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Homologation, Hydrogenolysis, and Dehydrogenation of Ethane on SiO_2- and SiO_2–Al_2O_3-Supported Reduced Molybdenum Oxide Catalysts

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Kinetics and reaction mechanisms of homologation, hydrogenolysis, and dehydrogenation of ethane were studied on reduced molybdenum oxides supported on SiO_2 and SiO_2–Al_2O_3. It was found that homologation of ethane to propane occurs via (1) dehydrogenation of ethane to ethylene, (2) homologation of ethylene to propylene, and (3) hydrogenation of propylene to propane. The rate-determining step was found to be hydrogenation of adsorbed propylene or that of adsorbed C_2H_5 species with an activation energy of 10.7 kcal/mole. In addition to homologation products, significant amounts of hydrogenolysis and dehydrogenation reaction products were also found. Dehydrogenation of ethane to ethylene had an activation energy of 25 kcal/mole, and it was quite similar to that for desorption of ethylene. Consequently, the dehydrogenation rate was assumed to be controlled by desorption of ethylene formed.

INTRODUCTION

The catalytic conversions of thermodynamically stable alkanes to their homologs are important reactions to study in energy research. In general, these reactions occur with difficulty. Only a few reports have appeared in the literature on the homologation of alkanes (*1–6*). O'Donohoe *et al.* (*1, 2*) and Sarakany *et al.* (*3, 4*) have reported detailed studies of alkane homologation of W, Rh, Pd, Mo, and Nb films and supported transition metal catalysts. In addition to hydrogenolysis and dehydrogenated products, the authors observed the formation of homologs. The yield of homologs was found to depend on the structure and chain length of the parent hydrocarbon, and the partial pressure of hydrogen in the reactant mixture. While the straight chain alkanes were more efficiently homologated than the isoalkanes, the cyclo- or neopentane gave no detectable amount of homologated product. The yield increased with the CH_2/CH_3 ratio in the normal alkanes and seemed to have a limit at C_7 to C_9.

The alkane homologation is believed to occur via an olefin intermediate. Since the discovery of olefin homologation on Mo/γ-Al_2O_3 (*7*), it has been known that metals, as well as metal oxides, catalyze the reaction (*8–13*). The olefin homologation recently has received much interest since the reaction is related to the Fischer–Tropsch reaction (*12*) as well as to olefin metathesis (*7, 13*). It consists of the addition of surface species (CH_x) to the α-olefin via an assumed metallocyclobutane which yields higher olefin which is subsequently hydrogenated to corresponding paraffin (*1–4*). The insertion of the CH_x species is considered to be the key step in the reaction. As the alkane homologation is usually performed in the presence of hydrogen, methane is simultaneously formed by hydrogenolysis of the alkane and/or of the product(s). An interesting point arises as to whether the CH_x species participating in the homologation is the same as that which acts as a precursor to methane formation in

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hydrogenolysis ($CH_x \rightarrow CH_4$), and whether methane can influence the formation of CH_x by the reverse reaction ($CH_4 \rightarrow CH_x$). Schleyer and co-workers (*14*) suggested that methane can supply this CH_x species to the homologation reaction of olefin on Ni catalysts.

In the reaction of ethane with hydrogen on SiO_2- and SiO_2–Al_2O_3-supported MoO_x catalysts propane is formed by homologation, in addition to methane and ethylene by hydrogenolysis and dehydrogenation of ethane, respectively. As mentioned above, homologation and hydrogenolysis of ethane may involve a common intermediate (CH_x). Stoichiometric reaction between organometallic μ^2-CH_2 and ethylene (*15*), which yields propylene, clearly suggests the significant role of a specific structure of active sites for ethylene homologation. In fact, a structural requirement is assumed in ethylene homologation on MoO_x/SiO_2 catalysts (*13, 16*). Ethane hydrogenolysis is interpreted to proceed on a cluster size of active metals (*17–20*), while dehydrogenation of alkanes does not depend on the structure of active sites (*17*). In this work, mechanistic studies were performed on ethane homologation and concurrently occurring ethane hydrogenolysis and dehydrogenation by measuring activation energies and preexponential factors of these reactions as well as by considering the active Mo species for the reactions. The influence of methane in the generation of CH_x species was also studied using labeled methane.

