyst to 0.8 cm^3/g and the reactions of propene and cyclopropane were virtually unaffected. When a pulse of C_2D_4 was passed over the catalyst at this point at 25°C using H_2 carrier gas, neither the activity nor the exchange pattern was altered by the chemisorbed CO_2. Again, this is in contrast with results for alumina (*13, 14*). A similar conclusion was reached in a tracer experiment in which cyclopropane was reacted at 90°C using He as carrier gas. In this case, the catalyst was first reduced with CO; the first pulse was cyclopropane-d_6 and the following ones were cyclopropane-d_0. Deuterium from polymer residues appeared in the products from the latter as previously reported (*5*).

NH_3. Since the facile isomerization of the cyclopropane ring requires protons (Brönsted acidity), basic molecules would be expected to poison this reaction. This proved to be true, but these chemisorptions were not very selective and the other reactions were poisoned also. Table 1 contains five rows of data describing NH_3 poisoning of the isomerization of cyclopropane at 90°C in He carrier gas. In the first experiment, a large amount of NH_3 was chemisorbed irreversibly at room temperature (19.9 cm^3/g); this poisoned the catalyst completely. In another experiment, NH_3 was adsorbed at room temperature and then evacuated at 300°C. The amount retained was lower (6.1 cm^3/g), but was still enough to completely poison the catalyst. The catalyst could not be evacuated at a higher temperature because the NH_3 decomposed and further reduced the catalyst. To avoid this problem, small doses of NH_3 were adsorbed at 25°C on a new sample of reduced catalyst. It was recognized that a serious chromatographic effect could develop and that nonuniform coverage of the bed length would undoubtedly occur. This should have the effect of increasing the size of the lethal dose, i.e., yield a site density that was too high. However, the remaining experiments using NH_3 (Table 1) showed that much smaller amounts of NH_3 were sufficient to deactivate the catalyst than the 6.1 cm^3/g measured by the "proper" experiment. The acid function was eliminated, as postulated, and NH_3 and C_5H_5N were the only poisons tested which accomplished this (see below). Note also that the mass loss (polymerization and/or strong

TABLE 2

Effect of Ammonia Poisoning on Cyclopropane and Propene Reactions[a]

	Reactant passed over poisoned or unpoisoned catalysts in pulse experiments[b]						
	Cyclop. (0 cm^3/g)	Propene (0 cm^3/g)	Cyclop. (0.3 cm^3/g)	Cyclop. (0.6 cm^3/g)	Propene (0.6 cm^3/g)	Cyclop. (0.8 cm^3/g)	Propene (0.8 cm^3/g)
	Product analysis (% of reactant)						
C_2H_4 and n-C_4H_8	20.9	22.9	13.2	1.3	23.8	0.7	14.7
Propene	29.8	50.9	25.2	4.7	64.4	3.6	79.1
Cyclopropane	26.0	—	49.1	94.0	—	95.7	—
Mass loss	23.3	26.2	12.5	0	11.8	0	6.2
	Poisoning (%)						
Isomerization							
(*c*)	—	—	24	88	—	92	—
(*d*)	—	—	31	92	—	94	—
Mass loss							
(Δ)	—	—	46	100	—	100	—
(C_3H_6)	—	—	—	—	55	—	76
Metathesis	—	—	—	—	0	—	36

[a] Catalyst weight 1.00 g; CO reduced, 0.9 *e*/Mo; reaction temperature, 90°C; pulse size, 1.45×10^{19} molecules; He carrying gas. The data shown correspond to a pulse passed after the catalyst is lined out.

[b] Reactant and amount of ammonia used as poison (cm^3(NTP)/g).

[c] Calculated from Σ olefin/Δ^0 for poisoned and clean catalyst.

