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Cyclopropane Hydrogenolysis on Clean and Chemically Modified Mo(100) Surfaces

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Catalytic hydrogenolysis of cyclopropane (CP) to propane, ethane, and methane has been investigated over initially clean Mo(100) single-crystal surfaces and over surfaces chemically modified by adsorbed carbon, oxygen, and sulfur. Catalyst preparation was performed in ultrahigh vacuum with surface characterization by LEED and Auger. Catalytic hydrogenolysis under 1 atm pressure was monitored by gas chromatography. Initially clean Mo(100) surfaces and surfaces modified by 1 ML of atomic carbon or oxygen are active for single hydrogenolysis to propane and double hydrogenolysis to ethane and methane. The Mo(100) surface with 0.8 ML of sulfur is completely inactive. The reaction is first order in hydrogen and zero order in CP. The activation energy, determined from Arrhenius plots over the temperature range 300–523 K, is 37 ± 4 kJ/mol and is the same for all active surfaces. The product distribution (ca. 17% CH_4, 17% C_2H_6, and 66% C_3H_8) is also the same for all active surfaces and is independent of temperature. The initially clean Mo(100) surface is ca. five times more active than either the carbon- or oxygen-modified surfaces which have approximately the same activity. Since the selectivity of CP hydrogenolysis has previously been shown to be sensitive to Mo chemical state, the data indicate that the same catalytic site is operative on all active surfaces. Comparison to literature data for supported Mo catalysts indicates that the observed selectivity is characteristic of low-valent Mo rather than of the oxide or carbide. Prior knowledge that adsorbed carbon and oxygen block fourfold hollow sites on the (100) crystal plane coupled with the higher activity observed for initially clean Mo(100) suggests (1) that the active sites for hydrogenolysis are open fourfold hollows and (2) that the open hollow sites are present as defects on the carbon- or oxygen-modified surfaces. The catalysts are inactive for hydrogenolysis of propane, indicating that CH_4 and C_2H_6 are primary products. Likewise, propene is not an intermediate since propene conversion in H_2 is exclusively to propane and metathesis products. The absence of the C_4 products of metathesis from cyclopropane suggests that hydrogenolysis does not proceed via a metallacyclobutane surface intermediate. Therefore, the most likely mechanism involves a 1,3-diadsorbed surface intermediate. © 1989 Academic Press, Inc.

INTRODUCTION

In this paper we report on an experimental investigation of cyclopropane hydrogenolysis catalyzed by the clean (100) crystal plane of molybdenum and by Mo(100) surfaces modified with monolayers of carbon, oxygen, and sulfur. Cyclopropane hydrogenolysis provides a means for investigating both catalyst activity and selectivity. Two parallel reactions occur on Mo at temperatures below 700 K: ring opening (single hydrogenolysis, hydrogenation) with addition of one molecule of H_2 to form propane, and fragmentation (double hydrogenolysis) with addition of two molecules of H_2 to form equal amounts of CH_4 and C_2H_6. Complete fragmentation to methane is not observed on Mo catalysts.

The surface structure and chemisorption properties of oxygen, carbon, and sulfur overlayers on Mo(100) have been characterized previously (*1–16*). Ion scattering and LEED (low energy electron diffraction) experiments have shown that carbon and oxygen occupy the fourfold hollow sites of the *bcc* Mo(100) surface (*5*). Surface oxidation states as a function of modifier identity and coverage have been determined (*2*). The chemisorption (Lewis acid–base) properties of many adsorbates have also been extensively investigated on these surfaces

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(*3, 4, 16*). Previous studies by our group have shown that the Lewis acidity (electron-accepting ability) of the Mo surface increases with increasing electronegativity of the surface modifier and with increasing coverage of a single modifier. This concept successfully explains the increase in desorption energies for Lewis bases, NH_3, $(CH_3)_2O$, propene, and ethene, as well as the decrease in desorption energies for Lewis acids, CO, and 3,3,3-trifluoropropene, when the oxidation state of Mo is increased (*3, 4, 16*).

Hall (*17*), Burwell (*18–23*), and Ponec (*24*) have studied cyclopropane hydrogenolysis reactions over supported Mo catalysts. Their results show that catalyst activity and selectivity is dependent on the Mo oxidation state. Unlike hydrogenation reactions, hydrogenolysis of cyclopropane is not a facile reaction on Mo surfaces. For example, at 227 K, turnover frequencies for the hydrogenation of propene on supported Mo catalysts are between 1.8 and 5.6 sec^{-1}, while turnover frequencies for cyclopropane hydrogenolysis range from 0.02 sec^{-1} at 300 K to 1.5 sec^{-1} at 400 K (*19*). This difference in specific activity can be attributed to the differences in the bonding interactions required by the two reactions. Hydrogenolysis requires dissociatively chemisorbed hydrocarbon intermediates, which may be multiply bonded to the surface by metal–carbon σ bonds. Hydrogenation, on the other hand, does not require these intermediates, but may proceed by π-bonded intermediates (*25*).

The focus of this work is to investigate the nature of the active sites and mechanism of cyclopropane hydrogenolysis on modified Mo(100) surfaces. These experiments also provide insight as to whether modified Mo(100) surfaces are good models for the corresponding bulk Mo oxide, carbide, and sulfide catalysts. Furthermore, the experiments test whether the catalytic chemistry of the chemically modified Mo surfaces can be understood within the context of surface Lewis acid–base concepts.

METHODS

A schematic diagram of the experimental apparatus is shown in Fig. 1a. The UHV chamber is equipped with two ion pumps and a titanium sublimator. Typical base pressures are in the range 2–5 × 10^{-10} Torr (1 Torr = 133.3 N m^{-2}). Surface preparation and analytical equipment include a quadrupole mass spectrometer, a variable 0–5 kV ion gun, LEED optics, and cylindrical mirror analyzer for Auger electron spectroscopy (AES).

