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Oxygenates from syngas over highly dispersed cobalt catalysts

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Abstract

Highly dispersed cobalt metal catalyst has been prepared by the deposition of $Co_2(CO)_8$ on silicagel in an oxygen-free condition and has been characterized with EXAFS. This catalyst exhibited high activity for the formation of C_2^+ oxygenates from syngas without any modification. The formation of hydrocarbons was strongly suppressed and the selectivity of oxygenates, especially C_2-oxygenates, was enhanced by the modification with alkali or alkaline earth cations. From the modification effects on CO hydrogenation and by the studies of in situ FT-IR, these basic cations were considered to reduce the hydrogenating ability of the catalyst by controlling the electronic state of the active cobalt site. Noble metals such as iridium and ruthenium have little effect on the catalyst of CO hydrogenation. Similar cobalt catalysts were prepared from $Co_2(CO)_8$ on other oxide supports and some oxides showed a similar effect on the basic additives. The effect of the cations and the reaction mechanism for the formation of oxygenates were discussed.

Keywords: Syngas reaction; Cobalt catalyst; Cobalt carbonyl; Oxygenates; Alkaline cations

1. Introduction

Direct synthesis of C_2^+ oxygenates from syngas is attractive for the development of new processes for fuels or basic chemicals from alternative feedstocks. Cobalt metal has long been thought to be a catalyst for Fischer-Tropsch synthesis to produce higher hydrocarbons, but not for the formation of oxygenates [1]. Cobalt is often used as a promoter in the catalysts for C_2^+ alcohols synthesis such as modified methanol synthesis catalysts and molybdenum sulfide catalysts, because cobalt is considered to promote the carbon chain growth [2-5]. However, several recent works indicate that cobalt could be the main active species for the formation of oxygenates [6-10]. We have also reported that noble metal promoted $Co(A)/SiO_2$ catalysts derived from cobalt acetate and Co/SiO_2 catalyst from cobalt carbonyl compound were active for the formation of oxygenates and the selectivities of oxygenates, especially C_2-oxygenates, greatly enhanced by the modification with alkali or alkaline earth cations to the catalyst [11-15]. The main active site of the catalysts for the reaction was revealed to be highly dispersed cobalt metal.

In this paper, we report the preparation and

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the activities of Co/SiO_2 catalyst derived from dicobaltoctacarbonyl ($Co_2(CO)_8$). We then study the modification effects of basic additives and noble metals comparing the effects on Co(A)/SiO_2 catalyst. The effect of supports was also studied.

2. Experimental

$Co_2(CO)_8$ was deposited on oxide supports by the impregnation from hexane solution under oxygen-free conditions. Silicagel (Davison#57, 330 m^2/g, dried in vacuo at 473K) was mainly used as a support, although several other metal oxides were also examined. After removing hexane, the catalysts were loaded in a reactor without contact to air and activated with a flowing H_2 at 723K just before the reaction. Alkali or other basic modifiers had been impregnated on the oxide support using their acetate compounds and calcined in H_2 flow at 523K before the deposition of cobalt. The contents of cobalt on supports were measured with XRF after used. For references, other cobalt catalysts were prepared by an ordinary incipient wetness impregnation on silicagel from aqueous solution of cobalt(II) nitrate, chloride and acetate. They are denoted as Co(N)/SiO_2, Co(Cl)/SiO_2 and Co(A)/SiO_2, respectively.

CO hydrogenation was carried out using a fixed bed type flow reactor. The standard reaction conditions were; $CO/H_2/Ar = 30/60/10$, 2.1 MPa, 473–553K and 6l/h (GHSV = 2000 h^{-1}). Argon was mixed in the reactant gas as a internal standard for analysis of the products. Effluent gas was introduced directly to a on-line GC system for analysis. Product selectivities were calculated based on carbon efficiencies of consumed CO. As esters were considered to be secondary products, methyl and ethyl acetate produced were summed up to corresponding alcohols and acid. Analytical data shown in this report were obtained in the stationary state of the reaction to which reached 4–6 h after starting.

Cobalt species in the catalysts were characterized by extended X-ray adsorption fine structure (EXAFS) measured using EXAFS facilities of Photon Factory of National Laboratory for High Energy Physics, Tsukuba. As the catalysts were so air-sensitive, they were prepared, hydrogenated and measured in a specially designed in situ cell with a CAPTON window [16]. Adsorbed CO species on the catalysts were characterized in the reaction conditions by a in situ FT-IR. Catalysts were also prepared and hydrogenated in a in situ cell before the measurement [17].

3. Results

3.1. Preparation of catalyst

Although $Co_2(CO)_8$ is relatively stable in air, it changes to be very air-sensitive after deposited on SiO_2, and the color varies immediately from red to blue by a short contact to air. To clarify the change of the features of cobalt species in the preparation process of the catalyst, EXAFS was measured using the in situ cell as described. Fig. 1 exhibits κ^3-weighed Fourier transforms of Co K-edge EXAFS of cobalt carbonyl and Co/SiO_2 catalysts prepared. Loading amount of Co and Sr were ca. 5 wt% and 7.5 wt% to SiO_2 as metals. Peaks at 2.51×10^{-1} and 2.10×10^{-1} nm were ascribed to Co–Co and Co–O bonds of $Co_2(CO)_8$ powder, respectively (a). These peaks slightly shifted and relative peak amplitude of Co–O bond to Co–Co bond changed after deposited on silicagel (b). The EXAFS(b) could be assigned to be $Co_4(CO)_{12}$. After calcined in hydrogen stream at 723K, main peaks were detected at 2.14 or 2.12×10^{-1} nm (d). This peak was ascribed to Co–Co metal bond from the reference peak of cobalt metal foil (f). The EXAFS study indicated that $Co_2(CO)_8$ changed to $Co_4(CO)_{12}$ on silicagel as reported by Iwasawa et al. [18], and then thermally decomposed to metal particles in H_2 stream at an elevated temperature. The cobalt metal particles on the prepared catalysts were highly dispersed from following results; (1) the peak amplitude of Co–Co bond of the catalyst was much lower, (2) Co–Co bond distance was smaller, (3) the second nearest Co–Co bond were much smaller, than those of standard cobalt metal foil. No XRD peaks assigned to cobalt species were observed for the catalyst. The average particle size of cobalt metal in Co/SiO_2 may be estimated ca. 1 nm from the amplitude of the peaks [15]. Cobalt–oxygen bond of 1.68×10^{-1} nm in (d) appeared probably by the incomplete decomposition to metal, or by the oxidation of Co carbonyl or Co metal by leaked air in spite of the careful handling. The cobalt metals rapidly oxidized by a short contact to air (g) and the features of EXAFS profile was quite similar to $Co(A)/SiO_2$ catalyst derived from cobalt acetate (i). The transformation of attached $Co_2(CO)_8$ is proposed as in Fig. 2.