[d] Calculated from (100 − Δ) for poisoned and clean catalysts.

adsorption of hydrocarbons) was also susceptible to poisoning with NH_3. Care must be exercised in evaluating the effectiveness of the poison for the several reactions. When the isomerization of cyclopropane is partially poisoned, the propene pressure available for polymerization and metathesis is decreased and the poisoning effect therefore exaggerated. Consequently, it was necessary to evaluate the poisoning of these latter reactions using propene as the reactant. Data for the two reactions are compared in Table 2 and poisoning plots are shown in Fig. 2. It is evident that isomerization is the most sensitive, polymerization next, and metathesis the least sensitive to poisoning by NH_3; the extrapolated amount of poison required to completely kill the catalyst (upper limit) was below 1.2 cm^3 (NTP)/g or about 3.2×10^{19} molecules/g. These figures may be compared with the loading of 5×10^{20} Mo/g and the anion vacancy concentration (expected from CO_2 evolution on reduction with CO) of about 1.2×10^{20}/g. The relative insensitivity of metathesis to poisoning by NH_3 is remarkable.

Pyridine. Pyridine was tried as a poison in the same manner as NH_3. A catalyst was

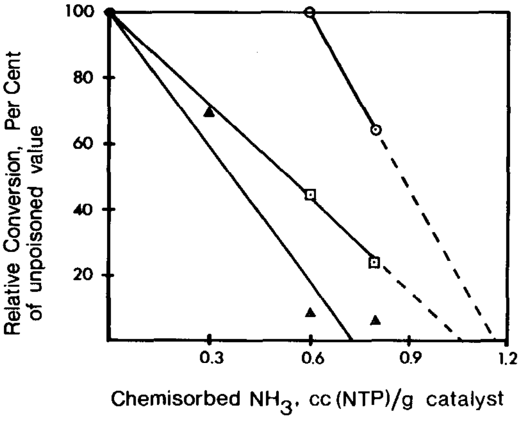


FIG. 2. Poisoning by NH_3 of the isomerization of cyclopropane (△), and the polymerization (□) and metathesis (○) of the propene by NH_3.

reduced to 1.5 e/Mo and evacuated. It was then exposed to pyridine and evacuated at 400°C; a large chemisorption [4.7 cm^3(NTP)/g] was observed. This completely poisoned the catalyst for all reactions tested.

N_2O. The catalyst (after reduction to 0.9 e/Mo) chemisorbed 0.2 cm^3(NTP)/g of N_2O irreversibly at 25°C. This chemisorption did not affect the rate of either hydrogenation of propene or its metathesis. In another experiment, the catalyst was reduced to about the same extent and contacted with N_2O at room temperature; it was then evacuated at 90°C, after which it retained 0.05 cm^3/g. Neither the isomerization of cyclopropane (in He) nor the metathesis was affected.

CO and NO chemisorption. These molecules were studied in the greatest detail because preliminary tests showed them to be the most promising. Moreover, by analogy with coordination chemistry, these compounds would be expected to interact strongly with coordinatively unsaturated molybdenum ions, with NO adsorbing more strongly than CO. On the other hand, they would not be expected to be adsorbed by Brönsted sites nor be as strongly adsorbed on a partially dehydroxylated alumina surface as, for example, CO_2 or NH_3. Volumetric adsorption studies confirmed these assumptions. Figure 3 shows that while the oxidized catalyst did not adsorb measureable amount of either CO or NO, on reduction the irreversible chemisorptions of these molecules at room temperature increased linearly with □/Mo. Curiously, the intercept was not at the origin, but at about 0.05 □/Mo. A similar result was noted earlier (*4*) for metathesis. The slopes of these curves indicated that only about 6% of the vacancies were populated with CO and 37% with NO.

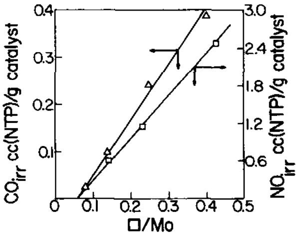


FIG. 3. Relationship between irreversible chemisorption of CO and NO and anion vacancy concentration (□); slopes are 0.063 CO/□ and 0.37 NO/□. (0.1 cm^3 of gas/g catalyst = 5.4 × 10^{-3} gas molecules/Mo (total).)

