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Hydrogenation of Ethylene over Molybdena–Alumina Catalysts

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The hydrogenation of ethylene was studied at 25 and −76°C over a molybdena–γ-alumina (8% Mo) catalyst which had been reduced to different extents (from 0.2 to 1.6 e/Mo). Both a static reactor (with recirculating gas) and a microcatalytic pulse reactor were used in this work. The catalytic activity increased with the extent of reduction of the catalyst. Nearly 100% $C_2H_4D_2$ was obtained from a 1:1 mixture of C_2H_4 and D_2 as the initial product at low and intermediate extents of reduction (in the circulation system). At the highest extent of reduction, ethane-d_2 was still the chief deuterated species but now accounted for only 60% of the initial products. Similar results were obtained with less reduced catalysts when the D_2/olefin ratio was greatly increased and with the pulse reactor. In all cases, the unreacted ethylene showed very little exchange. These results are discussed in terms of the current literature. It is suggested that formation of a carbene intermediate is responsible for the multiple exchange pattern. The relationship of the results to polymerization and olefin metathesis is pointed out.

INTRODUCTION

Molybdena–alumina catalysts are used for both hydrodesulfurization and for coal liquefaction. Consequently, knowledge about their catalytic properties has become a matter of increasing importance. The present work is concerned with the mechanism of the catalytic hydrogenation of the simplest olefin available, C_2H_4.

The catalytic hydrogenation of ethylene over metals has been widely studied and certain generalities have been developed. The reaction is thought to occur via the following steps:

$$H_2(g)+2_* \rightleftarrows 2H\text{-}_*, \tag{1}$$

$$C_2H_4(g)+2_* \rightleftarrows {}_*\text{-}CH_2\text{-}CH_2\text{-}_*, \tag{2}$$

$$_*\text{-}CH_2\text{-}CH_2\text{-}_* + H\text{-}_* \rightleftarrows 2_* + {}_*\text{-}CH_2\text{-}CH_3, \tag{3}$$

$$_*\text{-}CH_2\text{-}CH_3 + H\text{-}_* \rightarrow 2_* + C_2H_6(g). \tag{4}$$

In accordance with this scheme, the reaction of C_2H_4 with D_2 leads to multiple exchange of the ethylene and a distribution of ethanes of the form $C_2H_{6-x}D_x$, due to the reversibility of steps 2 and 3. A characteristic of this distribution is the appearance of sizable amounts of $x = 0$ and $x = 1$ ethanes and a nearly binomial distribution over higher values of x. Active hydrogenation catalysts are also effective in H_2–D_2 equilibration, although not during hydrogenation. This is consistent with the implied dissociative adsorption of hydrogen in the above scheme. However, if this is the general behavior over metals, some exceptions have been reported in which the starting reactant was only slightly ex-

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changed and the hydrogenated product was mainly dideuterated (*1*, *2*).

In contrast with the many detailed studies of the hydrogenation of C_2H_4 over metals, relatively little work has been done with oxides. It has been shown that some transition-metal oxides such as Cr_2O_3 (*3*), Co_3O_4 (*4*, *5*), ZnO (*6*, *7*), TiO_2 (*8*), and NiO (*9*) catalyze the hydrogenation of ethylene and the exchange of H_2 with D_2 when the oxide has been pretreated at elevated temperature, e.g., 500°C. A characteristic feature of the hydrogenation of ethylene over oxide catalysts is the preservation of molecular identity of hydrogen in the product ethane, e.g., the reaction of C_2H_4 with D_2 results in 1,2-dideuterioethane as almost the sole product.

The present work was undertaken to determine whether the main features of the reaction over reduced molybdena–alumina catalysts are similar to those over the unsupported oxides. Hall and Lo Jacono (*10*) have studied the reduction of this catalyst and have generated a model describing its surface chemistry. The model characterizes the surface in terms of the amount of hydrogen held irreversibly and the number of oxygen vacancies, □, related to Mo^{+4}. By varying the extent of reduction, catalysts having defined surface chemistry can be prepared. It was of interest to characterize the activity and exchange patterns for these different surfaces for the deuteration of ethylene.

EXPERIMENTAL

Catalyst Pretreatment

The catalyst and procedures were those developed earlier (*10*). Dry O_2 was passed through the reactor overnight at 500°C to remove possible adsorbed hydrocarbons from the catalyst. After evacuation for 40 min at this temperature, a known amount of H_2 was admitted and circulated over the catalyst. The drop in pressure was measured and at the end of the reduction the catalyst was evacuated for 90 min. The average extent of reduction (below Mo^{+6}), reported as H_e/Mo, was calculated from the amount of H_2 consumed in the reduction by substracting the amount of reversible adsorption (H_R). Alternatively, the extent of reduction is also given as e/Mo (where e/Mo is the average number of electrons placed on Mo^{+6}, i.e., $e/Mo = 1.0$ means the average valence state is Mo^{+5}, although Mo^{+6}, Mo^{+5}, and Mo^{+4} may all be present simultaneously). This symbolism was adopted so that the extents of reduction obtained when CO was used as the reducing agent could be compared with those for H_2. The amounts of hydrogen irreversibly held (H_I) and the vacancies produced were estimated using graphs obtained in an earlier work (*10*). The following relationship holds:

$$H_e/Mo = e/Mo = 2\square/Mo + H_I/Mo.$$

In some cases CO was used as a reducing agent instead of H_2. The procedure was exactly the same although the calculations were slightly different. A portion of the CO was irreversibly adsorbed in a way analogous to H_I.