3.2. Catalytic activity of the cobalt catalyst

The catalytic activity and the product distribution for various Co/SiO_2 catalysts on CO hydrogenation are shown in Table 1. The prepared catalyst exhibited the highest activity for the hydrogenation. More than 20% of the products were oxygenates. The cobalt catalyst was demonstrated to be active to produce oxygenates without any modification. Most of the products were n-paraffins, linear 1-olefins and linear 1-alcohols. Both of the carbon number distributions of hydrocarbons and oxygenates obeyed Schultz–Flory rule as shown in Fig. 3. The chain growth probability (α-value, $C > 2$) was ca. 0.65. However, if small amount of air had been contaminated to the catalyst in the preparation process, catalytic activity suppressed and only hydrocarbons were produced, while other cobalt catalysts prepared from ni-

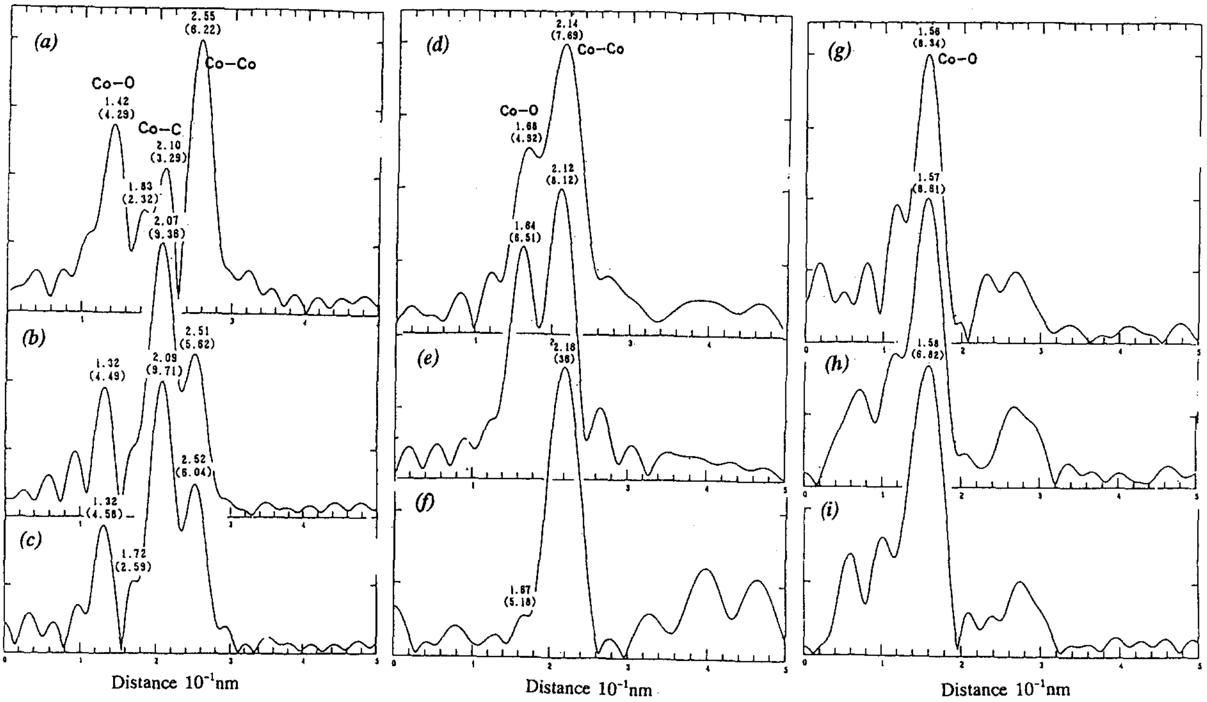

Fig. 1. Fourier transforms of $k^3\chi(k)$ of Co k-edge EXAFS. (a) $Co_2(CO)_8$ powder, (b) $Co_2(CO)_8/SiO_2$ and (c) $Co_2(CO)_8$–Sr/SiO_2, just after impregnation and in nitrogen atmosphere, (d) $Co_2(CO)_8/SiO_2$ and (e) $Co_2(CO)_8$–Sr/SiO_2, after treatment with H_2 stream at 450° for 3 h and measured in situ, (f) Co metal foil, (g) $Co_2(CO)_8/SiO_2$ and (h) $Co_2(CO)_8$–Sr/SiO_2, exposed to air after treatment with H_2 stream at 450°C, (i) $Co(A)/SiO_2$, after treatment with H_2 stream at 450°C.

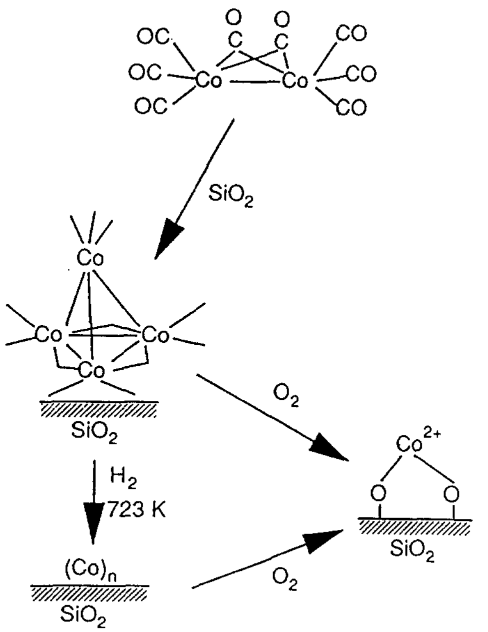

Fig. 2. Proposed transformation of attached $Co_2(CO)_8$.

trate, chloride or acetate showed lower activity and produced little oxygenates but hydrocarbons and/or carbon dioxide. Cobalt particles on $Co(N)/SiO_2$ and $Co(Cl)/SiO_2$ were metallic and those of $Co(A)/SiO_2$ were divalent from the studies of X-ray photo electron spectra [16]. The average particle sizes of them were ca. 4.3, 20, 1 nm, respectively, from the results of XRD and TEM [19]. It is considered that highly dispersed cobalt metal particles are important for the formation of oxygenates from syngas.

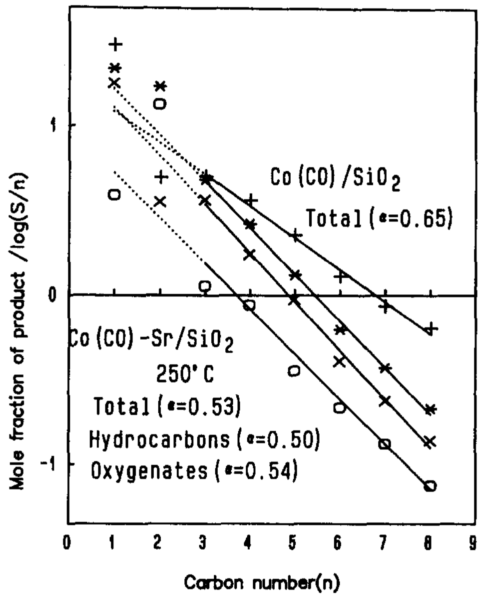

Fig. 3. Carbon number distributions of the products over (a) Co/SiO_2 (4.2/100) and (b) $Co–Sr/SiO_2$ (3.4–14.8/100) catalysts. Reaction conditions; $CO/H_2 = 1/2$, 2.1 MPa, 493 K for Co/SiO_2 and 523 K for $Co–Sr/SiO_2$, GHSV: 2000^{-1}. Symbols and α-value; +: over-all products ($\alpha = 0.65$) by Co/SiO_2, O: oxygenates ($\alpha = 0.54$), ×: hydrocarbons ($\alpha = 0.50$), and *: for over-all products ($\alpha = 0.53$) by $Co–Sr/SiO_2$.

