JOURNAL OF CATALYSIS **106**, 354–361 (1987)

Kinetics and Catalytic Studies of Ethene Homologation over Silica–Alumina Supported Reduced MoO_3 Catalysts

ASHIM K. GHOSH,[1,2] KATSUMI TANAKA,[2] AND ISAMU TOYOSHIMA

Research Institute for Catalysis, Hokkaido University, Sapporo, 060 Japan

Received August 19, 1986; revised March 23, 1987

Silica–alumina (28.61% Al_2O_3) supported reduced MoO_3 catalysts were found to be most active and selective for ethene homologation at a sufficiently low partial pressure of H_2 in the reactant. The insertion of surface species (CH_x) into the adsorbed olefin is considered to be the rate-determining step for ethene homologation, with an apparent activation energy of 5.5 kcal/mol. At a high reaction temperature (above ~300°C) the rate of the homologation decreases due to a competing reaction of ethene fragmentation. Hydrogen was found to enhance the ethene homologation but decreases its selectivity significantly due to increases in hydrogenation and fragmentation. The increased loading enhances the homologation reaction linearly with the loading at low MoO_3 levels, apparently due to formation of an increased number of active sites. © 1987 Academic Press, Inc.

INTRODUCTION

The chain-lengthening of hydrocarbons yielding the next higher homologs is a novel catalytic reaction. In 1972, O'Neil and Rooney (*1*) first reported the direct transformation of ethene to propene over an olefin metathesis catalyst. Since then only a few studies have appeared in the literature of the homologation of alkenes (*1–6*) and alkanes (*7–11*). Of these, O'Donohoe *et al.* (*7, 8*) and Sarakany *et al.* (*9, 10*) reported detailed studies of the homologation of alkanes over W, Rh, Pd, Mo, and Nb films and supported transition metals (Ni, Co, Ru, Rh, Pd, Os, Ir, Pt, and Re). In an earlier paper (*12*), we have reported ethane homologation over various supported reduced MoO_3 catalysts.

It is generally accepted that alkane homologation occurs via an olefin intermediate. It consists of the addition of surface species (CH_x) to the adsorbed olefin via an assumed metallocyclobutane (*7–10*), a commonly accepted intermediate for the olefin metathesis reaction. Recently, Tanaka *et al.* (*13*) have shown that the metathesis and homologation occur via different intermediates. It is apparent that in the homologation of alkanes and alkenes the key steps involve the adsorption of olefin and the insertion of CH_x into the latter.

We have found that the impregnated, reduced MoO_3 catalyst is most active and selective for ethene homologation. In the present study we report the results of a study of ethene homologation kinetics over silica–alumina supported reduced MoO_3 catalyst.

EXPERIMENTAL

The catalyst support used in this work was silica–alumina (28.61% Al_2O_3, surface area 511 m^2/g, pore volume 0.93 ml/g) donated by the Catalysis Society of Japan. Ammonium paramolybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, used for the preparation of the supported MoO_3 catalyst, was obtained from Wako Pure Chemical Industries. High-purity ethene (99.9%), obtained from

---

[1] JSPS Fellow (1985–1986). Present address: Department of Chemistry, University of Houston, Houston, TX 77004.

[2] To whom correspondence should be addressed.

0021-9517/87 $3.00

Takachiho K.K., was used as reactant without further purification. Prepurified H_2 was further treated by passing through palladium reactor at 400°C.

Various MoO_3 loaded catalysts were prepared by impregnating the support with an aqueous solution containing the desired amount of ammonium paramolybdate. (Note that the loading is reported in this paper as wt% Mo). Typically 10 g of the support was mixed with 100 ml of aqueous solution of the molybdate. The water was then slowly evaporated while stirring on a hot plate. The catalyst was dried at 110°C overnight and subsequently calcined at 550°C for 1 h.

