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Effects of modification of highly dispersed cobalt catalysts with alkali cations on the hydrogenation of carbon monoxide

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In the hydrogenation of carbon monoxide, alkali cations were found to be effective as modifiers for highly dispersed cobalt catalyst to improve the selectivities of C_2-oxygenated compounds, especially acetic acid and acetaldehyde, and to increase the olefin/paraffin ratio of hydrocarbons. These effects are ascribed to depression of the hydrogenating ability of the catalyst by modification with alkali cations.

Keywords: Hydrogenation of carbon monoxide; cluster derived cobalt catalyst; alkali cations; C_2-oxygenated compounds

1. Introduction

Chemical modification of catalysts with metal cations often brings about important effects on catalytic activity and selectivity in the hydrogenation of carbon monoxide [1,2]. It has been reported that some cobalt catalysts modified with transition metals and/or basic metal oxides gave C_2-oxygenated compounds in high selectivities [3–9]. In a previous paper, we described that highly dispersed cobalt catalysts supported on SiO_2 derived from dicobalt octacarbonyl ($Co_2(CO)_8$) were active for the formation of oxygenated compounds on the hydrogenation of carbon monoxide, and that modification with alkaline earth cations such as strontium remarkably improved the selectivity of C_2-oxygenated compounds, especially ethanol [3]. In this paper, we describe that the modification with alkali cations enhances the formation of acetic acid and acetaldehyde as well as ethanol over the cobalt catalysts derived from $Co_2(CO)_8$. This is the first report that acetic acid and acetaldehyde are the principal products in C_2-oxygenated compounds over precious metal free cobalt catalysts.

2. Experimental

Silica-gel (Davison #57, 16–32 mesh, specific surface area 330 m^2/g) were impregnated by aqueous solution of alkali metal acetates, and were calcined in a hydrogen stream at 573 K. Three ml (about 1.2 g) of them were then impregnated by a hexane solution of $Co_2(CO)_8$ under nitrogen atmosphere. After removal of the solvent, the catalysts were loaded in a reactor without any contact of air, and activated in situ in a hydrogen stream at 723 K for 2 h just before the reaction. After use, cobalt contents in the catalysts were measured by X-ray fluorescence analysis by a Rigaku 3080 spectrometer. Hydrogenation of carbon monoxide was carried out using a fixed bed type flow reactor made of SUS-316 stainless steel. Typical reaction conditions were $CO/H2/Ar = 3/6/1$ (molar ratio), 2.1 MPa, 573–653 K and GHSV 2000/h. Argon was used as an internal standard for analysis. Products were analyzed by a GC system as previously described [3–6]. Product selectivities were based on carbon efficiencies of reacted carbon monoxide. As esters were supposed to be secondary products, methyl and ethyl acetates produced were summed up to corresponding alcohols and acid.

3. Results and discussion

The effect of modification with alkali metals on the hydrogenation of carbon monoxide is summarized in table 1. Activities of the catalysts decreased during ca. 4 h at the initial stage of the reaction. Table 1 shows the results obtained at a stationary state after 6 h from the starting of the reaction. The effect of strontium is also shown as a reference, [3]. All alkali metals were effective for the improvement of the selectivity of oxygenated compounds, especially C_2-oxygenated compounds, although catalytic activities decreased. In these aspects, the effect of alkali metals was similar to the case of strontium. However, there are some differences between alkaline earth and alkali metals in the ratio of C_2-oxygenated compounds. Almost all of the C_2-oxygenated compounds were ethanol in the case of strontium, while acetaldehyde and acetic acid were obtained in high ratio in the case of alkali metals. This is the first example that aldehydes and/or acids are obtained as the principal products in oxygenated compounds with catalysts other than rhodium. It was also noticeable that the ratios of olefins in C_2 to C_4 hydrocarbons were significantly higher for alkali metals compared with alkaline earth metals.

The ratio of acetaldehyde to acetic acid depended on reaction temperature as shown in fig. 1 for the $Co\text{-}Na/SiO_2$ catalyst. Acetaldehyde was the principal product in C_2-oxygenated compounds at 493 K, whereas, at higher temperature, the formation of acetic acid increased to reach the maximum selectivity of about 12% at 508–523 K. The selectivity decreased beyond 523 K with increasing

Table 1
Effect of alkali cations on Co/SiO_2 catalyst for CO hydrogenation[a]

