JOURNAL OF CATALYSIS **105**, 530–535 (1987)

A Study of Ethene Homologation over Supported MoO_3 Catalysts: Effect of Catalyst Support and Pretreatment

The catalytic transformation of short-chain hydrocarbons to higher homologs is an important reaction. Since 1972, when O'Neil and Rooney (*1*) first reported the transformation of ethene to propene, only a few reports have appeared in the literature on the homologation of alkenes (*1–6*) and alkanes (*7–11*). In general, the yield of the homologated product was found to be sensitive to the structure and chain length of parent hydrocarbon and partial pressure of hydrogen used in the reaction. The yield was found to increase with the CH_2/CH_3 ratio in the *n*-alkanes, starting from ethane and propane, which showed little or no activity (*8, 10*), and tending to an upper limit with C_7 to C_9 alkanes. In a previous study, we found that various impregnated reduced MoO_3 catalysts are active for ethane homologation, which presumably occurs via insertion of active surface species (CH_x) into adsorbed ethene (*12*). This note reports the results of ethene homologation over the various supported MoO_3 catalysts.

The catalyst supports used in this work were TiO_2 (anatase grade, Titanium Pigment Corporation), ZrO_2 (Kanto Chemicals), SiO_2 (Kieselgel 60, Merck), SiO_2–Al_2O_3 (13.75% Al_2O_3), SiO_2–Al_2O_3 (28.61% Al_2O_3), and γ-Al_2O_3. The alumina and silica–alumina were donated by the Catalysis Society of Japan. The various supported MoO_3 (2.7 wt% Mo) catalysts were prepared by impregnating the support with an aqueous solution of ammonium salt of paramolybdate.

The catalytic studies were performed using an all-glass closed circulating system of total internal volume ca. 260 cm^3. A standard pretreatment for catalyst samples was used: 0.5 g of catalyst sample placed between two thin layers of quartz wool in a U-shaped reactor was evacuated while increasing the temperature to 550°C at which the evacuation was continued for 1 h. After evacuation, 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. After the reduction, excess hydrogen was briefly pumped off and the sample was cooled down to the desired reaction temperature for catalytic tests.

Following the pretreatment of catalyst samples a measured quantity of ethene was admitted into the reactor. Except for experiments in which kinetic data were collected all reactions were carried out at 250°C. For each catalytic run a fresh catalyst sample was used. The gases were recirculated using a Pyrex pump. The reaction products were analyzed at different reaction times using an on-line gas chromatograph. 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 the initial product formation. The product selectivity was calculated as

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

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%.

The results of a catalytic reaction of ethene in a circulating reactor are shown in Fig. 1. It shows that the ethene homologation producing propene is the dominant reaction at all reaction times. A trace amount of methane was observed in the products.

0021-9517/87 $3.00

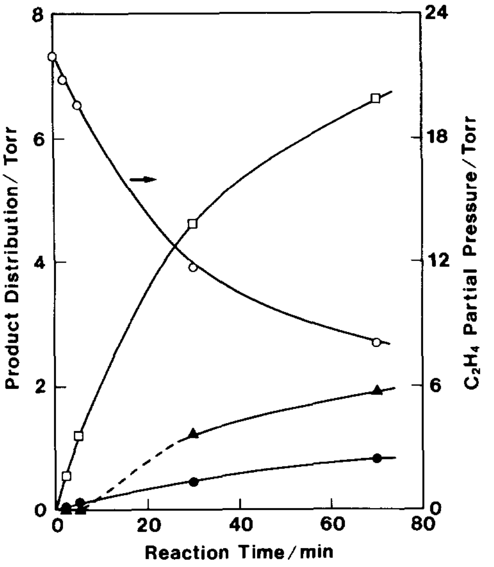

FIG. 1. Ethene conversion and product distribution as a function of reaction time in a circulating reactor. ○, Ethene; □, propene; ●, butenes; ▲, ethane. Reaction conditions: Catalyst (0.5 g) SiO_2–Al_2O_3 (28.61% Al_2O_3) supported MoO_3 pretreated at standard conditions described in text; $p^0_{C_2H_4}$ = 22 Torr, T = 250°C.

Small amounts of 1-butene and isobutene (1-butene/isobutene ratio ca. 0.6) were detected and their formation was found to be dependent on propene formation. In addition, hydrogenation of ethene was found to occur with an induction period of >5 min.

