CO_2 Hydrogenation to Alcohols over Highly Dispersed Co/SiO_2 Catalysts Derived from Acetate

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Highly dispersed Co(A)/SiO_2 catalysts were prepared from acetate, and used for CO_2 hydrogenation to alcohols under the reaction conditions of T = 493 K, P = 2.1MPa, H_2/CO_2 = 3/1, and GHSV = 2000 h^{-1}. Catalytic activity was greatly improved by adding a small amount of Ir to the catalyst, and methanol (ca. 20%) was formed, in contrast with Co(N)/SiO_2 catalyst derived from nitrate. Ethanol selectivity was increased up to 8% by adding Na salt to the Ir/Co(A)/SiO_2 catalyst.

Catalytic hydrogenation is one of the most promising ways of CO_2 fixation from view points of the efficiency and the diversified products.[1] Methanol (MeOH) synthesis by CO_2 hydrogenation has been extensively studied over mainly Cu-based catalysts, and even a bench scale test is now in progress.[2] On the contrary, only several investigations have been reported on the direct conversion of CO_2 to ethanol (EtOH). Okamoto et al.[3] and Inui et al.[4] developed combined catalyst systems based on K/Fe–Cu–ZnO(–Al_2O_3), respectively, and high STY of EtOH was obtained. The concept of the catalyst design is reported to be the combination of C–C bond formation catalysts and catalysts for oxygenate formation. Rh-based catalysts were reported by Kusama et al.[5] Rh is known as the typical catalyst species for oxygenate production from synthesis gas (CO/H_2 mixture). The concept of the catalyst design is the modification of the electronic state of Rh, resulting in application to CO_2 hydrogenation. Ru-based homogeneous catalyst system was also reported by Tominaga et al.[6] The noble metal catalysts are financially limited for wide application in industrial scale.

Cobalt is well known as typical catalyst for Fischer–Tropsch (F–T) synthesis to form hydrocarbons. However, it is reported that some oxygenates are also formed in F–T reaction, when Co is highly dispersed.[7] The catalysts for CO hydrogenation is generally applicable to CO_2 hydrogenation, too. Thus, Co/SiO_2 catalysts with high-dispersion were prepared from acetate, and tried to use for CO_2 hydrogenation to oxygenates.

Silica gel (Fuji–Davison #57, 16–32 mesh size, S = 260 m^2g^{-1}, V_p= 1.2 cm^3g^{-1}, D_p= 18 nm) was impregnated with aqueous solution of cobalt acetate or nitrate by the incipient wetness method to form 5 wt%-Co/SiO_2 catalysts (denoted as Co(A)/SiO_2 and Co(N)/SiO_2, respectively). Alkali and alkaline earth metal (M) acetate were added by co-impregnation. After pre-treatment in H_2 flow at 573 K for 3 h, $Ir_4(CO)_{12}$ was added to Co–M/SiO_2 by the vapor phase deposition method at 433 K *in vacuo*. After reducing the Ir/Co–M/SiO_2 catalysts at 723 K for 3 h, CO_2 hydrogenation was carried out under reaction conditions of T = 473–508 K, P = 2.1 MPa, H_2/CO_2 = 3/1, GHSV = 2000 h^{-1}. Effluent gas from the fixed bed reactor was analyzed by on-line gas chromatography.

The reaction results at 493 K were summarized in Table 1. The amounts of the additives were Ir/Co/M = 0.13 / 1.0 / 0.67 in atomic ratio. Since almost no deactivation was observed, the results at time-on-stream of t = 4–6 h were listed. The conventional catalyst Co(N)/SiO_2 showed relatively high activity without additives, and the main product was CH_4, as commonly recognized.[8] In contrast, the catalyst derived from acetate without additives, Co(A)/SiO_2, showed almost negligible activity. The results of XPS and H_2 chemisorption measurement indicated that Co in Co(N)/SiO_2 could be reduced to metallic state, Co^0, while that Co in Co(A)/SiO_2 was hardly reduced. However, by adding Ir to Co(A)/SiO_2 (Ir/Co = 0.13 in atomic ratio), CO_2 conversion was greatly improved, and MeOH was formed. Since Ir/SiO_2 itself did not show any activity in CO_2 hydrogenation, the improvement is thought to be a synergistic effect between Ir and Co(A)/SiO_2. The TPR result indicated that Ir/Co(A)/SiO_2 was easily reduced as low as 540 K, while that Co(A)/SiO_2 was not reduced below 1070 K. The XPS results showed that %-reduction to Co^0 (or $100 \times Co^0/(Co^0+Co^{2+})$) on Ir/Co(A)/$SiO_2$ surface was %-Co^0 = 75%, which was almost comparable to Co(N)/SiO_2 surface, %-Co^0 = 73%, as shown in

Table 1. CO_2 hydrogenation over Co-based catalysts[a]