3.3. Modification with basic additives and transition metals

Alkali, alkaline earth or rare earth metals were effective for suppressing the formation of hydrocarbons and enhancing the formation of oxygenates, especially C_2-oxygenates, for the

Table 1
Effects of cobalt precursors of Co/SiO_2 catalysts for CO hydrogenation [a]

Catalysts [b]	Temp. (°C)	CO conv. (%)	Product selectivity(%)							
			CO_2	CH_4	C_{2-4} [c]	C_{5+} [d]	MeOH	EtOH	C_2–O [e]	C_{3+}O [f]
Co/SiO_2^*	220	10.5	2	25	30	24	5.1	5.3	5.6	10.2
$Co(N)/SiO_2$	220	5.9	2	10	14	62	0.3	0.4	1.5	0.2
$Co(Cl)/SiO_2$	250	0.5	26	31	29	13	0	0	0.8	0.2
$Co(A)/SiO_2$	250	1.7	3	30	22	42	1.8	0.4	0.6	0.6

[a] Reaction conditions; $CO/H_2/Ar = 30/60/10$, press. 2.1 MPa, GHSV 2000 h^{-1}.
[b] Catalysts; Co: 5 wt% to SiO_2 (*4.2 wt%) as metals. Precursors; Co(N):$Co(NO_3)_2 \cdot 6H_2O$, Co(Cl):$CoCl_2 \cdot 6H_2O$, Co(A):$Co(CH_3COO)_2 \cdot 4H_2O$, Co(CO):$Co_2(CO)_8$.
[c] Sum of C_2–C_4 hydrocarbons.
[d] Sum of C_5 + hydrocarbons.
[e] Sum of EtOH, AcOH and AcH.
[f] Sum of C_3–C_8 oxygenates.

noble metal promoted Co(A)/SiO_2 catalysts [20]. Similar effects were obtained for the Co/SiO_2 catalyst from $Co_2(CO)_8$. The effects of the modification for CO hydrogenation are summarized in Table 2. These additives are in the forms of cations such as oxides in the catalysts [21]. In the case of alkaline earth cations, the activity decreased in the order; none $\geq$ Mg > Ca > Sr > Ba, and that of the oxygenates selectivity was; Ba, Sr $\gg$ Ca $\gg$ Mg $\geq$ none. The latter order for Co(A) catalysts was Sr, Ca > Ba > Mg > none [20]. Most of the oxygenates were alcohols except for Ba, by which acetic acid was also produced significantly. Carbon number distributions of C_3 to C_8 obeyed Schultz–Flory rule for both oxygenates and hydrocarbons as shown in Fig. 2 for Co–Sr/SiO_2 catalyst, although C_2 compounds were extremely deviated from the rule. α-Values were 0.53, 0.54 and 0.50 for total product, oxygenates and hydrocarbons, respectively, which values were lower than the unmodified catalyst. Olefin ratio in hydrocarbons (C_2–C_4) increased by the modification.

The effects of strontium contents are exhibited in Fig. 4. Activity of the catalyst strongly decreased by a small amount of Sr, although it kept rather constant by further addition. The selectivities of methane and other hydrocarbons decrease loosely. The optimum content of Sr for oxygenates was ca. 80–180 mmol in 100 g of SiO_2. The values were ca. 1.2–2.7 times of Co loaded as molar ratio and much higher than the case of Co(A) catalysts [11].

Alkali metals more strongly decrease the activity of the catalyst. They are also effective for depressing hydrocarbons and increasing the selectivity of oxygenates. Quite smaller amount of alkali metals were required for the effect compared to alkaline earth metals. Fig. 5 exhibits the effects of potassium contents. 25 mmol of K (K/Co mole ratio = ca. 0.4) was enough to

Table 2
Effect of additives on Co/SiO_2 catalyst for CO hydrogenation

Additives		Co	Temp.	CO	Product selectivities (%)									olefin [e] (%)
mmol [a]		(wt%)	(°C)	Conv. (%)	CO_2	CH_4	HC_{2-8} [b]	MeOH	EtOH	AcH	AcOH	C_2-O [c]	C_{3-8}O [d]	
none	–	4.2	220	10.5	2.0	25	54	5.1	5.3	0.3	0	5.6	10.2	29
Mg	127	3.5	220	9.0	1.0	23	59	4.2	6.1	0.3	0	6.3	7.2	35
Ca	127	3.5	250	11.0	2.6	21	44	3.8	15.8	0.7	0.2	16.6	11.9	43
Sr	169	3.4	220	1.5	0	18	35	3.1	21.9	3.8	0.4	26.1	16.9	72
Sr	169	3.4	250	5.5	3.3	18	35	3.9	24.4	2.0	0.3	26.7	15.0	61
Ba	127	3.7	250	4.0	9.7	14	32	4.6	18.8	2.0	5.8	27.6	12.0	65
Li	26	4.2	250	15.3	4.8	10	52	1.2	9.1	2.1	2.8	14.7	16.1	72
Li	50	4.0	220	2.1	0	10	49	2.2	14.4	7.3	3.9	25.4	13.2	81
Li	104	3.7	220	1.3	0	9	37	4.6	23.0	9.9	3.9	36.8	12.4	81
Na	26	3.9	250	2.2	11.4	8	38	2.0	7.6	9.0	10.5	27.2	13.7	92
Na	52	4.3	220	0.2	0	11	30	0.8	18.8	15.8	3.1	37.7	19.2	86
K	26	3.8	235	0.6	0	12	43	1.1	4.2	20.0	10.6	34.8	8.6	91
K	26	3.8	250	1.4	7.6	10	42	1.4	5.1	13.2	10.0	28.3	11.0	88
Rb	13	4.6	235	0.6	0	9	43	1.1	5.4	20.8	10.2	36.5	10.5	87
Rb	13	4.6	250	2.4	7.2	9	44	2.4	4.9	11.6	6.5	23.1	13.3	85
Cs	13	4.9	220	0.5	0	11	50	0.8	4.2	21.5	3.6	29.3	9.4	84
Cs	13	4.9	250	4.9	5.8	13	51	0.8	4.7	9.3	2.6	16.5	12.7	77
La	127	5.0	220	14.1	0.9	22	61	2.5	6.2	0.3	0	6.5	7.7	38

Reaction conditions; CO/H_2/Ar = 30/60/10, Pressure: 2.1 MPa, GHSV: 2000/h.

[a] Mmol on 100g · SiO_2.

[b] Hydrocarbons from C_2 to C_8.

[c] Sum of EtOH, AcH and AcOH.

[d] Sum of oxygenated compounds from C_3 to C_8.

[e] Molar ratio of olefins in C_2–C_4 hydrocarbons.

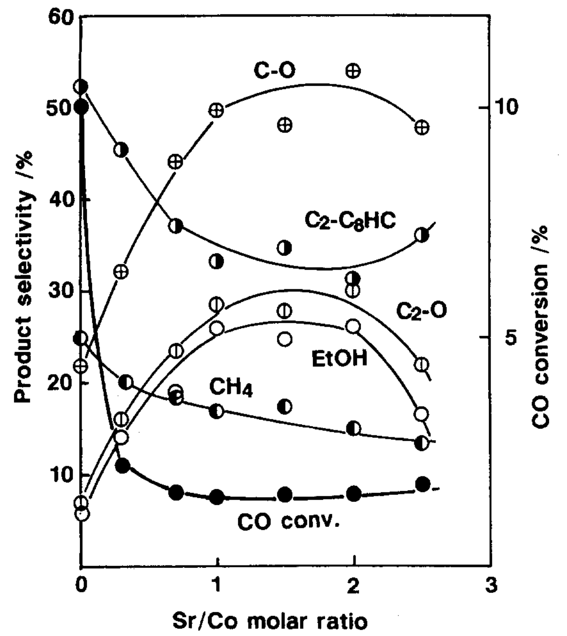

Fig. 4. Effect of strontium content on Co/SiO_2 (4.2±0.3/100 in weight) catalyst. Reaction conditions: $CO/H_2/Ar = 3/6/1$, temp. 523 K, press. 2.1 Mpa, GHSV:2000^{-1}.

