

A Study of Ethane Homologation over Various Supported Reduced MoO₃ Catalysts

The catalytic transformation of ethane to propane is considered to be one of the useful reactions of alkane homologation (1). In our previous study (2) of ethane homologation on reduced MoO₃ supported on SiO₂ and SiO₂-Al₂O₃, the reaction was found to occur via (i) dehydrogenation of ethane to ethylene, (ii) homologation of ethylene to propylene, and (iii) hydrogenation of propylene to propane. The active surface species (CH_x) was assumed to be involved in step (ii) and play a key role in the homologation. It was found that molybdenum species on the supported catalysts are the active sites for the reaction but that catalytic activity seemed to show a dependence on the nature of the support. In this note, we report the results of ethane homologation on various supported reduced MoO₃ catalysts and their characterization by X-ray photoelectron spectroscopy.

The details of experimental procedures have been described elsewhere (2). Supports used in this work were ZnO (Kadox-15, New Jersey Zinc Company), TiO₂ (anatase grade, Titanium Pigment Corporation), ZrO₂ (Kanto Chemicals), SiO₂ (Kieselgel 60, Merck), γ -Al₂O₃, SiO₂-Al₂O₃ (SAH-1) (28.61% Al₂O₃) and SiO₂-Al₂O₃ (SAL-2) (13.75% Al₂O₃). The alumina and silica-aluminas were supplied by the Catalysis Society of Japan. Various supported MoO₃ catalysts were prepared by impregnating the support into an aqueous solution of ammonium paramolybdate to obtain catalysts containing 2.67 wt% Mo. The catalyst was dried in air at 110°C for 16 h and subsequently calcined at 550°C for 1 h in air.

Samples of supported MoO₃ catalysts were placed between two thin layers of glass wool in a U-shaped glass reactor which was connected to an all-glass circulating system with an internal volume of 260 cm³. The sample was evacuated at 550°C for 1 h and was then reduced in H₂ ($p_{\text{H}_2}^0 = 30$ Torr) at 550°C by recirculating the hydrogen for 1 h. A liquid N₂ trap was used to remove water produced during the catalyst reduction. H₂ consumption for MoO₃ reduction was calculated from the amount of H₂O produced. After the reduction, the ethane reaction was carried out at 475°C using a 1:1 mixture of ethane and hydrogen ($p_{\text{total}}^0 = 76$ Torr). The products were analyzed at different reaction times using an on-line gas chromatograph.

XPS spectra of the catalysts were recorded on a VG ESCA-3 spectrometer with Mg K α radiation ($h\nu = 1253.6$ eV). The samples of calcined supported MoO₃ catalysts were mounted on a holder and transferred to the ESCA preparation chamber. XPS spectra were recorded at room temperature at a residual pressure of $<10^{-7}$ Torr at analyzer chamber. The binding energies (BE) were corrected with reference to C(1s) peak at 284.8 eV.

The results of specific loading (Mo/cm² of support), H₂ consumption during catalyst reduction, and average Mo valence state are collected in Table 1. In all cases, the MoO₃ catalysts were partially reduced. Particularly in SiO₂-, Al₂O₃-, and SiO₂-Al₂O₃-supported catalysts which have low specific loading, $(0.3-0.8) \times 10^{14}$ Mo/cm², the average Mo valence state lies between +4.8 and +5.2. The ZrO₂-, TiO₂-, and ZnO-

TABLE 1
Specific Loading, H₂ Consumption during Reduction and Extent of Reduction of Various MoO₃ Catalysts

MoO ₃ support	Surface area of support (m ² /g)	Specific loading (Mo/cm ²)	H ₂ consumption (mol/mol MoO ₃)	Average Mo valence state
SiO ₂	487	0.34×10^{14}	0.38	+5.2
SiO ₂ -Al ₂ O ₃ (SAH-1)	511	0.33×10^{14}	0.60	+4.8
SiO ₂ -Al ₂ O ₃ (SAL-2)	560	0.30×10^{14}	0.60	+4.8
Al ₂ O ₃	200	0.83×10^{14}	0.30	+5.4
ZrO ₂	21	8.16×10^{14}	1.56	+2.9
TiO ₂	13	13.07×10^{14}	1.21	+3.6
ZnO	11	14.94×10^{14}	1.41	+3.2

supported MoO₃ catalysts were reduced readily to a lower valence state, as one would expect, because of their higher specific loadings. In the case of the former catalysts, interaction between the supports and MoO₃ has been reported and the reduction is expected to be difficult.

