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Hydrogenation of carbon monoxide over highly dispersed cobalt catalysts derived from cobalt(II) acetate

T. Matsuzaki *, K. Takeuchi, T. Hanaoka, H. Arakawa, Y. Sugi

National Institute of Materials and Chemical Research, AIST, Tsukuba, 305 Japan

Abstract

Highly dispersed cobalt metal catalysts supported on SiO_2 were prepared by using cobalt(II) acetate as a precursor promoted with noble metals such as Ir, Ru, Rh, Re, Pt or Os. The catalysts were active for the formation of oxygenates by CO hydrogenation and the vapor phase hydroformylation of ethene. The selectivity of oxygenates, especially C_2-oxygenates, was strongly enhanced by a further modification with basic additives such as alkali and alkaline earth cations.

By the characterization of the catalysts using XPS, EXAFS, XRD, FT-IR, etc., it is revealed that highly dispersed Co^{2+} particles are formed on SiO_2 by the decomposition of Co(II) acetate at an elevated temperature in flowing H_2. The noble metals promote the reduction of the Co^{2+} particles to cobalt metals by spilt-over hydrogen activated on the noble metal sites. The effects of the basic additives were discussed.

Keywords: Carbon monoxide hydrogenation; Cobalt catalysts

1. Introduction

Cobalt has been known as the catalyst for Fischer–Tropsch synthesis to produce hydrocarbons. Product distributions are varied with the nature of cobalt catalysts. We previously reported that highly dispersed cobalt catalysts derived from cobalt carbonyl clusters were active in the formation of oxygenates in the CO hydrogenation; the selectivity of oxygenates, especially C_2-oxygenates, was greatly enhanced by the modification with alkali and alkaline earth cations on the catalyst [1,2]. Furthermore, the Co/SiO_2 catalyst derived from cobalt(II) acetate was also active in the formation of oxygenates by the addition of Re, Ru and Ir; alkaline earth metal cations similarly enhanced the formation of the oxygenates [3–5]. The main active site of the catalysts for the reaction was found to be highly dispersed cobalt metal and the effects of the transition metals were ascribed to promote the reduction of cobalt(II) species to form cobalt particles [6].

In this paper, we describe the preparation of highly dispersed cobalt catalysts from cobalt(II) acetate and their application to the hydrogenation of carbon monoxide and the vapor phase hydroformylation of ethylene. Moreover, the effects of basic additives to the catalysts are examined.

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* Corresponding author.

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2. Experimental

All the catalysts used were supported on silicagel (Davison, grade 57, specific surface area: about 300 m^2/g, 16–32 mesh) which was dried in vacuo at 473 K for 2 h before use. An aqueous solution of cobalt(II) acetate was deposited on the SiO_2 by a incipient wetness impregnation. After aging for 24 h, the resulting sample was dried in vacuo at 373 K and then treated in a H_2 stream at 573 K for 3 h. The catalyst prepared is denoted $Co(A)/SiO_2$. Standard content of cobalt in the $Co(A)/SiO_2$ was 5 wt.% as metal based on silicagel. In the cases that the catalyst was modified with basic additives such as alkali metals, alkaline earth metals and rare earth metals, they were impregnated together with cobalt compounds using acetate. Transition metals, such as Ru, Ir, Rh, Re, Os and Pt were deposited on SiO_2, $Co(A)/SiO_2$ or $Co(A)–M_2/SiO_2$ (M_2:basic additives) by dry mixing method in vacuo using carbonyl clusters for Ru, Ir, Rh and Os, or incipient wetness impregnation of NH_4ReO_4 for Re and $Pt(OCOCH_3)_2$ for Pt [6]. Finally, all catalysts were activated in a H_2 stream at 723 K for 3 h.

Some other silica-supported cobalt catalysts were also used as references. $Co(N)/SiO_2$ and $Co(Cl)/SiO_2$ were prepared from Co(II) nitrate and Co(II) chloride, respectively, in a similar way as $Co(A)/SiO_2$ catalysts. $Co(CO)/SiO_2$ catalysts were prepared by the impregnation of a hexane solution of dicobaltoctacarbonyl ($Co_2(CO)_8$) in a air-free condition as described elsewhere [1].