obtain the optimum selectivity of oxygenates. Considerable amount of acetic acid and acetaldehyde were produced as well as ethanol as C_2 oxygenates by the modification with alkali metals. This is the first example except for rhodium based catalysts for the formation of carboxylic acid as one of the main products by syngas reaction. The selectivity of oxygenates depended on reaction temperature as shown in Fig. 6 for $Co–Na/SiO_2$ catalyst. Acetaldehyde was the principal product in C_2-oxygenated compounds at 493K, whereas, at higher temperature, the formation of acetic acid increased to reach maximum selectivity of about 12% at 508–523K, and the selectivity decreased beyond 523K with increasing formation of carbon dioxide. However, the selectivity of ethanol and the ratio of olefins in hydrocarbons did not vary significantly from 493 to 543K. Selectivities of other oxygenates and hydrocarbons did not change so much in the range of temperature. Olefin ratios in the hydrocarbons were quite higher than the case of alkaline earth metals. As ethanol and alkanes are considered to be produced by the hydrogenation of acetaldehyde and alkenes, respectively, alkali cations may more strongly reduce the hydrogenating ability of the cobalt catalyst. The formation of acetic acid

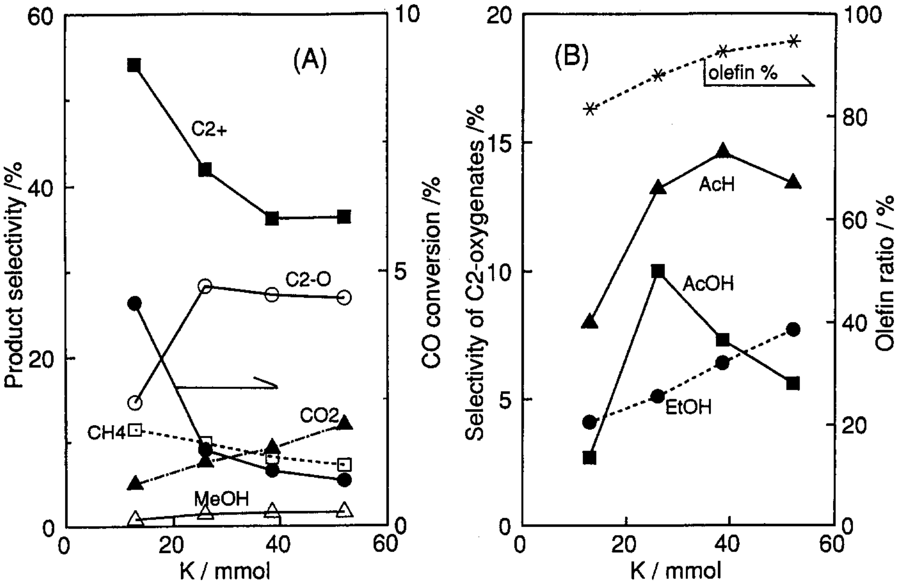

Fig. 5. Effect of potassium content on Co/SiO_2 (4.2 ± 0.3/100 in weight) catalyst. (A) CO conversion and product selectivities. (B) Selectivities of C_2-oxygenates and olefin/hydrocarbon ratio. Reaction conditions: $CO/H_2/Ar = 3/6/1$, temp. 523 K, press. 2.1 Mpa, GHSV:2000^{-1}.

may be enhanced by stronger hydrophilicity of alkyl cations than that of alkaline earth cations.

Lithium exhibited rather similar natures as modifier to barium. The effects of Mg and La were much less compared to other alkali and alkaline earth cations, although they were effective for the noble metal promoted Co(A)/SiO_2 catalysts derived from cobalt acetate [20]. The effects of the cations were, approximately, Na, K, Rb, Cs > Li > Sr, Ba > Ca ≫ Mg, La. The order indicates stronger base is more effective and suggests that the effects of the cations are electronic. Moreover, it is also suggested that the Co/SiO_2 catalysts require stronger basicity for the synthesis of oxygenates than the case of the promoted Co(A)/SiO_2 catalysts, although both of the catalysts have the similar active species, from the following results; (1) calcium is less effective than barium, (2) higher contents of alkaline earth cations are required, and (3) magnesium and lanthanum are less effective, compared to the Co(A) catalysts.

3.4. EXAFS and FT-IR studies on the modification

Significant differences were not found in the Fourier transformed profiles of EXAFS by the modification with strontium as shown in Fig. 1 (c and h). The structure of cobalt species seemed to be unchanged basically by the modification. However, slight differences were observed in the hydrogenated catalysts (Fig. 1, d and e). The amplitude of Co–O bond increased and bond distance of Co–Co was shifted from 2.14 to 2.12×10^{-1} nm by the modification. The result suggest that Co metal is higherly dispersed, and harder to be decomposed to metal or easierly oxidized by the modification. It is possible to suppose that the basic additives control the agglomeration of cobalt particles to keep highly dispersed as discussed elsewhere [13].

Fig. 7 shows in situ FT-IR spectra of CO species adsorbed on Co/SiO_2, Co–Ba/SiO_2 and Co–Mg/SiO_2. Catalysts were prepared,

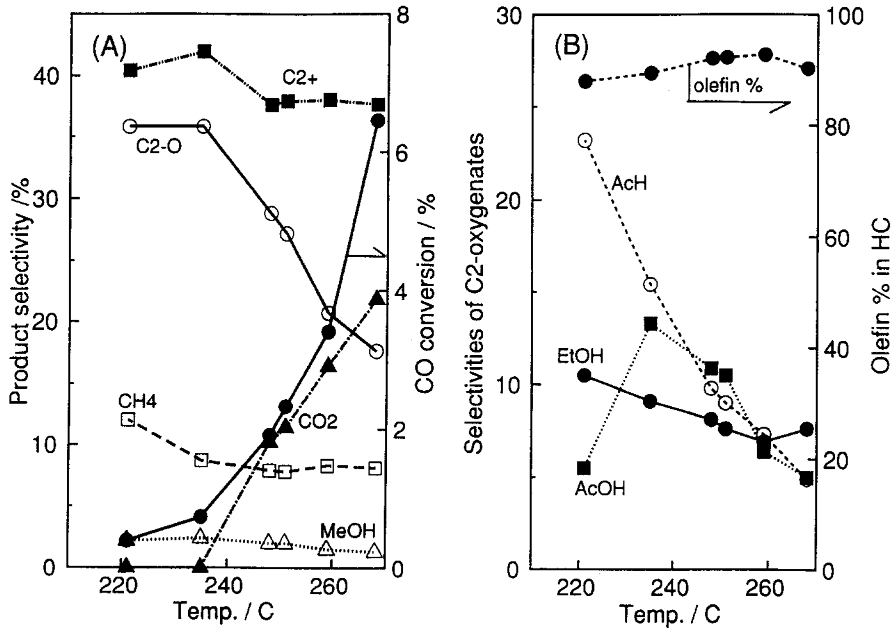

Fig. 6. Influence of reaction temperature on CO hydrogenation over Co–Na/SiO_2 (3.9–1.0/100) catalyst. (A) CO conversion and product selectivities. (B) Selectivities of C_2-oxygenates and olefin/hydrocarbon ratio. Reaction conditions: CO/H_2/Ar = 3/6/1, press. 2.1 Mpa, GHSV:2000^{-1}.

calcined by hydrogen and measured in a in situ cell. For Co/SiO$_2$ catalyst, most of linear and bridged-CO species on supported Co$_2$(CO)$_8$ (a) disappeared by heating until 473K, and only a linear-CO (2009 cm^{-1}) and a bridged − CO (1882 cm^{-1}) remained (b). By supplying syngas under room temperature and pressure, many linear CO species (around 2030–2080 cm^{-1}) and some bridged-CO species (1826–1946 cm^{-1}) appeared (c), however, only one linear-CO at 2069 cm^{-1} and a small bridged-CO species at 1880^{-1} were observed at 493K (d). Under the reaction conditions (493K, 2.1 MPa), a sharp linear band at 2075 cm^{-1} were observed (e). Other small adsorbed bands around 1946 and 1890 cm^{-1} were assigned to bridged-CO species and a band around 1600 cm^{-1} was thought to be carbon dioxide species.