Reactants

C_2H_4 was Matheson research grade. The C_2D_4 was prepared by exchanging C_2H_4 and D_2 over a very pure γ-alumina following the procedure reported by Larson *et al.* (*11*). Deuterium was purified by diffusion through a Pd thimble.

Procedure

(*i*) *Circulation system.* The experiments were conducted either at room or at dry-ice temperature in an all-glass recirculating system. The gases were pumped over a catalyst and into a mixing chamber which contained about 95% of the system volume. The exit stream from this could be sampled for glc analysis. Less than 1% of the circulating gas was removed for each analysis.

Percentage conversion was calculated as 100 multiplied by the fraction of ethane in ethane plus ethylene. The reactant mixtures were prepared by introducing a measured amount of ethylene first into the circulation system, where it was frozen and outgassed before H_2 and/or D_2 were admitted in the desired amounts. Except where otherwise indicated a $H_2:C_2H_4 \simeq 1:1$ ratio was used. The gases were thoroughly mixed before contacting the catalyst.

(*ii*) *Pulse reactor.* The same reactor and glc column used for the static experiments (recirculating system) could be connected to a microcatalytic pulse system. Pulses of ethylene were injected into the hydrogen carrier gas using a 1.15-ml doser and were passed over the catalyst at 1 atm of total pressure. The products emerging from the catalyst were collected in a −195°C trap for 20 min and then flashed into the chromatographic column. The separation of ethane and ethylene was achieved in a 4 ft × 0.25 in. (o.d.) Durapak 80- to 100-mesh column thermostated at −20°C.

The H_2–HD–D_2 mixtures were analyzed using a 6 ft × 0.25 in. column packed with an Fe^{+3}-doped alumina (*12*). To increase the sensitivity, the hydrogen was converted to water over CuO at 550°C before entering the detector.

Mass Spectrometric Analysis

Provisions were made to recover the products at the exit of the glc column for mass spectrometric analysis. The ethylenes were analyzed at 11 eV to minimize the peaks due to fragmentation. In the case of ethane the ionization potential of the molecular ion does not differ significantly from the appearance potential of ethylene ion; hence the elimination of fragmentation peaks was not possible. Therefore, the mass spectra were obtained at 70 eV where calibrations were made with C_2H_6 and C_2D_6. The cracking patterns for the other exchanged ethanes were calculated from these data using the method of Amenomiya and Pottie (*13*).

RESULTS

Surface Stability of Reduced Mo–γ-Alumina toward Further Reduction

It was essential to choose reaction conditions for the hydrogenation experiments such that the catalyst would not undergo further reduction by reaction with H_2 during the period of an experiment. To check this, the catalyst was reduced to a certain extent at say 500°C and then quenched to 0°C, and the H_2 was circulated for 1 hr at this lower temperature. If no change in pressure was detected, the temperature was increased in a stepwise fashion each hour until a temperature was reached at which reduction became apparent. This was repeated for different extents of reduction ranging from 0.2 to 1.8 e/Mo. It was concluded that by working below approximately 200°C, no appreciable further reduction occurred even at low extents of reduction, where the catalyst was most susceptible to further reduction.

Adsorption of Reactants

Ethylene was adsorbed at 25°C on a catalyst reduced to an intermediate extent (e/Mo = 1.1). Initially 23 ml/g of C_2H_4 were admitted at a pressure of 40 Torr. The ethylene uptake was rapid during the first few minutes, but slowed down considerably during the first hour. The ethylene which disappeared from the gas phase could not be recovered by evacuation at room temperature into a liquid nitrogen trap. Moreover, readmission of an equal amount of ethylene led to further irreversible adsorption by the catalyst, although at a slower rate. The initial adsorption corresponded to about one C_2H_4 for each Mo (total Mo = 5.08×10^{20} atoms/g of catalyst). Since the introduction of more C_2H_4 led to a further uptake, and since all of the Mo ions were not involved, it may be deduced that polymerization of ethylene took place. Further characterization was not attempted because it has been known for a long time that molybdena–alumina catalysts are active for ethylene polymerization (*14*).