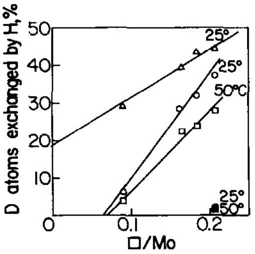


FIG. 4. Deuterium exchanged by hydrogen, (100/6) $\Sigma_i i h_i$, after different extents of reduction (where h_i is defined as the mole fraction of $C_3H_iD_{6-i}$) when cyclopropane-d_6 was reacted in pulse experiments using H_2 as a carrier gas. Cyclopropane (○, □) and propane (△) curves are shown. The effect of CO poisoning on exchange of cyclopropane is also shown (●, ■).

Tracer experiments were carried out over unpoisoned catalysts reduced to various extents with CO. Cyclopropane-d_6 was used as a test reactant and H_2 as the carrier gas. In an earlier study (*4*), it was reported that the isomerization of cyclopropane occurred about twice as fast in H_2 carrier as in He carrier. When pulses of cyclopropane-d_6 (92% C_3D_6, 8% C_3D_5H) were passed over a slightly reduced catalyst (Fig. 4), cyclopropane-d_6 and multiply exchanged propanes appeared. With catalysts reduced to still higher extents, both the cyclopropane and propane became multiply exchanged. In Figs. 4 and 5, the percentage of the D atoms exchanged by H into the unisomerized cyclopropane is shown. The extent of exchange in both cyclopropane and propane increased with extent of reduction. Since linear correlations exist between both the percentage of deuterium atoms exchanged by H (Fig. 4) and the CO and NO chemisorptions (Fig. 3) with the CUS concentration, □/Mo, it follows that the former must correlate with each other

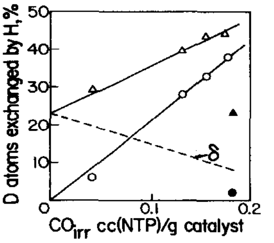


FIG. 5. Correlation of deuterium exchange in cyclopropane-d_6 (○) and propane (△) produced (pulse experiments of Fig. 4) with catalyst's ability to adsorb CO irreversibly as the catalyst was reduced to different extents. Solid points correspond to reaction over CO poisoned catalyst. Broken line shows difference in D exchanged between propane and cyclopropane.

(Fig. 5). Moreover, exchange was severely poisoned in the presence of chemisorbed CO (solid points). The exchange with cyclopropane was almost completely poisoned by CO while the reaction of H into the propane was only partially poisoned. Of course, one H was introduced into the propane molecule from the Brönsted acid site as the ring was opened. This could account for the intercepts for the propane curves of Figs. 4 and 5 if it is assumed that the Brönsted sites undergo facile exchange with the H_2 carrying gas.

The CO which was irreversibly chemisorbed in this experiment (0.18 cm^3/g or 4.9 × 10^{18} molecules/g), corresponded to only about 1% of the total Mo on the surface or to 4.6% of the available 107 × 10^{18} anion vacancies, which were related to the exchange of cyclopropane in Fig. 4. This chemisorbed CO also reduced the rate of isomerization from 63 to 17%. Moreover, while the deuterium exchange in cyclopropane dropped from 37 to 2%, in propane it decreased only from 44 to about 20% (Fig. 5); the latter value was about the same as the extrapolated values for the unreduced catalyst and is about equivalent to the exchange introduced by proton transfer as the ring is opened.

When propene and hydrogen were reacted in the same system over a catalyst reduced to 0.9 *e*/Mo and poisoned with 0.18 cm^3/g of CO, the hydrogenation rate was decreased by 75% while the metathesis rate remained unchanged (Table 1).

When a catalyst reduced to about *e*/Mo = 0.9 was exposed to excess NO and then evacuated, 1.15 cm^3(NTP)/g was irreversibly chemisorbed. The microcatalytic isomerization of cyclopropane and the secondary metathesis reaction were only slightly affected by this chemisorption (Table 1), whereas hydrogenation of propene was completely poisoned.