The catalytic and kinetic studies were performed using an all-glass, closed circulating reactor system with a total internal volume of ca. 260 cm^3. In this work a standard pretreatment for catalyst samples was used: 0.5 g of catalyst sample was placed between two thin layers of glass wool in a U-shaped reactor that was evacuated while increasing the temperature to 550°C, at which temperature the evacuation was continued for 1 h. After evacuating, the catalyst was reduced by recirculating H_2 ($p^0_{H_2} = 30$ Torr) for 1 h at the same temperature. A liquid nitrogen trap was used to remove any water produced during the reduction. The catalyst was then briefly evacuated ($\sim 10^{-3}$ Torr) and cooled to the desired reaction temperature for catalytic test.

Following the pretreatment of the catalyst sample, a measured quantity of ethene with or without H_2 was admitted into the reactor. For each catalytic run a fresh catalyst sample was used. The gases were recirculated using a Pyrex pump. The reaction products were analyzed at 30°C at different reaction times by using an on-line gas chromatograph (GC) (Hitachi-163) FID/TCD detector, equipped with a Shimadzu Chromatopac C-R3A data processor; column description: 4 m × 3 mm i.d. stainless-steel, packed with Chromosorb 105 (polyaromatic porous beads commercially available from Gaskuro Kohgyo, 60–80 mesh) or Sebaconitrile 25% Uniport C (60–80 mesh). The GC signals (suitably corrected for detector sensitivity) were used to calculate the conversion of ethene and the product distribution. The rate of conversion of ethene, or of formation of a product, is expressed as the number of moles of ethene consumed or, of a product formed, per gram of catalyst per second, determined from the slope of initial product formation. The product selectivity was calculated as follows:

$$\text{selectivity (\%)} = \left(R_i \Big/ \sum_i R_i\right) \times 100,$$

where R_i is the rate of formation of a product i, and $\Sigma_i R_i$ is the sum of the rates of all the products formed. The results of the catalytic runs were found to be within the experimental error of ±5%.

RESULTS

In this work, most of the experiments were done using samples of SiO_2–Al_2O_3 supported MoO_3 (3.3% Mo) catalyst. The BET surface area of this catalyst, after evacuating and reducing in H_2 at 550°C, was found to be 302 m^2/g. No hydrogen chemisorption was observed on the pretreated catalyst, indicating that no appreciable Mo metal was formed. In our earlier paper (*12*), X-ray photoelectron spectroscopy (XPS) results showed that the Mo ($3d_{5/2}$) peak of an unreduced MoO_3/SiO_2–Al_2O_3 catalyst was observed at a binding energy of 233.5 eV. This peak, attributed to Mo(VI), shifted to a lower binding energy after reduction of the catalyst in H_2 at 550°C. The intensity of the peak due to Mo(VI) was found to decrease upon reduction and peaks due to Mo(V) and Mo(IV) appeared at binding energies 231.45 and 229.4 eV, respectively. In the present work, the catalyst was reduced under the same conditions, and we assume that the catalysts possess mostly Mo(VI) and Mo(V), and some Mo(IV).

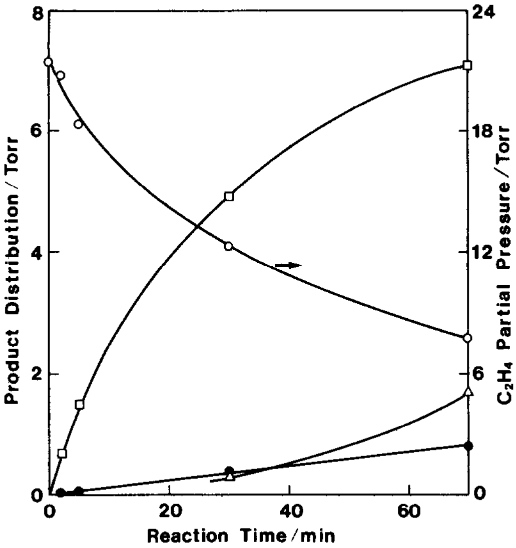

FIG. 1. Ethene conversion and product distribution as a function of reaction time in a recirculating reactor. ○, ethene; □, propene; ●, butenes; △, ethane. Reaction conditions: catalyst (0.5 g) supported MoO_3 (6.7% Mo) pretreated at 550°C, $p^0_{C_2H_4} = 22$ Torr, $p^0_{H_2} = 10^{-3}$ Torr, reaction temperature 250°C.