The adsorption of H_2 was measured at 25°C on a catalyst reduced at 500°C to 1.1 e/Mo. The isotherm between 75 and 500 Torr was approximately linear and at the highest pressure the adsorption was about 0.3 ml of H_2/g. After desorption for 1 hr at 25°C the isotherm was repeated. The difference between the two curves gave the amount of strongly chemisorbed hydrogen held by the catalyst at room temperature (0.1 ml of H_2/g). The data suggest two types of hydrogen adsorptions: one weak and reversible and the other strong and irreversible. Similar observations have been reported by Dent and Kokes (*6*) for ZnO and Tanaka *et al.* (*4*) for Co_3O_4. The amount of the strong adsorption corresponds to less than 1% of the Mo in the catalyst.

Blank Tests

Neither the γ-alumina support pretreated in the same way nor the oxidized molybdena–alumina catalyst hydrogenated ethylene at 25°C. Amenomiya reported (*15*), however, that preadsorbed C_2H_4 could be hydrogenated from alumina in this temperature range. Over a catalyst reduced to 1.5 e/Mo, ethane-d_0 did not exchange with D_2 at room temperature.

Hydrogenation of Ethylene in the Circulating System

(*a*) $C_2H_4 + D_2$. All the experiments in this series were carried out with an equimolecular mixture of reactants (130 ml). The reduced catalysts were found to be very active for the hydrogenation of ethylene. Products other than ethane were not detected in the gas phase in most cases. Significantly, in runs with highly reduced catalysts, however, small amounts of propane were found.

The rate of hydrogenation increased with the extent of reduction, which was varied between 0.87 and 1.62 e/Mo (decrease in average valence below Mo^{+6}). The rate of the reaction fell during a run. In one experiment, after a standard run of 1 hr, the reactor was evacuated for an additional hour and the experiment was repeated. The second run was definitely slower than the first confirming the deactivation. This could be explained by blocking of active sites due to strongly adsorbed or polymerized ethylene.

Figures 1 and 2 show the isotopic distributions in the ethane products versus the percentage conversion for various extents of reduction. At low extents (up to about 1 e/Mo) the only initial product (at 0% conversion) was $C_2H_4D_2$. At still higher extents of reduction, this compound was no longer the only species formed at low conversion, but it was still the chief product (over 60%). To avoid confusion, the small amounts of ethane-d_4 formed at higher extents of reduction are not shown in Fig. 2.

The first row of data in Table 1 gives the complete distribution data for the run with highest extent of reduction. Note that even after 44% conversion the ethylene is very little exchanged. The tracer data suggest that ethylene, once adsorbed, does not desorb; it leaves the catalyst only as ethane. The principal reaction is apparently simple 1–2 addition, but at higher extents of reduction another exchange process is superimposed which results in formation of multideuterated ethanes.

(*b*) C_2H_4:C_2D_4 + H_2:D_2. To characterize further the reaction at higher extents of reduction an experiment was made in which the different isotopic compounds were mixed in equimolecular amounts (30 ml of each reactant). The mixtures were prepared in a gas burette with a maximum error of 2%. The catalyst had been reduced to 1.45 e/Mo with a mixture of H_2 and D_2 and the reaction temperature was 25°C. The results are shown in the second row of Table 1.

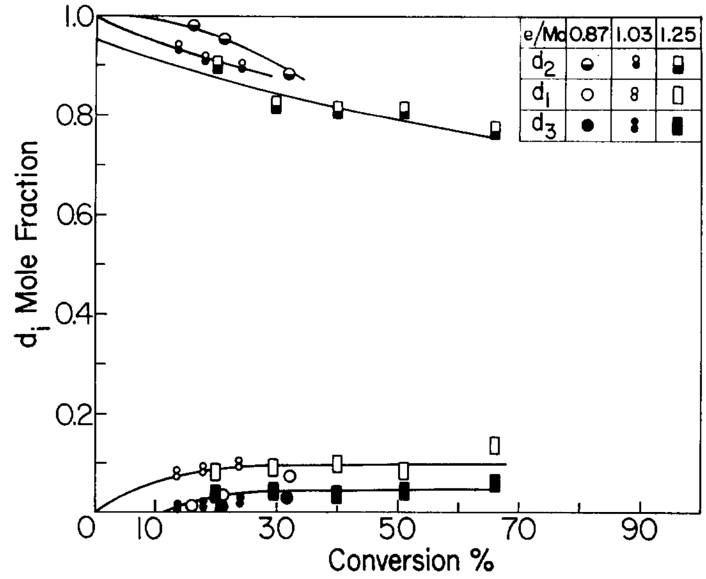


FIG. 1. Isotopic distribution in ethanes produced by reactions of C_2H_4 with D_2 over reduced Mo–γ-Al_2O_3 catalysts. Closed recirculation system: 130 ml of a 1:1 mixture of reactants, 1 g of Mo–Al_2O_3 catalyst, 25°C.