The hydrogenation of propene was studied in the circulating system. The effects of NO poisoning on this hydrogenation and metathesis are presented in Fig. 6. In the first series of experiments, the catalyst was reduced to 0.9 *e*/Mo and then saturated with NO at room temperatue (1.15 cm^3/g). The activity for hydrogenation at 21°C was close to zero (Fig. 6) while the metathesis activity was unaffected by the NO. In a second experiment, made after the catalyst had been reoxidized and reduced to 0.9 *e*/Mo, NO was adsorbed at room temperature and desorbed at 200°C; volumetric measurements indicated that 0.67 cm^3 of

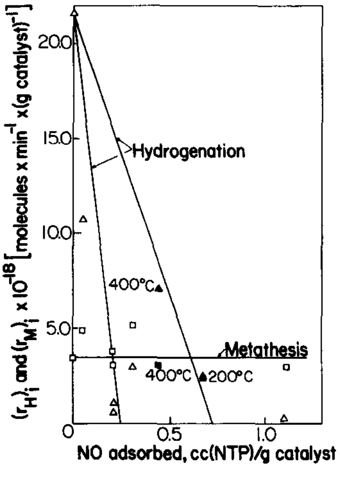


FIG. 6. The poisoning of hydrogenation (vs metathesis) of propene by varying amounts of NO. Experiments made at 21°C in the recirculating static reactor. The catalyst was reduced to 0.9 *e*/Mo; NO desorption temperatures are indicated (▲, ■). In all other experiments, NO was adsorbed at room temperature (△, □); 1 cm^3(NTP) = 2.69 × 10^{19} molecules or 0.054 molecules/Mo.

NO remained adsorbed on the catalyst. However, when the gas recovered was analyzed by mass spectrometry, it was found that it contained about 20% N_2O; no O_2 or N_2 was detected. Consequently, some reoxidation occurred at the catalytic sites. Nevertheless, the catalytic activity for hydrogenation increased somewhat compared with the previous experiment, suggesting that another portion of the active sites was freed in the process. In a third experiment, NO was again adsorbed at room temperature but desorbed at 400°C and 40% N_2O was detected in the gas phase. The hydrogenation activity again increased compared with the previous experiments as shown in Fig. 6. The extent of reoxidation suggested by the amount of N_2O produced was still small compared with the overall extent of reduction (see Fig. 3).

In a second series of experiments, small pulses of NO were added successively. As noted before, this technique should effectively increase the size of the lethal dose. However, the open triangles in Fig. 6 show that the actual concentration of active sites determined in this way was much lower than that suggested by the previous series of experiments. The 0.2 to 0.3 cm^3/g, which was sufficient to poison the active sites for hydrogenation, is in fair agreement with the value deduced from CO poisoning experiments. If 0.2 cm^3/g is a fair estimate of the active site concentration, then no more than about 5×10^{18} site/g or about 1% of the total Mo is active and this is less than 20% of the total NO chemisorption.

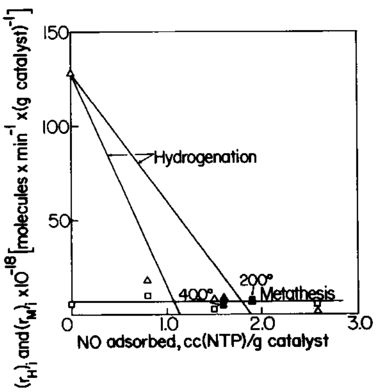


FIG. 7. The poisoning of hydrogenation (vs metathesis) of propene by varying amounts of NO. The catalyst was reduced to 1.35 e/Mo; NO desorption temperatures are indicated (▲, ■). In all other experiments, NO was adsorbed at room temperature (△, □). Conditions were otherwise the same as those of Fig. 6.

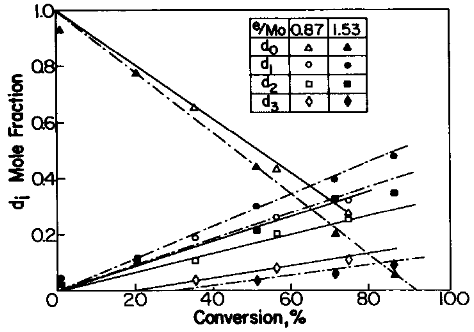


FIG. 8. Istopic distribution in the propene produced by reactions of propene-d_0 with D_2 over 1 g of catalyst reduced to different extents. The recirculation system contained 22 cm^3(NTP) of C_3H_6 and 110 cm^3(NTP) of D_2. The reaction was carried out at 21°C.