CO hydrogenation and ethylene hydroformylation were carried out using a fixed-bed type flow reactor. Standard reaction conditions were: $CO/H_2/Ar = 30/60/10$ (Ar:internal standard), 2.1 MPa, 473–553 K and 61/h (GHSV = 2000 h^{-1}) for CO hydrogenation [6] and $C_2H_4/CO/H_2/Ar = 30/30/30/10$, 1.1 MPa, 423–503 K for the hydroformylation [7]. After reaching the stationary state, effluent gas was introduced directly to an on-line GC system for analysis. Product selectivities were calculated based on carbon efficiencies of consumed CO or ethene, respectively.

X-ray diffraction (XRD) measurements were conducted under atmospheric conditions on a Phillips PW-1700 diffractometer employing Ni-filtered Cu K-α radiation. X-ray photoelectron spectra (XPS) were measured by a Shimadzu ASIX 1000 surface analyzer using Al K-α radiation. Just before measurements, pelletized catalysts were treated with H_2 at 573–673 K in a high pressure chamber fitted with the analyzer. The extended X-ray adsorption fine structure (EXAFS) spectra were measured using EXAFS facilities of Photon Factory of National Laboratory for High Energy Physics, Tsukuba [1,8].

3. Results and discussion

3.1. Characteristic features of $Co(A)/SiO_2$ catalysts

Cobalt(II) acetate supported on SiO_2 is hardly reduced under the condition in a H_2 stream at 723 K, although it is itself easily reduced to metallic cobalt under similar conditions, whereas cobalt(II) nitrate and chloride are readily reduced to metallic cobalt on SiO_2 even at lower temperatures such as 623 K. Fig. 1 shows XPS of various Co/SiO_2 catalysts after in situ treatment in a H_2 stream at 623 K. A large part of cobalt particles of $Co(N)/SiO_2$ and $Co(Cl)/SiO_2$ is zero-valent (777.9 eV), while only a divalent cobalt peak (782.2 eV) is observed for $Co(A)/SiO_2$.

Fig. 2 exhibits Fourier transforms of Co K-edge EXAFS of Co/SiO_2 catalysts. Metallic cobalt species with low dispersion were observed for $Co(N)/SiO_2$ and $Co(Cl)/SiO_2$ after in situ treatment in a H_2 stream at 727 K. While in the case of $Co(A)/SiO_2$, only similar C–O bonds to cobalt(II) acetate were detected even after the same treatment. Quite different patterns were observed in XRD analyses among these catalysts (Fig. 3). $Co(Cl)/SiO_2$ had sharp diffraction peaks due to cobalt crystals (α-Co). Its average crystal size was estimated around 20 nm. The pattern of Co(N)/SiO_2 showed a mixture of cobalt metal (β-Co) and cobalt oxide (CoO). CoO may be formed by the oxidation of metallic particles during the measurement. The particle radius was estimated at ca. 4.3 nm. On the other hand, Co(A)/SiO_2 gave no diffraction peaks. The particle size observed by TEM was below 1 nm [9].

From all the results described above, it is considered that divalent cobalt is strongly connected with Si of the SiO_2 through oxygens for the Co(A)/SiO_2 catalyst even after H_2 treatment at a high temperature as 723 K [8]. The structure of the cobalt oxide may be similar to cobalt(II) acetate according to the results of the EXAFS. Scheme 1 exhibits the proposed mechanism to form the oxide. Similar cobalt oxides were prepared from cobalt(II) nitrate mixed with carboxylic acids such as citric acid or maleic acid [10]. The peculiarity of the carboxylate may be explained as follows: coordinated ligands such as acetate are more strongly connected to cobalt cation compared to counter

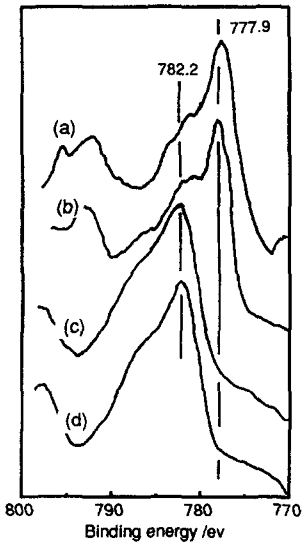


Fig. 1. X-ray photoelectron spectra of Co(2p) of (a) Co(Cl)/SiO_2, (b) Co(N)/SiO_2, (c) Co(A)/SiO_2 after in situ treatment with H_2 at 573 K for 30 min, and (d) $Co(OCOCH_3)_2$ powder dried at 353 K.