The ethane product was nearly equilibrated although the distribution was displaced toward the hydrogen end. Note particularly, the very small amounts of d_0- and d_6-ethanes produced, as these were expected to be primary products. On the other hand, the ethylene product was essentially unexchanged in agreement with the results given above. No isotope effect between C_2H_4 and C_2D_4 was found. Following the above experiment, the catalyst was evacuated for 4 hr (residual pressure $\leq 10^{-5}$ Torr)

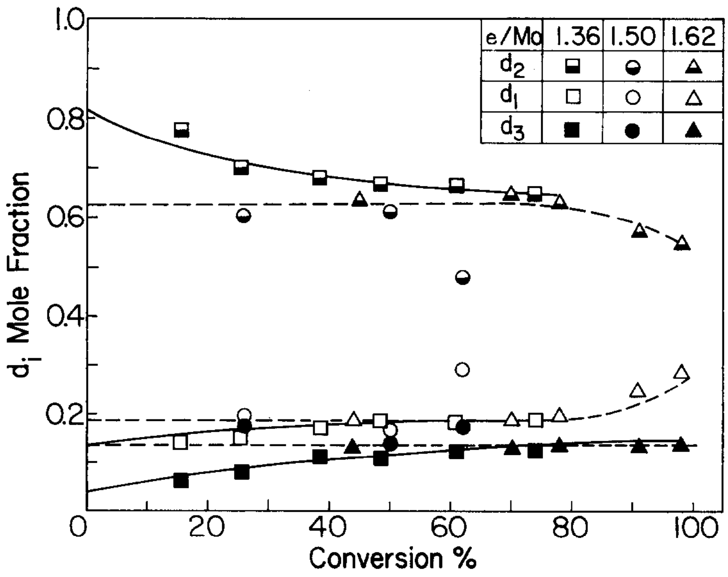


FIG. 2. Isotopic distribution in ethanes produced by reaction of C_2H_4 with D_2 over highly reduced catalysts. Reaction conditions identical to those in Fig. 1.

TABLE 1

Ethylene Hydrogenation over Mo(8%)–γ-Al_2O_3 Catalyst[a]

Reactant	Extent of reduction[b]			Reaction temperature	Conversion (%)	Reaction system	Ethylene					Ethane						
	$\frac{H_c}{Mo}$	$\frac{\square}{Mo}$	$\frac{H_I}{Mo}$				d_0	d_1	d_2	d_3	d_4	d_0	d_1	d_2	d_3	d_4	d_5	d_6
$C_2H_4 + D_2$ (1:1)	1.62	0.63	0.36	25	44.0	Recirculation	97	3	—	—	—	—	19.0	64.0	13.5	3.5	—	—
$C_2H_4 + C_2D_4 + H_2 + D_2$ (1:1:1:1)	1.45	0.48	0.5	25	21.3	Recirculation	52.0	—	—	5.0	43.0	0.8	18.1	37.0	17.5	14.5	7.7	4.4
					72.6		52.3	0.3	0.4	5.4	41.6	1.0	17.3	38.1	17.5	14.0	7.6	4.5
$C_2H_4 + H_2 + D_2$ (1.0:0.5:0.5)	1.45	0.48	0.5	25	42.0	Recirculation	99.6	0.4	—	—	—	37.5	44.4	16.7	1.4	—	—	—
					84.5		99.2	0.8	—	—	—	40.2	41.9	16.5	1.4	—	—	—
$C_2H_4 + D_2$ (1:5)	1.13	0.36	0.5	−78	76.0	Recirculation	95.9	2.4	1.7	—	—	—	10.6	61.9	17.3	8.4	1.8	—
$C_2D_4 + H_2$ (carrier)	1.52	0.5	0.5	25	100.0	Pulse	—	—	—	—	—	—	3.0	17.4	18.8	58.6	1.2	1.0
$C_2D_4 + H_2$ (carrier)	0.35	0.09	0.17	25	16.1	Pulse	—	—	0.6	9.7	89.7	—	2.9	17.8	19.1	57.8	1.3	1.1
C_2D_4 (starting material)										9.6	90.4							

[a] One gram of catalyst was used in all experiments. In recirculation experiments, 120–130 ml of reactant was used. In the pulse experiments, the H_2 flow rate was 60 ml/min, and the slug size, 0.42 ml.

[b] $\square/Mo$ and H_I/Mo calculated from Fig. 1 of Ref. (*10*). $H_c/Mo = e/Mo = 2\square/Mo + H_I/Mo$.

and then treated with O_2 at 500°C in the circulating system. CO_2 and H_2O were trapped at $-195°C$ and then separated by distillation. At $-78°C$, 14.8 ml of CO_2 were recovered corresponding to 7.4 ml of ethylene strongly adsorbed. The water formed, which came from both combustion and surface oxidation, was analyzed mass spectrometrically giving the following results: $H_2O = 36.1\%$, $HDO = 45.4\%$, $D_2O = 18.5\%$.

(*c*) $C_2H_4 + H_2{:}D_2$. This experiment was designed to determine whether hydrogen is consumed faster than deuterium during hydrogenation. That this was so is shown by the data contained in the third row of Table 1. The data also suggest that HD formed by exchange of H_2 with D_2 becomes an important reactant.