EXPERIMENTAL

Materials

Supports used in this work were SiO_2 (Kieselgel 60, Merck) and SiO_2–Al_2O_3 (28.61% Al_2O_3) (donated by the Catalysis Society of Japan). Ammonium paramolybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, used for the preparation of supported MoO_3 catalysts, was obtained from Wako Pure Chemicals. High-purity ethane (99.9%) obtained from Takachiho K.K. and ^{13}C-labeled methane (^{13}C, 94%) from Amersham International (UK) were used without further purification. H_2 was purified by passing through Pd/Ag thimbles.

Catalyst Preparation

Supported MoO_3 (typically 4 wt%) catalysts were prepared by impregnating the support with a solution of ammonium salt of paramolybdate. Typically 10 g of the support was mixed with 100 cm^3 aqueous solution of the molybdate containing the desired loading and the liquid phase was slowly evaporated while stirring on a hot plate. The catalyst was dried in air at 110°C overnight and subsequently calcined at 550°C for 1 h. The concentration of the ammonium paramolybdate solution was varied in order to obtain various MoO_3 loading. Note that loading is reported as weight percent of MoO_3.

Catalyst sample (0.5 g) was held between two thin layers of glass wool and was evacuated while increasing the temperature to 550°C, whence evacuation was continued for 1 h. After evacuation, the catalyst was reduced in H_2 ($p^0_{H_2} = 30$ Torr) for 1 h at the same temperature in an all-glass closed circulating reactor system with an internal volume of 260 cm^3. A liquid nitrogen trap was used to remove water produced during the reduction. H_2 consumed for MoO_3 reduction was calculated from the amount of H_2O produced. The sample was briefly evacuated to a pressure of 10^{-3} Torr and was then cooled down to desired reaction temperature.

In order to examine the effect of catalyst reduction on the activity and selectivity for the ethane reactions, SiO_2–Al_2O_3-supported MoO_3 samples were first evacuated at 550°C for 1 h, as described before, and then were reduced in H_2 varying reduction temperature (450, 500, and 500°C) and reduction time (1 to 5 h at 550°C).

Catalytic Studies

The reaction was carried out in a closed circulating reactor system using 38 Torr of ethane at C_2H_6/H_2 ratio unity. The reaction products were analyzed at 30°C at different reaction times using an on-line gas chromatograph (Hitachi 163, FID detector) equipped with a data processor (Shimadzu Chromatopac C-R3A). A 4-m-long (3-mm-i.d.) stainless-steel column packed with Chromosorb 105 (polyaromatic porous bead commercially available from Gaskuro Kohgyo, 60–80 mesh) was used. The rates of conversion of ethane, and of formation of a product, were expressed as the number of moles of ethane converted, or of a product formed, per gram of catalyst per second, which were calculated from the initial slope of product formation.

XPS Measurements

X-ray photoelectron spectra were recorded on a Vacuum Generators ESCA-3 with Mg*Kα* radiation ($h\nu = 1253.6$ eV). The samples of MoO_3 supported on SiO_2 and $SiO_2–Al_2O_3$ were mounted on a holder and transferred to the ESCA preparation chamber. They were first evacuated at room temperature overnight and then at 550°C for 1 h at $<10^{-7}$ Torr. The catalysts were then reduced in H_2 (ca. 10 Torr) at 550°C for up to 4 h. H_2 was flushed at an interval of 10 min during this reduction process. XPS spectra were recorded each time at room temperature at a residual pressure of $<10^{-7}$ Torr in an analyzer chamber. The binding energies (B.E.) were corrected with reference to the peak at 103.4 eV for Si 2*p* in SiO_2 (*21, 22*).

RESULTS

MoO_3 Catalyst Reduction

In order to elucidate the effect of reduction on the molybdenum, XPS spectra of Mo 3*d* were recorded on calcined catalysts and on reduced samples of 4 and 10% MoO_3 on $SiO–Al_2O_3$ and 4% MoO_3 on SiO_2. The XPS spectra of these samples were essentially the same and spectra of 4% MoO_3 on $SiO_2–Al_2O_3$ recorded at different stages are shown in Fig. 1. The unreduced sample showed a Mo $3d_{5/2}$ peak with binding energy (B.E.) at 234.1 eV which is assigned to Mo^{6+} species (Fig. 1a). On evacuation and subsequent reduction at 550°C in H_2, the Mo peak broadened and shifted to lower binding energy at 232.1 eV (Fig. 1c), indicating the presence of Mo oxidation states ranging from +4 to +6, with Mo^{5+} being the predominant species in both SiO_2- and $SiO_2–Al_2O_3$-supported MoO_3 catalysts.