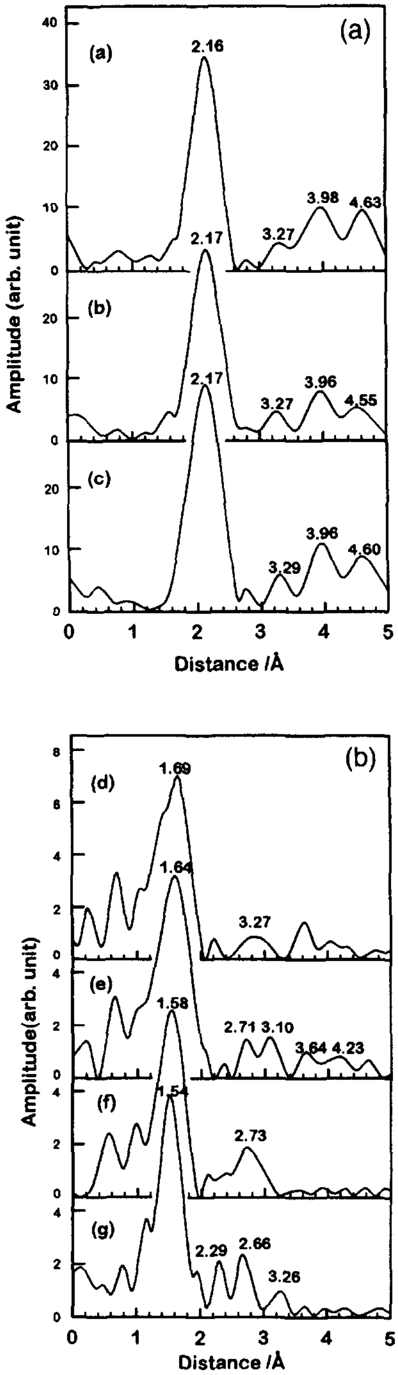


Fig. 2. Fourier transforms of Co K-edge EXAFS of (a) Co metal foil, (b) Co(Cl)/SiO_2, (c) Co(N)/SiO_2, (d) $Co(OCOH_3)_2$ anhydrated powder, (e) $Co(OCOCH_3)_2$ /SiO_2 dried, (f) Co(A)/SiO_2, (g) Co(A)/SiO_2. Samples (b), (c), (f) were measured after in situ treatment with H_2 flow at 723 K for 3 h, and sample (g) was leaked to air after the treatment.

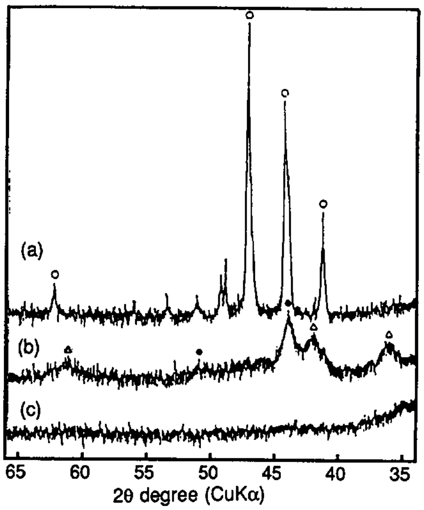


Fig. 3. X-ray diffraction spectra of (a) Co(Cl)/SiO_2, (b) Co(N)/SiO_2, (c) Co(A)/SiO_2 catalysts. ○: Co, ●: Co, △: CoO.