Kinetic Studies

The results of a catalytic run of the ethene reaction in a circulating reactor are shown in Fig. 1. It can be seen that ethene homologation yielding propene was the dominant reaction occurring at all reaction times. A small amount of 1-butene and isobutene (1-butene/isobutene = 0.6) and traces of methane were also formed. As the reaction proceeded, propene tended to reach an equilibrium. At this low partial pressure of hydrogen (ca. 10^{-3} Torr), hydrogenation of C_2H_4 occurred after an induction period of about 30 min.

All kinetic data were obtained from the initial rates of formation. The data were fitted to an Arrhenius equation,

$$r_0 = A \exp(-E/RT) p^n_{C_2H_4} p^m_{H_2},$$

with the parameters shown in Table 1. The dependence of the rates on the temperature was determined at C_2H_4 and H_2 partial pressures of 20 and 10^{-3} Torr, respectively. (Note that the catalyst was reduced in H_2 followed by brief pumping off to a pressure of ca. 10^{-3} Torr, and no further H_2 was added to the reactant). Under these conditions, the ethene homologation reaction was found to occur most selectively. From the Arrhenius plots (Fig. 2) an apparent activation energy of 5.5 kcal/mol was obtained for ethene homologation at reaction temperatures between 120 and 250°C. This value is much smaller than the activation energy of 10 kcal/mol found for but-1-ene homologation over an iron catalyst (*2*), but is close to the value of 4–7.6 kcal/mol found for *n*-pentane homologation over a supported Ni catalyst (*10*). The rate of the homologation decreased above ~300°C, with an apparent negative activation energy of 7.5 kcal/mol. The apparent activation energy for the hydrocarbon fragmentation was found to be 1.7 kcal/mol below ~300°C and 15.3 kcal/mol above ~300°C. It is worth noting that at the lower temperatures the apparent activation energy for ethene homologation is much higher than that for hydrocarbon fragmentation although significantly higher activity for the homologation is found. The higher activity must be accounted for by the preexponential factor rather than the activation energy.

TABLE 1

Kinetic Behavior of Silica–Alumina Supported MoO_3 (3.33% Mo) Catalyst

Reaction	Temperature range (°C)	E^a	A^b	n^c	m^d	$T(n,m)^e$ (°C)
C_2 (hom)	120–250	5.5	3.3×10^4	1.32	0.63	450
				1.38	0 or –	250
C_2 (hyd)	—	—	—	—	0.75	450
					1.07	250
HC (frag)	100–300	1.7	2.4	0.81	0.83	450
	300–450	15.3	2.1×10^6		1.45	
				0.81	1.52	250

[a] Apparent activation energy, kcal/mol, determined from the temperature dependence of the initial rate (r_0) at ethene and hydrogen partial pressures of 20 and 10^{-3} Torr, respectively.

[b] Preexponential factor, mol × 10^9 s^{-1}/g^{-1}_{cat}.

[c] Exponent on ethene pressure in experimental power rate law.

[d] Exponent on hydrogen pressure in experimental power rate law.

[e] Temperature at which exponents on ethene and hydrogen pressures was determined.

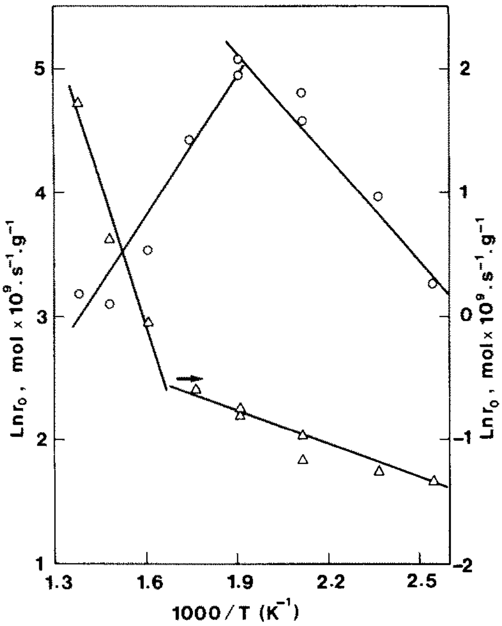

FIG. 2. The Arrhenius plots for ethene homologation (O) and hydrocarbon fragmentation (△). Catalyst (0.5 g) supported MoO$_3$ (3.3% Mo) pretreated at 550°C, $p^0_{C_2H_4}$ = 22 Torr, $p^0_{H_2}$ = 10^{-3} Torr.