Modifier		Co	Temp.	CO conv.	Product selectivities (%)									olefin[f]
	(%)[b]	(%)[b]	(K)	(%)	CO_2	CH_4	HC_{2+}[c]	MeOH	EtOH	AcH	AcOH	C_2-O[d]	$C_{3-8}O$[e]	(%)
none		4.2	493	10.3	0	25	54	5.1	5.3	0.3	0	5.6	10.2	29
Li	0.3	4.0	493	1.9	0	10	45	2.2	11.3	8.6	3.2	23.1	19.3	81
Na	0.6	3.9	523	2.2	11.4	8	38	2.0	7.6	9.0	10.5	27.2	13.7	92
K	1.0	3.8	523	1.4	7.6	10	42	1.4	5.1	13.2	10.0	28.3	11.0	88
Rb	2.2	4.6	523	2.4	7.2	9	44	2.4	4.9	11.6	6.5	23.1	13.3	85
Cs	3.3	4.9	523	4.9	5.8	13	51	0.8	4.7	9.3	2.6	16.5	12.7	77
Sr	17.7	3.9	523	5.5	3.3	18	35	3.9	24.4	2.0	0.3	26.7	15.0	61

[a] Reaction conditions; $CO/H_2/Ar = 3/6/1$, press.: 2.1 MPa, GHSV: 2000/h.

[b] wt% of metals to SiO_2.

[c] Sum of hydrocarbons from C_2 to C_8.

[d] Sum of EtOH, AcH and AcOH.

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

[f] Olefin ratio in C_2 to C_4 hydrocarbons.

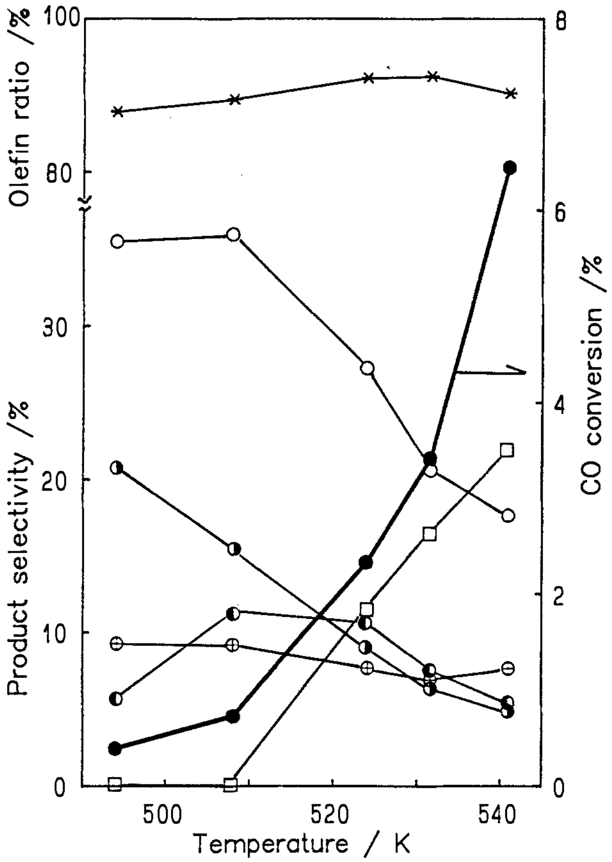

Fig. 1. Effect of reaction temperature on CO conversion (●), product selectivities and olefin ratio in C_2 to C_4 hydrocarbons (*). Catalyst: Co-Na/SiO_2 (3.9:1.0:100 in weight). Reaction conditions: CO/H_2/Ar = 3/6/1, press. 2.1 MPa, GHSV = 2000/h. Product selectivities; ⊕: ethanol, ◐: acetic acid, ◑: acetaldehyde, ○: sum of ethanol, acetic acid and acetaldehyde, □: carbon dioxide.

formation of carbon dioxide. However, the selectivity of ethanol and the ratios of olefins in hydrocarbons did not vary significantly from 493 to 543 K. Selectivities of other oxygenated compounds and hydrocarbons did not change so much in the range of temperature.

Fig. 2 shows the effect of potassium content on the hydrogenation of carbon monoxide. Catalytic activity of the non-modified catalyst was too high to give reasonable data at the same reaction conditions. The activity decreased and the ratio of olefins increased by an increasing amount of alkali content, while the selectivity of the total C_2-oxygenated compounds reached the maximum at about 1.0 wt% of SiO_2. The optimum content for the selectivity of oxygenated compounds was 25–50 mmol to 100 g of SiO_2 for alkali metals. This value was too small for alkaline earth metals to enhance the selectivity of C_2-oxygenated compounds [3]. The optimum content of alkaline earths was 150–200 mmol to