The formation of butenes apparently arises due to the subsequent homologation of propene formed. It is worth noting that SiO_2-supported MoO_3 catalysts were found to be active for alkene metathesis reaction at room temperature (*14*); but in this work propene metathesis, which yields ethene and 2-butene, was not found to occur during the ethene homologation reaction.

In previous work we studied ethene homologation at reaction temperatures between 120 and 450°C over a silica–alumina-supported MoO_3 catalyst (*13*). The rate of the reaction was found to decrease at above 300°C due to a competing reaction of ethene hydrogenolysis. In the present work we have restricted the temperature range to 120 to 250°C to avoid the complication of this competing hydrogenolysis reaction. We therefore believe that the trace quantities of methane detected in these experiments are the products of propene hydrogenolysis and not of ethene hydrogenolysis as it is well known that propene is more readily fragmented than ethene.

Various MoO_3 catalysts, used after standard pretreatment, are shown to be very active and selective for ethene homologation. As seen in Table 1 and Fig. 2, the catalyst support has a significant influence on the activity for ethene homologation.

TABLE 1

Ethene Homologation over Various Supported MoO_3 Catalysts Pretreated at Standard Conditions (Described in Text)

MoO_3 support	Rate of homologation (r_0) (mole × $10^9 \cdot s^{-1} \cdot g^{-1}$)	Percentage propene[a]	S(%)
TiO_2	0.30	0.03	54.22
ZrO_2	1.75	0.31	84.49
Al_2O_3	6.61	9.31	84.85
SiO_2	7.56	2.28	95.86
SiO_2–Al_2O_3 (13.75% Al_2O_3)	16.06	15.63	94.00
SiO_2–Al_2O_3 (28.61% Al_2O_3)	118.10	38.03	89.35

Note. Reaction conditions: 0.5 g catalyst sample pretreated at 550°C, $p^0_{C_2H_4}$ = 22 Torr, T = 250°C.

[a] Percentage propene (C_1–C_4 normalized to 100%) in circulating reactor after 70-min reaction.

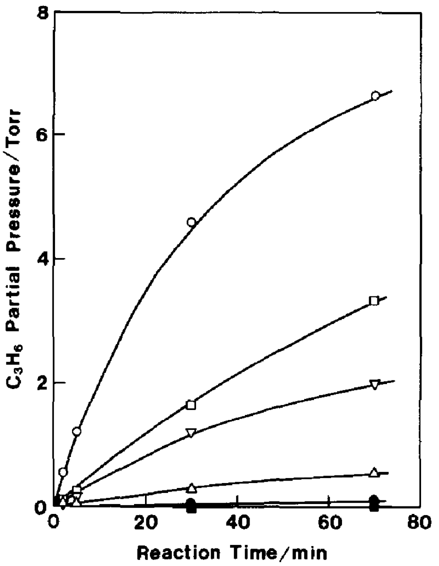

FIG. 2. Partial pressure of propene in a circulating reactor at different reaction times of ethene homologation over various supported MoO_3 catalysts. ○, SiO_2–Al_2O_3 (28.61% Al_2O_3); □, SiO_2–Al_2O_3 (13.75% Al_2O_3); ▽, Al_2O_3; △, SiO_2; ●, ZrO_2; and ■, TiO_2 supported catalysts pretreated at standard conditions described in text; $p^0_{C_2H_4}$ = 22 Torr, T = 250°C.

TABLE 2

Kinetic Behavior of Various Supported MoO_3 Catalysts for Ethene Homologation

MoO_3 support	Temperature range (°C)	E^a	A^b
SiO_2	120–250	1.2	3.2
SiO_2–Al_2O_3 (28.61% Al_2O_3)	120–250	5.5	10.2
Al_2O_3	120–250	6.9	8.5
ZrO_2	150–250	9.0	9.2

[a] Apparent activation energy, kcal/mole, determined from the temperature dependence of the initial rate (r_0) of propene formation at ethene pressure of 22 Torr.

[b] Preexponential factor, mole × 10^9/s/g_{cat}.

The initial rate of the reaction increases in order of the support: $TiO_2 < ZrO_2 < Al_2O_3 < SiO_2 < SiO_2$–$Al_2O_3$ (13.75% Al_2O_3) $\ll$ SiO_2–Al_2O_3 (28.61% Al_2O_3). The SiO_2- or Al_2O_3-supported catalysts are found to be moderately active, whereas the SiO_2–Al_2O_3 is found to be the most effective support. With the increase of alumina content in silica–alumina the effectiveness of the support increases. This is in agreement with our previous results that the SiO_2–Al_2O_3 (28.61% Al_2O_3)-supported MoO_3 catalyst showed the highest activity for ethane homologation, which presumably occurs via an ethene intermediate.