The high-pressure reactor, which has been described previously (*26*), permits exposure of the sample to atmospheric pressures of reactant gases, while maintaining pressures of 1–8 × 10^{-7} Torr in the UHV chamber. In addition, the reactor consists of a small-volume (0.1 liter) stainless-steel reaction loop equipped with a bakeable Metal Bellows circulation pump, shown in Fig. 1b. The reaction products are monitored with a Varian Model 3700 gas chromatograph equipped with a 20% BEEA on ChromPAW column.

The 9-mm-diameter Mo single-crystal disk is oriented to ±1° of the (100) plane by back-reflection Laue. The crystal is first polished with successively finer grades of alumina (Buehler) down to 0.03 μm, then bulk cleaned by heating in 5 × 10^{-7} Torr O_2 at ~1400–1500 K for 36 hr. The sample is mounted edge-on to a precision manipulator by spot-welding to stainless-steel support rods. The sample can be heated resistively to 1300–1400 K through the supports. The temperature is monitored by a chromel–alumel thermocouple spot-welded to the side of the crystal away from the stainless-steel support rods.

The modified Mo surfaces are prepared by cleaning the surface with Ar^+ sputtering followed by annealing to restore surface order. The crystal is exposed to various modifiers (O_2, C_2H_4, H_2S) through a microcapillary array doser. The dosing is performed with the crystal at ~1300 K to drive off hydrogen. Following the dose, the modifier

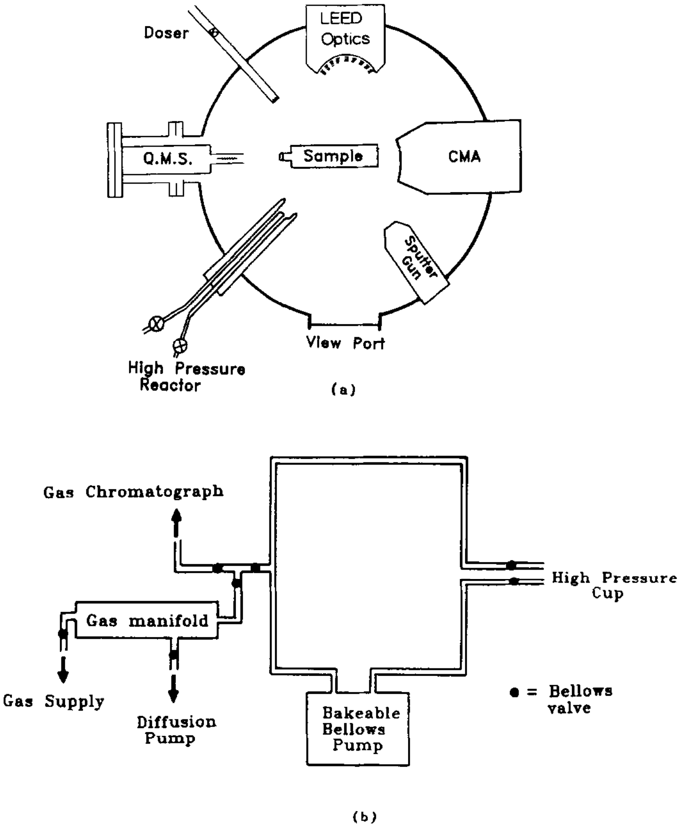


FIG. 1. (a) UHV chamber. (b) Reaction loop.

coverage is determined by Auger using peak-to-peak ratios and sensitivity factors obtained by signal calibration against the saturated β-CO adsorption state. The coverage determination by AES is accurate to $\sim\pm 0.1$ monolayer (ML). A further check of overlayer coverage is by comparison with previously determined LEED patterns (*1*, *7*). LEED is especially useful for determining oxygen coverages close to one monolayer where fourfold site filling may be incomplete. For example, it has been previously determined that small variations in oxygen coverage near one monolayer are responsible for the presence of a propene desorption peak at high temperature (*3*, *16*). This peak is attributed to desorption from vacant fourfold hollow sites. At coverages below one monolayer, propene dissociation is observed; this is not observed at higher oxygen coverages. There are several LEED patterns observed in the vicinity of 1-ML O: (1) A LEED pattern composed solely of a $\sqrt{5} \times \sqrt{5}\, R26°$ pattern is indicative of an oxygen surface coverage which is slightly below 1 ML; (2) a LEED pattern composed of both the $\sqrt{5} \times \sqrt{5}$ and a $p(1 \times 2)$ pattern is indicative of 1-ML O; (3) a LEED pattern composed solely of the $p(1 \times 2)$ pattern is indicative of an oxygen surface coverage greater than 1 ML. To obtain coverages close to 1-ML O, the sample was annealed in UHV at $\sim$1300 K several times, with examination of the LEED patterns between heating cycles. When the $\sqrt{5} \times \sqrt{5}$ plus the $p(1 \times 2)$ pattern was observed, the heating cycles were terminated.

Various spots on the crystal surface were examined with LEED prior to reaction to assure surface structure uniformity. Reactions were run on surfaces cleaned by the sputter and anneal technique as well as on surfaces which could be cleaned by just annealing. The reaction rates on these surfaces were similar. It can thus be concluded that the methods of surface preparation used here do not induce variation in activity.

Since one objective of these studies is to evaluate differences in activity of the various chemical modifications, it is crucial to minimize inadvertent surface contamination by impurities in the reaction mixture. This was particularly difficult to achieve for oxygen carriers such as H_2O and O_2 because of their affinity for the Mo surface. The concentration of oxygen-carrying contaminants must be reduced to below ~1 ppb. Reagent gases are Matheson UHP H_2 and 99.0% purity cyclopropane (c-C_3H_6). Manganese(II) oxide and silica traps are utilized for further removal of O_2 and H_2O. Additional purification of c-C_3H_6 is achieved by a freeze–pump–thaw cycle. H_2 is passed through a liquid N_2-cooled trap. The gas-handling lines were leak-checked with the mass spectrometer in the UHV chamber, and pressures of $\sim 10^{-8}$ Torr in these lines could be achieved. While these purification procedures eliminate oxygen-carrying species, they do not eliminate other hydrocarbon impurities from the cyclopropane. Typical hydrocarbon impurities, as determined by GC, are 0.09% propene, 0.008% propane, and <0.005% ethane.