(*d*) $C_2H_4 + 5D_2$. This experiment over the catalyst reduced to 1.13 e/Mo was run at $-78°C$ because otherwise the reaction was too fast. The results shown in line 4 of Table 1 were similar to those obtained at higher extents of reduction, but with lower hydrogen concentrations, i.e., with high hydrogen to olefin ratios, ethane-d_2 was not the only initial product. The ethylene was, as always, very slightly exchanged.

(*e*) *Exchange among olefin, deuterium, and hydrogen.* The experiments reported in Table 2 were performed so as to assay the H_2–D_2–HD composition remaining in the gas phase (by glc) to compare with the deuterium distributions in the ethanes formed.

(*i*) $C_2H_4 + H_2{:}D_2$. The data in the first row of Table 2 show that a rapid equilibration occurs between H_2 and D_2. However, this equilibration involves the participation of adsorbed olefin hydrogens as shown by the excess H_2 and HD over D_2. C_2H_5D was a chief product.

(*ii*) $C_2H_4 + D_2$. The previous experiment explained the appearance of important amounts of ethane-d_1 and -d_0 in terms of rapid olefin–H_2–D_2 exchange processes. To check this explanation an experiment was made with the catalyst reduced to 0.95 e/Mo. Figure 1 shows that in this case ethane-d_2 was the only product at 0% conversion. Consistent with this behavior the second experiment in Table 2 showed very little HD formed at low conversions. Above 50% conversion, however, the exchange had become sufficient to produce some ethane-d_1 and -d_3.

H_2–D_2 *Exchange*

In a separate experiment the exchange of H_2 with D_2 was studied at 25 and $-78°C$. In both cases the exchange was very fast and only a lower limit for the rate of exchange could be estimated (in the first case the system was already at equilibrium within 12 min).

After reduction to 1.5 e/Mo and evacuation at 500°C the catalyst still retained 4.5 ml of H_2 strongly adsorbed (H_I). This hydrogen was not exchanged to any measurable extent with the gas-phase hydrogen at temperatures below 25°C. It was necessary to increase the temperature above 250°C before H_I began to exchange into the gas phase. Evidently, H_I does not function in the hydrogenation reaction.

D_2-*Reduced Catalyst*

In order to ascertain the role of D_I in the hydrogenation of ethylene, an experiment was made in which the catalyst was reduced to 1.02 D_e/Mo. This catalyst contained 4.5 ml of D_2 irreversibly adsorbed. A mixture of 10 ml of C_2H_4 and 10 ml of H_2 was then reacted over the catalyst at 25°C. No trace of deuterated ethylenes or ethanes was detected. The limit of detection was below 0.5%. This was consistent with the previous experiment and demonstrated that irreversibly adsorbed hydrogen was not involved in the hydrogenation reaction at room temperature.

Diffusion Limitations

The low exchange in ethylene compared with the product ethanes suggested that

TABLE 2

Ethylene and H_2–D_2 Exchange over $Mo(8\%)$–γ-Al_2O_3[a]

Reactant	Extent of reduction[b]			Reaction temperature (°C)	Conversion (%)	Reaction time (min)	Ethylene			Ethane				H_2	HD	D_2
	$\frac{H_0}{Mo}$	$\frac{\square}{Mo}$	$\frac{H_1}{Mo}$				d_0	d_1	d_2	d_0	d_1	d_2	d_3			
$C_2H_4 + H_2 + D_2$ (1.0:0.5:0.5)	1.45	0.48	0.5	25	86	17	98.0	1.7	0.3	39.8	40.1	18.9	1.2	44.1	40.3	15.6
$C_2H_4 + D_2$ (1.0:1.0)	0.95	0.24	0.47	25	10.2	45	99.8	0.2	—	—	1.1	98.9	—	—	1.8	98.2
					54.1	220	98.5	1.5	—	0.2	9.7	85.8	4.3	1.7	16.4	81.9
$H_2 + D_2$ (1.0:1.0)	1.48	0.48	0.5	−78	80	12								31.2	39.5	29.3
$H_2 + D_2$ (1.0:1.0)	1.5	0.5	0.5	25	98	12								25.5	48.8	25.7

[a] Recirculation reactor. The same reaction conditions as in Table 1.

[b] See Table 1.

pore-diffusion limitations may have played a role in this system. To check for this, one experiment was made using 100-mesh catalyst particles reduced to 1.5 e/Mo. A mixture of $C_2H_4 + D_2$ was reacted over this catalyst, but the results were the same as those obtained with 40-mesh particles.

Hydrogenation of Ethylene in the Microcatalytic Pulse Reactor

(*a*) *Catalytic activity.* A series of experiments was performed at room temperature with catalysts reduced to various extents with either H_2 or CO. These results are presented in Fig. 3 as percentage conversion versus slug number. A couple of interesting phenomena appeared. Catalysts reduced with CO were at least as active as those reduced with H_2. With the very active catalyst having the highest extent of reduction, the activity did not decline with slug number, i.e., the reaction did not appear to be self-poisoning. With the different lower extents of reduction, however, an abrupt decay in activity occurred between the first and second slugs. This was followed by a continuous, but much slower decrease in activity. The catalyst having the lowest extent of reduction also escaped this initial decay.