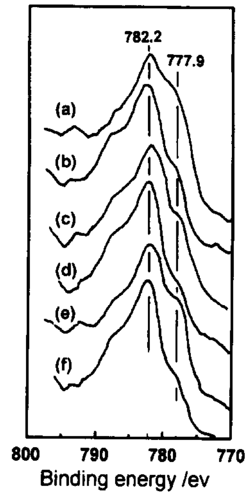


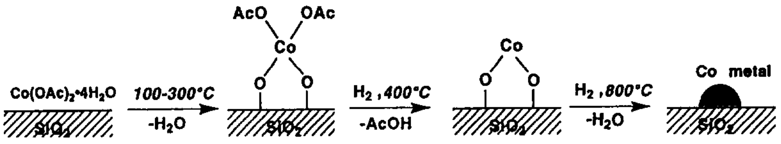
Fig. 4. X-ray photoelectron spectra of Co($2p_{2/3}$) of modified Co(A)/SiO_2 catalysts after in situ treatment with H_2 at 573 K for 0.5 h. (a) Co(A)–Ru/SiO_2, (b) Co(A)–Ir/SiO_2, (c) Co(A)–Re/SiO_2, (d) Co(A)–Rh/SiO_2, (e) Co(A)–Os/SiO_2, (f) Co(A)–Pt/SiO_2. Co: 5 wt.%, Ru: 2.7%, Ir: 5.2%, Re: 5%, Rh: 2.7%, Os: 5.2%, Pt: 5.2%.

anions such as nitrate or chloride, and the structure of the Co–O bonds is kept under the reduction conditions. Furthermore, uncoordinated counter anions such as nitrate or chloride are more easily removed from cobalt cation and the cation is easily reduced to cobalt metal in H_2 stream below 673 K. When some carboxylic acids are mixed to the cobalt(II) salts, these counter anions can be exchanged to the coordinated ligands at lower temperature than the reduction conditions.

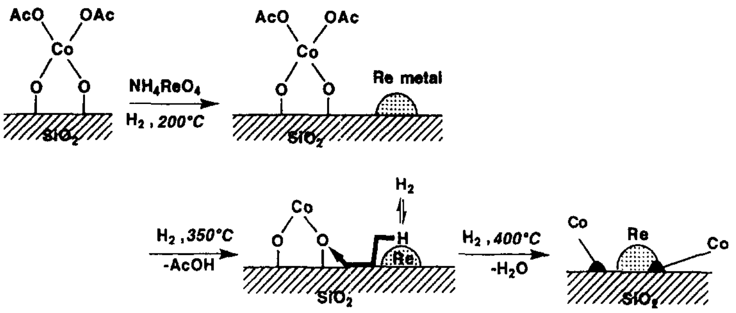
The Co(A)/SiO_2 catalyst is not active for CO hydrogenation, however, it may be a precursor for highly dispersed cobalt metal catalysts. We tried to prepare highly dispersed cobalt catalysts from the cobalt(II) species on Co(A)/SiO_2.

3.2. The modification of Co(A)/SiO_2 with transition metals

A part of Co^{2+} species on Co(A)/SiO_2 were reduced to Co^0 by the addition of a small amount of some transition metals at 723 K in a H_2 stream. Noble metals such as Ir, Rh, Ru, Re, Pt and Os were effective for the reduction while Pd and Au were less effective [6]. The XPS of Co($2p_{3/2}$) of the modified Co(A)/SiO_2 are shown in Fig. 4. Peaks or shoulders by Co^0 (777.9 eV) appeared at the modification. They became larger at longer treatment and/or at higher temperature treatment with hydrogen. No diffraction peaks for cobalt species were ob-



Scheme 1. Proposed decomposition procedure of Co(II) acetate on SiO_2.



Scheme 2. Proposed reduction procedure of Co species of Co(A)–Re/SiO_2.

served in the XRD analyses. Fig. 5 shows Fourier transforms of Co K-edge EXAFS measured after in situ treatment with H_2 at 723 K for the Co(A)/SiO_2 catalysts modified with Ru or Ir. Cobalt–cobalt bonds were detected at about 2.15 Å for these catalysts. Parts of cobalt particles were metallic. Moreover, the peak amplitudes of the nearest Co–Co bonds of them were much lower compared to cobalt metal foil shown in Fig. 2a and the next nearest Co–Co bonds were not clearly observed for the catalysts, which indicated that Co particles in these catalysts were highly dispersed [1].

All these results show that the transition metals promote the reduction of the Co^{2+} species to cobalt metal keeping Co particles highly dispersed. The divalent cobalt may be reduced by spilt-over hydrogen activated on the noble metals because they are known to have high capacity for hydrogen activation. The mechanism of the preparation of the highly dispersed Co/SiO_2 catalysts are proposed in Scheme 2.