C_2H_4 pressure dependence. The dependence of the rate of ethene homologation on the partial pressure of ethene was determined at reaction temperatures 250 and 450°C. In these experiments, the hydrogen pressure was kept constant at ca. 10^{-3} Torr, and the C_2H_4 pressure was varied between 4 and 38 Torr. The results are shown in Fig. 3. At both 250 and 450°C, the reaction order of ethene homologation with respect to C_2H_4 was found to be 1.35 ± 0.03. At 450°C, the reaction order of hydrocarbon fragmentation was 0.81 in the pressure range studied. At 250°C, this rate of fragmentation was not possible to determine an ethene partial pressure below about 18 Torr due to insufficient formation of methane. As a result, the order of the fragmentation at 250°C was determined between the partial pressures of 18 and 38 Torr and was found to be the same as that obtained at 450°C.

H_2 pressure dependence. In general, hydrogen enhanced the rates of ethene homologation, hydrogenation, and hydrocarbon fragmentation. The rate dependence of ethene homologation was determined between the H_2 partial pressures of 3 and 20 Torr at a constant partial pressure of ethene (20 Torr) at a reaction temperature of 450°C. The reaction order was found to be 0.63 (see Fig. 4). Between H_2 pressures of 20 and 40 Torr (that is, $p^0_{H_2}/p^0_{C_2H_4}$ = 1–2), the rate of ethene homologation remained somewhat unchanged, and above this hydrogen/ethylene ratio, it started to decline. The present results are in good agreement with those of Sarakany *et al.* (*10*) who reported that the rate of alkane homologation passes through a maximum at a H_2/HC pressure ratio of about 2. The hydrogenation of C_2H_4 was found to be 0.75 order on partial pressure of H_2. The dependence of hydrocarbon fragmentation on

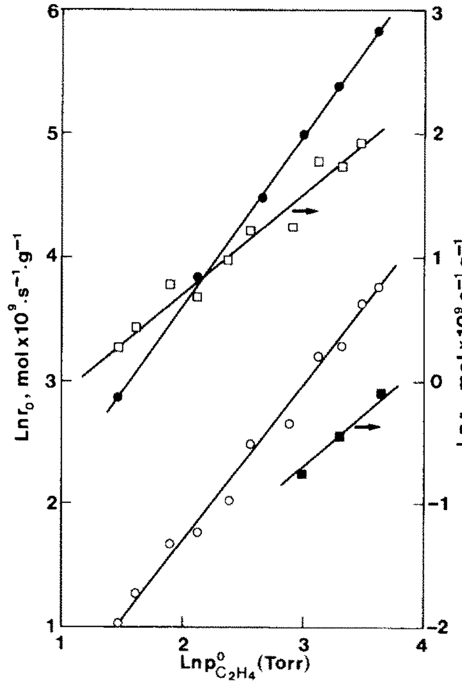

FIG. 3. C_2H_4 pressure dependence of ethene homologation (O, ●) and hydrocarbon fragmentation (□, ■) at reaction temperatures of 450°C (open symbols) and 250°C (closed symbols). Catalyst (0.5 g) supported MoO$_3$ (3.3% Mo) pretreated at 550°C, $p^0_{H_2}$ = 10^{-3} Torr.