The apparent activation energy, E, for the ethene homologation over the catalysts was determined from the initial rate of formation of propene (r_0). All data were fit with the Arrhenius equation,

$$r_0 = A \exp(-E/RT),$$

with the parameters shown in Table 2. The Arrhenius plots are shown in Fig. 3. It is noted that the apparent activation energy changes with the catalyst support. The reaction occurs over the SiO_2-supported catalyst with a very low activation energy (1.2 kcal/mole). The values of E in the case of

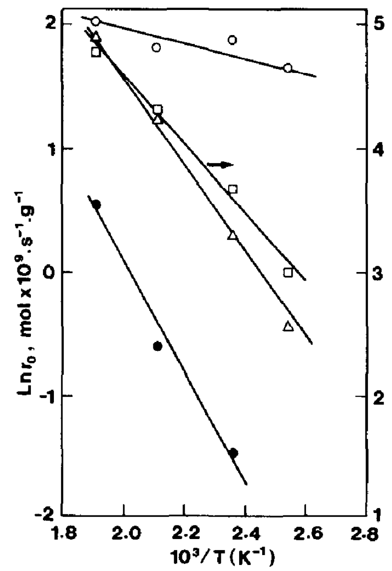

FIG. 3. The Arrhenius plots for ethene homologation over various supported MoO_3 catalysts pretreated at standard conditions described in text. ○, SiO_2; □, SiO_2–Al_2O_3 (28.61% Al_2O_3); △, Al_2O_3; ●, ZrO_2. Reaction condition: $p^0_{C_2H_4}$ = 22 Torr.

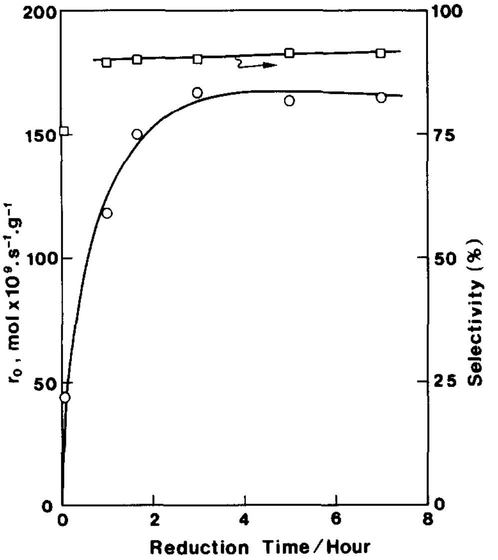

FIG. 4. Effect of length of reduction time at 550°C in H_2 ($p^0_{H_2}$ = 30 Torr) on the rate of ethene homologation and its selectivity. Catalyst SiO_2–Al_2O_3 (28.61% Al_2O_3) supported MoO_3 evacuated at 550°C for 1 h before reduction. Reaction conditions: $p^0_{C_2H_4}$ = 22 Torr, T = 250°C.

the other supported catalysts are much higher and lie in the range 5.5–9.0 kcal/mole. These values are close to the apparent activation energy of 4.0–7.6 kcal/mole for *n*-pentane homologation over a supported Ni catalyst (*10*) and of 10 kcal/mole for but-1-ene homologation over an iron catalyst (*2*). It is noted that the apparent activation energy for the homologation over the silica–alumina-supported catalyst is much higher than that obtained over the silica-supported catalyst, although the former showed higher activity for the reaction in the temperature range studied. As seen in Fig. 3, the SiO_2-supported catalyst would be more active than the other supported catalysts for the homologation at a low reaction temperature; whereas the latter catalysts are highly active at a high temperature. This is explained by the preexponential factor. The change in the activity as well as the apparent activation energy due to the catalyst support indicates that the support must have electronic (*4*) and/or structural (*14*) effects on the molybdenum.

The most active of the catalysts studied was MoO_3 on a SiO_2–Al_2O_3 (28.61% Al_2O_3) support. We used this catalyst to study the effect of reduction on the activity and selectivity for ethene homologation. As seen in Fig. 4, with increasing length of catalyst reduction time at 550°C the rate of homologation increases sharply, indicating that the reaction occurs preferentially on lower valence Mo sites. Under these reduction conditions, we have previously found that Mo^{6+} sites are reduced to Mo^{5+} and Mo^{4+} (*12*) and these are the active sites for ethene homologation. The formation of the active sites is apparently completed in about 3 h reduction at 550°C, as no appreciable change was seen in the rate of the reaction with further catalyst reduction.

