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Alcohol synthesis by catalytic hydrogenation of CO_2 over Rh–Co/SiO_2†

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The effect of the cobalt additive on Rh/SiO_2 catalysts prepared by co-impregnation was examined to improve the reactivity in CO_2 hydrogenation. The CO_2 conversion increased significantly with the amount of cobalt added. Although the methanol selectivity was very low over nonpromoted Rh/SiO_2 catalyst, more than 10% selectivity to methanol was obtained over the catalysts with cobalt added in the range of Co/Rh = 0.1–1 (atomic ratio). The methanol yield over Rh–Co/SiO_2 catalyst was higher than the sum of the yields of Rh/SiO_2 and Co/SiO_2 catalysts. Physically mixed Rh/SiO_2 and Co/SiO_2 catalysts did not promote methanol formation. Based on the results of X-ray diffraction and X-ray photoelectron spectroscopy, it was suggested that Rh–Co alloy was formed on the catalyst surface to change the electronic states of rhodium, resulting in promotion of methanol formation. **Copyright © 2000 John Wiley & Sons, Ltd.**

Keywords: Rh–Co/SiO_2 catalysts; CO_2 hydrogenation; alcohol synthesis

INTRODUCTION

Global warming caused by a remarkable increase of carbon dioxide emission into the atmosphere is an important and urgent problem to be solved. Catalytic hydrogenation of CO_2 has recently been attracting considerable attention as one of the chemical fixation and recycling technologies for emitted CO_2. Therefore, extensive studies on this technology are now being conducted.[1]

Catalytic hydrogenation of CO_2 has some advantages over other countermeasures such as CO_2 deposit and disposal. It is noted that catalytic hydrogenation can fix and convert CO_2 very quickly. In addition to the reduction of CO_2 emission into the atmosphere, it can produce valuable chemicals from emitted and useless CO_2, resulting in saving of other carbon resources, such as petroleum and natural gas. The present industrial process for syngas (CO–H_2) conversion, such as methanol synthesis, provides another advantage to CO_2 hydrogenation, because those production facilities may be easily applicable to the CO_2–H_2 conversion process without any significant replacement.[1]

Under these circumstances, CO_2 hydrogenation to methanol over Cu–ZnO catalysts has been investigated most extensively.[2] In contrast, the direct conversion process of CO_2 to more valuable feedstocks, such as higher alcohols, carboxylic acids, and light olefins, has not been pursued to such an extent, except for a few studies over iron-based,[3] molybdenum-based[4] and rhodium-based catalysts.[5–7]

In our previous paper, the feasibility of CO_2 hydrogenation to ethanol was studied over Rh–Fe/SiO_2 catalysts.[8] Iron addition to Rh/SiO_2 catalysts improved the ethanol selectivity remarkably, as well as the CO_2 conversion.

In the present study, the effect of cobalt addition to Rh/SiO_2 catalysts was examined to improve the reactivity in CO_2 hydrogenation. Cobalt is well known as one of the effective metals for alcohol production by CO hydrogenation.[9] Various kinds of characterization method, such as H_2 chemisorption, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy were also applied to determine properties of catalysts.

Experimental

The support used in this work was SiO_2 derived from Fuji–Davison (#57). $Rh(NO_3)_3$ and $Co(NO_3)_2 \cdot 6H_2O$ purchased from Soekawa Chemi-

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Table 1 Effect of cobalt addition on catalytic performance (5 wt% Rh)[a]

Co/Rh (atomic ratio)	CO_2 conversion (%)	Product selectivity (%)						Chemisorbed H_2 ($cm^3\ g^{-1}$)	Turnover frequency (h^{-1})
		MeOH	EtOH	CO	CH_4	C_2H_6	C_3H_8		
0	3.0	3.3	0.3	70.3	26.1	0.1	0	1.83	12
0.1	6.0	14.2	1.2	57.2	27.3	0.1	0	1.86	24
0.5	15.9	19.9	1.4	21.8	55.8	0.8	0.3	1.76	68
1	25.2	13.4	1.2	9.8	73.1	1.7	0.8	1.51	126
2	42.8	2.2	0.7	1.5	86.6	4.2	4.1	1.47	218
Co/SiO_2[b]	26.9	3.2	0.6	2.3	89.3	2.6	1.8	0.07	2989
$Rh/SiO_2 + Co/SiO_2$[c]	27.3	3.8	0.4	2.6	88.3	2.4	1.6	—	—