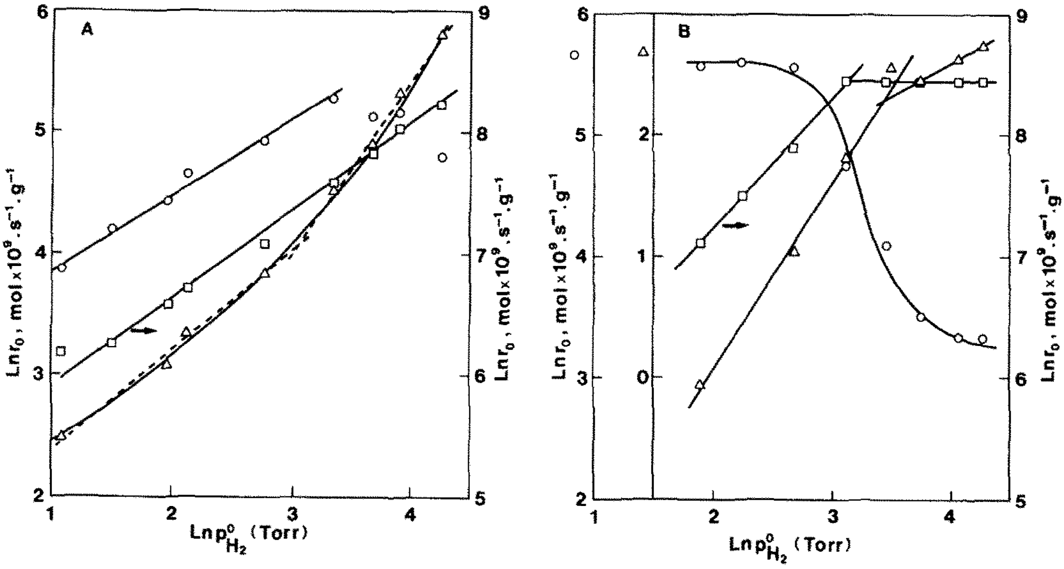

FIG. 4. Hydrogen pressure dependence of ethene homologation (○), hydrogenation (□), and hydrocarbon fragmentation (△) at reaction temperatures of (A) 450°C and (B) 250°C. Catalyst (0.5 g) supported MoO_3 (3.3% Mo) pretreated at 550°C, $p^0_{C_2H_4} = 20$ Torr.

hydrogen did not show a linear relation in the pressure range studied, and seems to have two different reaction orders: $m = 0.83$ and 1.45 at hydrogen partial pressures 3–20 Torr and 20–70 Torr, respectively.

Rather complex kinetics exist at a reaction temperature of 250°C, as can be seen in Fig. 4. In the low hydrogen pressure region (i.e., $p^0_{H_2} <$ ca. 16 Torr), the rate remained almost unchanged, but declined above this hydrogen pressure (Fig. 4B), following a trend seen at high H_2 pressure at the higher reaction temperature of 450°C (Fig. 4A). The order of the ethene hydrogenation with respect to hydrogen is found to be 1.07 at a H_2 pressure of up to about 23 Torr. This order is higher than that obtained for the low coverage condition. The rate of the hydrogenation remained the same above this hydrogen partial pressure (23 Torr) due to the maximum conversion already seen at this H_2 pressure. Hydrocarbon fragmentation showed a reaction order of 1.52 below $p^0_{H_2}$ of 33 Torr. This order is close to that obtained at the low surface coverage at hydrogen partial pressure 20 Torr.

Catalytic Studies

As was seen earlier, the product distribution is very dependent on the partial pressure of hydrogen. It can be seen from Table 2 that at a very low partial pressure of H_2

TABLE 2

Effect of Reaction Temperature on the Transformation of Ethene and Product Selectivity: Hydrocarbon Fragmentation (HC (frag)), Ethene Homologation (C_2 (hom)) and Formation of C_4 Compounds (C_4)

Reaction temperature (°C)	$-R_{C_2H_4}$ (mol × 10^9 s^{-1} g^{-1})	Selectivity (%)		
		HC (frag)	C_2 (hom)	C_4
100	10.35	2.32	93.14	4.54
120	27.29	1.03	95.53	3.44
150	60.47	0.46	89.22	10.32
200	131.92	0.26	91.14	8.60
250	168.40	0.27	91.03	8.70
300	95.42	0.49	88.13	11.38
350	47.24	1.99	73.01	25.00
400	44.48	5.48	64.39	30.13
450[a]	48.66	11.65	49.51	24.27

Note. Reaction conditions: catalyst 0.5 g, supported MoO_3(3.3% Mo), pretreated at 550°C, $p^0_{C_2H_4} = 22$ Torr, $p^0_{H_2}$ = ca. 10^{-3} Torr.