Figure 1 shows the distribution of products over various catalysts at 475°C as a function of reaction time. In all cases, methane, ethylene, propylene, and propane were found to be the products. As the reaction proceeded, the distribution of products changed appreciably. Except methane, whose concentration increased, all products reached equilibrium, or their concentration decreased, probably because of their subsequent fragmentation to methane. Under the present experimental conditions, we assume that the methane was produced mainly through propane fragmentation, since propane is more readily fragmented than either ethane or ethylene (3). The decrease of ethylene, which is pronounced in the case of SiO₂-Al₂O₃ (SAH-1) and Al₂O₃-supported catalysts, may be due to its fragmentation and/or conversion to C₃ hydrocarbons.

The initial rate of formation of ethane reaction product was calculated from the slope of initial product formation. In this work, the sum of rates of formation of propylene and propane was considered to

be ethane homologation. The catalytic activities of the supported catalysts for ethane homologation are shown in Table 2. The ethane homologation was found to be dependent on the MoO₃ catalyst support and to decrease in order SiO₂-Al₂O₃ (SAH-1) > Al₂O₃ > SiO₂-Al₂O₃ (SAL-2) > SiO₂ > ZnO > ZrO₂ ≈ TiO₂. In this work, SiO₂, SiO₂-Al₂O₃, and Al₂O₃ were found to be more effective than the other supports. This is in agreement with our previous work in which reduced MoO₃ catalysts supported on Al₂O₃, SiO₂, and SiO₂-Al₂O₃ were shown to be more highly active for ethylene homologation than the MoO₃ catalysts supported on TiO₂ and ZrO₂ (4). However, this is in contrast to the results reported by Yamaguchi *et al.* (5), who found that WO₃ catalysts on ZrO₂ and TiO₂ supports showed better activity for ethylene homologation than the WO₃ catalysts supported on SiO₂ and Al₂O₃. The variation in activity with the change of the supports may be attributed to the specific loading and an electronic and/or structural effect on the molybdenum.

The interaction of molybdenum with the supports was investigated by means of X-ray photoelectron spectroscopy. The binding energies (BE) of Mo(3d_{5/2}, 3d_{3/2}) and the full width at half maximum (FWHM) of Mo(3d_{5/2}) peak are listed in Table 3. The width of Mo(3d_{5/2}) peak changes with the