Reaction conditions for the experiments reported here are 40 Torr c-C_3H_6, and 715 Torr H_2 unless otherwise noted. The range of temperatures investigated was 300 to 523 K. Under these conditions, the untreated stainless-steel reactor loop was found to be an efficient propene hydrogenation catalyst. Therefore, the walls of the reactor were passivated by circulation of 760 Torr H_2S with simultaneous heating of the reactor to 600–700 K. After passivation, no activity was observed from the reactor walls. Negligible activity at 523 K was obtained from a stainless-steel blank inserted in place of the Mo crystal.

Activity associated with the back of the single-crystal disk can have a significant contribution to the activity measured from a small area catalyst. The back side of the Mo(100) surface was passivated by circulation of ~40 Torr H_2S and 720 Torr H_2 in the reaction loop. The sample temperature was 423 K for this passivation procedure. Elevated temperatures are necessary to dissociate H_2S, but excessive temperatures (over 700 K) cause extensive bulk contamination of the Mo(100) crystal. The front surface of the Mo(100) sample was then sputtered by Ar^+ to remove the sulfur layer. After sputtering, the sample was annealed to restore surface order, as described above. This procedure achieves preparation of modified Mo(100) surfaces on the front side, while passivating the back side of the crystal. Dosing and cleaning procedures were performed on the front of the sample only. Sulfur could only be removed by sputtering; it was not possible to remove sulfur by heating the sample to 1300 K in O_2. UHV sample preparation techniques, therefore, are not likely to alter the back side of the sample after it has been passivated.

A typical reaction run involves the following steps. The prepared surface is first sealed in the high-pressure reactor. The reaction mixture is then introduced into the reaction loop, followed by careful opening of the valves separating the sample from the loop. The circulation pump is started, and a GC sample is taken immediately. The room temperature GC sample provides an indication of impurity levels for the particular reaction mixture, and provides an initial value for all products and reactants. Hydrogenation of the propene impurity proceeds rapidly at room temperature; circulation for ~5 min is sufficient for complete propene hydrogenation to propane before the hydrogenolysis reaction is begun. Next, the sample temperature is increased to the desired reaction temperature. Constant volume GC samples are removed from the reaction mixture by first evacuating the small tee, shown in Fig. 1b, on the pump side of the reaction loop. The tee is isolated from the pump and the loop is then opened to the tee, followed by opening of the GC sampling loop valve. The sampling procedure removes ~5% of the reaction loop volume. This loss is taken into account when evaluating chromatographic peak heights for each product. At the conclusion of each reaction the molybdenum crystal is allowed to cool in the circulating reaction gases prior to evacuating the reactor loop.

The ethane and propane present as impurities can represent a significant portion of the chromatographic peak height, especially at low reaction temperatures. Peak heights for these impurities, obtained from the first chromatograph, were subtracted from the peak heights for each product. This procedure is adequate for ethane, but not for propane at low reaction temperature since there are three sources of propane; the initial impurity, hydrogenated propene, and hydrogenolysis product. The propane formed from single hydrogenolysis at low temperature is less than the amount of propane and propene initially present as impurities. Thus, the error due to subtraction can be large.

RESULTS

Cyclopropane hydrogenolysis was observed on the clean (less than 0.5 ML total modifier precoverage) and the 1-ML O- and C-modified Mo(100) surfaces over a temperature range 300–523 K. At 523 K, ~5% cyclopropane conversion occurs in 2 hr over the initially clean surface. The rate is first order in hydrogen partial pressure and zero order in cyclopropane partial pressure. No reaction at any temperature was observed on 0.8-ML S-modified surfaces. At higher temperatures, and in the presence of H_2, sulfur segregates from the bulk to the surface of the Mo cyrstal causing deactivation. Thus, higher reaction temperatures were not investigated. The phenomenon of sulfur segregation has been observed previously (*27, 28*).

TABLE 1

Product Distribution: Mo(100) Catalysts

Surface	Temp	%CH_4	%C_2H_6	%C_3H_8
Clean Mo	373	15.5	15.4	69.0
Clean Mo	423	17.7	15.8	66.5
Clean Mo	423	19.1	17.6	63.5
Clean Mo	423	17.0	16.4	66.6
Clean Mo	473	17.8	16.9	65.4
O/Mo	473	6.73	7.42	85.8
Clean Mo	523	19.1	18.0	63.0
O/Mo	523	17.3	17.2	65.5
O/Mo	523	17.3	16.2	66.5
O/Mo[a]	523	16.3	15.2	68.6
C/Mo	523	18.5	17.4	64.1
C/Mo	523	14.7	13.7	71.6

[a] The oxygen coverage for this run was 1.8 ML.

Product distributions are reported in Table 1. Substantial and equal amounts of CH_4 and C_2H_6 are formed, indicating that, in addition to ring opening to form C_3H_8, the single-crystal catalysts are active for double hydrogenolysis but not for triple hydrogenolysis. Minor amounts of propene were formed at temperatures above 473 K. Metathesis products were not observed from these surfaces. Except for one run on the O-modified surface, the product distribution is independent of reaction temperature. The product distribution is independent of cyclopropane partial pressure; however, it is dependent on H_2 partial pressure. The ratio of double hydrogenolysis to single hydrogenolysis products increases as the H_2 partial pressure increases. At 423 K, the percentage of double hydrogenolysis products increased from 9% at a H_2 partial pressure of 40 Torr to 32% at a H_2 partial pressure of 715 Torr. No hydrogenolysis of propane was observed (in separate experiments), indicating that propane is not an intermediate to the formation of CH_4 and C_2H_6. Propene is not an intermediate either since propane is the predominant product from the reaction of propene and H_2 along