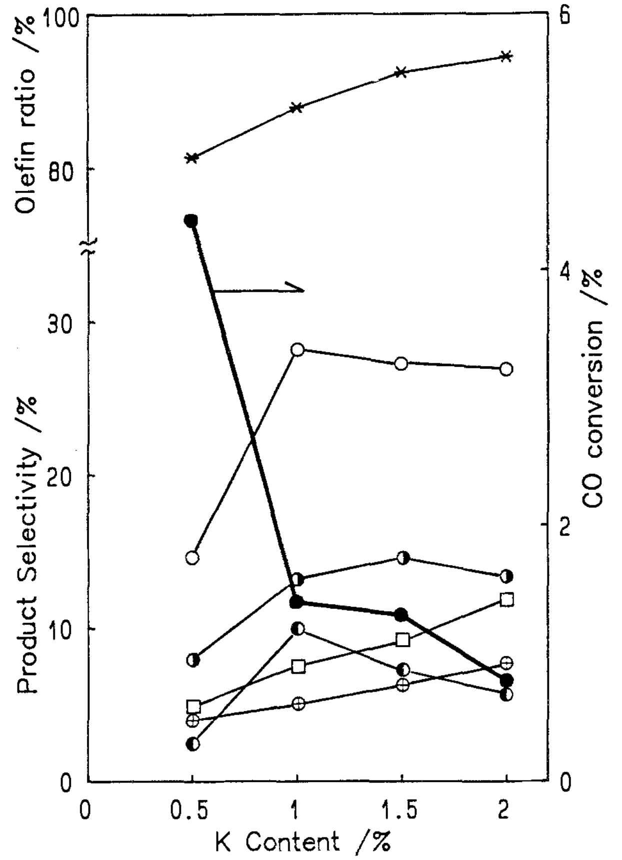

Fig. 2. Effect of potassium content on CO conversion (●), product selectivities and olefin ratio in C_2 to C_4 hydrocarbons (*). Catalyst: Co-K/SiO_2 (3.9:X:100 in weight). Reaction conditions: $CO/H_2/Ar = 3/6/1$, temp. 523 K, press. 2.1 MPa, GHSV = 2000/h. Product selectivities; ⊕: ethanol, ◐: acetic acid, ◑: acetaldehyde, ○: sum of ethanol, acetic acid and acetaldehyde, □: carbon dioxide.

100 g of SiO_2 for the selectivity of C_2-oxygenated compounds. This difference indicates that alkali cations were more effective as modifiers than alkaline earth cations. Selectivities of C_2-oxygenated compounds decreased in the order of Ba > Sr > Ca > Mg for alkaline earth metal, and K > Na > Li for alkali metal. The orders for catalytic activity were in reverse order. These results suggest that the effectiveness is closely related to the basicity of modifiers.

In the hydrogenation of carbon monoxide, alkali cations are often used as modifiers to enhance the productivity of methanol for palladium catalysts [10,11], and a wide range of alcohols for cobalt or ruthenium catalysts [12,13]. However, the features of the cations for our catalysts are different from these results. They enhance the selectivity of C_2-oxygenated compounds, especially acetaldehyde and acetic acid as well as ethanol. The selectivities of methanol and oxygenated compounds higher than C_2 were not so much enhanced by the cations. These effects of alkali cations may be characteristic for highly dispersed cobalt catalysts and rather similar to the case of rhodium catalysts [14,15].

The important role of these cations is the electronic effect because of influences of their basicity as we previously observed in the case of rhodium catalysts [14]. The effects of alkali cations in this paper are also similar to those over potassium modified iron catalysts for Fischer-Tropsch synthesis [2,16]. The following tendencies for our cobalt catalysts were observed by the modification of alkali cations: 1) the overall reaction rate decreased, 2) the mole fraction of methane in hydrocarbons decreased, 3) the mole fraction of alkenes increased, 4) the kind of oxygenated compounds was shifted from alcohols to aldehydes. These results suggest that the hydrogenating ability of our cobalt catalysts may be weakened by electronic effects of alkali cations.

As paraffins and ethanol are secondary products formed by the hydrogenation of olefins and acetaldehyde, respectively, the ratios of olefins in hydrocarbons and acetaldehyde to ethanol show the extent of the depression of the hydrogenating ability of the catalyst. These ratios were increased by the modification with alkali and alkaline earth metals, and alkali metals were much more effective. These results suggest that alkali cations more strongly reduce the hydrogenating ability of cobalt catalyst than alkaline earth cations. Acyl-cobalt complex is considered to be a common intermediate for the formation of oxygenated compounds and hydrocarbons over our cobalt catalysts [3–6]. Acetaldehyde is formed by reductive elimination of the acyl complex, and acetic acid is produced by the interaction of the complex with adsorbed hydroxyl group. Alkali cations are effective to retard the hydrogenation of the acyl-cobalt intermediate to the hydroxyalkyl complex, and to control the dehydroxylation of the latter complex to hydrocarbons. Alkali cations may also increase the formation of the adsorbed hydroxyl group on the surface. Moreover, no contribution is expected by the electron donating alkyl group only for C_2 compounds in the dehydroxylation of hydroxyalkyl intermediates to hydrocarbons and higher products. Consequently, alkali cations promote the reductive elimination of the acyl complex to acetaldehyde, and the reaction of the complex with the hydroxyl group to acetic acid, in contrast with the decrease of the production of hydrocarbons.

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