Figure 6 shows that in all these experiments, the metathesis activity was remarkably constant. In another set of experiments, in which the catalyst was reduced to an average extent of 1.35 e/Mo, the same behavior was found. The addition of successive small amounts of NO, as shown in Fig. 7, yielded data suggesting an active site concentration for hydrogenation of about 2.7×10^{19}/g (or about 5% of the Mo). For this catalyst, this is equivalent to nearly 20% of the vacancies.

The reaction of propene with D_2 was studied over the catalyst reduced to 0.9 and 1.5 e/Mo, respectively. The reactant mixture consisted of 22 cm^3 of C_3H_6 and 110 cm^3 of D_2. The data of Figs. 8 and 9 show extensive exchanges in both sets of reaction products. In a similar experiment, the catalyst was reduced to 0.9 e/Mo and exposed to excess NO at 25°C. On evacuation, 1.1 cm^3(NTP) was retained. With identical reactant the metathesis reaction proceeded at its usual rate, but less than 2% propane was formed in several hours (by

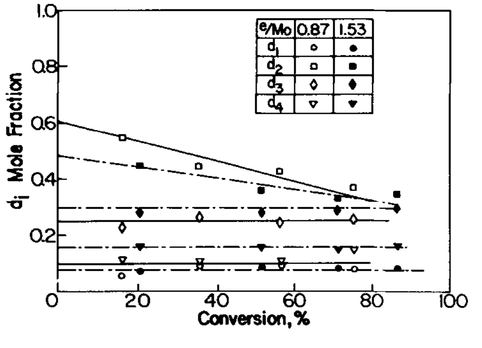


FIG. 9. Isotopic distribution in propanes produced by reactions of Fig. 8.

the time metathesis was close to equilibrium). This is longer than it would take to completely hydrogenate the C_3H_6 on the same catalyst in the absence of NO. Mass spectrometric analysis of the propene showed that it contained less than 2% propene-d_1; essentially all of the hydrogenated product was propane-d_2.

Oxygen. Oxygen was selectively chemisorbed on reduced catlaysts in a way similar to NO (*15*, *16*). In a poisoning experiment, 0.35 cm^3/g of O_2 was retained irreversibly by the catalyst at 25°C (compared with 1.1 cm^3 NO/g) after reduction to 0.9 e/Mo. The hydrogenation of propene was completely poisoned by this chemisorption, while the metathesis activity remained unchanged. Previously, using a modified technique to determine the chemisorption, we showed that the O_2 chemisorption mimicked Fig. 1, and indeed a linear curve was obtained when the hydrogenation rate was plotted against the amount so adsorbed.

In other experiments made with the same poisoning conditions, pulses of cyclopropane were passed over the catalyst at 90°C using He carrier gas. Metathesis was tested with the same system using propene pulses. Both reactions (isomerization and metathesis) decreased in conversion in the way expected if the catalyst had been reoxidized to around 0.3 e/Mo. However, the amount of O_2 available was only enough to reoxidized the catalyst from 0.9 to 0.8 e/Mo.

DISCUSSION

The present work has taught us several lessons. The first of these is that the reactions studied occurred on only a small fraction of the surface. Consequently, attempts to characterize reaction intermediates or active sites in terms of the major components which are easily measurable are apt to prove futile. The catalyst studied contained about 5×10^{20} Mo/g. The numbers of anion vacancies, Mo^{4+} and Mo^{5+} centers, and new hydroxyl groups introduced during reduction (H_I) were all within an order of magnitude of this figure. The poisoning experiments proved that the numbers of sites which are active for these reactions are at least another order of magnitude smaller. Consequently, the application of spectroscopic techniques which integrate over all surface observables will tend to show the major species, and not those of interest to catalysis. An interesting corollary to this rule is that detailed spectroscopic studies of the chemisorbed poison are likely to be more rewarding than searching for reaction intermediates. For example, we have shown (*16*) that the NO molecules which poison hydrogenation are chemisorbed to form dinitrosyl surface compounds, i.e., they select sites which expose two or more coordinatively unsaturated positions. Kokes' studies (*17*) of ZnO catalysts present an interesting contradiction to this view. Kokes and co-workers proved that the chemisorbed species observed by infrared spectroscopy were the active intermediates. The apparent conflict disappears when it is realized that the intermediates on ZnO were relatively stable, the rates were zero order and probably controlled by desorption, and, in addition, side reactions were negligible. Thus, Kokes' work may be considered the exception which proved the rule.