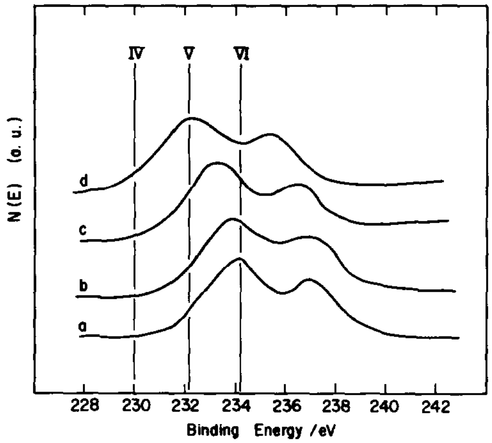

FIG. 1. XPS Mo 3*d* spectra of MoO_3 (4 wt%) catalyst supported on $SiO_2–Al_2O_3$ recorded after various pretreatments: (a) unreduced catalyst evacuated at room temperature overnight, (b) evacuated at 550°C for 2 h, and (c and d) subsequently reduced in H_2 (10 Torr) at 550°C for (c) 2 h and (d) 4 h. IV, V, and VI represent valences of Mo ion.

The results of H_2 consumption for the reduction and average valence state of Mo are collected in Table 1. The average valence state of Mo was found to be +5.2 for SiO_2 and +4.8 for $SiO_2–Al_2O_3$-supported catalysts reduced at 550°C in H_2 for 1 h. With the increase in the reduction time to 5 h (at 550°C), the average valence state of Mo was decreased to +4.4.

Catalytic Studies

The distribution of products in ethane reaction on SiO_2- and $SiO_2–Al_2O_3$-supported molybdenum catalysts is shown in Fig. 2 as a function of reaction time at reaction temperature 475°C. As analyzed after 5 min, the products were methane, ethylene, propylene, and propane. With reaction time,

TABLE 1

Reduction of 4% MoO_3 Catalysts Supported on SiO_2 and SiO_2–Al_2O_3

MoO_3 support	Reduction time[a]	[H_2] consumption mole/mole MoO_3	Average Mo valence state
SiO_2	1 h	0.38	+5.2
SiO_2–Al_2O_3	(a) 5 min	0.25	+5.5
	(b) 1 h	0.60	+4.8
	(c) 3 h	0.70	+4.6
	(d) 5 h	0.81	+4.4

[a] After evacuation at 550°C for 1 h, catalyst was reduced in H_2 ($p^0_{H_2}$ = 30 Torr) circulating at 550°C for different periods.

the product distribution changed appreciably. For both catalysts the amount of methane in the circulating system increased with time. All other products, in the case of SiO_2–Al_2O_3-supported catalyst, decreased with time, while in the case of SiO_2-supported catalyst, ethylene decreased but propylene and propane were not found to decrease even after 5 h reaction time.

In the present work the following reactions are believed to occur.

$$C_2H_6 + H_2 = 2CH_4 \quad (1)$$

$$C_2H_6 - H_2 = C_2H_4 \quad (2)$$

$$3C_2H_4 = 2C_3H_6 \quad (3)$$

$$C_3H_6 + H_2 = C_3H_8. \quad (4)$$

In addition to ethane hydrogenolysis (1), any of the products (ethylene, propylene, and propane) may readily undergo hydrogenolysis reaction producing methane.

The SiO_2–Al_2O_3-supported catalyst was found to be more effective than the SiO_2-supported catalyst for ethane conversion under the same experimental conditions. The former catalyst showed activity for the

