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CO_2 hydrogenation to ethanol over promoted Rh/SiO_2 catalysts

Hitoshi Kusama, Kiyomi Okabe *, Kazuhiro Sayama, Hironori Arakawa

Department of Surface Chemistry, National Institute of Materials and Chemical Research, MITI, Tsukuba, Ibaraki 305, Japan

Abstract

Hydrogenation of CO_2 to ethanol was carried out over Rh/SiO_2 based catalysts. The main product over the unpromoted catalysts was methane. By adding various metal oxide promoters to the catalysts, CO_2 conversion and selectivity to alcohols (methanol and ethanol) increased. Among the promoters, Li salts showed the most prominent effect on ethanol production. Reaction conditions were optimized for ethanol formation over $Rh-Li/SiO_2$ catalysts. An ethanol selectivity of 15.5% and a CO_2 conversion of 7.0% were obtained at $P = 5$ MPa and $T = 513$ K in a flow of H_2–CO_2 premixed gas ($H_2/CO_2 = 3$) with a flow-rate of 100 cm^3/min. By in situ FT-IR analysis of the adsorbed species on the catalysts, the reaction was suggested to proceed via CO intermediate(s).

Keywords: Carbon dioxide hydrogenation to ethanol; Rh/SiO_2 catalysts

1. Introduction

Catalytic hydrogenation of CO_2 to chemical feedstocks has been paid much attention as one of the most promising recycling technologies of emitted CO_2 from power stations, iron mills and so forth, which may cause global warming. Under the circumstances, hydrogenation of CO_2 to methanol has been investigated most extensively on supported Cu–ZnO, precipitated $Cu-ZnO-Cr_2O_3-Al_2O_3$, and precipitated $Cu-ZnO-TiO_2$ catalysts, including in our previous papers [1–3]. In contrast, the direct processes of CO_2 hydrogenation to more valuable feedstocks, such as higher alcohols, carboxylic acids, and light olefins, have not been attempted yet so much, except for the few cases over Fe-based and Rh-based catalysts [4–6], and Ru-based complex catalysts. In the present paper, the feasibility of CO_2 hydrogenation to ethanol was studied over Rh/SiO_2 catalysts, based on the results obtained through syngas conversion [7]. The effect of additives was also examined to improve conversion and selectivity.

2. Experimental

Silica gel (Fuji-Davison, #57), sieved into 16–32 mesh size range and evacuated at 473 K for 2 h, was impregnated with an aqueous solution of $RhCl_3$ or $Rh(NO_3)_3$ together with additives by the incipient wetness method, to form $Rh-M/SiO_2$ catalysts (M = additive). After drying at 473 K in vacuo, 1.0 g of catalyst was packed in a fixed-bed flow type reactor, and was pretreated in situ at 623 K for 30 min in a H_2 flow of 200 cm^3/min. After cooling to

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* Corresponding author.

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room temperature, the H_2 gas was switched into H_2-CO_2 premixed gas ($H_2/CO_2 = 3$) containing 1% of Ar as an internal standard for GC analysis, and the reaction was carried out under appropriate conditions. The effluent gas was analyzed by on-line gas-chromatography.

The dispersion and particle size of Rh on the catalysts were estimated by CO adsorption at 308 K. The electronic states of catalyst surfaces were investigated by XPS, after the in situ H_2 pretreatment within the prechamber. The reaction intermediates and surface species adsorbed on the catalysts were characterized by an in situ FT-IR spectrometer (JEOL, JIR-100) with a high-pressure high-temperature IR cell [8].