[a] Reaction conditions: temperature, 533 K; pressure, 5 MPa; H_2/CO_2 ratio, 3; flow rate, 100 $cm^3\ min^{-1}$.
[b] Cobalt loading was the same as the catalyst of Co/Rh = 1.
[c] Physical mixture of Rh/SiO_2 and Co/SiO_2.

cals were used as precursor salts. Silica gel, which was sieved into the 16–32 mesh size range and was evacuated at 473 K for 2 h, was impregnated with an aqueous solution of a mixture of $Rh(NO_3)_3$ and $Co(NO_3)_2{\cdot}6H_2O$. After drying at 473 K *in vacuo*, the catalyst was reduced at 623 K for 1 h in a hydrogen flow at 100 $cm^3 min^{-1}$ to prepare the $Rh–Co/SiO_2$ catalysts.

Hydrogenation of CO_2 was conducted by using a pressurized fixed-bed, flow-type micro-reactor. Prereduced catalyst (1 g) was packed in the reactor tube and pretreated *in situ* at 623 K for 0.5 h in a hydrogen flow at 200 $cm^3\ min^{-1}$. After cooling to room temperature, the gas was switched to the $H_2–CO_2$ premixed one ($H_2/CO_2 = 3$) containing 1% argon as the internal standard for gas chromatography (GC) analysis, and reaction was carried out. The effluent gas was analyzed by on-line GC.

Hydrogen chemisorption was measured at 308 K using a Micromeritics ASAP 2000.

Powder XRD analysis was carried out using a MAC Science MXP18. The diffracted X-ray was the Cu Kα line ($\lambda = 0.154\ 05$ nm).

X-ray photoelectron spectra (XPS) of catalysts were recorded with a Shimadzu ESCA-850 without exposure to open air, after pretreatment at 623 K for 0.5 h in a hydrogen flow of 200 $cm^3\ min^{-1}$ within the prechamber of the apparatus. The binding energies of the XPS were referred to the evaporated gold on the surface as an internal standard with the Au $4f_{7/2}$ level at 83.8 eV.

RESULTS

Reaction behavior

Table 1 shows the effect of cobalt addition to a 5 wt% Rh/SiO_2 catalyst on the CO_2 hydrogenation reaction. The amount of cobalt added was 0–2 to rhodium by atomic ratio. The CO_2 conversion increased significantly with the amount of cobalt added. Co/SiO_2 catalyst, for which the cobalt loading was the same as for the catalyst in which Co/Rh = 1 (by atomic ratio), itself was active in CO_2 hydrogenation. This result suggests as if the reactivity of $Rh–Co/SiO_2$ catalysts might be the simple sum of the reactivity of Rh/SiO_2 and Co/SiO_2 catalysts.

However, more than 10% of methanol was formed over the catalysts with cobalt added in the range of Co/Rh = 0.1–1 (atomic ratio). Although the methanol selectivity was very low over nonpromoted Rh/SiO_2 catalyst, the yield of methanol over the $Rh–Co(1:1)/SiO_2$ catalyst was much higher than the sum of those over Rh/SiO_2 and Co/SiO_2 catalysts. The reactivity to hydrocarbon, such as methane, increased monotonously and that of CO decreased with the amount of cobalt added.

In order to confirm whether the reactivity over $Rh–Co/SiO_2$ catalyst was simply the sum of those of Rh/SiO_2 and Co/SiO_2 catalysts or not, CO_2 hydrogenation over the physical mixture of Rh/SiO_2 and Co/SiO_2 catalysts was tried. As listed in Table 1, product selectivity over physically mixed catalyst was similar to that over Co/SiO_2 rather than Rh/SiO_2, and methanol promotion was not observed.

Hydrogen chemisorption

In order to investigate the mechanism of methanol promotion effect brought about by the cobalt addition, various kinds of characterization for catalysts were performed.

First of all, hydrogen chemisorption on the

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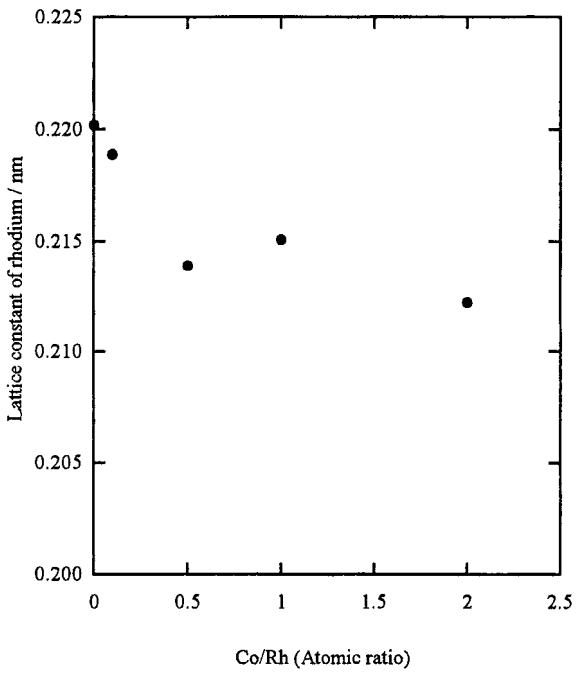

Figure 1 Effect of cobalt addition on lattice constant of Rh (111) determined by XRD measurement.