Some earlier indications of low active site density have been reported. In one instance, the catalyst acidity was tested by reacting cyclopropane. Approximately 2 ×

10^{20} H_I/g were introduced when our catalyst was reduced with H_2 to 0.9 *e*/Mo (*2*). It was suspected that these OH groups might be Brönsted sites and indeed a linear correlation was obtained (*4*) when the percentage conversion of cyclopropane was plotted against H_I/Mo or against $(H_I + \square)$/Mo. It was later found (*5*), however, that when the catalyst was reduced with CO, almost the same activity level was developed. In this case, no new OH groups were introduced, yet $\sim 10^{20}$/g were still present and unreplaced by $(MoO_4)^{-2}$ groups at the 8% Mo loading level. Moreover, from the results of tracer experiments, it could be estimated that about 1% of these ($\sim 10^{18}$/g) had become active Brönsted sites. Neither NH_3 nor pyridine proved to be very selective poisons for these sites, yet it was found that isomerization could be drastically reduced by 0.6 cm^3(NTP)/g; polymerization was completely eliminated and the metathesis activity lowered by this same 1.6×10^{19} molecules/g, and this figure is obviously considerably too high.

In a similar vein, it was initially reported that metathesis activity correlated with $\square$/Mo (4), but later work (*5*) revealed that only about 2×10^{18}/g carbene centers (required for metathesis) formed on a catalyst reduced by about 0.9 *e*/Mo, i.e., about $1.7 \times 10^{-2}/\square$. In the present work, the metathesis activity was nearly invariant with extent of reduction, i.e., the correlation with $\square$/Mo was not confirmed. The earlier work (*4*) was carried out with cyclopropane as the source of olefin, using the pulse technique; hence, the olefin pressure increased with extent of conversion, which in turn increased with the extent of reduction. Consequently, the earlier result reflected the increasing olefin pressure, not an increasing number of active sites. In the earlier work (*4*), it was also found that metathesis decreased with increasing $\square$/Mo in H_2 carrying gas. This was attributed to competition with hydrogenation on the same sites. The present work also showed that this was not so, because hydrogenation could be eliminated by poisoning with NO or CO without noticeably affecting the metathesis conversion. The reaction network shown as Scheme 1 affords several possible explanations for this result when it is recalled that the experiments were made at different temperatures as well as with different partial pressures of the reactants. The blank runs shown in Fig. 1 suggest that H_2 is not the factor controlling the selectivity for metathesis.

It is of considerable interest that metathesis was not noticeably affected by chemisorbed NO (which completely eliminated hydrogenation), but was substantially poisoned by comparable quantities of NH_3. The carbene mechanism for metathesis would be expected to require sites having multiple coordinative unsaturation together with at least two available electrons (Mo^{4+}). It is on this kind of center that NO and CO would be expected to adsorb. However, this finding has been confirmed by the experiments of Engelhardt (*18*) who found that metathesis of propene was completely poisoned, not by NO, CO, or O_2, but by a form of hydrogen which is chemisorbed at high temperature and which we have characterized (*1, 2, 4*) as H_R. This hydrogen does not poison the hydrogenation of C_3H_6. Evidently, a key element is missing in our present understanding of the nature of the site requirements for these reactions.