3. Results and discussion

3.1. Effect of additives

Hydrogenation of CO_2 was carried out over unpromoted 5 wt.% Rh/SiO_2 catalyst at various pressures (P). The main product was CH_4 even at 5 MPa, and ethanol was not detected, as listed in Table 1. In comparison with the results

Table 1
Effect of additives on CO_2 hydrogenation over Rh/SiO_2 catalysts (5 wt.% Rh) [a]

Additive [b]	Precursor	CO_2 conv./ %	Selectivity/C%				
			MeOH [c]	EtOH [d]	CO	CH_4	DME [e]
None		12.4	0.2	0.0	0.1	99.7	0.0
Li	LiCl	7.0	5.2	15.5	15.7	63.5	0.0
Na	NaCl	7.2	0.7	0.0	0.1	99.2	0.0
K	KCl	1.9	2.2	0.0	5.5	92.3	0.0
Mg	$MgCl_2 \cdot 6H_2O$	34.7	0.0	0.0	0.0	100.0	0.0
Ca	$CaCl_2$	33.3	0.1	0.0	0.1	99.9	0.0
Sr	$SrCl_2 \cdot 6H_2O$	2.8	7.6	2.5	27.1	62.6	0.3
Ba	$BaCl_2 \cdot 2H_2O$	3.7	3.9	0.0	0.6	95.5	0.0
Fe	$FeCl_3 \cdot 6H_2O$	10.4	16.0	3.2	6.8	73.9	0.1
Co	$CoCl_2 \cdot 6H_2O$	3.7	27.4	0.0	8.6	63.6	0.4
Ni	$NiCl_2 \cdot 6H_2O$	6.4	8.3	0.0	2.1	89.6	0.0
Ru	$RuCl_3 \cdot H_2O$	31.1	0.0	0.0	0.0	100.0	0.0
Pd	$PdCl_2$	1.9	26.2	0.0	16.6	56.8	0.4
Ir	$IrCl_3 \cdot 3/2H_2O$	7.0	0.8	0.0	0.2	99.0	0.0
Pt	$H_2PtCl_6 \cdot 6H_2O$	4.5	11.6	0.0	81.2	7.0	0.2
Cu	$CuCl_2 \cdot 2H_2O$	0.4	9.6	0.0	83.6	4.4	2.3
Ag [f]	$AgNO_3$	2.1	7.4	1.8	30.7	60.2	0.0
Ti	$TiCl_4$	67.9	0.0	0.0	0.0	100.0	0.0
V	$VOCl_3$	56.2	0.1	0.0	0.0	99.9	0.0
Mn	$MnCl_2 \cdot 4H_2O$	44.8	0.1	0.0	0.4	99.6	0.0
Zr	$ZrCl_2O \cdot 8H_2O$	76.0	0.0	0.0	0.0	100.0	0.0
Nb	$NbCl_5$	69.4	0.0	0.0	0.0	100.0	0.0
Mo	$MoCl_5$	43.0	0.0	0.0	0.1	99.7	0.2
Re	$ReCl_3$	46.2	0.2	0.0	0.1	99.6	0.1
Zn	$ZnCl_2$	0.3	11.6	0.0	62.6	5.7	20.1
Sn	$SnCl_2 \cdot 2H_2O$	2.8	43.1	0.0	51.4	4.9	0.5
La	$LaCl_3 \cdot 7H_2O$	53.9	0.0	0.0	0.0	100.0	0.0
Ce	$CeCl_3 \cdot 7H_2O$	46.6	0.0	0.0	0.0	100.0	0.0
Sm	$SmCl_3 \cdot 6H_2O$	33.1	0.0	0.0	0.0	100.0	0.0

[a] Reaction conditions: $T = 513$ K, $P = 5$ MPa, flow-rate = 100 cm^3/min, and $H_2/CO_2 = 3$.
[b] Rh: additive = 1:1 (atomic ratio).
[c] Methanol.
[d] Ethanol.
[e] Dimethyl ether.
[f] Rh precursor = nitrate.

obtained through syngas conversion, namely that more than 60% of the products are C_2-oxygenates (i.e. ethanol, acetaldehyde, acetic acid, and so on) at the same pressure [7], it is suggested that CO_2 is more easily hydrogenated than CO, resulting in high CH_4 selectivity in CO_2 hydrogenation even at high pressures.