3.3. CO hydrogenation and ethylene hydroformylation over the modified Co(A) / SiO_2 catalysts

Although the activity of the Co(A)/SiO_2 was low for CO hydrogenation and produced only a small amount of hydrocarbons, it acquired high activity for the reaction by the promotion with the noble metals. Table 1 exhibits the examples of the activities and product distributions by various catalysts supported on SiO_2 for the

Table 1
Catalytic behaviors of various SiO_2 supported catalysts for CO hydrogenation

Catalyst (wt.% to SiO_2)	Temp. (K)	CO conv. (%)	Product selectivity (%)						
			CO_2	CH_4	C_2^+	MeOH	EtOH	C_2–O	C_3^+–O
Co(N)(5)	493	5.9	2	10	76	0.3	0.4	1.5	0.2
Co(CO)(4.2)	493	10.5	2	25	54	5.1	5.3	5.6	10.2
Co(A)(5)	523	1.7	3	30	64	1.8	0.4	0.6	0.6
Co(A)–Ir(5–5.1)	493	12.4	0	27	48	6.9	8.7	9.4	8.9
Co(A)–Ru(5–2.7)	493	17.0	3	20	56	0.9	5.7	7.5	12.3
Co(A)–Re(5–5)	493	7.7	2	31	41	3.4	10.8	11.6	11.0
Co(A)–Rh(5–2.7)	493	9.7	0	41	30	7.7	8.1	11.6	8.7
Co(A)–Pt(5–5.2)	493	7.8	3	21	61	4.2	6.8	7.2	3.6
Ir(5.1)	553	0.2	26	53	17	0	0	0	0
Ru(2.7)	523	16	1	36	55	1.1	1.9	4.5	2.4
Re(5)	523	0.3	34	36	30	0	0	0	0
Rh(2.7)	523	2.3	6	52	12	1.5	6.2	16.9	5.5
Pt(5.2)	523	0.2	32	9	2	55	0	0	0

Reaction conditions: Ar/CO/H_2 = 10/30/60, pressure 2.1 MPa, GHSV 2000 h^{-1}.

Table 2
Vapor phase hydroformylation of ethene over SiO_2 supported catalysts

Catalyst	Temp. (K)	Ethene conv. (%)	Oxygenates selectivity (%)
Co(N)/SiO_2	463	14	17
Co(CO)/SiO_2	463	49	36
Co(A)/SiO_2	463	1.7	5
Co(A)–Ir/SiO_2	443	27	47
Co(A)–Ru/SiO_2	443	17	54
Co(A)–Re/SiO_2	443	26	43
Co(A)–Pt/SiO_2	443	25	58
Ir/SiO_2	443	0.8	13
Co(A)/SiO_2 + Ir/SiO_2 [a])	443	11	42
Ir/SiO_2 + Co(A)/SiO_2 [b])	443	5.5	28
Ru/SiO_2	443	7.2	48
Re/SiO_2	443	1.8	12
Pt/SiO_2	443	6.1	43

Reaction conditions: $Ar/CO/CH_4/H_2 = 1/3/3/3$, 1.1 MPa, GHSV 600 h^{-1}. Catalysts: Co, 5; Ir, 5.1; Ru, 2.7; Re, 5; Pt, 5.2 wt.% on SiO_2

[a] Mixture of catalysts. [b] Two layers divided by quartz wool.

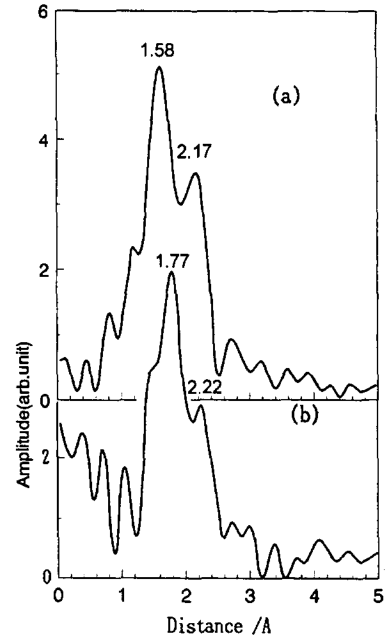


Fig. 5. Fourier transforms of Co K-edge EXAFS of (a) Co(A)–Ru/SiO_2 (b) Co(A)–Ir–Sr/SiO_2 measured after in situ treatment with H_2 flow at 723 K for 3 h.