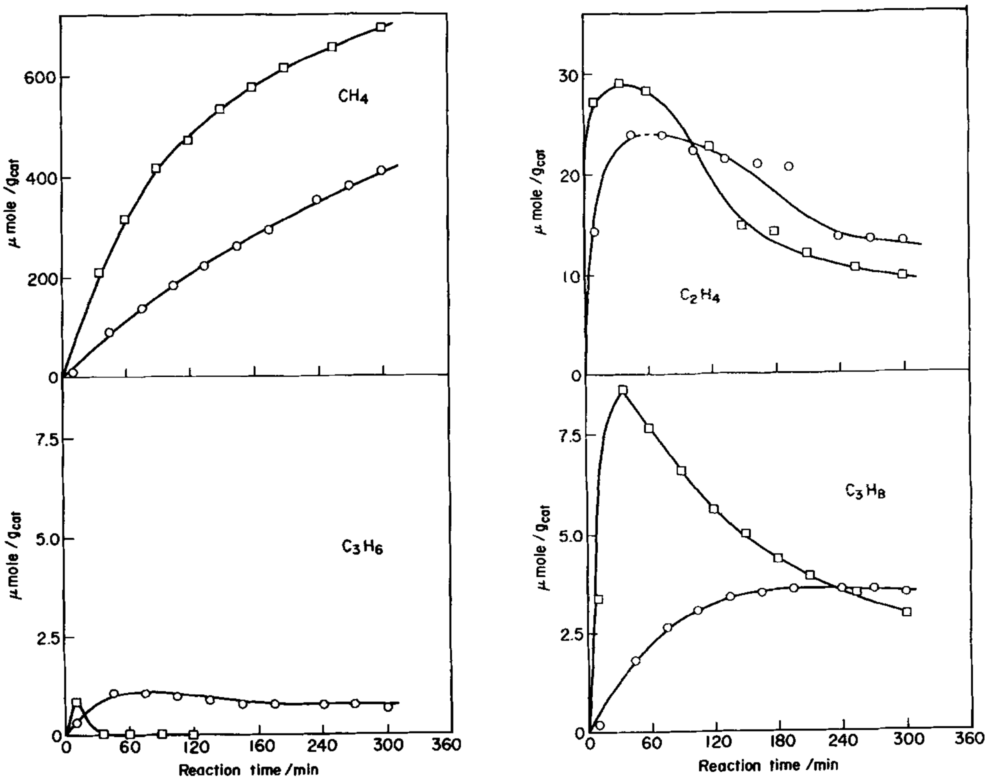

FIG. 2. Product distribution of ethane reaction as a function of reaction time over reduced MoO_3 (4 wt%) catalysts supported on (○) SiO_2 and (□) SiO_2–Al_2O_3. Samples of 0.5 g catalyst were reduced in H_2 at 550°C; reactant C_2H_6 (38 Torr) was mixed with H_2 at 1 : 1 ratio; reaction temperature was 475°C.

TABLE 2

Kinetic Behavior of Reduced MoO_3 (4%) Supported Catalysts for Ethane Reactions

MoO_3 support	Temperature range (°C)	E_a (kcal/mole)			A (molecules · s^{-1} · g^{-1})		
SiO_2	350–475	17.55	25.62	10.77	2.55×10^{21}	7.8×10^{23}	6.8×10^{17}
SiO_2–Al_2O_3	300–475	9.09	24.51	10.71	3.69×10^{19}	8.2×10^{23}	1.1×10^{19}

reactions even at 200°C but no reaction occurred on the SiO_2-supported catalyst below 300°C.

The apparent activation energies, E_a, for the formation of CH_4, C_2H_4, and C_3H_8 were calculated from their initial formation rates on reduced MoO_3 supported on SiO_2 and SiO_2–Al_2O_3 catalysts. All data were fitted to the Arrhenius equation,

$$r = A \exp(-E_a/RT),$$

with the parameters shown in Table 2. A marked difference can be seen in the apparent activation energy for the formation of methane over the two catalysts. The value of E_a was 17.6 kcal/mole for MoO_3/SiO_2 catalyst, which is almost twice that found for MoO_3/SiO_2–Al_2O_3 (9.1 kcal/mole). The activation energies for the dehydrogenation over the catalysts were similar (about 25 kcal/mole). Although different activities were observed for the catalysts in Fig. 2, the apparent activation energies for the homologation of ethane were the same on both catalysts (10.7 kcal/mole).