More than 30 additives were examined with an atomic ratio of Rh:M = 1:1 (M = additive) in order to improve ethanol production, since pronounced effect of additives has been reported on syngas conversion to C_2-oxygenates [9]. Some of the reaction results are tabulated in Table 1. By adding Ca, V, Mn and Re, CO_2 conversion increased with slight formation of methanol but no ethanol. In contrast, ethanol was formed by adding Li, Sr, Fe and Ag. Among them, Li addition gave rise to the highest ethanol selectivity.

3.2. Optimization of CO_2 hydrogenation over Rh–Li / SiO_2 catalysts

The CO_2 hydrogenation was optimized over Rh–Li/SiO_2 catalyst, which showed the highest ethanol production in Table 1. Table 2 shows the effect of added amounts of Li. The conversion decreased with Li amount, along with the decrease in the numbers of active sites estimated by CO adsorption. This result indicates that the turnover frequency (TOF) did not change significantly by the Li addition. By changing the Li/Rh ratio, the highest selectivity to ethanol was obtained at Li/Rh = 1, with CH_4 selectivity higher than 60%. The increase in ethanol formation implies that further hydrogenation of reaction intermediates to CH_4 was suppressed to some extent over Rh/SiO_2 based catalysts by adding Li. In comparison with the cases of syngas conversion, in which CH_4 selectivity is less than 20% under similar conditions, it is suggested that CO_2 is more easily hydrogenated to CH_4 than CO over Rh–Li/SiO_2 catalysts, as well as Rh/SiO_2 catalyst. Both the selectivities to methanol and CO increased with ethanol selectivity. The good correlations among them suggest that the reaction proceeds consecutively via common intermediates.

By using 5 wt.% Rh–Li/SiO_2 catalysts (Rh/Li = 1), which showed the highest selectivity to ethanol, the reaction conditions were optimized. Table 3 shows the effect of pressure at a temperature $T = 513$ K with a flow-rate of 100 cm^3/min, and $H_2/CO_2 = 3$. The CO_2 conversion increased with pressure. Ethanol was formed at higher pressure than 1 MPa, with suppression of CH_4 formation. Ethanol selectivity, as well as methanol selectivity, increased almost proportionally with pressure. As is expected by equilibrium, ethanol formation needs pressurized conditions, and higher pressure is favorable to ethanol selectivity.

Table 2
Effect of added amount of Li on CO_2 hydrogenation over Rh–Li/SiO_2 catalysts [a]

Li/Rh [b]	CO_2 conv. /%	Selectivity/C%				CO adsorbed / cm^3 g^{-1}
		MeOH [c]	EtOH [d]	CO	CH_4	
0.0	12.4	0.2	0.0	0.1	99.7	3.11
0.5	8.4	4.1	10.4	8.8	76.8	2.43
1.0	7.0	5.2	15.5	15.7	63.5	1.58
2.0	6.6	4.6	12.7	14.0	68.7	1.22

[a] Reaction conditions: $T = 513$ K, $P = 5$ MPa, $H_2/CO_2 = 3$, flow-rate = 100 cm^3/min, and loading amount of Rh = 5 wt.%.
[b] Atomic ratio.
[c] Methanol.
[d] Ethanol.

Table 3
Effect of pressure on CO_2 hydrogenation over 5 wt.% Rh–Li/SiO_2 catalysts (Rh/Li = 1) [a]

Pressure / MPa	CO_2 conv. / %	Selectivity /C%			
		MeOH [b]	EtOH [c]	CO	CH_4
0.1	3.7	0.0	0.0	0.5	99.5
1	3.6	0.9	2.7	14.2	82.3
3	5.4	2.8	9.9	17.9	69.4
5	7.0	5.2	15.5	15.7	63.5

[a] Reaction conditions: $T = 513$ K, flow-rate = 100 cm^3/min, $H_2/CO_2 = 3$.
[b] Methanol.
[c] Ethanol.

Table 4
Effect of reaction temperature on CO_2 hydrogenation over 5 wt.% Rh-Li/SiO_2 catalysts (Rh/Li = 1) [a]

Temperature / K	CO_2 conv. / %	Selectivity /C%			
		MeOH [b]	EtOH [c]	CO	CH_4
473	1.4	5.3	7.3	55.2	32.2
493	3.0	6.0	12.8	36.6	44.7
513	7.0	5.2	15.5	15.7	63.5
533	15.7	3.2	9.4	6.2	81.3

[a] Reaction conditions: $P = 5$ MPa, $H_2/CO_2 = 3$, flow-rate = 100 cm^3/min.
[b] Methanol.
[c] Ethanol.