reaction. Co(N)/SiO_2 was active, however, most of the products were wide-range hydrocarbons. The catalytic activities of the noble metals were very low except Ru. Furthermore, in the case of the noble metal-modified Co(A)/SiO_2 catalysts, oxygenates were also produced with about 20% selectivity. Hydrocarbons were composed of n-paraffins and 1-olefins. The carbon number distributions of hydrocarbons and oxygenates obeyed the Schultz–Flory rule (α-values are 0.65–0.75). The activities and product distributions of the catalysts closely resemble to each other in spite of the different activities of the noble metals. They were also quite similar to those of the Co(CO)/SiO_2 catalyst, in which metallic cobalt particles were highly dispersed [1]. These results suggest that the main active site of the modified Co(A)/SiO_2 catalysts are highly dispersed cobalt metals, as previously discussed [6,11].

Table 3
Modification effects of Co/SiO_2 catalyst with transition metals and strontium for CO hydrogenation

Catalyst	CO conv. (%)	Product selectivity (%)						
		CO_2	CH_4	C_2^+	MeOH	EtOH	C_2–O	C_3^+–O
Co(A)–Sr	0.8	16	31	53	0	0	0	0
Co(A)–Ir–Sr [a]	2.2	0	12	22	8.7	37.0	41.1	14.2
Co(A)–Ir–Sr	8.7	5	16	28	7.0	26.0	33.0	11.0
Co(A)–Re–Sr	4.5	7	18	32	4.4	22.5	30.4	8.2
Co(A)–Re–Sr	5.0	6	18	39	2.8	20.4	25.2	9.0
Co(A)–Rh–Sr	5.2	11	23	26	8.3	16.9	23.0	9.0
Co(A)–Pt–Sr	5.8	8	15	35	8.9	18.4	21.2	11.9
Co(A)–Os–Sr	4.5	7	17	40	1.8	15.8	22.3	11.9
Co(CO)–Sr [b]	5.5	2	19	33	6.0	24.9	26.8	13.1

Reaction conditions: $Ar/CO/H_2 = 1/3/6$, 2.1 MPa, 523 K ([a] 483 K), GHSV: 2000 h^{-1}. Catalysts: Co, 5 wt.%; Sr, 5 wt.% on SiO_2. ([b] Co: 4.2%, Sr: 14.8%). Transition metals/Co = 0.32 (mole ratio).

These modified Co(A)/SiO_2 catalysts were also active for the vapor phase hydroformylation of ethene as shown in Table 2. Similar activity was obtained by the Co(CO)/SiO_2 catalyst [12]. These results indicate that highly dispersed cobalt metal has an ability for the CO insertion to adsorbed hydrocarbon. The mechanically mixed catalyst of Co(A)/SiO_2 and Ir(CO)/SiO_2, both of which were inactive for the reaction, was also active, indicating Co(A)/SiO_2 was activated by spilt-over hydrogen formed on Ir/SiO_2.

3.4. Effects of basic additives on the Co(A)/SiO_2 catalysts for CO hydrogenation

Further modification with basic additives such as alkali, alkaline earth or rare earth metals enhanced the formation of oxygenates, especially C_2-oxygenates, although the activities decreased. Table 3 shows the effect of strontium on the noble metal modified Co(A)/SiO_2 catalysts for CO hydrogenation. The differences on the catalytic activities and product distributions by the noble metals were less when modified with Sr. The selectivity of C_2-oxygenates greatly increased and reached 25–40% under our reaction conditions. The main product of the C_2-oxygenates was ethanol, however, acetaldehyde and acetic acid were also produced. The formation of hydrocarbons was strongly suppressed by the addition of strontium, while the ratios of olefins to paraffins were increased. Strontium was considered to reduce the dissociative adsorption and hydrogenating ability of the catalysts. The carbon number distributions of hydrocarbons and oxygenates obeyed the Schultz–Flory rule except for C_2 compounds, although the chain growth probabilities were decreased (ca. 0.45 for oxygenates and ca. 0.5 for hydrocarbons). The yields of C_2-oxygenates were much higher and C_2-hydrocarbons were lower than expected by the rule.