When Co$_2$(CO)$_8$ was deposited on Ba/SiO$_2$ (f), some differences were found on the IR spectra from the case on SiO$_2$, i.e., bridged-CO bands around 1938 cm^{-1} were larger and new large band at 1543 cm^{-1} appeared. These differences suggest that the structure of cobalt species of supported cobalt carbonyl was changed by the presence of barium oxide in

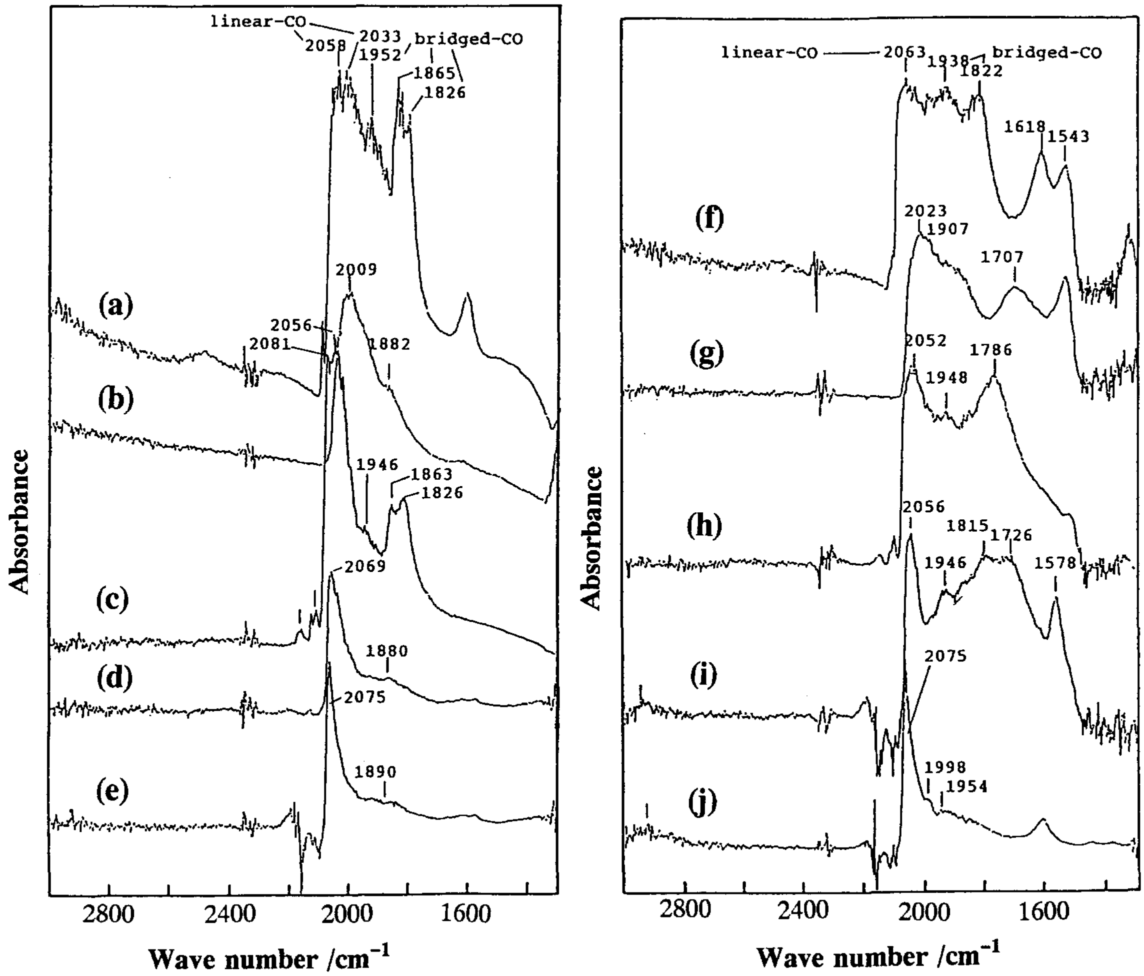

Fig. 7. in situ FT-IR spectra of adsorbed species on the catalysts. (1) Co/SiO$_2$(5/100); (a) Co$_2$(CO)$_8$ on SiO$_2$, 303 K, in He flow (0.1 MPa) (b) 473 K, in He flow (0.1 MPa) (c) in syngas flow, 303 K, 0.1 MPa (d) in syngas flow, 493 K, 0.1 MPa (e) in syngas flow, 493 K, 2.1 MPa. (2) Co-Ba/SiO$_2$(5–17/100); (f) Co$_2$(CO)$_8$ on Ba/SiO$_2$, 303 K, in He flow (0.1 MPa) (g) 303 K in He flow (h) in syngas flow, 303 K, 0.1 MPa (i) in syngas flow, 493 K, 2.1 MPa. (3) Co–Mg/SiO$_2$(5–5/100); (j) in syngas flow, 493 K, 2.1 MPa.

Table 3
Effect of Ru and Ir on Co/SiO_2 catalysts for CO hydrogenation [a]

Catalyst [b]	Ru, Ir (wt%)	Temp. (°C)	CO conv. (%)	Product selectivity (%)							olefin [f] (%)
				CO_2	CH_4	C_{2+} [c]	MeOH	EtOH	C_2-O [d]	C_{3+}O [e]	
Co	–	220	10.3	0	25	54	5.1	5.3	5.6	10.2	29
Co–Ru	0.9	220	12.9	0	32	48	3.6	7.4	7.8	9.5	20
Co–Ru	2.7	220	14.4	0	29	50	4.1	7.0	7.2	9.3	20
Co–Ir	2.1	220	7.5	0	24	44	7.4	8.6	9.8	10.7	20
Co–Sr	–	260	5.5	2	19	33	6.0	24.9	26.8	13.1	61
Co–Ru–Sr	2.7	250	5.7	4	19	29	6.6	29.4	31.1	11.4	42
Co–Ir–Sr	1.0	250	5.3	6	17	31	7.4	23.1	28.4	9.7	30
Co–Ir–Sr	5.2	250	5.1	6	20	26	11.8	26.3	29.7	7.1	12
Co–Ba	–	250	4.0	10	14	32	4.9	18.8	27.6	15.5	65
Co–Ru–Ba	2.1	250	2.4	10	15	29	5.9	24.5	29.6	10.5	67
Ru–Sr *	2.7	250	1.7	16	25	38	5.5	5.1	7.6	8.0	46
Ru–Ba	2.1	250	0.8	27	19	21	20.8	7.9	8.6	3.5	49

[a] Reaction conditions: $CO/H_2/Ar = 30/60/10$, press. 2.1 MPa, GHSV 2000 h^{-1}.
[b] Catalysts: Co 4 (±0.3) wt%, Sr 14.8 wt%, Ba 17.8 wt% as metals to SiO_2 (* Sr 5 wt%).
[c] Sum of hydrocarbons from C_2 to C_8.
[d] Sum of EtOH, AcOH and AcH.
[e] Sum of oxygenates from C_3 to C_8.
[f] Ratio of alkenes in C_2–C_4 hydrocarbons.

spite of the results of EXAFS. The bridged-CO species were more stable at higher temperature by the modification with barium (g). Bands at 1707 and 1543 cm^{-1} were also remaining. Under flowing syngas at room temperature and pressure, smaller linear-CO at 2052 cm^{-1} and larger bridged-CO species compared Co/SiO_2 were observed as well as a big band at 1786 cm^{-1} (h). Under the reaction conditions, some linear-CO species at around 2056 cm^{-1} and bridged-CO species at 1946 and 1815 cm^{-1} were observed (i). Band at 1578 × 10^{-1} may be assigned to carbon dioxide. Band at 1726 × 10^{-1} may be to monodentated acetic acid or bidentated CO species on cobalt and barium. In the case of Co–Mg/SiO_2, the features of adsorbed CO species were almost same as Co/SiO_2 except for CO_2 species around 1600 cm^{-1} (j).