Catalyst[b]	CO_2 conv. / C-%	CH_4 selec. / C-%	$C_{2\text{-}8}$[c] selec. / C-%	CO selec. / C-%	MeOH selec. / C-%	EtOH selec. / C-%
Co(N)/SiO_2	9.2	93.8	3.4	0.0	2.7	0.1
Co(A)/SiO_2	0.5	15.0	0.8	67.0	17.1	0.0
Ir/SiO_2	0.5	9.4	0.5	90.1	0.0	0.0
Ir/Co(A)/SiO_2	10.0	68.2	1.5	9.6	20.3	0.4
Ir/Co(A)–MgO/SiO_2	11.9	64.5	2.2	10.9	21.9	0.6
Ir/Co(A)–CaO/SiO_2	5.4	21.9	0.8	41.0	35.2	1.1
Ir/Co(A)–SrO/SiO_2	4.7	32.1	0.9	38.7	27.0	1.2
Ir/Co(A)–Li_2O/SiO_2	5.6	49.7	7.1	24.4	16.3	2.5
Ir/Co(A)–Na_2O/SiO_2	7.6	35.7	9.6	38.5	7.8	7.9
Ir/Co(A)–K_2O/SiO_2	7.8	28.5	4.2	55.6	5.6	6.1

[a] Reaction conditions: T = 493 K, P = 2.1 MPa, H_2/CO_2 =3/1, GHSV = 2000 h^{-1}. [b] Ir / Co / M = 0.13 / 1.0 / 0.67 (in atomic ratio); M = Mg, Ca, Sr, Li, Na, K.
[c] C_{2-8} hydrocarbons.

Table 2. %-Co^0 determined by XPS, and H_2 volume adsorbed

Catalyst	Ir/Co[a]	Na/Co[a]	%-Co^0	H_2 ads. / cm^3 g^{-1}
Co(N)/SiO_2	-	-	73.1	0.195
Co(A)/SiO_2	-	-	4.4	0.001
Ir/SiO_2		-	-	0.278
Ir/Co(A)/SiO_2	0.03	-	22.6	0.156
Ir/Co(A)/SiO_2	0.07	-	31.0	0.217
Ir/Co(A)/SiO_2	0.13	-	75.0	0.316
Ir/Co(A)–Na_2O /SiO_2	0.13	0.67	74.9	0.279

[a] Atomic ratio. [b] 2wt%Ir/SiO_2.

Table 2. The similar effects of reduction by Pt and Ru addition have been also reported on Co-based catalysts for F–T synthesis.[9] However, no XRD peaks were observed on the Co(A)/SiO_2 and Ir/Co(A)/SiO_2 catalysts, implying that the crystallite size of Co metal of these catalysts was smaller than 3 nm. On the other hand, the crystallite size of Co of Co(N)/SiO_2 was estimated at about 6 nm by the XRD line broadening. These results suggest that the highly dispersed Co catalyst is obtained from acetate and activated by adding Ir, and that the high dispersion is responsible for oxygenate selectivity. The effect of the adding amount of Ir to the Co(A)/SiO_2 catalyst was investigated in the range of Ir/Co = 0.03–0.26. Although H_2 adsorption amount was increased with Ir amount, CO_2 conversion and selectivity were slightly affected in the range.

The effect of alkaline earth metal (M) additives on CO_2 hydrogenation was investigated over Ir/Co(A)/SiO_2 catalyst (M/Co = 0.67 in atomic ratio). CO_2 conversion and CH_4 selectivity tended to be decreased, and CO selectivity was increased, with the basicity of alkaline earth metal additives. The highest MeOH selectivity up to 35% was obtained over Ir/Co(A)–CaO/SiO_2 catalyst, which showed moderate selectivity for CH_4 and CO. The catalyst with high hydrogenation activity may show the highest CH_4 selectivity, for CH_4 is the most extremely hydrogenated product. Since CO_2 adsorbed on the catalyst surface is consecutively hydrogenated to CH_4 via CO adsorbed species, CH_4 selectivity is generally traded off with CO selectivity. Thus, CO formation as well as moderate hydrogenation activity may be prerequisite to MeOH formation.

Effects of alkali metal additives were also examined. Methane selectivity was decreased and CO selectivity was increased with the basicity of the additives, in a similar manner as alkaline earth metal additives. In contrast with alkaline earth metal addition, however, selectivity for C_{2+} hydrocarbons increased, and EtOH, instead of MeOH, was formed by adding alkali metal additives. The C–C bond formation of reaction intermediates was presumably promoted by alkali metal addition, resulting in EtOH selectivity. The selectivity was hardly varied in the conversion range of 5–26%. The highest selectivity up to 8% was obtained over Ir/Co(A)–Na_2O/SiO_2 catalyst.

In conclusion, highly dispersed Co(A)/SiO_2 catalyst obtained from acetate was drastically activated by impregnating with Ir, resulting in MeOH formation in CO_2 hydrogenation. By adding alkaline earth and alkali metal salts to Ir/Co(A)/SiO_2 catalysts, the selectivity for MeOH and the selectivity for EtOH were increased, respectively. Since conversion was increased without significant change in EtOH selectivity at a higher temperature below 523 K, the highest STY of EtOH up to 7.9 g dm^{-3} h^{-1} was obtained over Ir/Co(A)–Na_2O/SiO_2 catalyst at 508 K.

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