The effects of other basic additives were examined on Co(A)–Ir/SiO_2 catalysts and are summarized in Table 4. Alkali and alkaline earth metals were highly effective for enhancing the C_2-oxygenate selectivities except Mg, and Mg and rare earths were less effective. The ratios of ethanol in C_2-oxygenates were lower and the ratios of olefins in hydrocarbons were higher in the case of the catalysts modified with alkali metals compared to those of alkaline earth metals. As ethanol and paraffins are considered to be formed by the hydrogenation of acetaldehyde and olefins, respectively, the results indicate that alkali metals more strongly reduce the hydrogenating ability of the catalysts. The ef-

Table 4
Modification effects of Co(A)–Ir/SiO_2 catalyst with alkali, alkaline earth and rare earth metals for CO hydrogenation

Modifier	M/Co	Temp. (K)	CO conv. (%)	Product selectivity (%)									Olefin (%)
				CO_2	CH_4	C_2^+	MeOH	EtOH	AcH	AcOH	C2–O	$C3^+$–O	
None		493	10.5	0	23	60	5.6	5.6	0.2	0.1	5.9	5.5	1.4
Li	0.85	493	3.5	0	10	38	6.0	24.9	2.7	3.0	30.8	15.9	24
Na	0.3	523	5.6	15	9	31	6.3	14.9	2.0	6.0	23.0	16.4	20
K	0.45	523	2.8	13	13	29	6.6	15.1	1.9	9.3	26.3	12.5	29
Rb	0.3	523	4.6	8	12	39	6.3	12.5	2.6	3.7	18.7	17.1	23
Cs	0.3	508	2.7	6	13	38	5.1	11.2	3.0	2.4	16.6	19.6	32
Mg	0.67	493	10.1	0	24	49	6.7	8.9	0.3	0.4	9.7	10.5	14
Ca	0.67	493	4.5	0	18	32	8.5	28.4	0.8	1.5	30.8	11.2	11
Sr	0.67	519	6.3	4	15	33	5.3	24.9	1.1	3.5	29.5	13.4	16
Ba	0.67	523	2.8	8	19	29	12.9	22.0	0.6	2.6	25.3	7.2	13
La	0.6	493	9.1	0	25	49	7.6	10.6	0.4	1.0	12.0	6.5	13
Ce	0.42	493	8.3	0	28	46	7.6	10.5	0.2	0.5	11.2	7.2	1.6

Reaction conditions: Ar/CO/H_2 = 1/3/6, 2.1 MPa, GHSV:2000 h^{-1}. Catalysts: Co, 5 wt.%; Ir, 2.1 wt.% on SiO_2. M/Co: mole ratio of modifiers to Co.

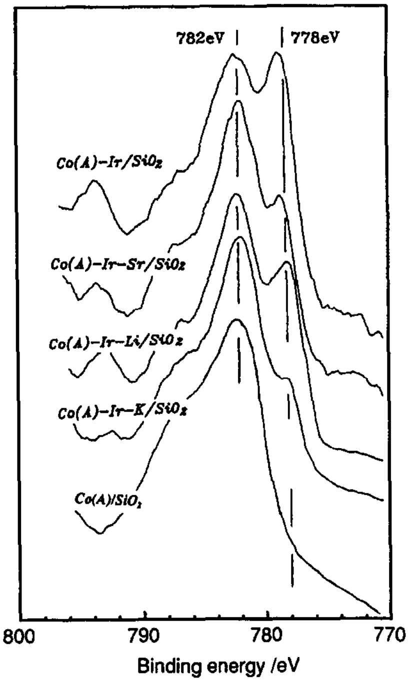


Fig. 6. X-ray photoelectron spectra of Co($2p_{2/3}$) of modified Co(A)–Ir/SiO_2 catalysts after in situ treatment with H_2 at 683 K for 2 h. Co: 5 wt.%, Ir: 2.1%, Sr: 5%, Li: 0.5%, K: 1.5%.

fects were generally in the order of alkali > alkaline earth > rare earth, and heavier metals were more effective in alkali and alkaline earth metals.