Summarizing the results of the FT-IR study, it is noticeable that the structure of cobalt species of cobalt carbonyl varied on SiO_2, and the ratio and stability of bridged-CO species increased even under the reaction conditions by modification with barium. While, linear CO species was predominant on Co and Co–Mg catalysts. These results suggest that the electronic state of cobalt is affected by barium, and bridged CO species is important for the formation of oxygenates. Similar results were obtained by Co(A)–

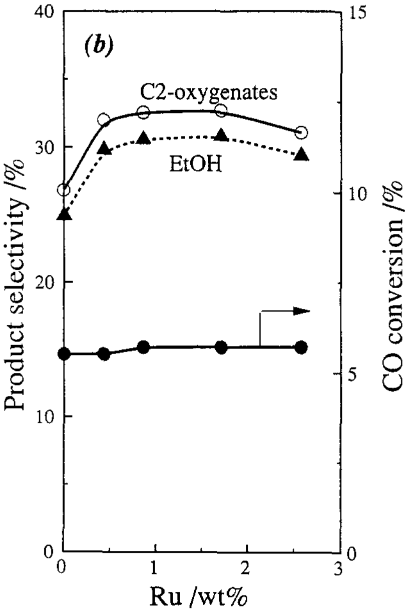

Fig. 8. Effect of ruthenium content on Co-Sr/SiO_2 (4.5±0.3-14.8/100) for CO hydrogenation. Reaction conditions: $CO/H_2/Ar = 3/6/1$, press. 2.1 Mpa, GHSV:2000^{-1}.

Table 4
Natures of oxides supports

oxides		sp. sur. area (cm^2/g)	ap. sp. weight (g/ml)
SiO_2	Davison #57, pellet	330	0.4
Al_2O_3	Ketjen CK-300, spherical	198	0.67
TiO_2	Merck anatase, powder	9.8	1.1
ZnO	Merck, powder	5.8	1.7
ZrO_2	$Zr(OH)_2$, powder calcined in air at 673 K	114	0.95
MgO	Kanto Chemicals, powder	16.8	0.67
La_2O_3	Wako Chemicals 99.8%, powder	3.1	1.6
CeO_2	Wako Chemicals 99.8%, powder	26.5	1.95

Re/SiO_2 catalyst and Rh/SiO_2 catalysts [22–24].

3.5. *Effect of noble metals*

Some noble metals such as iridium and ruthenium are indispensable promoters for $Co(A)/SiO_2$ catalyst [14]. They are considered to activate the catalyst by reducing Co^{2+} species to Co^0 by spilt-over hydrogen activated on the noble metal site. It is interesting to know whether these metals are effective or not for the present Co/SiO_2 catalyst. Table 3 and Fig. 8 exhibit the effect of ruthenium and iridium. Ruthenium and iridium were impregnated on SiO_2, Sr/SiO_2 or Ba/SiO_2 by dry mixing from their carbonyl compounds and calcined in hydrogen stream at 723K before the deposition of cobalt [14]. It was found that these metals had only a little effect for C_2 oxygenates formation and almost no effect for the activity for the Co/SiO_2 catalysts whether they were modified with basic additives or not. From the result, it is obvious that these metals are not important when cobalt particles are metallic.

3.6. *Effect of supports*

The effects of metal oxides were examined as supports. Specific surface areas and apparent

Table 5
Effect of supports of Co catalysts on CO hydrogenation

catalyst	Co (%)	wt. (g)	vol. (ml)	CO conv. (%)	product selectivities (%)									Ol/HC (C_{2-4})
					CO_2	CH_4	HC_{2-8}	MeOH	EtOH	AcH	AcOH	C_2–O	$C_{3+}O$	
Co/SiO_2	4.2	1.2	3.0	10.3 *	0	25	54	5.1	5.3	0.3	0	5.6	10.2	29
$Co-Sr/SiO_2$	3.2	1.4	3.0	5.5	3	18	35	3.9	24.4	2.0	0.3	26.7	15.0	61
Co/Al_2O_3	3.6	1.2	1.8	15.8 *	1	19	64	3.0	5.1	0.2	0.1	5.3	8.1	41
$Co-Sr/Al_2O_3$	3.1	1.2	1.6	6.6	4	21	44	2.2	15.3	3.3	0.5	19.1	10.8	64
Co/ZnO	1.3	3.4	2.0	8.4 *	0	25	55	2.3	4.9	0.4	0.4	5.7	9.4	51
Co/TiO_2	1.9	2.2	2.0	0.3	0	21	50	3.5	6.5	11.2	2.6	20.3	5.9	86
$Co-Sr/TiO_2$	1.8	2.3	2.0	1.0	0	16	45	2.0	3.9	13.9	1.5	19.2	18.2	90
Co/ZrO_2	3.0	1.9	2.0	3.7	0	23	50	6.0	12.5	0.7	0.4	13.6	7.0	29
$Co-Sr/ZrO_2$	3.2	1.9	2.0	5.4	0	21	51	1.8	8.6	3.2	0.2	12.0	13.2	70
Co/MgO	2.3	1.2	1.8	3.2	0	22	49	5.7	6.4	4.1	1.6	12.1	11.0	67
$Co-Sr/MgO$		2.2	2.0	2.4	6	25	34	5.4	6.2	9.1	0.6	15.9	13.5	75
Co/La_2O_3	1.2	3.2	2.0	3.7	0	28	50	7.2	5.0	3.3	0.3	8.6		70
Co/CeO_2	1.7	3.9	2.0	6.3	3	38	39	2.4	6.4	1.1	1.0	8.5	9.1	43

Catalyst; Sr: 0.13 mole (14.8 g)/100 g · SiO_2. Reaction conditions; $CO/H_2 = 1/2$, 2.1 MPa, 250°C (* 220°C), gas flow rate: 6 l/h.

specific weight of the oxides used are summarized in Table 4. Powder samples were pelletized by a press machine at 1 ton/cm^2 and crashed to 16–32 mesh. Catalysts were prepared in a similar way to Co/SiO_2. The results of CO hydrogenation are exhibited in Table 5. Cobalt contents measured by XRF, catalyst weight and volumes for each catalysts are shown in the table. The effect of the modification with strontium was also examined. Alumina and ZnO had similar properties to SiO_2 as supports because the activities, product distributions and the modification effect with Sr were similar to SiO_2. In the case of TiO_2 and ZrO_2, the selectivities of oxygenates were higher without any modification with basic additives, and the effect of Sr was little. Magnesia, La_2O_3 and CeO_2 showed the similar effects as modifiers and Sr had a low effect. These results indicate that highly dispersed cobalt metals can be prepared on each of the oxides, and some basic oxide supports have the similar effects to cation modifiers on Co/SiO_2.

4. Discussion

4.1. Cobalt species as active site

Cobalt species of the catalyst derived from $Co_2(CO)_8$ was revealed to be metallic and highly dispersed on oxide supports. The catalyst was active for oxygenates formation from syngas without modification with transition metals. The cobalt catalyst was also found to be active for the hydroformylation of ethylene [25]. These results indicated that the highly dispersed cobalt metal has enough ability for the activation of hydrogen and for the migratory insertion of CO. Some other researchers such as Yermakov et al. [7], Nakamura et al. [26], Bertholomew et al. [27], and Fukuoka et al. [28] also have reported the cobalt catalysts derived from $Co_2(CO)_8$ for syngas reaction, however, only Yermakov et al. claimed to produce oxygenates as one of the main products, and only a small amounts of oxygenates were produced by others. That may be because the preparation and the handling of the catalysts were different among the researchers.