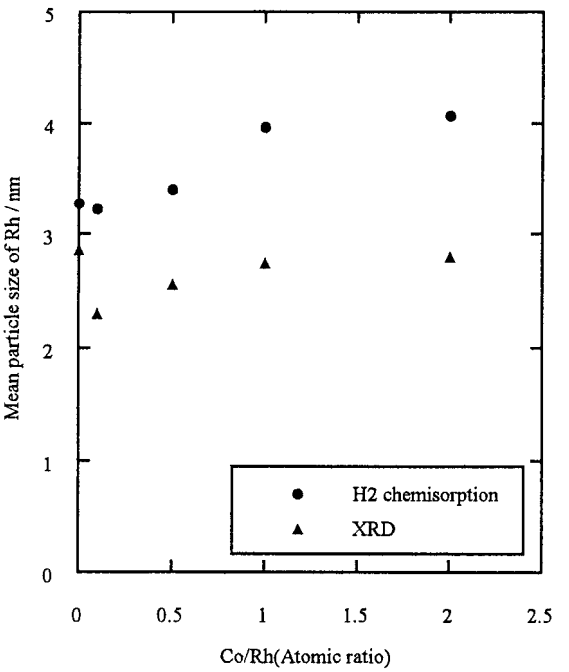

Figure 2 Effect of cobalt addition on rhodium mean particle sizes determined by hydrogen chemisorption and XRD line broadening.

catalysts was carried out. As listed in Table 1, on the whole, the amount of chemisorbed hydrogen decreased slightly with the amount of cobalt added. It was speculated that most of the hydrogen was chemisorbed on the rhodium surface because there was little chemisorption on the Co/SiO_2 catalyst. The results of CO_2 hydrogenation reaction and hydrogen chemisorption indicate that the turnover frequency (specific rate per unit active site) of the catalysts increased with cobalt addition (Table 1).

XRD

Secondly, XRD measurements were carried out in order to investigate crystallite structure. The diffraction peak of Rh (111) at $2\theta = 41\,^\circ$ shifted to higher angles with cobalt addition. Figure 1 shows the lattice constant of Rh (111) determined by the Bragg's formula. The rhodium lattice constant decreased with cobalt addition, becoming close to Co (111) ($d = 0.204\,67$ nm).

The rhodium mean particle sizes determined by hydrogen chemisorption and XRD line broadening of the Rh (111) peak width from Scherrer's formula are depicted in Fig. 2. It was noteworthy that the mean particle size of rhodium determined by hydrogen chemisorption was somewhat larger than that determined by XRD line broadening. In the method of hydrogen chemisorption, the hydrogen could not be adsorbed on rhodium particle surfaces attached to silica, so the rhodium mean particle size determined by hydrogen chemisorption might be somewhat larger than that determined by XRD line broadening. The rhodium mean particle size estimated by both methods decreased with cobalt addition in the Co/Rh range 0–0.1, and then increased.

XPS

The electronic states of rhodium and cobalt were analyzed by XPS measurement. Figure 3 illustrates the percentage reduction to Rh^0 and Co^0 determined by peak separation at the Rh $3d_{5/2}$ and Co $2p_{3/2}$ levels. The percentage of Co^0 was less than under 10% and the percentage of Rh^0 was about 80% after hydrogen reduction at 623 K, indicating that cobalt was far more difficult to reduce than rhodium. The percentage Rh^0 reached a minimum

