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CO_2 Hydrogenation for C_{2+} Alcohols Synthesis over Silica–Supported Ir–Mo Catalysts

Masahiro KISHIDA,* Keiki YAMADA, Hideo NAGATA, and Katsuhiko WAKABAYASHI
Department of Chemical Engineering, Faculty of Engineering,
Kyushu University, Hakozaki, Higashi–ku, Fukuoka 812

CO_2 hydrogenation over silica-supported catalysts was carried out to investigate the synthesis of C_{2+} alcohols (ethanol, propanol and butanol). The Ir–Mo bimetallic system among the catalysts investigated was found to produce C_{2+} alcohols. The catalytic performance of the Ir-Mo catalysts was examined as a function of Mo/Ir molar ratio. It was revealed that the highest selectivity to C_{2+} alcohols was obtained in the Mo/Ir ratios of around 0.3.

Recently, the global warming resulting from an increasing atmospheric concentration of CO_2 is one of the most serious environmental problems, and the development of the technologies for the utilization of CO_2 is considered to be important among many countermeasure technologies. With regard to the utilization of CO_2, the catalytic CO_2 hydrogenation into chemicals and fuels is a promising process.[1–3] However, the synthesis of C_{2+} alcohols from the CO_2 hydrogenation has been scarcely studied.[4–6] In this work, the CO_2 hydrogenation were investigated to obtain the C_{2+} alcohols (ethanol, propanol and butanol), using Rh, Pd, Ru, Ir, Mo and their bimetallic catalysts which showed an interesting performance in the CO hydrogenation.[7–9]

Catalysts were prepared by impregnating SiO_2 (Fuji-Davison Chemical Ltd., Cariact–50) with aqueous metal chloride solutions except $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and then by reducing in H_2 at 400 °C for 2 h. Bimetallic catalysts, Pd*Ru, Ir*Ru and Ir*Mo, were prepared by co–impregnation of two components unless otherwise noted. Ir–doped Mo//SiO_2 was prepared by loading Mo firstly and then Ir, and Mo–doped Ir//SiO_2 by loading Ir and then Mo. All the catalysts were pre–reduced under the above–mentioned conditions before subjected to reaction. The hydrogenation reaction was carried out in a fixed bed flow microreactor at the pressure of 4.9 MPa (H_2:CO_2:Ar=6:3:1). The effluent gas was directly led to gas chromatographs for analysis. The CO_2 conversion and the product selectivities were time–independent after 1 to 3 h on stream.

The results of the CO_2 hydrogenation over various catalysts are listed in Table 1. C_{2+} alcohols were formed neither over all the monometallic catalysts nor over Pd*Ru and Ir*Ru ones. Only the Ir*Mo catalyst, however, showed a slight activity for ethanol and propanol. Butanol were not detected over all the catalysts.

The CO_2 hydrogenation over the Ir–Mo system catalysts were further carried out to investigate the effects of the impregnation sequence and the molar ratio of Mo to Ir. The impregnation sequence for Ir and Mo system had a great influence on the catalytic activity as shown in Table 1. The CO_2 conversion decreased in the following order; Ir–doped Mo > Ir*Mo > Mo–doped Ir. The selectivity to C_{2+} alcohols over the Ir–Mo system catalysts was not significantly dependent on the impregnation sequence. Propanol was not detected only over the Mo–doped Ir catalyst. With regard to the CO hydrogenation over the Ir–Mo system catalysts, we reported in a previous paper that the CO conversion decreased in the same order; Ir–doped Mo > Ir*Mo > Mo–doped Ir, and that the selectivities of these catalysts to C_{2+} alcohols were invariable at about 16 C–mol%.[7] Taking these results into consideration, it is likely that C_{2+} alcohols may be synthesized via CO in the CO_2 hydrogenation. The selectivity to C_{2+} alcohols in the CO_2 hydrogenation was lower than that in the CO hydrogenation, which also suggests that C_{2+} alcohols might be the secondary products in the CO_2 hydrogenation.