We have already reported that Co(A)/SiO_2 catalysts derived from cobalt acetate and promoted by some noble metals were also active for oxygenates formation, and discussed that the main active site for the syngas reaction was the highly dispersed cobalt metal [14]. In this study, it is revealed that the oxidation states, the particle size of cobalt species, catalytic activity, product distribution and the modification effect of basic additives of the present cobalt catalyst are basically similar to the noble metal promoted Co(A)/SiO_2 catalysts. Moreover, it was demonstrated that EXAFS profile of the air-leaked Co/SiO_2 was quite similar to Co(A)/SiO_2, and noble metals such as ruthenium and iridium had little effects for the Co/SiO_2 catalyst. These result suggest that the structure of cobalt species are similar to each of the cobalt catalysts and noble metals have not a important role as active site of Co(A)/SiO_2 catalysts. From these considerations, it is concluded that the CO hydrogenation principally proceeds on the nearly common active site, i.e., highly dispersed cobalt metal site for both of the cobalt catalysts.

However, it is apparent that active cobalt site of the cobalt catalysts are resembled but not same. The effects of basic additives are partly different from each other in detail. For example, olefin ratio in hydrocarbons are higher, and stronger basicity are required for the present Co/SiO_2 catalysts than for the promoted Co(A)/SiO_2 catalysts. The differences may be because of the presence of transition metals in Co(A)/SiO_2. These metals naturally form minor active sites in the catalysts or have some effects on the main cobalt site.

4.2. Effect of cations

The effects of alkali and alkaline earth cations are summarized as follows; (1) reduce the over-all reaction rate, (2) reduce the formation of hydrocarbons, (3) enhance the formation or selectivities of oxygenates, especially C_2-oxygenates, (4) increase the olefin ratio in hydrocarbons, and (5) decrease (or not increase) the probability of carbon chain growth.

Alkali or alkaline earth cations have been very often used as modifiers to enhance the productivity or selectivity of oxygenates for syngas reaction. It has been well-known that addition of potassium to Fischer–Tropsch iron catalyst enhanced the formation of ethanol [29–31]. Alkali metal increased the formation of C_2^+ alcohols in the methanol synthesis [32]. Kikuzono et al. exhibited that methanol productivity remarkably increased by addition of alkali metals for palladium catalysts [33]. Supported rhodium catalysts were improved by lithium for C_2-oxygenates synthesis [34,35]. Most of the recently proposed catalysts for C_2^+ alcohols consist of alkali metals as indispensable component for enhancing wide range of alcohols, c.g. modified methanol synthesis catalysts [2,3,36], molybdenum sulfide catalysts [2,37], molybdenum [38,39] or ruthenium [40] catalysts. In most of these cases, alkali cations decrease the overall reaction rate, decrease the formation of hydrocarbons, enhance the formation of C_2^+ alcohols, increase the ratio of olefins to paraffins and increase the probability of carbon chain growth. It is obvious that alkali cations reduce the hydrogenating ability of the catalysts.

Although most of the effects are adapted to our cobalt catalysts, it is a very rare case except for rhodium catalysts that the cations strongly enhance C_2 oxygenates, especially acetic acid, and methanol and C_3^+ oxygenates are not so much increased. It is also rare that α-values are decreased or not increased. These effects of the cations may be characteristic for our highly dispersed cobalt catalysts.

From the syngas reactions and the characterizations of the catalysts, it is demonstrated that the cations decrease the hydrogenating ability of the catalysts and the effect of the cations is electronic. In the case of promoted Co(A) catalysts, the X-ray photoelectron spectroscopy (XPS) exibited that the cations control the reduction of Co^{2+} species to cobalt metal decreasing the ratio of Co^0/Co^{2+} [20]. In the case of the present cobalt catalysts, EXAFS study exhibited that the ratio of Co–O bond to Co–Co bond was increased by the modification with strontium. The result indicates that the cations decrease the Co^0 site in the catalyst in spite that no hydrogenation required in the preparation of the catalysts. The decrease of the Co^0 site is the cause for reducing over-all reaction rate, however, it does not fully explain the effect of the cations because product distributions were strongly changed by the modification. Blanchard et al. [8] and Burch et al. [9] reported that oxygenates were formed in the conditions of the co-existence of Co^0 and Co^{2+} in good balance. In this case, for example, CO is dissociatively adsorbed on Co^0 sites and migratory CO insertion occurs on the Co^{2+} sites. Tatsumi et al. claimed the similar system for molybdenum catalysts [39]. However, in the case of the $Co(A)/SiO_2$ catalyst, in which most of the cobalt species are divalent, oxygenates were not produced but only a small amount of hydrocarbons, and had little activity for the hydroformylation of ethylene [41]. From the analogies of the two kind of cobalt catalysts, it is hard to consider the participation of Co^{2+} species in the synthesis of oxygenates for our cobalt catalysts.

It is possible to consider that cations not only decrease the Co^0/Co^{2+} ratio, but affect the oxidation state of cobalt active site. The in situ FT-IR study indicated that the ratio of bridged/linear adsorbed CO species increased by the modification, and the results suggests that the oxidation state of cobalt species is affected by the cations. Ponec claimed that pure metal site gives only hydrocarbons and no oxygenates [42]. Somorjai et al. reported that slightly oxygenated rhodium metal is effective for the synthesis of oxygenates [43]. Ichikawa et al. also reported that ethanol formation was enhanced when the electronic state of rhodium was between Rh^0 and Rh^{1+} by XPS studies

[44]. Probably, in our case, the cations keep cobalt active site slightly cationic and that weaken the hydrogenating ability of the catalysts and stabilize the acyl-cobalt intermediate against hydrogenation.

Another important effect of the cations is preventing the agglomeration of cobalt particles. These cations may block cobalt species to move and keep cobalt particles highly dispersed. It is concluded that the effects of the cations on the cobalt catalysts for CO hydrogenation are performed by controlling the electronic and dispersive state of active cobalt site.

4.3. Discussion for reaction mechanism

As cobalt has a strong ability to adsorb CO dissociatively, the initial step of the Fischer–Tropsch reaction must be the dissociative adsorption of CO on the catalysts, although methanol may be formed by the hydrogenation of non-dissociatively adsorbed CO species. Migratory CO insertion to surface alkyl species is important for the formations of oxygenates. The highly dispersed cobalt catalysts have an enough ability for the CO insertion as discussed. The chain growth may proceed mainly via the CO insertion. The direct chain growth by the reaction of surface carbene species with surface alkyl group which leads to higher hydrocarbons may also occur, however, the rate of the reaction may be low when the particle size of the active sites are small. Basic additives suppress the ability of the catalyst for CO dissociation reaction and the possibility of the direct chain growth, and enhance the CO insertion reaction. Therefore, both of hydrocarbons and oxygenates may be mainly produced via acetyl–cobalt complex for our catalysts.

Alcohols may be produced mainly by the hydrogenation of aldehydes which are the product of the reductive elimination of the complex. Carboxylic acids may be formed by the reaction of the complex with surface OH-group and the reaction should be enhanced by the presence of the basic additives, especially alkali cations. If the complex is hydrogenated to hydroxy–alkyl-complex, the latter may proceed to olefins, or to the further chain growth via the CO insertion. The basic additives weaken the hydrogenating ability of the catalysts and stabilize the acyl-complex against the hydrogenation, resulting to decrease the ratio of paraffin to olefin, the ratio of alcohols to aldehydes, the yield of hydrocarbons and the chain growth probability.