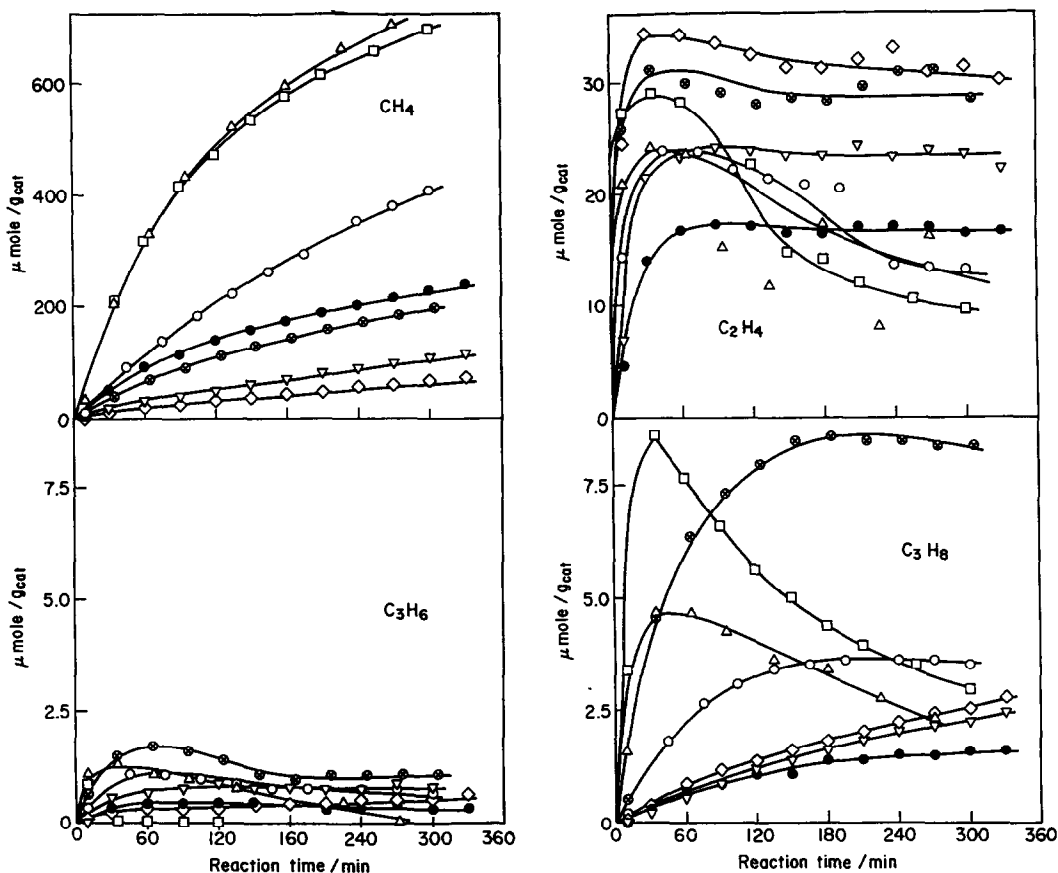


FIG. 1. Product distribution of ethane reaction over various supported reduced MoO_3 catalysts at 475°C . MoO_3 supports: \square , $\text{SiO}_2\text{-Al}_2\text{O}_3$ (SAH-1); \triangle , Al_2O_3 ; \circ , SiO_2 ; \otimes , $\text{SiO}_2\text{-Al}_2\text{O}_3$ (SAL-2); \diamond , ZnO ; \bullet , ZrO_2 and ∇ , TiO_2 .

TABLE 2

Rates of Ethane Reactions over Various Supported MoO_3 Catalysts

MoO_3 support	Rate of formation ($10^9 \text{ mol s}^{-1} \text{ g}^{-1}$)		
	Homologation	Dehydrogenation	HC fragmentation
ZrO_2	0.3	15.6	18.8
TiO_2	0.3	22.8	15.2
ZnO	0.8	83.2	5.2
SiO_2	1.8	48.9	32.6
$\text{SiO}_2\text{-Al}_2\text{O}_3$ (SAL-2)	4.0	87.6	20.3
Al_2O_3	9.0	71.0	119.2
$\text{SiO}_2\text{-Al}_2\text{O}_3$ (SAH-1)	14.5	92.4	111.5

Note. Catalysts 0.5 g pretreated at 550°C , reactant C_2H_6 ($p^0 = 38 \text{ Torr}$) mixed with hydrogen at $\text{HC}/\text{H}_2 = 1.0$, reaction temperature 475°C .

TABLE 3
XPS Binding Energies of Mo(3d) in Various
Supported MoO₃ Catalysts

MoO ₃ support	Binding energies ^a (eV)	
	Mo(3d _{5/2})	Mo(3d _{3/2})
ZnO	233.4 (1.61)	236.5
TiO ₂	233.4 (2.06)	236.6
ZrO ₂	233.5 (2.30)	236.6
SiO ₂	233.4 (2.51)	236.3
SiO ₂ -Al ₂ O ₃ (SAL-2)	233.4 (2.86)	236.6
SiO ₂ -Al ₂ O ₃ (SAH-1)	233.5 (2.91)	236.3
Al ₂ O ₃	233.5 (3.51)	236.6

^a Binding energies are referenced to C(1s) at 284.8 eV, and values in parentheses are FWHM.

change of the catalyst support and the FWHM of this peak decreases in the order Al₂O₃ > SiO₂-Al₂O₃ (SAH-1) > SiO₂-Al₂O₃ (SAL-2) > SiO₂ > ZrO₂ > TiO₂ > ZnO. Peak broadening may be interpreted as due to the presence of different Mo(VI) on the support surface (6) or interaction between the support and MoO₃ (7, 8). Previous workers have observed such interaction between MoO₃ and the support. For example, on Al₂O₃, SiO₂-Al₂O₃ and SiO₂ supports, a small amount of chemically interacted molybdenum may coexist with weakly adsorbed molybdenum (9). There seems to be a correlation between the effectiveness of the various supports for the homologation activity and the observed peak width (FWHM) for the Mo(3d) peak. So, it appears that the interaction of MoO₃ with the support is at least one of the reasons for the dependence of catalytic activity on the nature of the support.