Table 5
Effect of H_2/CO_2 ratio on CO_2 hydrogenation [a] over Rh-Li/SiO_2 catalysts [b]

H_2/ CO_2	CO_2 conv. / %	Selectivity /C%			
		MeOH [c]	EtOH [d]	CO	CH_4
0.6	1.7	1.0	12.3	38.1	48.6
1.0	2.4	1.8	13.0	30.4	54.9
3.0	5.4	2.8	9.9	17.9	69.4
4.0	6.5	2.9	8.5	7.2	81.1
9.0	13.4	3.5	5.5	5.1	85.8

[a] Reaction conditions: $T = 513$ K, $P = 3$ MPa, flow-rate = 100 cm^3/min.
[b] Loading amounts: Rh = 5 wt.%, Li = 0.3 wt.%.
[c] Methanol.
[d] Ethanol.

Table 4 shows the effect of reaction temperature at $P = 5$ MPa with a flow-rate of 100 cm^3/min and $H_2/CO_2 = 3$. The CO_2 conversion increased with temperature. The main product was CO at low temperature, and CH_4 at higher temperature. The highest selectivity to ethanol was obtained at 513 K. The highest yield of ethanol was accomplished in the range $T = 513$–533 K. By assuming that conversion and CH_4 yield reflect overall reaction rate and the rate of a hydrogenation step to CH_4, the apparent activation energies of them were estimated at 87 and 121 kJ/mol, respectively. The higher activation energy of the latter implies that higher temperature is favorable to CH_4 formation, and consequently ethanol selectivity decreases.

Table 5 shows the effect of H_2/CO_2 ratio at $P = 3$ MPa and $T = 513$ K with a flow-rate of 100 cm^3/min. The CO_2 conversion increased and ethanol selectivity decreased with H_2/CO_2 ratio. The selectivity to CO was almost proportional to ethanol selectivity. The selectivities to CH_4 and methanol increased with H_2/CO_2 ratio.

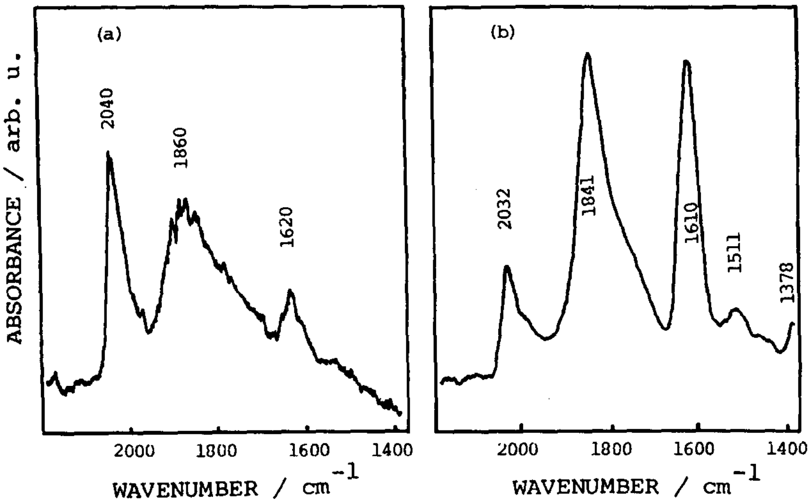

Fig. 1. In situ FT-IR spectra of adsorbed species on (a) 5 wt.% Rh/SiO_2 and (b) 5 wt.% Rh-Li/SiO_2 (Rh/Li = 1:1) catalysts at $T = 533$ K, $P = 5$ MPa, and $H_2/CO_2 = 3$.