5. Conclusions

Silica-supported cobalt catalyst was prepared from dicobaltoctacarbonyl in an oxygen-free conditions. Cobalt species of the catalyst was revealed to be metallic and highly dispersed by the studies of extended X-ray adsorption fine structure(EXAFS). The catalyst was found to be active for the formation of oxygenates in CO hydrogenation. By the modification with alkali or alkaline earth cations to the catalyst, the formation of hydrocarbons was strongly depressed and the selectivity of oxygenates, especially C_2-oxygenates, was enhanced although the over-all reaction rate was decreased. While, transition metals had little effects as promoters. Similar cobalt catalysts were obtained from the carbonyl compound using some other oxide supports.

The properties of active site, effect of the cations and reaction mechanism were discussed. It is concluded that the cations affect cobalt active site on dispersive and electronic state, and then reduce the hydrogenating ability of the catalyst and stabilize the acyl–cobalt intermediate.

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References

[1] R.B. Anderson, Fischer–Tropsch Synthesis, Academic Press, Orland, 1984, p. 122.
[2] G. Herman, in: L. Guczi, Ed., New Trends in CO Activation, Studies on Surface Science and Catalysis 64, Elsevier Science B.V., Amsterdam, 1991, p. 265.
[3] P. Courty, D. Durand, E. Fruend and A. Sugier, J. Mol. Catal., 17 (1982) 241.
[4] D.J. Elliot and F. Pennella, J. Catal., 102 (1986) 464.
[5] N. Mouaddib and V. Perrichon, Proc. 9th Int. Congr. Catal., 2 (1988) 521.
[6] H. Hachenberg, F. Wunder, E.I. Leupoid and H.-J. Schmidt, Eur. Pat. Appl., 21330 (1981).
[7] A.Y. Lysitsyn, V.L. Kuznetsov, Yu.I. Yermakov, Kinetika i Kataliz, 24 (1983) 764; A.S. Lisytsyn, A.V. Golovin, A.L. Chuvilin, V.L. Kuznetsov, A.V. Romanenko, A.F. Danilyuk and Yu.I. Yermakov, Appl. Catal., 55 (1989) 235.
[8] M. Blanchard, H. Delule and P. Canesson, Catal. Lett., 2 (1989) 319.
[9] J.E. Baker, R. Burch and S.E. Golunski, Appl. Catal., 53 (1989) 279; J.E. Baker, R. Burch, S.J. Hibble and P.K. Loader, Appl. Catal., 65 (1990) 281; J.E. Baker, R. Burch and Niu Yuqin, Appl. Catal., 73 (1991).
[10] Y. Kintaichi, Y. Kuwahara, H. Hamada, T. Ito and K. Wakabayashi, Chemistry Lett., 1305 (1985).
[11] K. Takeuchi, T. Matsuzaki, H. Arakawa, Y. Sugi, Appl. Catal., 18 (1985) 325.
[12] K. Takeuchi, T. Matsuzaki, H. Arakawa, T. Hanaoka, Y. Sugi, Appl. Catal., 48 (1989) 149.
[13] 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, 1991, p. 249.
[14] T. Matsuzaki, K. Takeuchi, T. Hanaoka, H. Arakawa, Y. Sugi, Appl. Catal., A, 105 (1993) 159.
[15] K. Takeuchi, T. Matsuzaki, H. Arakawa, T. Hanaoka, Y. Sugi, K. Wei, J. Mol. Catal., 55 (1989) 361.
[16] K. Takeuchi, T. Matsuzaki, T. Hanaoka, H. Arakawa, Y. Sugi, N. Matsubayashi, J. Nat. Chem. Lab. Ind., 84 (1989) 549.
[17] H. Arakawa, T. Fukushima and M. Ichikawa, Appl. Spectrosc., 40 (1986) 884.
[18] Y, Iwasawa, M. Yamada, Y. Sato, H. Kuroda, J. Mol. Catal., 23 (1984) 95.
[19] Y. Kintaichi, K. Takeuchi, T. Matsuzaki, H. Arakawa, T. Hanaoka, T. Ito, Y. Sugi, Chemistry Express, 4 (1989) 129.
[20] T. Matsuzaki, K. Takeuchi, T. Hanaoka, H. Arakawa and Y. Sugi, Catal. Today, 28 (1996) 251.
[21] T. Matsuzaki, K. Takeuchi, T. Hanaoka, H. Arakawa and Y. Sugi, Sekiyu Gakkaishi, 37 (1994) 179.
[22] The Research Association for C_1 Chemistry, Progress on C_1 Chemistry in Japan, p. 143.
[23] H. Arakawa, K. Takeuchi, T. Matsuzaki and Y. Sugi, Sekiyu Gakkaishi, 31 (1988) 335.
[24] H. Arakawa, T. Fukushima, M. Ichikawa, K. Takeuchi, T. Matsuzaki and Y. Sugi, Chem. Lett., 4 (1984) 129.
[25] K. Takeuchi, T. Hanaoka, T. Matsuzaki, M. Reinikainen, and Y. Sugi, Catal. Lett., 8 (1991) 253.
[26] R. Nakamura, A. Oomura and E. Echigoya, Proc. 8th Int. Congr. Catal., Berlin, 1988, V–51.
[27] B.G. Johnson, C.H. Betholomew and D.W. Goodman, J. Catal., 128 (1991) 2318.
[28] A. Fukuoka, T. Fujimoto, F-S. Xiao and M. Ichikawa, Sekiyu Gakkaishi, 34 (1991) 125.
[29] F. Fischer and H. Tropsch, Brenstoff-Chem., $ (1923) 276.
[30] M.E. Dry, in: Catalysis-Science and Technology, Vol. 1, Springer-Verlag, Berlin, 1981, p. 159.
[31] D.J. Dwer, in: H.P. Bonzel, A.M. Bladshow and G. Ertl, Eds., Physics and Chemistry of Alkali Metal Adsorption, Elsevier Science B.V., Amsterdam, 1989, p. 307.
[32] G. Natta, U. Colombo and I. Pasqueon, in: P.H. Emmett, Ed., Catalysis, Vol. 5, Reinhold, NY, 1957, Ch.4.
[33] Y. Kikuzono, S. Kagami, S. Naito, T. Onishi and K. Tamaru, Faraday Discuss. Chem. Soc., 72 (1981) 135.
[34] S.C. Chuang, J.G. Goodwin and I. Wender, J. Catal., 95 (1985) 435.
[35] H. Arakawa, T. Hanaoka, K. Takeuchi, T. Matsuzaki and Y. Sugi, Proc. 9th Int. Congr. Catal., Calgary, 1988, Vol. 2, p. 602.
[36] E. Tronkoni, L. Lietti and I. Pasqueon, Appl. Catal., 47 (1989) 317.
[37] J.G. Santiesteban, C.E. Bogdan, R.G. Herman and K. Klier, Proc. 9th Int. Congr. Catal., Calgary, 1988 Vol. 2, p. 561.
[38] K. Fujimoto and T. Oba, Appl. Catal., 13 (1985) 289.
[39] T. Tatsumi, A. Muramatsu and H. Tominaga, Sekiyu Gakkaishi, 35 (1992) 233.
[40] M. Inoue, T. Miyake, Y. Takegami and T. Inui, Appl. Catal., 11 (1984) 103.
[41] K. Takeuchi, T. Hanaoka, T. Matsuzaki, Y. Sugi, S. Ogasawara, Y. Abe and T. Misono, Catal. Today, 20 (1994) 423.
[42] V. Ponec, in: L. Guczi, Ed., New Trends in CO Activation, Studies on Surface Science and Catalysis 64, Elsevier Science B.V., Amsterdam, 1991, p. 117.
[43] D.G. Castner, R.L. Blackadar and A. Somorjai, J. Catal., 66 (1980) 257.
[44] M. Kawai, M. Uda and M. Ichikawa, J. Phys. Chem., 89 (1985) 1654.