Tracer studies of a reaction mechanism provide another approach to relating catalyst function to surface chemistry. From such work a reaction scheme can be deduced which usually requires the postulation of surface intermediate species. This approach was taken in a study (*6*) of the reactions of C_2H_4 with D_2. The chemistry deduced suggested that hydrogenation, metathesis, polymerization, and isotope exchange between olefin and D_2 could all be accounted for by a common intermediate (adsorbed alkyl) on the same CUS molybdenum ions. The present poisoning experiments did not support this hypothesis; hydrogenation could be eliminated without affecting metathesis. Of course the site requirements might be quite similar, e.g., Mo^{4+} centers for metathesis (in plentiful supply) and Mo^{3+} (sparse) for hydrogenation. If so NO and O_2 chemisorb strongly only on the latter (*15, 16*) and it may be that hydrogen is chemisorbed in an active form only on these same sites.

Reaction Scheme 1 includes several implicit reaction steps, such as chemisorption (and the dissociation) of H_2, metathesis, and the bonding and insertion of monomer olefins to produce polymer. Moreover, these processes may be competitive. Consequently, it is not possible at this stage to be very explicit. What may be said is that the concentration of such sites is sufficiently small to require that some rather special conditions be fulfilled, e.g., that they contain a rare species such as Mo^{3+}, or that the concentration reflects the joint probability of finding two or more minor species at one site. The latter (multiplet) could, for instance, be what Siegel (*19*) has termed a CH site, i.e., a CUS site containing Mo–H, or, perhaps, the ensemble of Mars and co-workers (*20*), where chemisorption of substrate occurs on a higher valent ion (Mo^{5+}) while H_2 is chemisorbed on a neighboring ion of lower valence ($Mo^{3+}\square$). This model would be in agreement with our findings since NO is known to interact most strongly with the lower valence states of molybdenum (*21*). The sharp upturn in the hydrogenation rate at a reduction of about $e/\mathrm{Mo} = 1$ tends to support the multiplet theory. It is in this region that multiple coordinative unsaturation begins to develop; at lower extents of reduction, the anion vacancies are thought to appear randomly and mostly singly (*2*).

The tracer experiments on the unpoisioned catalyst revealed some similarities and differences with similar work with ethene (*6*). Ethene underwent negligible exchange with D_2, even at high conversions and ethane-d_2 was almost the sole product at low D_2/olefin ratios and extents of reduction. As these two factors increased, however, other deuterated ethanes appeared, i.e., the d_1, d_3, and d_4 species. This particular distribution was interpreted in terms of a carbene intermediate that allowed the production of ethane containing not more than four deuteriums per molecule (*6*). By contrast, propene exchanged continually with D_2 as the conversion increased and consequently the propanes contained a wider distribution of deuterated species (Figs. 8 and 9). Formation of an allyl intermediate could explain these results in the same manner as with ZnO where ethene was converted exclusively to ethane-d_2, while propene, as well as the product propane, became multiply exchanged (*17*). The distributions shown in Figs. 8 and 9 are remarkably similar to those obtained by Kokes and Dent (*17*), who discovered, using infrared, that a π-allyl specie was formed from propene on CUS sites.

NO was an excellent poison for hydrogenation. The intercept of Fig. 6 suggests that, at most, 0.25 cm^3 (NTP) of NO is enough to poison hydrogenation. This corresponds to 6.7×10^{18} active sites/g, a number two orders of magnitude smaller than the total molybdenum available on the catalyst. This NO is adsorbed on these sites as dinitrosyl species (*16*). NO has been shown to be an excellent poison for metathesis reactions occurring over molybdenum carbonyl supported on silica (*22*). However, over our reduced molybdena catalyst, NO did not affect the metathesis activity. We can offer no explanation for this interesting contradiction.

Some of the observations concerning poisoning might be attributed to selective reoxidation at the active sites. Thus, the chemisorption of O_2 at 25°C completely poisoned hydrogenation; it also lowered the isomerization activity for cyclopropane at 90°C so that it acted more like a catalyst reduced to about 0.3 e/Mo, rather than 0.9. However, even if the entire 0.35 cm^3(NTP) adsorbed was totally consumed to reoxidize the catalyst, the overally extent of reduction should have been lowered only slightly, i.e., from 0.9 to 0.82 e/Mo. A similar partial reoxidation process occurred when NO was desorbed at elevated temperature as N_2O was detected in the gas phase. Again, the extent of reoxidation by this process would not have been enough to explain the data of Figs. 6 and 7, were the adsorption not site specific.