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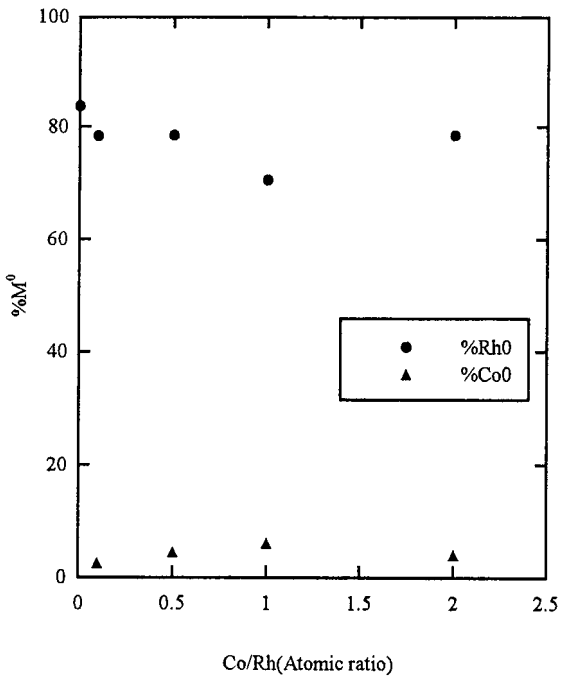

Figure 3 Effect of cobalt addition on percentage reduction to Rh^0 and Co^0 determined by peak separation of XPS binding energy.

and that of cobalt reached a maximum at the ratio Co/Rh = 1.

DISCUSSION

The effect of cobalt addition to Rh/SiO_2 catalyst was observed on the reactivity of CO_2 hydrogenation. Unpromoted Rh/SiO_2 catalyst showed low activity and alcohol selectivity. Cobalt-promoted Rh/SiO_2 catalysts improved methanol selectivity remarkably, as well as CO_2 conversion. In order to elucidate the reason why cobalt addition changed reactivity, the properties of the catalysts were investigated by various kinds of characterization.

As listed in Table 1, Co/SiO_2 catalyst itself showed high activity, so the reason why CO_2 conversion increased with cobalt addition may be an increase of active sites on the catalysts by cobalt addition. In other words, the active sites of rhodium and cobalt may exist on the surface independently and the reaction may occur on these sites separately. In the formation of CO and hydrocarbons, this hypothesis holds well, but the methanol yield over Rh–Co(1:1)/SiO_2 catalyst was much higher than the sum of the yields over Rh/SiO_2 and Co/SiO_2 catalysts. From these results, it was speculated that new active sites where methanol is produced peculiarly were formed on Rh–Co/SiO_2 catalysts.

As shown in Fig. 1, the lattice constant of Rh (111) determined by XRD measurement decreased with cobalt addition, becoming close to Co (111). This result suggested that Rh–Co alloy was formed on the Rh–Co/SiO_2 catalysts. As a result, the mean particle size determined by both hydrogen chemisorption and XRD line broadening (Fig. 2) became smaller by cobalt addition in the range Co/Rh = 0–0.1.

If the sites of the Rh–Co alloy on the surface promote methanol formation, physically mixed Rh–Co catalyst will not promote methanol formation. As expected, methanol formation was not promoted over physically mixed Rh–Co catalyst, as shown in Table 1.

In addition, the XPS results suggested that the electronic state of rhodium on the catalysts changed with cobalt addition (Fig. 3), correlating with methanol yield qualitatively. This effect of Rh–Co alloy is what is called a ligand effect.[10]

CONCLUSION

In the catalytic hydrogenation of CO_2 over Rh–Co/SiO_2 catalysts, the amount of cobalt added influenced methanol selectivity as well as CO_2 conversion. Based on the results of XRD and XPS, it was suggested that Rh–Co alloy was formed on the catalyst surface to change the electronic states of rhodium, resulting in promotion of methanol formation.

REFERENCES

1. Arakawa H. *Stud. Surf. Sci. Catal.* 1998; **114**: 19.
2. Arakawa H, Dubois JL, Sayama K. *Energy Conv. Mgmt.* 1992; **33**: 521.
3. Kaspar J, Graziani M, Rahman AM, Trovarelli A, Vichi EJS, Silva EC. *Appl. Catal. A* 1994; **117**: 125.
4. Tatsumi T, Muramatsu A, Tominaga H. *Chem. Lett.* 1985; 593.
5. Inoue T, Iizuka T, Tanabe K. *Appl. Catal.* 1989; **46**: 1.
6. Ikehara N, Hara K, Satsuma A, Hattori T, Murakami Y. *Chem. Lett.* 1994; 263.

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7. Solymosi F, Erdohelyi A, Bansagi T. *J. Catal.* 1981; **68**: 371.
8. Kusama H, Okabe K, Sayama K, Arakawa H. *Energy*, 1997; **22**: 343.
9. Catalysis Society of Japan. *C1 Chemistry*. Koudansha: Tokyo, 1984; 45–49.
10. Sachtler WMH, Plank PVD. *Surf. Sci.* 1969; **18**: 62.

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