The activities for hydrogenolysis, dehydrogenation, and homologation on the catalysts can be explained in terms of the preexponential factors rather than the activation energies. Preexponential factors for the dehydrogenation reaction were similar (8×10^{23}) and SiO_2- and SiO_2–Al_2O_3-supported catalysts, and they were larger than those for the other reactions by at least two orders of magnitude. It is noted that the preexponential factor for the homologation on MoO_3/SiO_2–Al_2O_3 catalyst (1.1×10^{19}) was larger than that on MoO_3/SiO_2 catalyst by a factor of 16, whereas the activation energies were the same. It is also noted that preexponential factors for the hydrogenolysis and homologation were of the same order on the MoO_3/SiO_2–Al_2O_3 catalyst.

Effect of MoO_3 Loading

To evaluate the effect of catalyst structure on the reactions, the variation of loading of MoO_3 in SiO_2- and SiO_2–Al_2O_3-supported catalysts for homologation, hydrogenolysis, and dehydrogenation of ethane was investigated. The rates of methane, ethylene, and propane formation on these catalysts are shown in Fig. 3 as a

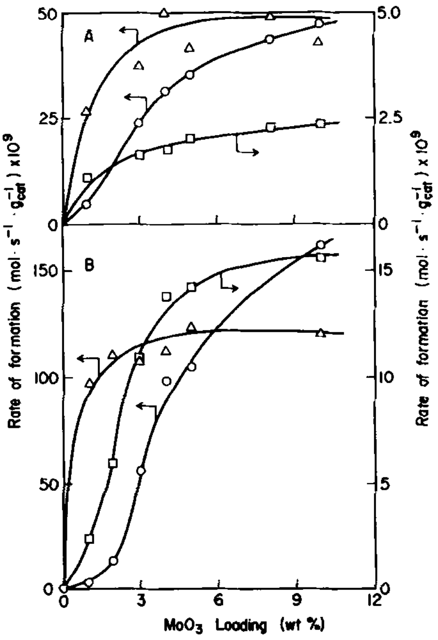

FIG. 3. Effect of MoO_3 loading in A SiO_2- and B SiO_2–Al_2O_3-supported MoO_3 catalysts in the activity of ethane reaction. Reaction conditions are the same as those described in Fig. 2.

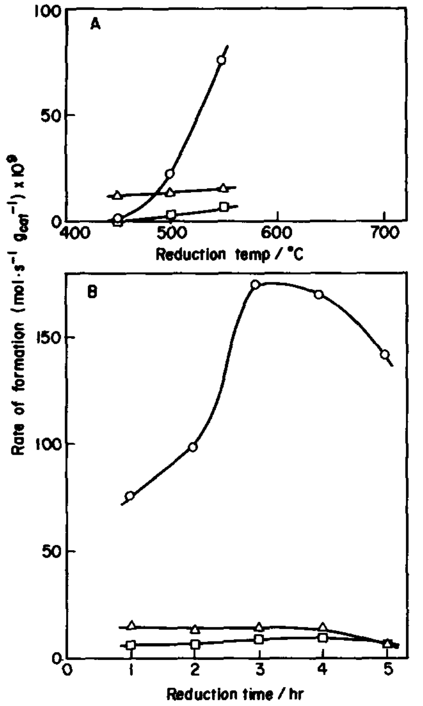

FIG. 4. Effect of catalyst reduction on the initial formation rates of (○) CH_4; (△) C_2H_4; and (□) C_3H_8 at 400°C. MoO_3 (4 wt%) catalyst supported on SiO_2–Al_2O_3 was reduced at different temperatures (A), and for different lengths of time at 550°C (B).

function of MoO_3 loading. The supports alone (SiO_2 or SiO_2–Al_2O_3) did not show any activity for the ethane reactions, suggesting that the molybdenum is responsible for the catalytic activity. Both SiO_2- and SiO_2–Al_2O_3-supported catalysts showed similar behavior. The hydrogenolysis and homologation reactions increased with MoO_3 loading, whereas the dehydrogenation activity sharply increased at low loading but remained unchanged above about 4% MoO_3 loading. In both cases the catalysts show that hydrogenolysis reaction activity is one order higher than the homologation activity.

Effect of Catalyst Reduction

The effect of catalyst reduction on the activity and selectivity for ethane reactions was studied using samples containing 4% MoO_3 in SiO_2–Al_2O_3-supported catalysts. As shown in Fig. 4, activity for dehydrogenation of ethane remained unchanged under the various conditions and degrees of catalyst reduction. In contrast, activities for homologation and, especially, hydrogenolysis reactions increased with the increased reduction of temperature or time.