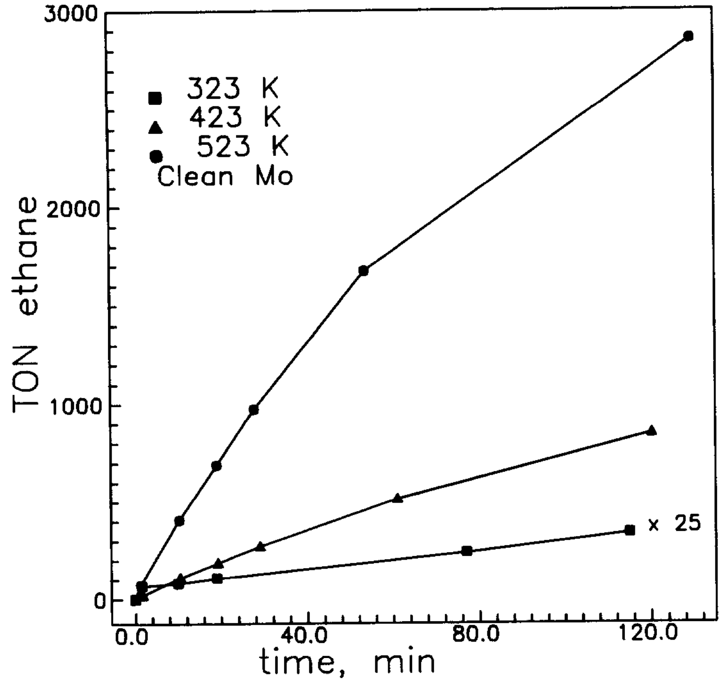


FIG. 2. Time evolution of ethane formation on initially clean Mo(100) at 323, 423, and 523 K.

with insignificant quantities of cyclopropane, ethane, and butane. These findings suggest that CH_4 and C_2H_6 are primary reaction products.

The accumulation of ethane at 323, 423, and 523 K from an initially clean Mo(100) surface is shown in Fig. 2. Deactivation is observed at temperatures greater than 373 K. Two possible causes of deactivation are carbon deposition and sulfur segregation. After reaction the measured carbon coverage on initially clean Mo surfaces is ~0.75 ML. After reaction at temperatures above 423 K, minor amounts of sulfur are detected on the Mo(100) surface by AES. It is not possible to accurately quantify the sulfur coverage because of interference between the 152 eV S peak and Mo peaks around 154 eV. However, from changes in AES peak ratios the sulfur coverage is estimated to be ~0.2 ML. In order to investigate the reversibility of deactivation by carbon, an initially clean Mo(100) surface at 423 K was exposed to a sequence of four fresh reaction mixtures. Following the fourth exposure, the sample was heated to ~1300 K in UHV, then replaced in the reaction loop and exposed for a fifth time. Turnover frequencies were calculated by using adjacent data points in the plots of product accumulation. The data is shown in Fig. 3. The dashed line indicates the behavior of an uninterrupted run. Initially the rate of ethane formation decreases rapidly, but eventually reaches a steady state. After refilling the reactor with a fresh reaction mixture the initial activity is lower than that prior to evacuation and lower than observed in the uninterrupted reaction. After an induction period the activity recovers to the level observed for the uninterrupted reaction. After heating under vacuum, the catalyst activity is the same as that at the end of the previous exposure, and the induction period is significantly shorter. These results indicate that there is both an irreversible component to the deactivation and a reversible component which is largely

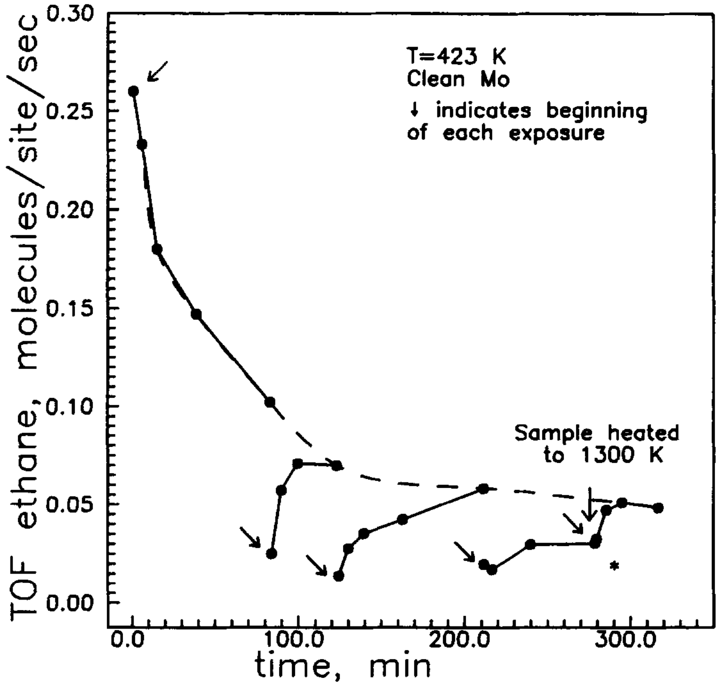


FIG. 3. Deactivation results from an interrupted series of reactions. An arrow marks the beginning of a new exposure. Uninterrupted reactions follow the behavior of the dashed line. The asterisk indicates two overlapping points. The activity at the end of the fourth exposure is approximately the same as the initial activity after the sample was heated to 1300 K.

removed by heating under vacuum. In a separate experiment the desorption of cyclopropane or propene was observed upon heating the surface under vacuum after a reaction run, suggesting that reversible hydrocarbon adsorption is responsible for the reversible deactivation component.

The induction periods for exposures 2, 3, and 4 in Fig. 3 can be explained by a stable hydrocarbon species, probably a C_3 species, that is removed by reaction at elevated sample temperatures. We propose that this C_3 species is formed when the sample is cooled in the reaction mixture prior to evacuation and that removal of this species is activated and rate limiting. This proposal is supported by the observation of a similar induction period following an increase in sample temperature from 323 to 423 K after 2 hr in the reaction mixture at the lower temperature. After heating the sample to 1300 K in UHV the initial activity is the same as that at the end of the previous exposure, and the induction period is short as shown in Fig. 3. The increased initial activity can be explained by the removal of the C_3 species upon heating under vacuum. The short induction period is then due simply to adsorption of cyclopropane while the sample is at room temperature following the refilling of the reaction loop. A short time period is required to reach a steady state of reactant on the surface. One might also expect to see a short induction period for the first exposure in Fig. 3. However, the time dependence of activity is dominated by deactivation in the initial stage of the reaction, so that the induction period is not observable.