The metathesis sites are most difficult to characterize. None of the poisons selectively affected metathesis. These sites appear to occupy only a small fraction of the surface (*5*). Moreover, Fig. 1 demonstrates that the metathesis activity was not much affected by the extent of reduction. Whatever their nature, two facts have been established, viz., they are rapidly formed at low extents of reduction and further reduction does not seem to increase their number; also, they are not affected by NO, but are poisoned by H_R. These two facts favor a higher oxidation state for the metathesis site than for the hydrogenation site.

ACKNOWLEDGMENTS

This work was supported by National Science Foundation Grant CHE74-11539 which we gratefully acknowledge.

REFERENCES

1. Hall, W. K., and Massoth, F. E., *J. Catal.* **34,** 41 (1974).

2. Hall, W. K., and Lo Jacono, M., *in* "Proceedings, 6th International Congress of Catalysis, London, 1976" (G. C. Bonds, P. B. Wells, and F. C. Tomkins, Eds.), Vol. 1, p. 246. The Chemical Society, London, 1977.

3. Abdo, S., Lo Jacono, M., Clarkson, R. B. and Hall, W. K., *J. Catal.* **36,** 330 (1975); Millman, W. S., Crespin, M., Cirillo, A. C., Abdo, S., and Hall, W. K., *J. Catal.* **60,** 404, (1979).

4. Lo Jacono, M., and Hall, W. K., *J. Colloid Interface Sci.* **58,** 76 (1977); *Colloid Interface Sci. Symp. Ser. San Juan, P.R.* **1,** 81 (1977).

5. Lombardo, E. A., Lo Jacono, M., and Hall, W. K., *J. Catal.* **51,** 243 (1978).

6. Lombardo, E. A., Houalla, M., and Hall, W. K., *J. Catal.* **51,** 256 (1978).

7. Larson, J. G., Hightower, J. W., and Hall, W. K., *J. Org. Chem.* **31,** 1225 (1966).

8. Begley, J. W., and Wilson, R. T., *J. Catal.* **9,** 375 (1967).

9. Lewis, M. S., and Wills, G. B., *J. Catal.* **15,** 140 (1969).

10. Luckner, R. C., McConchie, G. E., and Wills, G. B., *J. Catal.* **28,** 63 (1973).

11. Lin, C. J., Aldag, A. W., and Clark, A., *J. Catal.* **45,** 287 (1976).

12. Davie, E. S., Whan, D. A., and Kemball, C., *J. Catal.* **24,** 272 (1972).

13. Rosynek, M. P., and Hightower, J. W., *in* "Proceedings, 5th International Congress on Catalysis, Palm Beach, 1972" (J. W. Hightower, Ed.), Vol. 2, North-Holland, Amsterdam, 1973, and earlier references cited therein.

14. Larson, J. G., and Hall, W. K., *J. Phys. Chem.* **69,** 3080 (1965).

15. Millman, W. S., and Hall, W. K., *J. Catal.* **59,** 311 (1979).

16. Millman, W. S., and Hall, W. K., *J. Phys. Chem.* **83,** 427 (1979).

17. Kokes, R. J., and Dent, A. L., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 22, p. 1. Academic Press, New York, 1972, and earlier references cited therein.

18. Engelhardt, *J. Rec. Trav. Chim. Pays Bos* **96,** M-101 (1977).

19. Siegel, S., *J. Catal.* **30,** 139 (1973).

20. Fransen, T., Van der Meer, O., and Mars, P., *J. Phys. Chem.* **80,** 2103 (1976).

21. Hashimoto, K., Watanabe, S., and Tarana, K., *Bull. Chem. Soc. Japan* **49,** 12 (1976); *Nippon Kagaku Kaishi,* 409 (1974); *Nippon Kagaku Kaishi,* 591 (1975).

22. Howe, R., and Kemball, C., *J. Chem. Soc. Faraday Trans. 1* **70,** 1153 (1974).