3.3. *Characterization of reaction intermediates by in situ FT-IR spectroscopy*

It was shown that ethanol was formed by CO_2 hydrogenation over Rh–Li/SiO_2 catalysts. In order to speculate about the reaction mechanism, in situ FT-RI of adsorbed species on the catalysts was conducted. Fig. 1 illustrates FT-IR spectra on (a) 5 wt.% Rh/SiO_2 and (b) 5 wt.% Rh–Li/SiO_2 (Rh: Li = 1) catalysts at a condition of $T = 533$ K, $P = 5$ MPa, and $H_2/CO_2 = 3$. The CO species adsorbed on Rh were observed on both catalysts. For Cu–ZnO–Cr_2O_3–Al_2O_3 catalysts, it has been suggested that CO_2 is directly hydrogenated to methanol via adsorbed carbonate and formate species [2]. On the contrary, it is suggested that CO_2 is hydrogenated to methanol and ethanol via CO intermediate(s), by considering the facts that CO species adsorbed on Rh is observed in the FT-IR spectra, and that a pronounced amount of CO is detected in the effluent gas of the reaction over Rh–Li/SiO_2 catalysts when ethanol is formed. A plausible mechanism of ethanol formation is depicted in Fig. 2.

Two types of adsorbed CO species were observed in the FT-IR spectrum on the Rh/SiO_2 catalyst (Fig. 1a). The bands at 2040 and 1860 cm^{-1} were assigned to linear and bridged CO species adsorbed on Rh, respectively. They had almost the same intensity. In contrast, the bridged CO band was more intensive than the linear one on Rh–Li/SiO_2 catalyst, as shown in Fig. 1b. The difference in the relative intensity may reflect the different selectivity on the catalysts: The bridged species interacts with the surface Rh more strongly than the linear one, and the former occupies 2 Rh atoms on the surface. The more bridged CO species may provide smaller numbers of unoccupied Rh sites for H_2 adsorption, and the hydrogenation ability of the catalyst will be suppressed. Thus, over Rh–Li/SiO_2 catalysts, hydrogenation to CH_4 may be suppressed, and CO species can be inserted into a CH_3–Rh bond more easily, in comparison with the case of Rh/SiO_2 catalysts. Additionally, bonds assigned to formate species, which was supposed to be adsorbed on Li, were observed on Rh–Li/SiO_2 catalyst at 1511 and 1378 cm^{-1}.

Table 6
XPS binding energies [a] of Rh(–Li)/SiO_2 catalysts (Rh/Li = 1)

Catalyst	Rh $3d_{5/2}$ (eV)	O 1s (eV)	Si $2p_{3/2}$ (eV)
Rh/SiO_2	307.2 ± 0.2	532.9 ± 0.4	103.5 ± 0.2
Rh–Li/SiO_2	306.8 ± 0.1	532.7 ± 0.3	103.4 ± 0.2

[a] Values referenced to adsorbed Au with Au $4f_{7/2} = 83.8$ eV.

3.4. *Electronic state of catalyst surfaces*

The IR bands of adsorbed species on the catalysts shifted to a lower wavenumber side by adding Li, as shown in Fig. 1. This shift may imply that the electron density of surface Rh increases by Li, and that the C–O bond of adsorbed species is weakened by more back-donation electrons from Rh. The change in electronic state of surface Rh was also supported by XPS binding energies, as listed in Table 6. The addition of Li brought about a shift in Rh $3d_{5/2}$

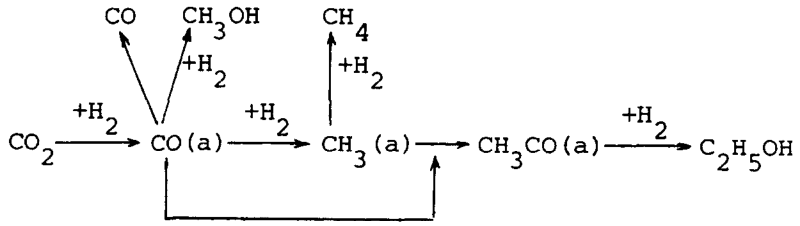

Fig. 2. A plausible reaction mechanism of CO_2 hydrogenation to ethanol.