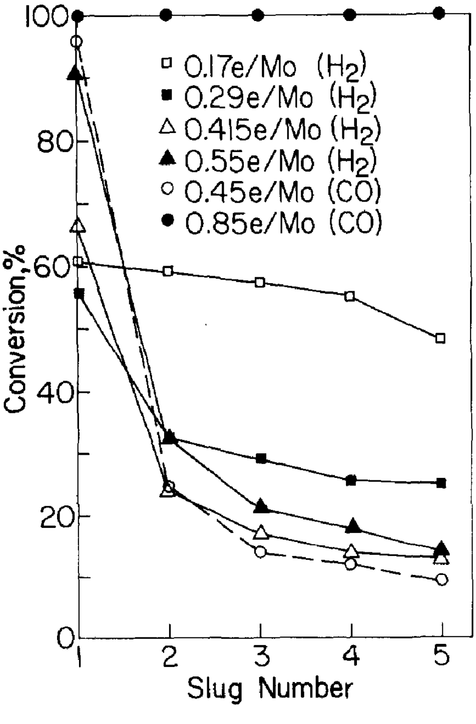


FIG. 3. Hydrogenation of C_2H_4 in microcatalytic pulse experiments. Slug size, 0.42 ml was 1.13×10^{19} molecules; 1 g of catalyst; H_2 flow rate = 60 ml/min; reaction temperature, 25°C.

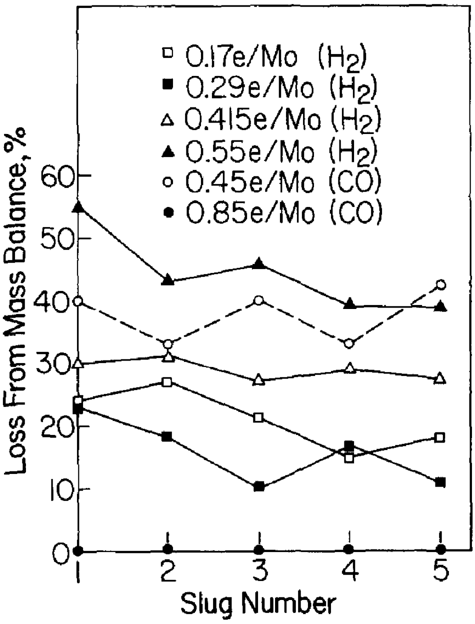


FIG. 4. Loss from mass balance in experiments shown in Fig. 3, given as percentage of the ethylene reactant. A 10% loss per slug corresponds to 1.13×10^{18} molecules of C_2H_4.

Figure 4 presents the data on the carbon mass balance for the different experiments. At a high extent of reduction where the conversion was complete, no loss was detectable. When the conversion was below 100%, however, the mass loss correlated with the extent of reduction and was about the same for each slug. The disappearance of ethylene in these experiments was consistent with results obtained in the circulation system. Three additional experiments made with catalysts reduced at 0.85 or higher extents of reduction also yielded 100% conversion with no detectable mass balance loss.

(*b*) *Tracer experiments.* Two experiments were performed using C_2D_4 as reactant in the flowing H_2 carrying gas stream. The data are shown in the last two lines of Table 1. The deuterium distributions in the products were quite similar even though the activity levels were quite different, corresponding to a small extent of reduction in one case and extensive reduction in the other. (With the latter the ethylene was totally converted to ethane.) Ethane-d_4 was the chief product as expected, but d_3 and d_2 ethanes were also major products. As usual, the ethylene was essentially unexchanged.

The similarity between the ethane distributions for the microcatalytic experiments (H_2 flow) with that for the experiment in the circulating system with the D_2:C_2H_4 = 5:1 (line 4 of Table 1) should be noted.

DISCUSSION

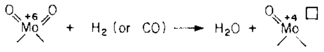
The kinetic and tracer studies of ethylene hydrogenation over molybdena–alumina revealed some important features of the hydrogenation mechanism. These bear upon the formation of active sites and on the behavior of the adsorbed species. They have extended our knowledge of the behavior of different oxide systems for the catalytic hydrogenation of olefins.

At room temperature in the absence of hydrogen, in contrast with the results for ZnO (*6*), ethylene was irreversibly adsorbed. The large amount of C_2H_4 retained by reduced molybdena–alumina suggested that polymerization had occurred. Furthermore, the data in Fig. 4 indicate that, even in presence of hydrogen, part of the reacting ethylene was strongly retained by the catalyst under reaction conditions. The polymerization ability of molybdena–alumina is well known (*14*). In fact, recent studies reported by Hashimoto *et al.* (*16*) have shown that a high-density linear polymer is formed from ethylene. This work was carried out under conditions very similar to those used here (200 Torr, 0–70°C) and with the catalyst reduced with either H_2, CO, or Na metal. No difference was found in the behavior of the catalyst with different reducing agents. This means that the polymerization must occur via an insertion mechanism, rather than by acid catalysis. This is interesting because our catalyst isomerized cyclopropane readily below 100°C (*17*), i.e., it has a strong Brönsted acid function.

