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HYDROGENATION OF CO OVER SILICA-SUPPORTED Mo-Ir CATALYSTS

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Silica-supported Mo-Ir bimetallic catalysts exhibited much higher activity than the monometallic Mo or Ir catalyst for the hydrogenation of CO at 220-240 °C and 21 atm. Alcohols up to four carbon atoms were found to be produced over the bimetallic catalysts.

Recently, attention has been focused on the activity of bimetallic catalysts for the hydrogenation of CO.[1] We have reported that Ir-Ru bimetallic alloy catalysts are effective for the formation of C_2-oxygenated compounds from synthesis gas.[2] This letter describes an excellent activity of Mo-Ir bimetallic catalysts for the hydrogenation of CO, although Mo[3] or Ir[4] catalyst has little activity by itself.

The catalysts were prepared by impregnating SiO_2 (Davison Grade 57, 12-20 mesh) with aqueous solutions of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $IrCl_4\cdot H_2O$, followed by reduction in H_2 at 500 °C for 3 h. Reactions were carried out at 21 atm of synthesis gas ($CO:H_2:Ar=3:6:1$) with a fixed-bed flow reactor (316 stainless steel). The effluent gas was introduced directly into gas chromatographs for analysis. Results obtained after 15 h on stream were presented. CO conversion was estimated by adding up the yields of products up to five carbon atoms. CO chemisorption measurements were made by a pulse technique in H_2 carrier gas at room temperature.

Table 1 shows the results of the hydrogenation of CO over various Mo-Ir/SiO_2 catalysts. Both Mo/SiO_2 and Ir/SiO_2 were almost inactive under the reaction conditions. The bimetallic catalysts, making a strong contrast with the monometallic catalysts, exhibited high activity. The co-impregnated Mo-Ir/SiO_2(IIIA) was about 500 times as active as Mo/SiO_2(I) or Ir/SiO_2(II) on the assumption that CO conversion was inversely proportional to space velocity. Similar synergetic effects were observed also for the following catalysts different in preparation: Ir-doped Mo/SiO_2(IV), Mo-doped Ir/SiO_2(V), and co-impregnated Mo-Ir/SiO_2(VI) that was air-calcined before H_2 reduction. The order of synergism efficiencies of these catalysts was as follows: IV > III$\approx$V > VI. In addition, alcohols up to four carbon atoms were found to be produced over the Mo-Ir bimetallic catalysts. It is noteworthy that Mo-containing catalysts such as alkali-metal promoted Ru-Mo,[5] Co-Mo-K,[6] and alkali-metal promoted Mo[7] have been reported to be effective for the synthesis of the alcohols.

Table 1. Hydrogenation of CO over silica-supported molybdenum-iridium catalysts[a)]

Catalyst no.	Metal loading wt% Mo	Metal loading wt% Ir	GHSV h^{-1}	CO conv. %	Carbon atom selectivity / % Hydrocarbons C_1	C_2	C_3	C_4	C_5	Alcohols C_1	C_2	C_3	C_4	CO_2
I[b)]	3.2	0	62	0.61	22	8.0	3.6	1.3	0	0	0	0	0	65
II[b)]	0	6.5	62	0.60	42	7.6	4.2	2.2	0.7	15	2.0	0.9	0	25
IIIA[b)]	2.5	5.0	6000	3.0	28	7.5	4.0	1.7	0.8	23	11	3.3	1.0	18
IIIB	2.4	6.2	2000	3.8	26	6.4	3.5	1.2	0.7	22	11	3.7	1.2	23
IV[c)]	2.5	6.4	2000	8.2	24	5.6	2.9	1.2	0.6	23	9.4	2.6	0.9	28
V[d)]	2.3	6.9	2000	3.4	25	6.3	3.2	1.1	0.6	24	10	3.7	1.5	24
VI[e)]	2.4	6.4	2000	0.65	27	7.9	4.3	2.4	1.0	19	12	4.0	1.4	19

a) Conditions: $CO:H_2:Ar=3:6:1$, 21 atm, 220 °C. b) Results obtained after 4 h on stream, 240 °C. c) Ir-doped Mo/SiO_2. d) Mo-doped Ir/SiO_2. e) After impregnation, the catalyst was calcined in air at 500 °C for 3 h and reduced in H_2.

Figure 1 shows the effect of Mo addition to Ir/SiO_2 on activity and CO uptake. The activity increased in proportion to the increase in Mo loading in the Mo/Ir ratios up to 0.2 and reached a maximum. Upon further addition of Mo, the activity remained constant. CO uptake decreased with the increase in Mo loading. The Ir particle size, according to the measurements by transmission electron microscopy, did not change by the Mo doping over the whole range of Mo loading. Thus, the decrease in CO uptake may be attributed to the covering of Ir surface with Mo. These findings suggest that the Mo forms the active sites for CO hydrogenation on the Ir surface and that the amount of the active sites increases in proportion to the increase in Mo loading below the Mo/Ir ratios of 0.2.

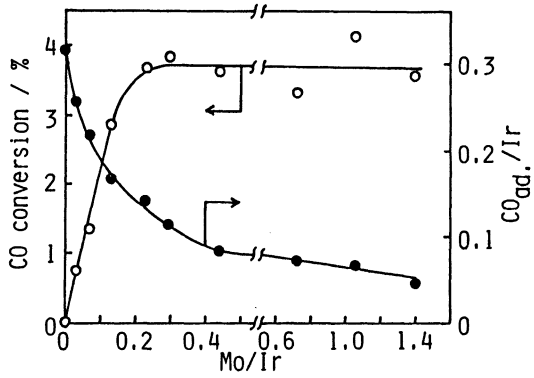

Fig. 1. Effect of Mo addition on activity and CO uptake
6.4 wt% Ir/SiO_2 was doped with Mo. Reaction conditions: $CO:H_2:Ar=3:6:1$, 21 atm, GHSV=2000 h^{-1}, 220 °C.

The roles of Mo and Ir in the bimetallic catalysts are now being investigated.

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References

1) M. Boudart and M. A. McDonald, J. Phys. Chem., 88, 2185 (1984). 2) H. Hamada, Y. Kuwahara, Y. Kintaichi, T. Ito, K. Wakabayashi, H. Iijima, and K. Sano, Chem. Lett., 1984, 1611. 3) C. B. Murchison and D. A. Murdick, Hydrocarbon Process., 60, 159 (1981). 4) M. A. Vannice, J. Catal., 37, 449 (1975); 50, 228 (1977). 5) M. Inoue, T. Miyake, Y. Takegami, and T. Inui, Appl. Catal., 11, 103 (1984). 6) T. Oh-ha and K. Fujimoto, Preprint of the Meeting of Catalysis Society of Japan, Sapporo, Aug. 1983, 3D17. 7) T. Tatsumi, A. Muramatsu, and H. Tominaga, Chem. Lett., 1984, 685.

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