The rate of reaction was computed from the product accumulation data. At 323 and 373 K, where no deactivation was observed, the rate was computed from a least-squares fit to the data. At higher temperatures steady-state rates are reported using the last two product accumulation data points at 1 and 2 hr. Arrhenius plots for ethane formation on clean, C- and O-modified Mo(100) surfaces are reported in Fig. 4. All top-layer Mo atoms are counted in the computation of turnover frequencies. As discussed later, this method for counting the number of active Mo atoms is likely to be in error and is thought to be responsible for the observed scatter in the turnover frequencies. The measured rates from C- and O-modified surfaces fall on a common Arrhenius curve which is parallel to and below the curve observed for the clean surface. Activation energies are the same for all surfaces: 37 kJ/mol with a standard deviation of 4 kJ/mol. However, the activity of initially clean Mo(100) is approximately five times greater than the activity of the modified surfaces.

It was not possible to obtain an Arrhenius plot for propane formation or accurate product distributions for the carbon- or oxygen-modified surfaces due to inaccuracies in subtracting the propane impurity contribution. The level of propane impurity is approximately the same as that of the propane formed by reaction, making all but the data at 523 K difficult to interpret. However, at 523 K qualitative agreement is found with the ethane data. The activity for propane formation by the C- and O-modified surfaces is similar, and the activity of the clean Mo surface is approximately three times greater than that of either modified surface.

DISCUSSION

The similarities in activation energy and product distribution found on all three single-crystal catalysts suggest that the same site is responsible for the catalytic activity. The fact that the activity is higher on the clean surface than on either modified surface indicates that the active sites are more numerous on the clean surface. The knowledge that adsorbed atomic carbon and oxygen block fourfold hollow sites on the (100)

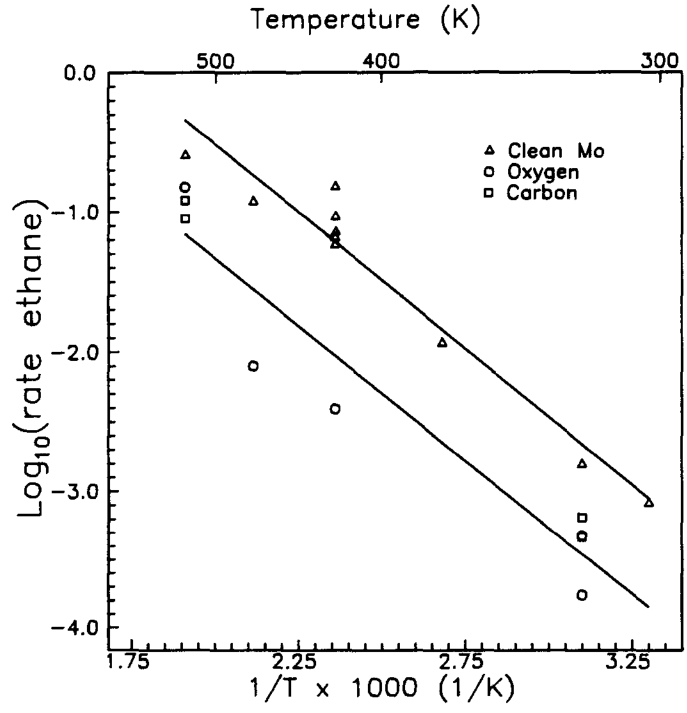


FIG. 4. Arrhenius plots for ethane formation on clean, C-, and O-modified Mo(100).

molybdenum crystal plane (*5*) coupled with the higher activity observed for initially clean Mo(100) surfaces provides strong evidence that the active sites for this reaction are open fourfold hollows which are present in high concentration on initially clean Mo(100) surfaces and as defects on the C- and O-modified surfaces. An estimate of the density of open fourfold hollows present on the C- and O-modified surfaces can be made by comparison of their activities with the initially clean surface. Since the coverage of open fourfold hollows on the initially clean surface is 0.25 ML after reaction and the initially clean surface has an activity ~5 times that of the C- and O-modified surfaces, then the fraction of open fourfold hollow sites present on the modified surfaces must be on the order of 0.05. One consequence of this model is that the turnover frequencies computed on the basis of counting all surface Mo atoms are in error. The actual turnover frequency per active site is higher by a factor of 4 to 20 depending on the surface under consideration. Another consequence of this model is that reproducible preparation of surfaces with the same active site coverage is difficult. We attribute the observed variations in activity to this effect.

The persistence of open fourfold sites under reaction conditions might seem improbable, given the reactivity of clean Mo surfaces. However, it is an experimental fact that the initially clean surface is not completely covered by carbon during reaction. It has been previously proposed that two adjacent open sites are required for CO decomposition (*7*). In agreement with this proposition ion-scattering experiments have shown that very high exposures of CO and C_2H_4 are required to completely fill the fourfold sites (*5*). The difficulty in filling the last of the fourfold sites is attributed to the absence of adjacent fourfold hollow sites available for the atomic fragments of dissociation. This suggests that isolated hollow sites are more stable than adjacent sites and that these sites are more likely to support catalytic activity rather than merely serving as sites for cyclopropane dissociation. It should be noted that the reaction conditions during formation of the carbon-containing overlayer are very different from those employed to prepare the C-modified surface, and that this leads to overlayers with very different chemical natures. On C-modified surfaces carbon is atomic and is located in fourfold hollow sites of the Mo(100) surface. Thermal desorption measurements indicate that the overlayer deposited during catalytic reaction contains significant quantities of undissociated cyclopropane and/or propene. The major factor responsible for the difference between the two overlayers is sample temperature. During surface modification, the sample temperature is sufficient for complete hydrocarbon decomposition, desorption of H_2, and ordering of the adlayer. The minimum temperature required to prepare an ordered carbon overlayer is 550 K (*16*). This does not occur to any significant extent at the reaction temperatures reported here.