These additives were existing as cations in the catalysts [11]. XPS studies indicated that they controlled the reduction of Co^{2+} species in decreasing the active site as shown in Fig. 6, probably by preventing the migration of spilt-over hydrogen. The order of the intensity of Co^0 peak was none > Li > Sr > K. This was just the same order of the catalytic activity. ESR and TG studies also supported that the cations controlled the reduction of the cobalt when it was reduced [11]. However, the effects of the cations were not fully explained by the decrease of the active site, because product distributions were changed by the modification. The hydrogenating ability of the catalysts was decreased by the cations. FT-IR studies indicated that adsorbed CO species on the catalyst changed by the modification with Sr [13]. The stronger basicity of the cations was more effective. All these results suggest that these additives affect the electronic states of active sites of the catalysts. In addition, the cations may play a role to prevent the agglomeration of cobalt particles and kept them highly dispersed from the XRD and EXAFS studies [1,5]. In conclusion, the basic additives are considered to control the electronic and dispersive states of the active site of the cobalt catalysts.

4. Conclusion

Highly dispersed cobalt metal catalysts supported on SiO_2 were prepared by using cobalt(II) acetate as a precursor by promoting with noble metals such as Ir, Ru, Rh, Re, Pt or Os. The catalysts were characterized by using with XRD, XPS, EXAFS, FT-IR, etc. The reduction of the highly dispersed Co^{2+} particles formed on SiO_2 were considered to be promoted by a spilt-over hydrogen activated on the noble metal sites.

These Co/SiO_2 were active for the formation of oxygenates by the CO hydrogenation and the vapor phase hydroformylation of ethene. The selectivity of oxygenates, especially C_2-oxygenates, was strongly enhanced by a further modification with basic additives such as alkali or alkaline earth cations. The basic additives may control the dispersive and electronic states of the cobalt species.

References

[1] K. Takeuchi, T. Matsuzaki, H. Arakawa, T. Hanaoka and Y. Sugi, J. Mol. Catal., 55 (1989) 361.

[2] T. Matsuzaki, K. Takeuchi, T. Hanaoka, Y. Sugi and M. Reinikainen, Catal. Lett., 10 (1991) 193.

[3] K. Takeuchi, T. Matsuzaki, H. Arakawa and Y. Sugi, Appl. Catal., 18 (1985) 325.

[4] K. Takeuchi, T. Matsuzaki, H. Arakawa, T. Hanaoka and Y. Sugi, Appl. Catal., 48 (1989) 149.

[5] T. Matsuzaki, K. Takeuchi, H. Arakawa, T. Hanaoka and Y. Sugi, in S. Yoshida, N. Takezawa and T. Ono (Eds.), Catalytic Science and Technology, Vol. 1, Kodansha, Tokyo, Japan and VCH, Weinheim, Germany, 1991, p. 249.

[6] T. Matsuzaki, K. Takeuchi, T. Hanaoka, H. Arakawa and Y. Sugi, Appl. Catal. A, 105 (1993) 159.
[7] K. Takeuchi, T. Hanaoka, T. Matsuzaki, Y. Sugi, S. Ogasawara, Y. Abe and T. Misono, Catal. Today, 20 (1994) 423.
[8] K. Takeuchi, T. Matsuzaki, T. Hanaoka, H. Arakawa, Y. Sugi and N. Matsubayashi, J. Natl. Chem. Lab. Ind., 84 (1989) 549.
[9] Y. Kintaichi, K. Takeuchi, T. Matsuzaki, H. Arakawa, T. Hanaoka, T. Ito and Y. Sugi, Chem. Express, 4 (1989) 129.
[10] Unpublished data.
[11] T. Matsuzaki, K. Takeuchi, T. Hanaoka, H. Arakawa and Y. Sugi, Sekiyu Gakkaishi, 37 (1994) 179.
[12] K. Takeuchi, T. Hanaoka, T. Matsuzaki, M. Reinikainen and Y. Sugi, Catal. Lett., 8 (1991) 253.
[13] H. Arakawa, K. Takeuchi, T. Matsuzaki and Y. Sugi, Sekiyu Gakkaishi, 31 (1988) 335.