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SELECTIVE SYNTHESIS OF C_2-OXYGENATES BY CO HYDROGENATION OVER SILICA-SUPPORTED Co-Ir CATALYST

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Silica-supported Co-Ir bimetallic catalyst was effective for the selective synthesis of C_2-oxygenates such as ethanol, acetaldehyde, and acetic acid by vapor-phase CO hydrogenation at 280-320 °C and 51 atm. It is suggested that Co-Ir catalyst may form an active species responsible for the synthesis of C_2-oxygenates.

Iridium is ranked as one of the less active metals in the group VIII metals for vapor-phase CO hydrogenation,¹⁾ and this may be the reason why Ir has received little attention. It has recently been reported that Ru-Ir²⁾ or Mo-Ir³⁾ bimetallic catalyst is effective for the selective synthesis of C_2-oxygenates such as ethanol and acetaldehyde or of C_1-C_4 alcohols. In addition to these two Ir-containing bimetallic catalysts, we have found a novel Co-Ir bimetallic catalyst which has, to our knowledge, the higher C_2-oxygenate selectivity than the Co-based multicomponent catalysts shown in the literature.⁴⁻⁶⁾

The catalysts were prepared by simultaneous impregnation of SiO_2 (Davison Grade 57, 20-32 mesh) with mixed aqueous solutions of chloride salts. They were then vacuum-dried at 120 °C for 1 h and reduced in a stream of H_2 at 500 °C for 3 h. Catalytic activities were evaluated by using a conventional flow reactor, to which pressurized (51 atm) gas composed of CO, H_2, and Ar at a ratio of CO:H_2:Ar =3:6:1 was fed. The effluent was analyzed by gas chromatographs. Argon was employed as an internal standard in order to calculate CO conversions and product yields. The activity and selectivity of Co-Ir bimetallic catalysts changed at the initial stage of reaction (3-4 h), and thereafter remained almost constant over 15 h. The results obtained after 15 h on stream were presented.

Figure 1 shows the activities of Co-Ir bimetallic catalysts as a function of metal composition. The catalysts containing both metals (Co-Ir/SiO_2) differed significantly from each catalyst containing one metal (Co/SiO_2 and Ir/SiO_2) in both activity and selectivity. CO conversion increased almost linearly as Ir mole fraction (x_{Ir}) was varied from 0 to

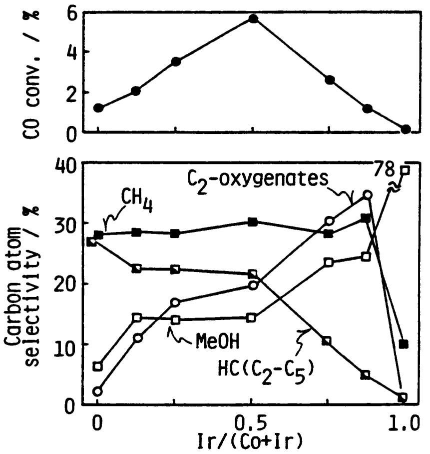

Fig. 1. CO hydrogenation over Co-Ir/SiO_2
Co+Ir=0.2 mmol/g-SiO_2.
Reaction conditions: CO:H_2:Ar=3:6:1, 51 atm, 280 °C, GHSV=2000 h^{-1}.

0.5. The product distribution obtained at x_{Ir}=0 (Co/SiO_2) changed abruptly by the inclusion of a small amount of Ir (x_{Ir}=0.12); C_2-oxygenates were produced in higher selectivity. The product distribution hardly changed in the x_{Ir} range 0.12 to 0.5. These results suggest that Co-Ir bimetallic system may form a new active species, the amount of which is proportional to x_{Ir} in the x_{Ir} range 0 to 0.5.

As x_{Ir} increased further above 0.5, CO conversion decreased. This may be due to the decrease in Co content. The product distribution changed markedly; C_2-oxygenate selectivity continued to increase with x_{Ir} up to 0.88. The improvement of C_2-oxygenate selectivity is attributable to the decrease in selectivity to C_2-C_5 hydrocarbons. Since the production of high molecurar weight hydrocarbons is shown to be suppressed upon the addition of an inactive diluting metal,[7,8] the decrease in selectivity to C_2-C_5 hydrocarbons may be caused by a diluting effect of Ir. Therefore, it is suggested that Ir may act as the diluent for the active species as well as be the component of the active species in the x_{Ir} region above 0.5.

The effect of CO/H_2 ratios of feed gas is shown in Table 1. It is evident that higher CO/H_2 ratios improve C_2-oxygenate selectivity. The selectivity reached 50% at a CO/H_2 ratio of 4.

Table 1. Effect of CO/H_2 ratios on catalytic activity of Co-Ir/SiO_2

CO/H_2	Temp	CO conv.	Carbon atom selectivity / %								
	°C	mmol(h·g-cat)$^{-1}$	ΣC_2-O$^{a)}$	EtOH	AcH	AcOH	MeOH	PrOH	CH_4	HC(C_2-C_5)$^{b)}$	CO_2
0.5	280	0.82	35	27	3.3	4.5	23	1.8	31	4.9	2.5
0.5	300	1.7	33	27	1.9	4.3	23	1.6	34	4.7	3.8
2	280	0.34	47	26	15	6.4	19	2.1	20	5.6	6.2
2	300	0.79	45	27	9.9	8.4	15	2.4	24	6.6	5.4
2	320	2.0	39	26	5.4	7.4	13	2.6	29	7.6	7.8
4	280	0.18$^{c)}$	48	23	14	11	14	2.1	19	7.9	7.7
4	300	0.44	50	22	17	11	13	1.9	20	8.1	5.0
4	320	1.1	43	23	10	10	10	2.2	25	9.3	9.1

Conditions: Co+Ir=0.2 mmol/g-SiO_2, Ir/(Co+Ir)=0.88, 51 atm, GHSV=2000 h^{-1}.
a) Total C_2-oxygenates. b) C_2-C_5 hydrocarbons. c) GHSV=670 h^{-1}.

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References

1) M. A. Vannice, J. Catal., 37, 449 (1975); 50, 228 (1977). 2) H. Hamada, Y. Kuwahara, Y. Kintaichi, T. Ito, K. Wakabayashi, H. Iijima, and K. Sano, Chem. Lett., 1984, 1611. 3) Y. Kuwahara, H. Hamada, Y. Kintaichi, T. Ito, and K. Wakabayashi, Chem. Lett., 1985, 205. 4) P. Courty, D. Durand, E. Freund, and A. Sugier, J. Mol. Catal., 17, 241 (1982). 5) A. S. Lisitsyn, V. L. Kuznetsov, and Yu. I. Ermakov., Kinet. Catal., 24, 652 (1983). 6) K. Fujimoto and T. Oba, Appl. Catal., 13, 289 (1985). 7) L. J. M. Luyten, M. v. Eck, J. v. Grondelle, and J. H. C. v. Hooff, J. Phys. Chem., 82, 2000 (1978). 8) J. A. Dalmon and G. A. Martin, Proc. Int. Congr. Catal. 7th, 402 (1981).

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