The assignment of open fourfold hollows as the active sites is consistent with previous studies of cyclopropane hydrogenolysis carried out over supported catalysts. Tables 2 and 3 list product distribution data from the literature for supported and film Mo catalysts, and other catalysts, respectively. The Mo catalysts prepared by Bowman via decomposition of $Mo(CO)_6$ on Al_2O_3 had average oxidation states ranging from 0 to +5 (*18*). Ponec and Merta prepared Mo film catalysts by vapor deposition of Mo (*24*). The catalysts used by Hall (*17*) and Burwell (*23*) were prepared by reduction of MoO_3 on alumina. The literature data shows product distributions that vary both as a function of temperature and Mo oxidation state. Double hydrogenolysis is reported on supported Mo(0) catalysts and Mo films over a temperature range similar to that reported here. Double hydrogenolysis was only observed by Hall on highly reduced MoO_3/Al_2O_3 catalysts; no activity was observed on unreduced or partially re-

TABLE 2

Product Distribution: Mo Catalysts

Ref.	Catalyst	Temp (K)	%CH_4	%C_2H_6	%C_3H_8
Ponec[a]	Mo film	273	17.4	17.6	65.0
Bowman[b1]	Mo(0.3)	273	35.4	32.6	32.0
Bowman[b2]	Mo(<0.3)	273	36.6	36.6	26.8
Verma[c]	10% Mo Al_2O_3	298	18.8	18.8	62.4
Bowman[b3]	Mo(+3)	298	5.0	5.0	90.0
Burwell[d]	Mo(0)	323	19	19	62
Bowman[b1]	Mo(0.3)	328	30.2	29.5	40.3
Bowman[b4]	Mo(+2)	338	12.6	12.5	74.9
Bowman[b5]	Mo(>3)	373	16.9	18.8	64.4
Bowman[b3]	Mo(+3)	373	11.7	9.6	78.7
Bowman[b4]	Mo(+2)	373	20.6	20.5	58.9
Bowman[b1]	Mo(0.3)	373	26.6	25.8	47.7
Bowman[b2]	Mo(<0.3)	373	42.9	42.3	14.7
Bowman[b6]	Mo(0)	373	39.5	39.2	21.4
Hall[e]	8% Mo Al_2O_3	664	6.4	8.1	85.4

[a] Ref. (*24*); evaporated Mo film.

[b] Ref. (*18*); catalysts prepared by decomposition of $Mo(CO)_6$ on Al_2O_3; oxidation state determined by activation procedure. (1) Dehydroxylated Al_2O_3 (DA), activated in He at 300–500°C; (2) dehydroxylated Al_2O_3 in H_2 at 300–500°C; (3) partially dehydroxylated Al_2O_3 (PDA) in H_2 at 300–500°C; (4) PDA in He at 300°C; (5) PDA in He at 400–500°C; (6) DA in He at 300–500°C followed by H_2 at 650–900°C.

[c] Ref. (*29*); commercial catalyst (Harshaw Mo-1201), reduced in flowing H_2 at 360°C, 18 hr.

[d] Ref. (*23*); Al_2O_3 impregnated with ammonium heptamolybdate, pretreated in O_2 at 500°C for 1 hr, then in He at 500°C. Catalysts were reduced in H_2 at 950°C for 1 hr.

[e] Ref. (*17*); Al_2O_3 impregnated with ammonium paramolybdate, pretreated in O_2 overnight at 500°C, then reduced in H_2 at 400–500°C.

duced MoO_3/Al_2O_3 catalysts (*17*). Burwell and Chung reported product distributions similar to those obtained here for their highly reduced MoO_3/Al_2O_3 catalyst (*23*). The oxidation state of the Mo in this catalyst was 0. Finally, propane is the only product observed on Cr_2O_3, Al_2O_3, and ZnO catalysts (*18*, *33*), and Mo oxides are not active hydrogenolysis catalysts in this temperature range. This leads to the conclusion that the active sites on our catalysts must contain low-valent Mo consistent with the model of open fourfold hollows as the active sites. The product distributions observed for C- and O-modified Mo(100) surfaces suggest that they are not good models for Mo oxide or carbide catalysts. This does not necessarily mean that the C- and O-modified surfaces lack oxide or carbide chemical functionality. It may simply reflect the fact that the catalytic character is dominated by very active low-valency sites present in low concentration. Additional evidence against carbide-like catalysts is that no induction period is observed in these experiments. An induction period should occur as the carbide layer forms during the course of reaction on the clean surface. On the contrary, all catalysts studied here deactivate with time.

The irreversible deactivation observed at higher reaction temperatures arises from two possible sources: filling of isolated fourfold hollow sites and sulfur segregation. The filling of stabilized, isolated fourfold hollow sites can occur by dehydrogenation of the hydrocarbon layer to produce coke. As discussed above, the carbon overlayer which forms during reaction is not simply atomic carbon since thermal desorption of cyclopropane and/or propene is observed, but a significant fraction of this overlayer does not desorb and will be a source of deactivation. Another model for the filling of isolated fourfold sites is the reorganization of deposited atomic carbon

TABLE 3

Product Distribution: Other Catalysts

Ref.	Catalyst	Temp (K)	%CH_4	%C_2H_6	%C_3H_8
Ponec[a]	Ni film	273	15.0	19.0	66.0
Verma[b]	14% Ni Al_2O_3	298	28.1	28.1	43.8
Verma[b]	40% Ni Al_2O_3	298	31.3	31.3	37.5
Sridhar[c]	40% Ni Al_2O_3	333	15.9	15.9	68.1
Sridhar[c]	14% Ni Al_2O_3	333	21.8	21.8	56.5
Goodman[d]	Ni(100)	400	22.5	21.3	56.0
Goodman[d]	Ni(100)	450	27.0	23.0	50.0
Goodman[d]	Ni(111)	488	24.0	12.0	64.0
Goodman[d]	Ni(111)	550	55.0	16.4	29.0
Verma[b]	35% Co Al_2O_3	298	14.6	14.6	70.8
Verma[b]	10% Os SiO_2	298	6.3	6.3	87.4
Various[e]	Pt, Pd, Rh	—	0.0	0.0	100.0

[a] Ref. (*24*).