[a] Ethene hydrogenation reaction was found to occur initially at this temperature.

TABLE 3

Effect of Hydrogen Partial Pressure on the Transformation of Ethene and Product Selectivity: Hydrocarbon Fragmentation (HC (frag)), Ethene Homologation (C_2 (hom)) and Formation of C_4 Compounds (C_4)

p_{H_2} (Torr)	$-R_{C_2H_4}$ (mol $\times 10^6$ s^{-1} g^{-1})	Selectivity (%)			
		HC (frag)	C_2 (hyd)	C_2 (hom)	C_4
2.93	0.56	2.11	86.34	8.43	3.12
7.13	0.84	2.57	85.18	9.90	2.35
8.38	0.97	2.94	84.04	10.92	2.10
15.93	1.38	3.32	85.29	9.96	1.44
28.50	2.24	4.06	86.94	8.71	0.29
39.41	2.83	4.72	88.60	5.97	0.72
49.46	3.48	5.91	88.59	5.01	0.49
70.43	4.13	6.26	90.57	2.94	0.23

Note. Reaction conditions: catalyst 0.5 g, supported MoO_3 (3.3% Mo), pretreated at 550°C, $p^0_{C_2H_4}$ = 20 Torr, reaction temperature 450°C.

(ca. 10^{-3} Torr) the conversion of ethene increased with increasing reaction temperature up to about 250°C, after which it decreased. At 250°C, the selectivity for ethene homologation was found to be >90%; while above this temperature the selectivity of C_4 hydrocarbon formation apparently increased. The rate of hydrocarbon fragmentation was found to be small at low reaction temperatures, but increased significantly above about 300°C with a higher apparent activation energy (see Fig. 2). It is noted that due to the low sensitivity of the thermal conductivity detector it was not possible to identify any small amounts of hydrogen that could have been desorbed from the surface. Hydrogen was identified in the product after the reaction at a high temperature (e.g., ca. 400°C) only.

The partial pressure of hydrogen was found to have a great influence on the activity and the product selectivity of ethene reactions (see Table 3). The rate of ethene consumption increased significantly with increasing partial pressure of hydrogen. It was noted that this increased ethene consumption was apparently due to increased rates of hydrogenation and hydrocarbon fragmentation. The selectivities for both of these reactions increased. While the selectivity for the homologation passes through a maximum at a HC/H_2 ratio of about 2, that of C_4 hydrocarbon formation regularly declines with the increased hydrogen partial pressure.

Variation of Mo loading. The catalytic activity of various MoO_3 loaded catalysts is shown in Fig. 5. The most important feature is under the reaction conditions $p^0_{H_2}$ = ca. 10^{-3} Torr, $p^0_{C_2H_4}$ = 22 Torr, reaction temperature 250°C, the dominant reaction is ethene homologation with a selectivity of >90%. It can be seen that the conversion of ethene and its homologation increase linearly with the loading at the low level, and at higher loading the activity seems to remain constant. The increased activity is tentatively attributed to the formation of an increased number of active sites.

DISCUSSION

In the present work the supported MoO_3 catalyst was reduced in H_2 at 550°C fol-

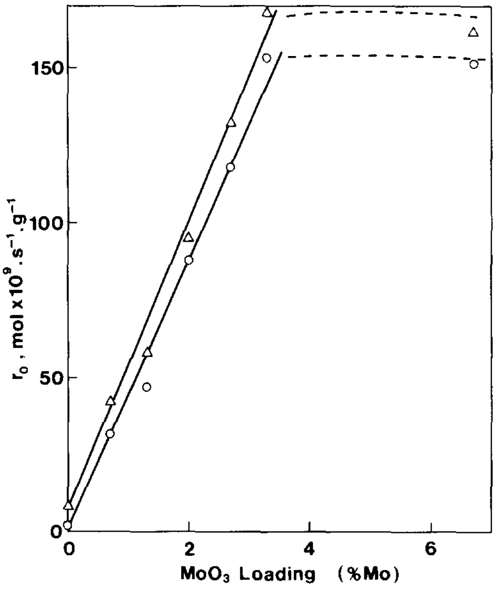

FIG. 5. Variation in Mo loading in the silica–alumina supported MoO_3 catalysts on the rates of ethene conversion (△) and homologation (○). Catalyst (0.5 g) pretreated at 550°C, $p^0_{C_2H_4}$ = 22 Torr, reaction temperature 250°C.