Table 7
Effect of $MnCl_2$ addition on CO_2 hydrogenation over 5 wt.% Rh–Li/SiO_2 catalysts (Rh/Li = 1) [a]

Temperature/K	Mn/Rh atomic ratio	CO_2 conv. %	Selectivity/%			
			MeOH [b]	EtOH [c]	CO	CH_4
473	0.0	1.4	5.3	7.3	55.2	32.2
	0.2	3.6	1.7	16.1	7.0	75.2
	0.5	6.3	1.0	8.9	2.4	87.7
	1.0	5.7	0.7	4.6	1.5	93.2
513	0.0	7.0	5.2	15.5	15.7	63.5
	0.2	16.1	1.3	7.7	2.4	88.6
	0.5	24.7	0.5	1.1	0.6	97.8
	1.0	27.4	0.1	0.1	0.2	99.5

[a] Reaction conditions: $P = 5$ MPa, $H_2/CO_2 = 3$, flow-rate = 100 cm^3/min.
[b] Methanol. [c] Ethanol.

levels to a lower binding energy side by 0.4 eV, although other levels, such as 0 1s and Si $2p_{3/2}$ levels, were unchanged. These results indicate that the addition of Li changes the electronic state of the catalysts, and that the increase in the intensity of bridged-bond CO species may be brought about by the changes in the qualitative characters of Rh.

3.5. CO_2 hydrogenation over Rh–Li–Mn/SiO_2 catalysts

It was pointed out in Section (3.1) that the addition of Mn promoter increased the CO_2 conversion. In order to increase ethanol yield, Mn promoter was added to Rh–Li/SiO_2 catalysts. Table 7 shows the reaction results at $T = 473$ and 513 K over Mn added 5 wt.% Rh–Li/SiO_2 catalysts (Rh/Li = 1). At $T = 513$ K, CO_2 conversion increased and ethanol selectivity decreased with the amount of Mn added. In contrast, at $T = 473$ K, the highest selectivity to ethanol (16.1%) was obtained over the Rh–Li–Mn/SiO_2 catalyst with an atomic ratio of Mn/Rh = 0.2. The CO_2 conversion increased by Mn addition, and the maximum yields of ethanol were 0.58 and 1.24% at $T = 473$ and 513 K, respectively, over the catalyst with Mn/Rh = 0.2.

4. Conclusion

In conclusion, effect of additives to 5 wt.% Rh/SiO_2 catalysts for CO_2 hydrogenation was examined. Among more than 30 additives, Li was the most favorable to ethanol formation. By optimizing the reaction conditions, the highest ethanol selectivity of 15.5% with a CO_2 conversion of 7.0% was obtained. The results of in situ FT-IR suggested that CO_2 was hydrogenated to ethanol via CO intermediate(s), which amount was increased by Li addition.

References

[1] T. Tagawa, G. Pleizier and Y. Amenomiya, Appl. Catal., 18 (1985) 285.
[2] H. Arakawa, J.L. Dubois and K. Sayama, Energy Convers. Mgmt., 33 (1992) 521.
[3] H. Arakawa, K. Sayama and K. Okabe, Stud. Surf. Sci. Catal., 77 (1993) 389.
[4] J. Kaspar, M. Graziani, A.M. Rahman, A. Trovarelli, E.J.S. Vichi and E.C. da Silva, Appl. Catal. A, 117 (1994) 125.
[5] T. Inoue, T. Iizuka and K. Tanabe, Appl. Catal., 46 (1989) 1.
[6] N. Ikehara, K. Hara, A. Satsuma, T. Hattori and Y. Murakami, Chem. Lett., (1994) 263.
[7] H. Arakawa, K. Takeuchi, T. Matsuzaki and Y. Sugi, Chem. Lett., (1984) 1607.
[8] H. Arakawa, T. Fukushima and M. Ichikawa, Appl. Sectrosc., 40 (1986) 884.
[9] F. Solymosi, A. Erdohelyi and T. Bansagi, J. Catal., 68 (1981) 371.