[b] Ref. (*29*).

[c] Ref. (*30*).

[d] Ref. (*31*).

[e] Refs. (*25*, *32*).

to produce adjacent open fourfold sites which are rapidly filled via dissociative adsorption of cyclopropane. This model requires that the atomic carbon be mobile, which is unlikely at the reaction temperatures employed. Slow deactivation caused by sulfur segregation may also occur. However, sulfur segregation is only observed at temperatures greater than 423 K. This cannot explain the deactivation observed below 423 K.

The inactivity of the S-modified surface can be explained by the fact that sulfur atoms are too large to fit into the fourfold hollow sites (*6*) and therefore block all active sites. Experimental evidence for this explanation comes from thermal desorption measurements of a series of molecules from S-modified surfaces (*4*, *16*). The desorption activation energies for all molecules were very low and indicative of very weak interaction with the surface.

The observed product distribution can be explained by several different mechanisms. The first mechanism,

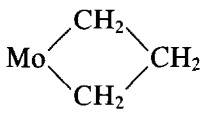
$$c\text{-}C_3H_6 \rightarrow n\text{-}C_3H_6 \rightarrow C_3H_8 \rightarrow CH_4 + C_2H_6$$

is a sequential reaction involving first the isomerization of cyclopropane to gas phase propene. Propene then undergoes hydrogenation to propane followed by propane hydrogenolysis to methane and ethane. This mechanism is ruled out since the single-crystal catalysts are not active for hydrogenolysis of propane. Furthermore, propene is observed only at temperatures greater than 423 K. Another possible mechanism is

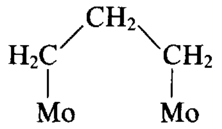
$$c\text{-}C_3H_6 \rightarrow n\text{-}C_3H_6 \rightarrow CH_4 + C_2H_6.$$

Evidence against this mechanism is that propene reaction at these surfaces yields only hydrogenation and metathesis products. The experimental data is only consistent with methane and ethane as primary products of reaction.

There are two different intermediates proposed for cyclopropane hydrogenolysis (*18*, *34*). The first intermediate, also proposed for olefin metathesis reactions, is a metallacyclobutane,

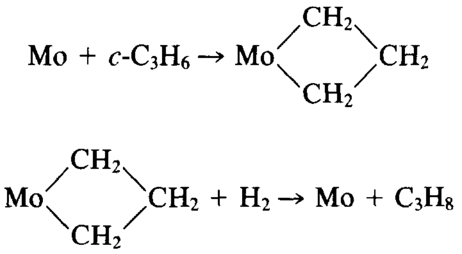


The second is a 1,3-diadsorbed cyclopropane molecule,



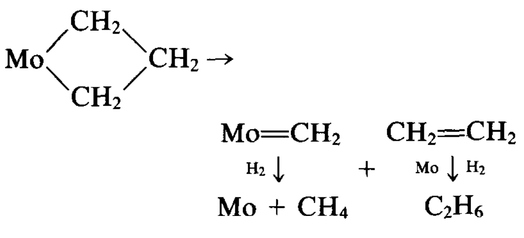
There have been numerous but similar mechanisms proposed for the cyclopropane hydrogenolysis reaction (*18*). The following mechanisms serve to illustrate product formation from the two different intermediates. In mechanism Ia a metallacyclobutane is formed by reaction of cyclopropane with a Mo site. H_2 dissociates on the Mo site, and the hydrocarbon portion of the metallacyclobutane is hydrogenated and removed as propane.

Mechanism Ia



Methane and ethane are formed by a mechanism resembling metathesis with formation of ethylene and a coordinated methylene species, followed by hydrogenation, shown in mechanism Ib.

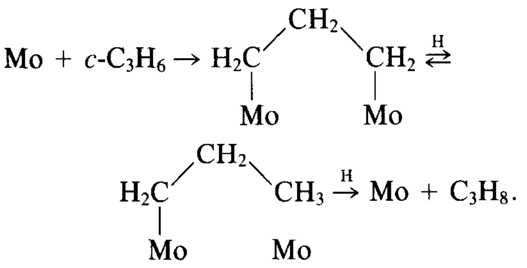
Mechanism Ib



Ethylene and coordinated methylene species have been observed by Gassman and Johnson (*35–37*) with homogeneous metathesis catalysts. Formation of a stable Mo=CH_2 carbene complex, identified by IR spectroscopy, has recently been reported following chemisorption of cyclopropane on a Mo/SiO_2 catalyst (*38*). The fact that C_4 metathesis products are not observed here suggests that the reaction does not proceed via a metallacyclobutane intermediate.

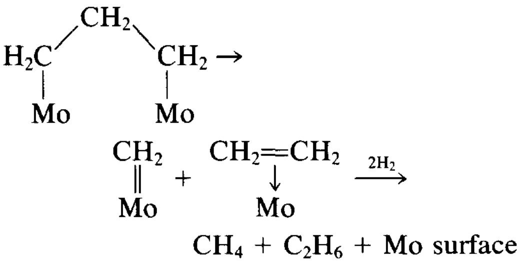
In mechanism IIa, the cyclopropane ring opens to form a 1,3-diadsorbed species, which is then hydrogenated forming propane.

Mechanism IIa

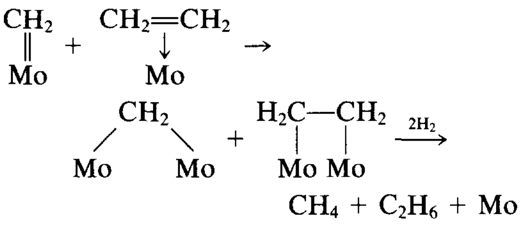


Methane and ethane may then be formed in several possible steps shown in mechanism IIb.