Effect of Addition of Methane and Ethylene during Ethane Reaction

As mentioned earlier, surface species, CH_x, must be supplied to C_2 species in order to yield C_3H_6, which subsequently hydrogenates to C_3H_8. The CH_x species may also be a precursor to the formation of methane by hydrogenating desorption of CH_x ($CH_x \rightarrow CH_4$). It is worthy investigating whether the CH_x species involved in homologation can be generated by the addition of methane by the reverse reaction ($CH_4 \rightarrow CH_x$). In order to investigate this, $^{13}CH_4$ was mixed with ethane and H_2 (see runs 2–4 in Table 3). The mass spectrometric analysis of the products showed that C_2 and C_3 compounds did not contain any ^{13}C, indicating that methane cannot be involved in the formation of CH_x species.

The reduced MoO_3/SiO_2 has been found to be very active for ethylene homologation, yielding propylene selectively even at room temperature (*11, 13*). Therefore if ethylene, formed by the dehydrogenation of ethane, is an active participant in the homologation reaction, the addition of ethylene into the reactants would be expected to enhance the formation of homologated products. As can be seen in runs 5–7 (Table 3), this was the case. It is worth noting that propylene was found to form in the initial products which in turn hydrogenated to propane; the latter step was dependent on partial pressure of H_2 (see runs 1 and 2 in Table 3), as would be expected.

DISCUSSION

MoO_3 Catalyst Reduction

In general, the reduction of supported MoO_3 catalysts occurs gradually and

TABLE 3

Results of ^{13}C-Labeled Experiments[a]

Catalytic run	Reactants (mmole)				Analysis of Component[b] (mole%)					C_3 (μmole)	^{13}C in C_2–C_3
	$^{13}CH_4$	C_2H_4	C_2H_6	H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8		
1	—	—	0.53	c	1.36	9.67	87.74	0.81	0.42[d]	6.52	—
2	0.42	—	0.52	c	55.08	5.30	39.06	0.38	0.18[d]	5.26	—
3	0.42	—	0.52	0.58	59.61	0.42	39.83	0.02	0.23	2.35	—
4	0.05	—	0.54	0.58	17.11	1.21	81.29	0.03	0.36	2.30	—
5	—	—	0.53	0.53	8.02	1.49	89.94	0.06	0.49	2.92	—
6	—	0.26	0.27	0.58	13.60	1.93	83.20	0.16	1.11	7.37	—
7	—	0.53	—	0.53	4.71	5.96	84.15	2.03	3.15	27.45	—

[a] Experimental conditions: catalyst 0.5 g of 5% MoO_3/SiO_2–Al_2O_3 pretreated at 550°C, reaction temperature 450°C.

[b] After 30 min of reaction: Percentage C_1–C_3 normalized to 100% (a trace amount of C_4 compound was observed when the formation of C_3 was high).

[c] $p^{o}_{H_2} < 10^{-3}$ Torr.

[d] Propane was not detected after 5 min of reaction time.

smoothly to lower valences of Mo without any definite intermediate state (*23*). Depending on reduction temperature and time, the species Mo^{6+}, Mo^{5+}, Mo^{4+}, and even lower valence states may exist. It is possible that at any one state of reduction, more than one valence of Mo is present. The present results show that MoO_3 catalysts supported on either SiO_2 or SiO_2–Al_2O_3 were partially reduced. Under H_2 circulation at 550°C for 1 h, the pretreatment which was used for most of the catalytic studies, the catalysts are shown to possess molybdenum cations of different oxidation states between +4 and +6 in various proportions. In our earlier study (*24*), H_2 chemisorption results suggested no appreciable formation of Mo metal, when 5% MoO_3 supported on SiO_2–Al_2O_3 was reduced in H_2 circulation at 550°C for 1 h. Our results