It has been found that in homologation of ethane, dehydrogenation of ethane to ethylene is an essential process that occurs before chain lengthening starts (2). The latter step is rather complex and consists of the addition of surface species, CH_x, to the adsorbed ethylene via an assumed metallacyclobutane (*1b,c*), which yields propylene and subsequently propane by hydroge-

nation. We previously carried out ethylene homologation on various supported reduced MoO₃ catalysts at relatively low temperatures and at a very low hydrogen content in the reactant mixture (4). We found that the ethylene homologation reaction occurs most selectively under these reaction conditions. In addition to propylene, only a small amount of methane was observed in the initial reaction products. We conclude that C-C bond breaking occurs, generating the active intermediate (CH_x), which selectively takes part in either homologation at a very low hydrogen content in the reactant mixture or hydrogenating desorption as methane (CH_x → CH₄) at a higher hydrogen content.

In this work, ZnO-supported MoO₃ catalyst was found to be as active as the silica-alumina- or alumina-supported catalysts for dehydrogenation of ethane, but was not so active for homologation and hydrocarbon fragmentation. This indicates that the ZnO-supported catalyst is not active for the C-C bond-breaking reaction, and hence the surface may not have the high flow of CH_x required for the homologation.

In conclusion, various supported reduced MoO₃ catalysts were shown to be active for ethane homologation. In addition to homologation, dehydrogenation of ethane and hydrocarbon fragmentation occurred predominantly. The activity of the catalyst for the homologation was found to be dependent on the support, possibly because of variations in the specific Mo loading and an interaction of the molybdenum with the supports. It seems that C-C bond breaking, producing an active intermediate (CH_x), controls the rate of ethane homologation.

ACKNOWLEDGMENT

The authors thank the Japan Society for the Promotion of Science (JSPS) for providing a fellowship to one them (AKG). We also acknowledge the help of Mr. H. Suzuki for measuring the surface areas of the supports.

REFERENCES

1. (a) Anderson, J. R., and Baker, B. G., *Proc. R. Soc. London A* **271**, 402 (1963); (b) O'Donohoe, C., Clarke, J. K. A., and Rooney, J. J., *J. Chem. Soc. Chem. Commun.*, p. 648 (1979), and *J. Chem. Soc. Faraday Trans. I* **76**, 345 (1980); (c) Sarakany, A., and Tetenyi, P., *J. Chem. Soc. Chem. Commun.*, p. 525 (1980); (d) Sarakany, A., Palfi, S., and Tetenyi, P., *React. Kinet. Catal. Lett.* **15**, 1 (1980), and *Acta Chim. Sci. Hung.* **111**, 633 (1982).
2. Ghosh, A. K., Tanaka, K., and Toyoshima, I., *J. Catal.* **108**, 143 (1987).
3. Nakamura, R., and Burwell, R. L., Jr., *J. Catal.* **93**, 399 (1985).
4. Ghosh, A. K., Tanaka, K., and Toyoshima, I., *J. Catal.* **105**, 530 (1987).
5. Yamaguchi, T., Nakamura, S., and Tanabe, K., *J. Chem. Soc. Chem. Commun.* p. 621 (1982).
6. Ratnasamy, P., *J. Catal.* **40**, 137 (1975).
7. Cimino, A., and DeAngelis, B. A., *J. Catal.* **36**, 11 (1975).
8. Gajardo, P., Grange, P., and Delmon, B., *J. Catal.* **63**, 201 (1980).
9. Gajardo, P., Pirotte, D., Grange, P., and Delmon, B., *J. Phys. Chem.* **83**, 1780 (1979).

ASHIM K. GHOSH^{1,2}
KATSUMI TANAKA²
ISAMU TOYOSHIMA

*Research Institute for Catalysis
Hokkaido University
Sapporo 060
Japan*

Received April 29, 1987

¹ JSPS Fellow (1985–86). Present address: Department of Chemistry, University of Houston, Houston, TX 77004.

² To whom correspondence should be addressed.