Active Co/SiO$_2$ Catalysts Prepared from Mixing Precursors for Slurry Phase Fischer-Tropsch Synthesis

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The catalysts prepared by mixing impregnation of cobalt (II) nitrate and cobalt (II) acetate displayed high activity. X-ray diffraction indicated that highly dispersed cobalt metal was the main active site on the catalyst prepared by mixing impregnation method. The metal reduced from cobalt nitrate promoted the reduction of Co^{2+} to metallic state in cobalt acetate by H$_2$ spillover mechanism during catalyst reduction process.

Supported cobalt catalysts are widely used in CO hydrogenation, leading to formation of methane and higher hydrocarbons,[1] which is very important for the production of synthetic fuel (Fisher-Tropsch synthesis, FTS). Iglesia et al.[2] pointed out that the overall hydrocarbon synthesis rates on cobalt catalyst were proportional of metal dispersion and independent of the metal oxide support nature, while the C$_{5+}$ selectivity slightly increased with increasing Co site density because of diffusion-enhanced readsorption of α-olefins.

Here, it is reported that using different cobalt salts as precursors has great effect on the cobalt catalyst activity and selectivity. Highly active cobalt catalysts made from the mixture of cobalt nitrate and cobalt acetate and their performance in the hydrogenation of carbon monoxide in slurry phase will be introduced.

The supported cobalt catalysts were prepared by incipient-wetness impregnation of cobalt (II) salts on silica gel (ID gel, Fuji Davison, 270 m^{2}g^{-1}, pore volume 1.22 cm^{3}g^{-1}), drying in air at 393 K for 12 h, and then calcining at 723 K for 2 h in air. After calcination, catalysts were activated in flowing hydrogen at 673 K for 10 h. The catalysts were passivated by 1% O$_2$ in N$_2$. For the sequentially impregnated catalysts, after the first impregnation step, the catalyst precursor was dried for 12 h at 393 K. Then, it was calcined in air at 723 K for 2 h and used for the second salt impregnation repeating the procedure.

The nomenclature for catalysts in this study consists of two parts [X/Y] or [X+Y]. The first part refers to the type of used cobalt metal salt: "N" indicates cobalt (II) nitrate, "A" indicates cobalt (II) acetate and "C" for cobalt (II) chloride. The second part gives the order of impregnation of metal salts: [X/Y] means that "X" was impregnated into the support before "Y", and [X+Y] means that X and Y were coimpregnated. The cobalt molar ratio of X/Y was 1.

Catalysts were tested in a semi-batch slurry-phase reactor (volume: 80 ml). All of the tests were conducted under 1.0 MPa at 513 K in a stream of CO/H$_2$ = 1/2 and W/F = 5 g-cat.h/mol. The amount of catalyst was 1 g. 20 ml of n-C$_{16}$H$_{34}$ was used as liquid medium. An X-ray diffractometer instrument (XRD, Rigaku) with monochromatized CuKα radiation was used for the X-ray measurements. The catalyst samples for XRD were at oxide state. Average Co$_3$O$_4$ particle sizes were calculated by the Scherrer equation. The diameter of a given Co$_3$O$_4$ particle could be used to calculate the diameter of metallic Co crystallite by the formula[3] below:

$$D\,(\mathrm{Co}^0) = 0.75\, d\,(\mathrm{Co_3O_4})$$

Thermal gravimetric (TG) measurements were conducted using a Shinku-Riko MTS 9000 instrument. The catalyst precursor after calcination was placed in the furnace and heated in a stream of H$_2$ to the desired temperature at a heating rate of 18 °C min^{-1} and held at this temperature for 10 min.

A quartz-made microreactor was used for Temperature-Programmed Reduction (TPR). 5% H$_2$ in Ar was used as reducing gas. The effluent gas was monitored by gas chromatography, while the temperature rising rate was 7 Kmin^{-1}.

Table 1. Catalytic behaviors of various Co (10 wt%)/SiO$_2$ catalysts for CO hydrogenation and particle size

Catalyst	CO conv./%	CH$_4$ sel./%	CO$_2$ sel./%	α	XRD/nm
Co (N)	29.8	6.58	1.64	0.85	15.5
Co (A)	9.2	1.62	1.63	N/A	N/A
Co (C)	1.6	24.63	0.42	N/A	N/A
Co (A/N)	31.3	6.65	1.19	0.85	12.1
Co (N+A)	33.5	8.89	1.27	0.84	6.2
Co (N/A)	42.5	6.27	1.82	0.86	10.1
Co (N)^a	9.0	4.67	0.71	0.86	14.8

Total cobalt loading amount: 10 wt%, a: 5 wt%. Reaction conditions: 1.0 MPa, 513 K, W/F = 5 g-cat.h/mol.