lowed by pumping off (10^{-3} Torr) at the same temperature. When this catalyst had been subjected to the ethene reaction without further addition of hydrogen to the reactant, the ethene homologation reaction occurs most selectively, and the reaction order is 1.35 with respect to C_2H_4, with an apparent activation energy of 5.5 kcal/mol in the lower temperature region i.e., 120–250°C. At sufficiently high temperatures (above ca. 300°C), the rate of the homologation decreases with an apparent negative activation energy of 7.5 kcal/mol. It is noted that a small activity for hydrocarbon fragmentation was seen at the low temperatures but that was increased significantly at high temperatures, with an apparent activation energy of 15.3 kcal/mol; this value is much higher than that found (1.7 kcal/mol) in the lower temperature region. The results indicate that the ethene homologation may occur in competition with fragmentation at a high temperature. A general reaction scheme for ethene homologation can be written as follows:

$$C_2H_4\ (g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_2H_4\ (a)$$

$$C_2H_4\ (a) \xrightarrow{k_2} C_3H_6\ (a)$$

$$C_3H_6\ (a) \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} C_3H_6\ (g)$$

One can recognize that step 2 is rather complex and, in reality, it may involve a series of steps. It is reported (*7–10*) that the adsorbed olefin picks up the so-called surface species CH_x which presumably play a key role in the occurrence of step 2. The generation of the CH_x may involve the following steps:

$$C_2H_4\ (a) \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} C_2H_x\ (a)$$

$$C_2H_x\ (a) \xrightarrow{k_5} CH_x\ (a)$$

If it is considered that step 2 is the rate-determining one for homologation, then the rate of propene formation is given by

$$\text{rate} = (k_2k_1/k_{-1})p_{C_2H_4}.$$

The observed apparent activation energy is related to the activation energies of the individual reactions by

$$E_{obs} = E_1 - E_{-1} + E_2 = 5.5\ \text{kcal/mol}.$$

It is generally accepted that hydrogenolysis of alkanes or alkenes occurs via an adsorbed, dehydrogenated, and cracked surface species. The activity for hydrogenolysis of C_3H_8 is much higher than that of C_2H_6 (*14, 15*), and from this analogy it may be considered that the trace amount of methane detected at a low reaction temperature is due to the fragmentation of C_3H_6 formed rather than C_2H_4 in a single or/and double hydrogenolysis:

$$C_3 \rightarrow C_2 + C_1 \qquad (1)$$

and/or

$$C_3 \rightarrow 3C_1 \qquad (2)$$

of which (2) is highly probable (*14*). In view of the fact that a significantly increased activity for the fragmentation has been seen at high temperatures, it is most likely that C_2H_4 undergoes fragmentation. The surface species CH_x (produced by step 5) yields CH_4 after hydrogenating desorption:

$$CH_x \overset{k_6}{\rightleftharpoons} CH_4$$

The surface may have a high flow of CH_x and the hydrogenating desorption may be considered to be rate-determining for ethene hydrogenolysis (*16*), although different views exist. The concentration of CH_x decreases due hydrogenating desorption, yielding methane, and this process decreases the rate of ethene homologation at high reaction temperatures.

The addition of hydrogen to the reactant plays a decisive role in the selectivity of the ethene reaction. The impregnated MoO_3 catalysts are shown to be highly active and selective for olefin homologation at a sufficiently low partial pressure of hydrogen.