The CO_2 conversion and the product selectivities are listed as a function of Ir/Mo molar ratios, as is seen from Table 2. No oxygenates were formed over Ir//SiO_2. With increasing Mo/Ir ratio, selectivities to methanol and CO increased, while that to methane decreased. The main product over Mo//SiO_2 was methanol. C_{2+} alcohols were formed below the Mo/Ir ratio of 2, and the selectivity to C_{2+} alcohols was the highest in the range of 0.2 to 0.3. CO_2 conversion was also the highest in the same region.

Table 1. Hydrogenation of CO_2 over various catalysts

Catalyst (metal cont. wt%)	Conv. %	Selectivity /C–mol%					
		Alcohols			H.C.		CO
		C_1	C_2	C_3	C_1	C_2–C_4	
Rh(2.0)	12.0	tr	0	0	99.3	0.6	tr
Pd(2.1)	3.5	2.9	0	0	5.7	tr	88.6
Ru(2.0)	47.1	0	0	0	99.1	0.9	0
Ir(6.5)	0.4	0	0	0	99.1	0.9	0
Mo(3.2)	0.5	65.7	0	0	13.3	0	19.2
Pd(1.1)*Ru(1.0)	4.7	1.5	0	0	91.5	6.4	0
Ir(6.5)*Ru(1.0)	1.6	0.2	0	0	97.6	1.1	0
Ir(6.5)*Mo(3.2)	7.0	9.7	3.8	0.5	37.2	6.6	41.7
Ir–doped Mo*)	8.4	8.3	3.4	0.4	57.6	4.9	25.0
Mo–doped Ir*)	5.0	9.1	2.9	0	37.7	4.1	46.1

Conditions ; H_2:CO_2:Ar=6:3:1, 200 °C, 4.9 MPa, GHSV:2000 h^{-1}
Reults obtained after 2 h on stream.
*) Ir content=6.5 wt%, Mo content=3.2 wt%.
tr; trace

Table 2. Dependence of products distribution over Ir*Mo//SiO_2 upon Mo/Ir molar ratio

Mo/Ir molar ratio	Conv. %	Selectivity /C–mol%					
		Alcohols			H.C.		CO
		C_1	C_2	C_3	C_1	C_2–C_4	
0.2	12.4	8.8	5.3	0.8	62.1	5.9	16.8
0.25	11.9	9.6	5.3	0.8	61.6	6.2	15.9
0.33	11.9	9.3	5.3	1.0	60.6	6.9	29.8
0.5	10.1	9.9	4.9	0.8	47.0	6.9	29.8
1.0	7.0	9.7	3.8	0.5	37.2	6.6	41.7
2.0	3.7	11.3	0	0	39.7	4.1	42.8

Conditions : H_2:CO_2:Ar= 6:3:1, 200 °C, 4.9 MPa, GHSV: 2000 h^{-1}, Ir content =6.5 wt%.
Results obtained after 2 h on stream.

References

1) G. D. Weatherbee and C. H. Barthromew, *J.Catal.*, **68**, 67 (1981).
2) M. Pijolat, V. Perrichon, M. Primet, and P. Bussieve, *J. Mol. Catal.*, **17**, 367 (1982).
3) A. Guerrero–Ruiz and I. Rodoriguez–Rawas, *React. Kinet. Catal. Lett.*, **29**, 93 (1985).
4) R. Fujii, *Nippon Kagaku Kaishi*, **64**, 1103 (1943).
5) T. Inoue, T. Iizuka, and K. Tanabe, *Appl. Catal.*, **46**, 1 (1989).
6) T. Tatsumi, A. Muramatsu, and H. Tominaga, *Chem. Lett.*, **1985**, 593.
7) Y. Kuwahara, H. Hamada, Y. Kintaichi, T. Ito, and K. Wakabayashi, *Chem. Lett.*, **1985**, 205.
8) W. Keim, M. Berger, and J. Schlupp, *J.Catal.*, **61**, 359 (1980).
9) M. M.Bhasin, W. J. Baetley, P. C. Ellegen, and T. P. Wilson, *J. Catal.*, **54**, 120 (1978).

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