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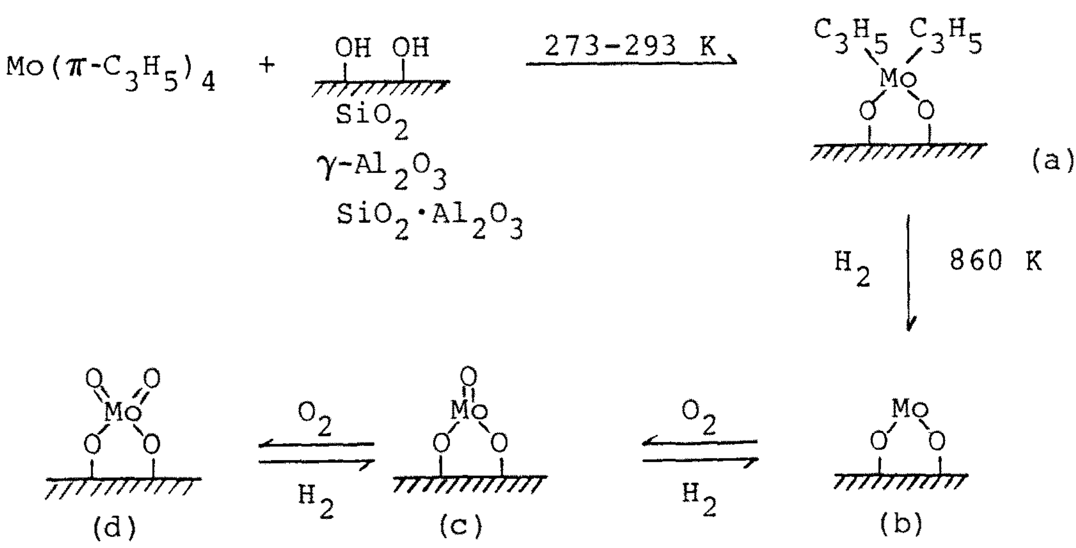
NOTE

Selective Ethane Formation by CO Hydrogenation on Inorganic Oxide-Attached Mo(II)–Monomer Catalysts

It has been demonstrated that specific supported metal catalysts can give particular products with high selectivities from syngas (CO and H_2); e.g., Co–Cd/A-zeolite (*1*) yields selectively propene (ca. 100%), Fe/graphite/K-naphthalenide (*2*) unusually produces acetylene (ca. 95% selectivity), and Cr/Zn/ZSM-5 (*3*) converts carbon monoxide to ethane with 83% selectivity. These phenomena were of great interest from viewpoints of chemical source problems as well as reaction mechanisms in pure C_1 chemistry although real understanding of catalysis on those multicomponent catalysts is open to future studies. In the present paper we report a selective ethane formation by CO hydrogenation on well-characterized one-component supported catalysts with molybdenum(II)–monomers which were prepared by attaching $Mo(\pi\text{-}C_3H_5)_4$ onto SiO_2, Al_2O_3, or $SiO_2 \cdot Al_2O_3$ followed by chemical treatments.

The SiO_2-, γ-Al_2O_3-, and $SiO_2 \cdot Al_2O_3$-attached molybdenum–monomer catalysts were prepared in a similar manner to that previously reported (*4, 5*) as follows:



The Mo(II)–monomers (b) and the Mo(IV)–monomers (c) used as catalysts were obtained by the quantitative reduction of the dioxomolybdenum(VI)–monomers (d) with H_2 at 860 K for 2 h (SiO_2) or 6 h (Al_2O_3 and $SiO_2 \cdot Al_2O_3$), and by the stoichiometric oxidation of the (b) thus obtained with O_2 at 273 K for 30 min, respectively. SiO_2, γ-Al_2O_3, and $SiO_2 \cdot Al_2O_3$ (Al_2O_3 content: 13%) were all commercially available. The Mo loadings in these catalysts were determined to be 1.5–1.9 wt% as Mo/support by chemical analysis.

The catalytic hydrogenation of carbon monoxide was carried out in a closed circulating system with a U-shaped liquid-N_2 trap (circulation rate: 90 $cm^3\ min^{-1}$) under reduced pressures (typically; CO = 150

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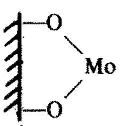
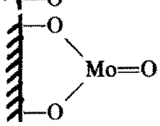
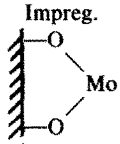
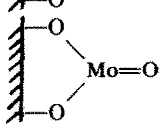
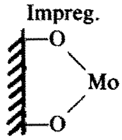
Torr, H_2 = 300 Torr, 1 Torr = 133.3 Pa) using 0.7 g of attached Mo catalysts. The reaction products trapped and in gas phase were analyzed at every 10- to 30-min intervals by gas chromatography using a 5A molecular sieve column (1.5 m) (H_2, CH_4, CO), a VZ-10 column (2 m) (C_2–C_5 and $C_2^=$–$C_5^=$), a Deactigel (SiO_2) column (1 m) (C_2, $C_2^=$, CO_2), and a series column of PEG 1500/Celite (4 m) and DOP/Chromosorb (1 m) (C_5–C_8, $C_5^=$–$C_8^=$, oxygenated compounds).