High conversion rates of ethene were found, more than 50% in 70 min of reaction time in the circulating reactor (Fig. 1). The production of C_4 hydrocarbons suggests the occurrence of a single or multiple reactions, such as

$$2C_3 \rightleftharpoons C_2 + C_4,$$

$$4C_3 \rightarrow 3C_4$$

and

$$2C_2 \rightarrow C_4.$$

The first two reactions are more probable since the formation of C_4 compounds was found to be dependent on C_3 formation.

In general, hydrogen enhances the rate of homologation but decreases its selectivity quite significantly. This increase in the rate of the homologation may be attributed to the increase of surface flow of CH_x which enhances step 2. It is apparent that even at a HC : H_2 ratio 10 : 1, ethene homologation is a process in competition with hydrogenation and fragmentation. In the hydrogenation of ethene

$$C_2H_4 \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} C_2H_6.$$

Step 7 is found to be very fast, as is the case of hydrogenating desorption of CH_x (step 6), thereby decreasing the selectivity of ethene homologation.

CONCLUSION

The following conclusions can be drawn from the present work:

(1) At a sufficiently low partial pressure of hydrogen in the reactant, the silica–alumina supported reduced MoO_3 catalysts are shown to be highly active and selective for ethene homologation. Hydrogen plays a decisive role in the selectivity of the reaction. It enhances the rate of the homologation reaction but decreases its selectivity significantly due to increases in ethene hydrogenation and hydrocarbon fragmentation.

(2) The rate-limiting step for ethene homologation is assumed to be the insertion of surface species (CH_x) into the adsorbed olefin with an apparent activation energy of 5.5 kcal/mol. At a high reaction temperature (above ca. 300°C) its rate decreases due to competition with ethene fragmentation.

(3) Ethene homologation is found to be enhanced by an increase in Mo loading, due to the formation of an increased number of active sites.

ACKNOWLEDGMENT

The authors wish to thank the Japan Society for the Promotion of Science (JSPS) for providing a fellowship to one of them (A.K.G.).

REFERENCES

1. O'Neil, P. P., and Rooney, J. J., *J. Amer. Chem. Soc.* **94,** 4383 (1972).
2. Strehlow, R. A., and Douglas, E. C., *J. Chem. Soc., Chem. Commun.*, p. 259 (1982).
3. Yamaguchi, T., Nakamura, S., and Tanabe, K., *J. Chem. Soc., Chem. Commun.*, p. 621 (1984).
4. Tanaka, K., and Tanaka, K., *J. Chem. Soc. Chem. Commun.*, p. 1626 (1984).
5. Hughes, F., Besson, B., and Basset, J. M., *J. Chem. Soc., Chem. Commun.*, p. 719 (1980).
6. Anpo, M., and Kubokawa, Y., *J. Catal.* **75,** 204 (1982).
7. O'Donohoe, C., Clarke, J. K. A., and Rooney, J. J., *J. Chem. Soc., Chem. Commun.*, p. 648 (1979).
8. O'Donohoe, C., Clarke, J. K. A., and Rooney, J. J., *J. Chem. Soc., Faraday Trans. 1* **76,** 345 (1980).
9. Sarakany, A., and Tetenyi, P., *J. Chem. Soc., Chem. Commun.*, p. 525 (1980).
10. Sarakany, A., Palfi, S., and Tetenyi, P., *Acta Chim. Acad. Sci. Hung.* **111,** 633 (1982).
11. Sarakany, A., Palfi, S., and Tetenyi, P., *React. Kinet. Catal. Lett.* **15,** 1 (1980).
12. Ghosh, A. K., Tanaka, K., and Toyoshima, I., *J. Catal.* submitted for publication.
13. Tanaka, K., Tanaka, K., Takeo, H., and Matsumura, C., *J. Chem. Soc., Chem. Commun.*, p. 33 (1986).
14. Guilleux, M. F., Dalmon, J. A., and Martin, G. A., *J. Catal.* **62,** 235 (1980).
15. Nakamura, R., and Burwell, R. L., Jr., *J. Catal.* **93,** 399 (1985).
16. Frennet, A., Degols, L., Lienard, G., and Crucq, A., *J. Catal.* **35,** 18 (1974).