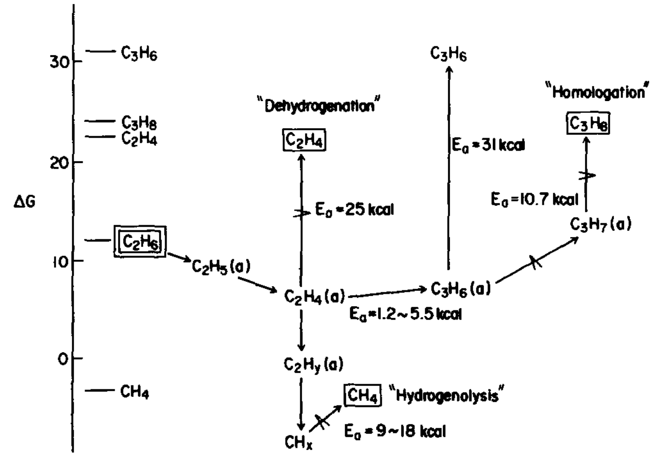

FIG. 5. Thermodynamic data at 427°C and reaction scheme of ethane reactions. E_a represents the activation energy of the respective steps.

are in agreement with those reported by previous authors who, by using the techniques of ESR (*25–27*), UV–Vis optical spectroscopy (*26, 27*), and XPS (*25, 28*), have shown that upon heating of MoO_3 catalysts supported on SiO_2 with molybdena loading of less than 8% in H_2 or CO atmosphere at 400–600°C, Mo^{6+}, Mo^{5+}, and Mo^{4+} ions were produced in various proportions.

Dehydrogenation of Ethane

Thermodynamic data (*29*) at 427°C and a reaction scheme for dehydrogenation, homologation, and hydrogenolysis of ethane are shown in Fig. 5. The activation energy (E_a) of dehydrogenation of ethane to ethylene on reduced MoO_3/SiO_2 and MoO_3/SiO_2–Al_2O_3 is about 25 kcal/mole with similar preexponential factors. In a temperature-programmed desorption (TPD) study it was found that adsorbed ethylene on reduced MoO_3/SiO_2 desorbed at around 50°C, giving an activation energy for desorption of ethylene of 19 kcal/mole (*30*). In the present work, the E_a value observed for dehydrogenation of ethane (25 kcal/mole) is close to that for desorption of ethylene, indicating that the rate-determining step for ethane dehydrogenation is probably the desorption of the ethylene formed. A similar value of E_a (27.5 kcal/mole) was reported for the dehydrogenation of ethane on Cr(VI)/SiO_2 (*31*), which may also be attributed to the same rate-determining step.

The catalytic activity for the dehydrogenation showed a plateau at a very low loading of MoO_3; no change in activity was observed above about 4% MoO_3 loading (Fig. 3). Russell and Stokes (*34*) reported that dehydrogenation activity of MoO_3 catalyst supported on Al_2O_3 increases linearly with increase of MoO_3 content up to the formation of a monolayer after which the activity remains unchanged. The possibility of formation of a monolayer has been reported for MoO_3 catalysts supported on SiO_2 at a low MoO_3 content (<8%) due to formation of silicomolybdate and polymolybdates (*26, 32, 33*).

Hydrogenolysis of Ethane

It is generally accepted that hydrogenolysis of alkane and alkene occurs on active metal sites. So far, there have been many studies of ethane hydrogenolysis. Especially on Ni catalysts it has been reported that the rate-determining step is C–C bond fission (*35, 36*), dissociative adsorption of ethane (*18, 37*), and hydrogenative desorption of adsorbed C_1 fragments (*38, 39*). Ethane hydrogenolysis activity has been found to decrease with a decrease in Ni in Cu–Ni alloy and it has been concluded that 12 Ni atoms unit participate in the reaction (*20*). Such structure sensitivity is generally accepted in hydrogenolysis reactions.

In our experiments, ethane hydrogenolysis activity is significantly enhanced by the increase in catalyst reduction temperature and time (Fig. 4). In addition, hydrogenolysis activity sharply increases with the MoO_3 loading at higher than 3% in MoO_3/SiO_2–Al_2O_3 (Fig. 3). These results infer that the active species for ethane hydrogenolysis is polymolybdate since it is formed at high MoO_3 loading and is more reducible (*40*). It is worth noting that Mo metal formation was not observed under our reduction conditions, and it seems that molybdenum cations of lowered oxidation number are involved in ethane hydrogenolysis.

Anderson and Avery (*41*) observed that hydrogenolysis of propane or higher alkanes occurred more rapidly than that of ethane. In agreement, Burwell and coworkers (*42, 43*) recently found that the rates of hydrogenolysis of propane and butane are similar and they are seven to eight times faster than those of ethane hydrogenolysis. Under our experimental conditions the concentration of propane in the circulating system was found to decrease with time (Fig. 2). This decrease can be interpreted in terms of a secondary hydrogenolysis reaction.