The catalytic results are compared in Table 1. The catalytic activity decreased in the order Co (N) >> Co (A) > Co (C). Catalyst Co (N) had the highest activity, because Co (N) began to be reduced at 523 K and the reduction was completed at 673K as shown in Figure 1. The reduction degree calculated by TG curve was about 93%. The catalyst Co (A) had small cobalt particle size, but some kinds of oxide species could not be reduced to cobalt metal even at 673 K for 10 h in H$_2$ as supported by the findings of Matsuzaki et al's result.[4] The results in Figure 1 also show that the Co (A) was reduced under the H$_2$ stream just at about 1000 K, although cobalt acetate in bulk compound state was easily reduced to metallic cobalt at less than 623 K as cobalt nitrate. This phenomenon may be due to the fact that Co^{2+} from cobalt acetate has strong interaction with the SiO$_2$ support,[5] and the Co-O bonds were still kept under reduced conditions. The catalyst Co (C) was inactive for CO hydrogenation. The results in Figure 1 show that the Co (C) was reduced under H$_2$ atmosphere at about 773 K. Furthermore, the cobalt metals crystallite from Co (C) was at α state, different from the cobalt crystallite from cobalt nitrate,

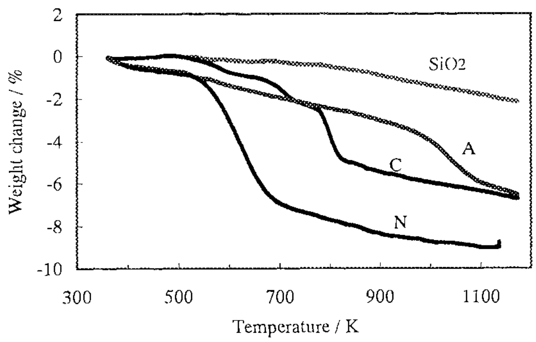

Figure 1. TG curves of catalysts Co (N), Co (A), Co(C) and pure SiO_2 in H_2 atmosphere.

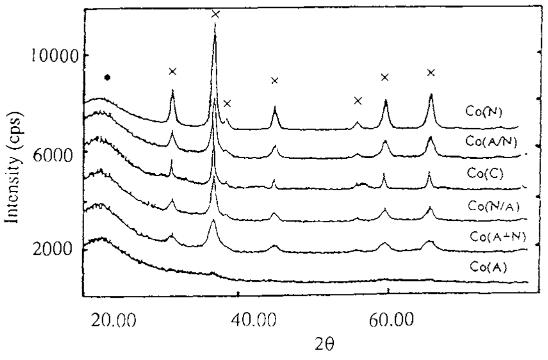

Figure 2. X-ray diffraction spectra of oxide state Co (N), Co (A/N), Co (C), Co (N/A) and Co (A) on silica × Co_3O_4 • SiO_2. Total loading: 10 wt%.

which was at β state.[4] It seems that the α state cobalt of metal was inactive for CO hydrogenation.

As in Table 1, the catalysts Co (A/N), Co (N/A) and Co (N+A) were active for CO hydrogenation and more active than Co (N)[a], although the catalyst Co (A) had little activity for CO hydrogenation. It should be noted that Co (N)[a] with 5 wt% cobalt showed only 9.0% conversion. Table 1 shows that the cobalt metal particle size decreased in the order Co (N) > Co (A/N) > Co (N/A) > Co (N+A) > Co (A). The order of catalytic activity was Co (N/A) > Co (N+A), Co (A/N) and Co (N) >> Co (A). Although the catalyst Co (N/A) had not the smallest particle size, it was the most active among the above catalysts. For 20 wt% total cobalt loading catalysts, the similar phenomena were observed. The catalysts made from mixture salt displayed remarkably higher activities than those from single salt.

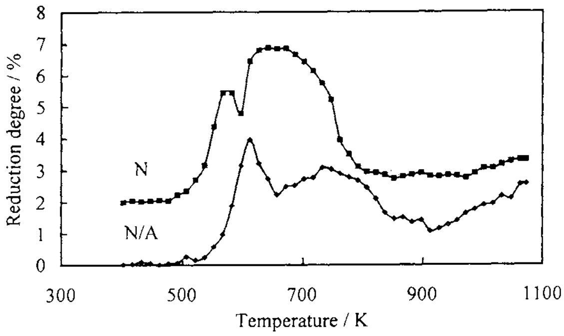

Figure 3. TPR profiles of catalysts Co (N) and Co (N/A).

From TPR spectra in Figure 3, it is found that the main peak of catalyst N/A was at 600 K, but the main peak of catalyst N distributed from 600 K to 800 K, centered at 670 K. Using a mixture of cobalt nitrate and cobalt acetate for impregnation could result in highly active cobalt silica catalyst. The cobalt acetate had stronger interaction with the SiO_2 than cobalt nitrate and was difficult to be reduced. It is considered that the reduction of cobalt acetate species could be promoted by spillover hydrogen activated on the cobalt metal from cobalt nitrate in Co (N/A) catalyst. It seems that the high reduction degree of Co (N/A) was one of important factors for its high activity. This phenomenon is similar to the fact that noble metals promoted the reduction of Co^{2+} species to cobalt metals, which was reported by Matsuzaki et al.[4,5]

As for Co (N+A) and Co (A/N) catalysts, structures and interactions among cobalt nitrate species, cobalt acetate species and SiO_2 might limit their activity. But the detailed information is not clear yet.

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