Murchison (*6*) demonstrated that molybdenum-based catalysts on high-surface-area supports like Al_2O_3 and particularly carbon can produce about 70% of the hydrocarbon products as LPG, most of which is ethane and propane, in the hydrogenation of carbon monoxide under suitable conditions. He also found that a carbon-supported Mo catalyst shows a very low rate of coking and high sulfur tolerance. The conventional Mo catalysts prepared by an impregnation method produced hydrocarbons and carbon dioxides as shown in Table 1 where the SiO_2-supported Mo catalyst gave 73% of the hydrocarbons produced as C_2–C_3 components under the conditions of CO = 150 Torr and H_2 = 300 Torr at 523 K similarly to 70% of LPG fraction reported by Murchison (*6*) although the reaction conditions were much different with each other. The Al_2O_3- and $SiO_2 \cdot Al_2O_3$-supported Mo catalysts yielded mainly methane, where C_2–C_3 components were only 38–53%. The Fischer–Tropsch (F-T) reactions on the impregnation catalysts using

TABLE 1

Activities and Selectivities of Attached and Impregnation Mo Catalysts for CO Hydrogenation at 523 K[a]

Catalysts	Supports	Rates[b]	Selectivities, %		Distributions, %				
			H.C.	CO_2	C_1	C_2	$C_2^=$	C_3	$C_3^=$
	SiO_2	41.9	71.6	28.4	13.1	68.9	0	14.4	3.7
	SiO_2	Very low	—	—	—	—	—	—	—
Impreg.	SiO_2	10.4	61.6	38.4	27.4	41.8	11.5	7.3	10.3
	Al_2O_3	53.1	75.4	12.8	59.0	30.6	0.9	7.3	2.2
	Al_2O_3	32.5	85.2	5.8	61.8	29.9	0	5.3	3.0
Impreg.	Al_2O_3	17.5	58.3	27.9	74.1	16.6	0	7.0	2.2
	$SiO_2 \cdot Al_2O_3$	57.9	66.6	23.9	37.3	51.1	1.5	9.5	0.7
Impreg.	$SiO_2 \cdot Al_2O_3$	14.8	83.3	16.7	46.9	25.3	3.9	4.5	2.7

[a] CO : H_2 = 150 : 300 Torr, 523 K.
[b] 10^{-5} mol h^{-1} (g Mo)$^{-1}$, Mo/SiO_2 = 1.7 wt%, Mo/Al_2O_3 = 1.5 wt%, Mo/$SiO_2 \cdot Al_2O_3$ = 1.9 wt%.

SiO_2, γ-Al_2O_3, or $SiO_2 \cdot Al_2O_3$ supports were not selective and the reaction rates were generally low, the activities decreasing in the order for supports, $Al_2O_3 > SiO_2 \cdot Al_2O_3 > SiO_2$.

In contrast to these traditional Mo catalysts, the Mo(II)–monomers (b) attached on SiO_2 were found to produce ethane at a high selectivity of ca. 70% as shown in Table 1, when the sum of C_2 and C_3 components attained to 87% of the hydrocarbons formed. Higher hydrocarbons than C_4 were negligible or never detected even by flash-heating to 673 K after the F-T reactions. The $SiO_2 \cdot Al_2O_3$-attached Mo(II) catalyst also gave mainly ethane (51%) in contrast to the low selectivity (25%) to ethane for the impregnation catalyst in Table 1. The surface hydroxyl groups of the $SiO_2 \cdot Al_2O_3$ employed may be located on mainly Si atoms according to NMR studies (*7*). The local structure of the Mo(II) species (b) on $SiO_2 \cdot Al_2O_3$ may partially be similar to that of the Mo(II) species (b) attached to SiO_2 surface, but it would be affected electronically and sterically by the presence of Al ions. Actually, the catalytic activity increased and the ethane selectivity decreased compared with the SiO_2-attached catalyst (Table 1). On Al_2O_3 support neither Mo(II) (b) nor oxo-Mo(IV) (c) species were effective to C_2–C_3 formation. The selectivity to ethane on the attached catalysts was about twofold larger in comparison with the impregnation catalysts. The catalytic activities of the three attached Mo(II) catalysts were 3–4 times higher than those of the corresponding impregnation catalysts. Consequently, the SiO_2-attached Mo(II)–monomers (b) provide an efficient one-component catalyst for selective ethane formation from syngas.

REFERENCES

1. Fraenkel, D., and Gates, B. C., *J. Amer. Chem. Soc.* **102,** 2478 (1980).
2. Jones, W., Schlögel, R., and Thomas, J. M., *J. Chem. Soc. Chem. Commun.*, 464 (1984).
3. Chang, C. D., Miale, J. N., and Socha, R. F., *J. Catal.* **90,** 84 (1984).
4. Yermakov, Yu. I., *Catal. Rev.* **13,** 77 (1976).
5. Iwasawa, Y., Nakano, Y., and Ogasawara, S., *J. Chem. Soc. Faraday Trans. 1* **74,** 2968 (1978); Iwasawa, Y., Ogasawara, S., and Soma, M., *Chem. Lett.*, 1039 (1978); Iwasawa, Y., and Ogasawara, S., *J. Chem. Soc. Faraday Trans. 1* **75,** 1465 (1979); Iwasawa, Y., Nakamura, T., Takamatsu, K., and Ogasawara, S., *J. Chem. Soc. Faraday Trans. 1* **76,** 939 (1980); Iwasawa, Y., Ichinose, H., Ogasawara, S., and Soma, M., *J. Chem. Soc. Faraday Trans. 1* **77,** 1763 (1981); Iwasawa, Y., Kubo, H., and Hamamura, H., *J. Mol. Catal.* **28,** 191 (1985).
6. Murchison, C. B., *in* "Proceedings, 4th International Climax Mo Conference, Colorado, 1982," p. 197.
7. Schreiber, L. B., and Vaughan, R. W., *J. Catal.* **40,** 226 (1975); Hall, W. K., Leftin, H. P., Cheselske, F. J., and O'Reilly, D. E., *J. Catal.* **2,** 506 (1963).

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