Turning to the mechanism of the homologation reaction, a general reaction scheme for ethene homologation can be written as

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

$$C_2H_4\ (a) \xrightarrow{k_2} C_3H_6\ (a) \qquad (2)$$

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

Reaction step (2) is rather complex and involves an insertion of active surface species (CH_x) into an adsorbed ethene. We found previously that an increase in hydrogen partial pressure increases the rate of ethane homologation significantly, and also increases the rate of methane production (*13*). We surmise that the active surface species, CH_x, is the precursor to both the important second step in the homologation reaction above and the reaction producing methane by hydrogenating desorption of the surface species ($CH_x \rightarrow CH_4$). To test this idea we have, in this study, investigated the homologation reaction, following pretreatment of the catalyst with methane, in the hope that the adsorbed methane will generate the surface active CH_x species by

TABLE 3

Results of Ethene Homologation on the Methane-Pretreated SiO_2–Al_2O_3 (28.61% Al_2O_3)-Supported MoO_3 Catalyst

Catalyst treatment[a]	Rate of formation (r_0) (mole × $10^9 \cdot s^{-1} \cdot g^{-1}$)			Percentage propene[b]
	CH_4	C_3H_6	C_4	
A. (1)[c]	0.38	118.10	13.70	38.03
B. $p^0_{CH_4}$ = 10 Torr at				
(2) 150°C/1 h	1.73	110.11	20.87	41.72
(3) 250°C/1 h	1.27	113.38	23.48	42.30
(4) 400°C/1 h	1.61	111.49	16.91	41.11
C. At 250°C/1 h				
(5) $p^0_{CH_4}$ (10 Torr) + $p^0_{H_2}$ (10 Torr)	1.30	134.47	17.34	42.38
(6)[d]	1.24[e]	130.12	18.09	40.13[f]
D. (7) (CH_4 added in C_2H_4)[g]	NC	120.45	18.39	NC[h]
E. (8) At 250°C				
$p^0_{H_2}$ = 10 Torr	0.49	124.67	18.61	41.21

[a] Prior to methane treatment the catalyst was pretreated at 550°C as described in the text.

[b] Percentage propene (C_1–C_4 normalized to 100%) in circulating reactor after 70-min reaction.

[c] Reaction carried out after standard pretreatment.

[d] Catalyst pretreated as in (5) using ^{13}C-labeled methane.

[e] Mass spectrometric analysis showed that methane contained ^{13}C (83.4%).

[f] Mass spectrometric analysis showed that propene contained no ^{13}C.

[g] After standard pretreatment methane was premixed with C_2H_4 ($p^0_{CH_4}$ = 10 Torr, $p^0_{C_2H_4}$ = 22 Torr).

[h] Not calculated.

the reverse reaction ($CH_4 \rightarrow CH_x$). Samples of silica–alumina-supported MoO_3 catalyst, after standard pretreatment, were treated with methane at different conditions as summarized in Table 3. As is seen, CH_4 treatment at 150, 250, or 400°C had no appreciable effect on ethene homologation (compare A and B in Table 3). In contrast, when the pretreated (at standard conditions) catalyst was further treated with hydrogen alone or premixed with methane at 250°C, a small increase was seen in the rate of the homologation. This may be attributed to higher surface coverage by hydrogen which enhances the rate of homologation (*13*). (Note that in this case hydrogen and methane were pumped off at 250°C after treatment, whereas in standard pretreatment H_2 was pumped off at 550°C after reduction.) When ^{13}C-labeled methane was used in the pretreatment, mass spectrometric analysis of the homologation products showed that the propene produced contained no ^{13}C, confirming that the methane does not generate active intermediate species for the homologation reaction. The present results are consistent with our previous study (*12*) in which we showed that the addition of methane to the reactant does not influence the rate of ethane homologation. It is worth mentioning that the methane pretreatment enhances the rate of formation of methane during the homologation reaction. This result suggests that the methane treatment deposits a different type of surface species which in turn desorb as CH_4, as detected by mass spectrometric analysis (see 6 in Table 3). It seems certain that these species are not active intermediates for the homologation reaction.

ACKNOWLEDGMENTS

The authors thank the Japan Society for the Promotion of Science (JSPS) for providing a fellowship to one of them (A.K.G.). Thanks to Dr. David Brown for his valuable discussions.

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Received September 6, 1986; revised January 20, 1987

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