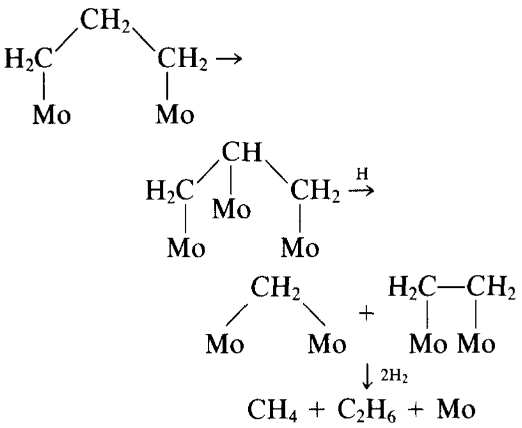
Mechanism IIb



or



or



The first possibility consists of breaking a C–C bond of the 1,3-diadsorbed intermediate leading to formation of ethylene and a coordinated methylene, which are then hydrogenated. The second possibility is that the methylene and ethylene form Mo–CH_2–Mo and Mo–CH_2–CH_2–Mo, respectively, before they are hydrogenated to methane and ethane. Finally the cyclopropane reacts to form the 1,3-diadsorbed species, which then loses hydrogen, forming a 1,2,3-triadsorbed (π-allyl) species. This intermediate can then decompose to form Mo–CH_2–Mo and Mo–CH_2–CH_2–Mo, which are then hydrogenated. These mechanisms both account for equal methane and ethane production.

There are several possibilities that might account for the increased activity of fourfold hollow sites relative to the activity of sites occupied by carbon or oxygen. One possibility is that no steric blocking of the 1,3-diadsorbed intermediate occurs in the absence of chemical modifiers. Alternatively, empty fourfold hollows may provide sites for hydrogen adsorption.

We attempt to assess the validity of these mechanisms by considering the possible bonding interactions of cyclopropane with the Mo(100) surface. The use of single-crystal catalysts provides greater insight into the allowed bonding geometries of the intermediate than is available with supported or polycrystalline catalysts. On the basis of

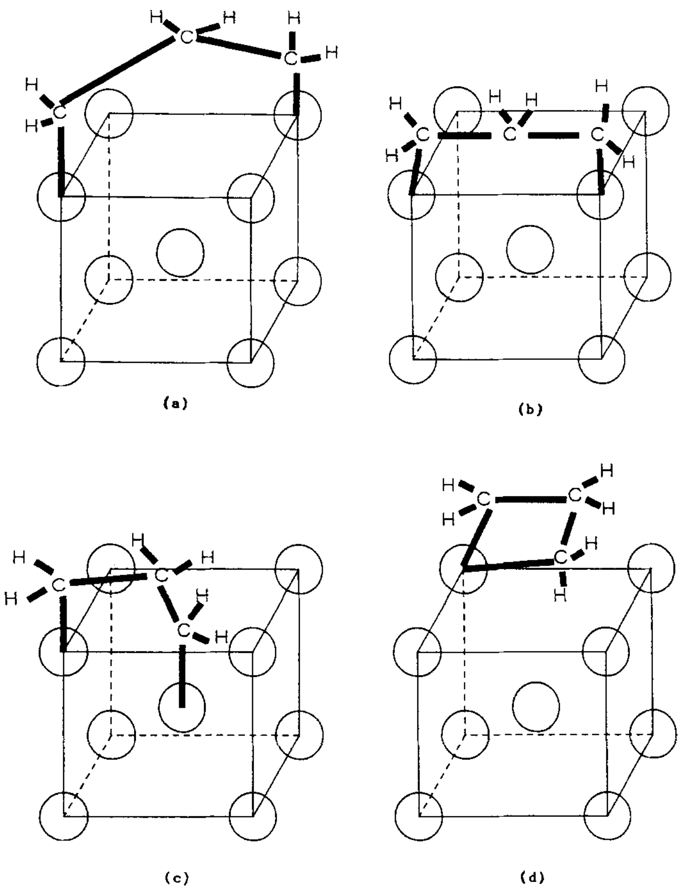


FIG. 5. Possible binding geometries for hydrogenolysis intermediates. (a) 1,3-diadsorbed species bridging diagonally across fourfold hollow site. (b) 1,3-diadsorbed species bonded to two adjacent top-layer Mo atoms. (c) 1,3-diadsorbed species bonded to one top-layer and one second-layer Mo atom. (d) Metallacyclobutane bonded to a top-layer Mo atom.

geometric and bond length arguments, three possible bonding interactions can be envisioned for the 1,3-diadsorbed intermediate. These are shown in Fig. 5a–5c. The first possibility is that cyclopropane bridges diagonally across a fourfold hollow site, forming Mo–C bonds with the 1,3 ends of the molecule. The Mo–Mo diagonal distance is 4.44 Å. In this configuration, the hydrocarbon fragment is close to the plane of the Mo(100) surface due to bond length constraints, and the central carbon atom is centered over the fourfold hollow. The second possible bonding configuration consists of the cyclopropane fragment bonded to two adjacent top-layer Mo atoms. The Mo–Mo distance is 3.14 Å in this case. This shorter distance allows the C_3 species to lie parallel to the plane of the Mo(100) surface, allowing interaction between the metal and the π-type orbitals of the C_3 fragment. The third possibility is that one end of the C_3 fragment binds to a second layer Mo at the bottom of a fourfold hollow, and the other end interacts with a top-layer Mo atom. In this case the Mo–Mo distance is 2.7 Å.

The most probable location for the formation of a metallacyclobutane intermediate is with a top-layer Mo atom, shown in Fig. 5d. It is unlikely that the entire C_3 fragment could fit into a fourfold hollow and bind to a second layer Mo atom.

CONCLUSIONS

Product distribution and activation energy data indicate that the same active site and the same mechanism operate on all active surfaces studied. We propose that the active sites for hydrogenolysis are open fourfold hollows of the Mo(100) crystal plane and that these sites are present as defects on the carbon- or oxygen-modified surfaces. The results reported here favor a 1,3-diadsorbed surface intermediate rather than a metallacyclobutane structure. Comparison of the results from the single-crystal catalysts with literature data from supported molybdenum catalysts suggests that the single-crystal catalysts have the character of low-valent Mo rather than oxide or carbide materials.

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