Reduced molybdena–alumina had a much higher activity for the hydrogenation of ethylene than that reported for Co_3O_4 (*4*), ZnO (*6*), and TiO_2 (*8*); it was comparable to that of activated chromium oxides (*3*). The main character of the results nevertheless corresponded quite well to that for ZnO (*6*) (see below).

The decline of the catalytic activity during the course of the reaction and between runs was probably due to the ethylene polymerization mentioned above. Fukushima and Ozaki (*5*) recently reported that C_2H_4 was strongly adsorbed on Co_3O_4, but no decline in catalytic activity occurred between runs. When H_2 was chemisorbed before the reaction, however, a sharp decline in the strongly adsorbed C_2H_4 was observed.

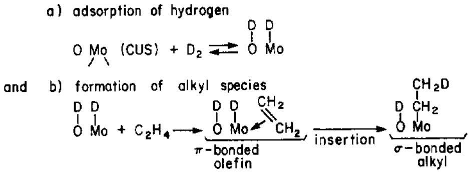
The increase in hydrogenation rate with increasing extent of reduction suggested that the active sites were coordinatively unsaturated molybdenum sites (CUS) generated during reduction. The Mo ions in the unreduced catalyst may reside in either tetrahedral or octahedral coordination (with the surrounding O^{-2}) and the CUS would be expected to form at these ions. The reduction of tetrahedral Mo^{+6} is illustrated below, based on the picture presented by Hall and Lo Jacono (*10*).



(5)

In this scheme, □ represents an anion vacancy created by formation of H_2O. A similar picture could be drawn for the octahedral sites. The active site participating in the first step of the reaction scheme could be this CUS Mo^{+4} species.

Aside from the higher activity of molybdena–alumina for hydrogenation, the main character of the results resembled those of Dent and Kokes (*6*) for ZnO. Ethane was formed largely by molecular addition, and exchanged ethylenes did not appear in the gas phase (no alkyl reversal). Consequently, it seems justified to write the following.

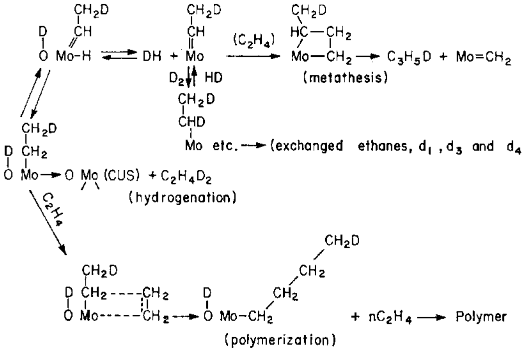


(6)

(7)

Reaction 6 is the well-documented heterolytic dissociation of H_2 which occurs on ZnO (*6, 7*) and presumably on Cr_2O_3 (*3*) and Co_3O_4 (*4, 5*). As with ZnO, C_2H_4 may become π-bonded at a second vacant ligand position and insert to form the alkyl as indicated by reaction 7. In any case the adsorption of olefin is very strong as evidenced by the fact that very little exchanged ethylene appeared in the products.

The major differences which appeared when molybdena–alumina was used instead of other metal oxides can be interpreted in terms of three parallel pathways involving intermediates formed as follows.



(8)

(9)

(10)

Metathesis and exchange with D_2 occurred presumably via the transformation of the metal alkyl intermediate to the metal carbene intermediate. This transformation was recently suggested by Laverty *et al.* (*18*), based on analogy with their results with homogeneous catalysts. An important role for metal hydrides was envisioned for various catalysts including all those discussed here. Supporting this scheme is the fact that, in the absence of hydrogen, reduced molybdena–alumina is a good metathesis catalyst (*17*). Even in the presence of H_2, when a 50–50 mixture of C_2H_4 and *cis*-C_4H_8 was hydrogenated over a highly reduced $Mo–Al_2O_3$ catalyst, propane appeared in the gas phase (*19*).

Reaction (8) provides an explanation for the exchange patterns found at high extents of reduction. The desorption of the olefin is not allowed; consequently extra deuterium atoms may be introduced into the alkyl intermediate and hence into the ethane product without deuteration of the reactant ethylene. Moreover, the combination of reactions (8) and (9) would yield ethane-d_1, -d_2, -d_3 and -d_4; no ethane-d_0, -d_5, or -d_6 should be produced. The experimental distribution for a catalyst reduced to 1.62 e/Mo was $d_1 = 19\%$, $d_2 = 62\%$, $d_3 = 14\%$, $d_4 = 5\%$; d_0, d_5, and d_6 were absent. Metathesis utilizing the carbene intermediate formed in reaction (8) may be the source of the very small amounts of propane detected when the ethylene hydrogenation proceeded on a highly reduced catalyst.