Frennet and co-workers (*39*) studied reactions of $C_2H_6 + D_2$ and $CH_4 + D_2$ on W, Rh, and Ru. They found that hydrogen exchange reaction occurs faster than hydrogenolysis in $C_2H_6 + D_2$, while ethane hydrogenolysis proceeds more rapidly than hydrogen exchange between CH_4 and D_2. From these results the authors concluded that the rate-determining step of ethane hydrogenolysis is hydrogenative desorption of CH_x species (step 4) in the following scheme:

$$C_2H_6 \overset{(1)}{\rightleftharpoons} C_2H_5\ (\mathrm{ads}) + H\ (\mathrm{ads}) \overset{(2)}{\rightleftharpoons}$$

$$C_2H_y\ (\mathrm{ads}) \xrightarrow{(3)} CH_x\ (\mathrm{ads}) \overset{(4)}{\rightleftharpoons} CH_4.$$

After results in Figs. 3 and 4 are compared it seems that hydrogenolysis of ethane is closely related to homologation. In fact, hydrogenolysis supplies CH_x species on the catalysts, which may be the propagating species to the homologation of ethane. In this work, labeled methane was added to the reactants of ethane homologation, and no ^{13}C was found in C_3 compounds. This indicates that the reverse reaction of step ($CH_x \leftarrow CH_4$) is either very slow or cannot occur under the experimental conditions used.

Homologation of Ethane

As shown in Table 3, addition of ethylene enhances the formation of propane in an ethane homologation reaction. It is apparent that the ethane homologation is fundamentally based on the ethylene homologation since reduced MoO_3 catalysts supported on SiO_2 and SiO_2–Al_2O_3 are very active for ethylene homologation (*11, 13, 44*). The activation energies for ethylene homologation were found to be 1.2 and 5.5 kcal/mole on reduced MoO_3/SiO_2 and MoO_3/SiO_2–Al_2O_3, respectively, with preexponential factors of the order of 10^9 molecules · s^{-1} · g^{-1}. If ethane homologation proceeds through gaseous ethylene, formed by dehydrogenation of ethane, then the activation energy should be larger than 25 kcal/mole, the activation energy found for the dehydrogenation of ethane reported above. As shown in Table 2, activation energies of ethane homologation on these catalysts are the same (10.7 kcal/mole). This result can be interpreted as follows: (i) Homologation of C_2 to C_3 proceeds via adsorbed ethylene, C_2H_4 (ads), which is formed by dehydrogenation of ethane and participates in homologation to form propylene. This is reflected by the fact that the ethylene homologation rate is controlled by the reaction on the surface. (ii) The rate-determining step of ethane homologation is the hydrogenation of adsorbed propylene, C_3H_6 (ads), and/or that of the adsorbed propyle intermediate, C_3H_7 (ads), and the activation energy of ethane homologation (10.7 kcal/mole) is observed in this step. The latter assumption is deduced from the analogy of the results of ethylene hydrogenation (*45*).

Preexponential factors of ethane homologation on the catalysts used in the present work are 10^4 to 10^6 times smaller than those of ethane dehydrogenation. They are 10^8 to 10^{10} times larger than those of ethylene homologation. This indicates that the number of active sites of ethylene homologation is quite low, and the number of active sites for hydrogenation of adsorbed propylene, which is produced on the active sites for ethylene homologation, is represented by the preexponential factor of ethane homologation. This clearly suggests that the rate-determining step of ethane homologation is hydrogenation of C_3H_6 (ads) or C_3H_7 (ads). The ethane homologation scheme is summarized as follows.

$$C_2H_6 \dashrightarrow C_2H_4\ (\mathrm{ads}) \underset{\nearrow\ CH_x}{\xrightarrow{E_a = 1.2\text{–}5.5\ \mathrm{kcal/mole}}} C_3H_6\ (\mathrm{ads}) \xrightarrow{E_a = 10.7\ \mathrm{kcal/mole}} C_3H_7\ (\mathrm{ads}) \xrightarrow{E_a = 10.7\ \mathrm{kcal/mole}} C_3H_8$$

$\dashrightarrow$ Dehydrogenation
$\longrightarrow$ Homologation
$- - \rightarrow$ Hydrogenation

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