In the pulse experiments C_2D_4 was hydrogenated in a large excess of flowing H_2. The H_2/olefin ratio on the surface may be even larger than in the circulation experiment with D_2/olefin = 5. In this experiment, according to the mechanism, ethand-d_4 should be the principal product, with ethane-d_3 and -d_2 being formed by exchange. Much smaller amounts of ethane-d_5 would be produced from the HD formed by exchange, as well as some -d_3 and -d_2 from the 9.6% ethylene-d_3 impurity in the reactant. The last two rows of Table 1 are consistent with these predictions.

Reaction (10) provides a possible route for formation of linear polyethylene as observed (*16*). Polymerization should lead to catalyst poisoning, especially in the absence of H_2 as has been observed (*17*).

An increase in extent of reduction favored hydrogenation. It also favored the metathesis reaction in the absence of gas-phase hydrogen (17, 19). Polymerization (residue formation) was also greater the more the catalyst was reduced. In the presence of H_2, hydrogenation was the fastest reaction. All these results are consistent with the proposed reaction scheme. When more and/or stronger CUS sites become available, reaction (6) will be displaced toward the right. This means that higher concentrations of the metal alkyl intermediate can be formed on the surface, thus promoting reactions (8)–(10). Propane (or propylene) should be formed to a very limited extent as found experimentally.

The effects produced by changing the H_2/olefin ratio may also be understood. An increase in the partial pressure of H_2 will displace reaction (6) toward the right making possible the formation of a larger number of alkyl intermediates. Reactions (8) and (9) should now be favored over (10).

The results shown in the first row of Table 2 are also consistent with reaction (8). The composition of the H_2–HD–D_2 mixture could not have been obtained from the reactant H_2 and D_2; it contained excess hydrogen which came from the olefin. Similarly, the second row of Table 2 shows that at lower extents of reduction the C_2H_4–D_2 exchange occurred much more slowly.

The H_2–D_2 exchange data fit nicely into the developing picture for metal oxides. After reduction and evacuation at 500°C the catalyst retained substantial amounts of bound hydrogen or carbon monoxide (H_I or CO_I). The data showed that H_I was not directly involved in the hydrogenation of olefins at the temperatures studied. Recently Massoth (*20*) inferred from kinetic studies that H_I was not involved in thiophene hydrogenolysis over a sulfided Mo/Al_2O_3 catalyst. Both the CO- and H_2-reduced catalysts had the same activity for a given extent of reduction. Furthermore, the H_2–D_2 exchange experiments proved that H_I was not exchanged below 250°C. This was consistent with the results obtained with both ZnO (*6*, *7*) and Co_3O_4 (*4*, *5*) where it was shown that strongly adsorbed hydrogen was present which did not intervene in the hydrogenation reaction at room temperature. It may be convenient to think of this as reductively adsorbed hydrogen in contrast with the heterolytically held gas used for hydrogenation.

Siegel (*21*) developed a model for olefin hydrogenation and exchange based on catalytic results for Co_3O_4 (*4*) and Cr_2O_3 (*3*).

He attributed the higher activity of these oxides to the existence of CUS sites having two or three vacant ligand positions. The model was derived by analogy with the chemistry of organometallic homogeneous catalysts and required that H_2 be oxidatively dissociated on transition ion centers. However, as pointed out recently by Burwell and Stec (*22*), oxidative chemisorption has not been demonstrated for heterogeneous systems, and, in homogeneous systems, it seems to be restricted to ions in low valence states. Nothing in the present work, nor in that of Burwell and Stec (*22*), suggested anything different from the well-known heterolytic cleavage found for ZnO (*6*, *7*). Moreover, Fukushima and Ozaki (*5*) failed to find evidence for the required type CH sites (*21*) when studying the H_2–D_2 exchange over Co_3O_4. In fact preadsorption of H_2 in Co_3O_4 reduced the activity of this catalyst for H_2–D_2 exchange at −196°C against predictions of the Siegel model. Since no drastic change occurs in the H_2–D_2 activity of the different metal oxides, hydrogen activation and probably the hydrogenation of olefins may occur through the same sort of mechanism over all of them. The basic requirements are the CUS *and* the electrons needed for bonding.

In summary, the hydrogen activation step seems to proceed in this system in the same way as with other metal oxides. The main difference found was the unique ability of the Mo catalyst (among the metal oxides studied so far) to form carbenes and catalyze the metathesis reactions. This provides an alternative to alkyl reversal for exchange. The mechanism presented here emphasizes the importance of a single intermediate for hydrogenation, exchange, metathesis, and, perhaps, polymerization. It is in agreement with the views recently advanced by Laverty *et al.* (*18*).

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