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SELECTIVE VAPOR PHASE HYDROFORMYLATION OF ETHYLENE OVER CLUSTER-DERIVED COBALT CATALYST

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Vapor phase hydroformylation of ethylene was studied with silica-supported metal catalysts. A cobalt metal catalyst derived from $Co_2(CO)_8$ gave propanal and its derivatives in as high selectivity of about 36% as Rh/SiO_2 catalyst under the reaction conditions of 1.1 MPa of a gas-mixture of $Ar:CO:C_2H_4:H_2 = 1:3:3:3$ at 423-503 K. On the other hand, conventional cobalt catalysts derived from cobalt nitrate, chloride, or acetate, and other noble metal catalysts (Pd/SiO_2 and Ir/SiO_2) produced mainly ethane.

Keywords: Vapor phase hydroformylation, ethylene, cobalt catalysts, $Co_2(CO)_8$, propanal, n-propanol

1. Introduction

In recent years, vapor phase hydroformylation of olefin has been attracted much attention of researchers since it is one of the most promising new alternative processes to the present homogeneous hydroformylation processes. It is also a good model reaction for CO insertion step in synthesis of oxygenated compounds from syngas. Several rhodium catalysts have been studied on their hydroformylation activities [1-4]. However, few heterogeneous catalysts other than rhodium catalysts have shown hydroformylation activity because their hydrogenation activity of olefin was much higher than hydroformylation activity [5-7]. In this report, we will describe the catalytic activity of a silica-supported cobalt catalyst derived from cobalt carbonyl cluster ($Co_2(CO)_8$) for vapor phase hydroformylation of ethylene comparing with those of conventional cobalt catalysts and some noble metal catalysts.

2. Experimental

All catalysts were prepared by an impregnation method. Silica gel (Davison grade 57, 330 m^2/g) evacuated at 473 K for 2 h, was impregnated with a n-hexane solution of $Co_2(CO)_8$ for a $Co(CO)/SiO_2$ catalyst, or with an aqueous solution of $RhCl_3.3H_2O$, $IrCl_4.nH_2O$, $PdCl_2.2H_2O$, $Co(OCOCH_3)_2.4H_2O$, $Co(NO_3)_2.6H_2O$, or $CoCl_2.6H_2O$ for other catalysts. A symbol of CO, Cl, N, or A in parenthesis in the name of a catalyst shows that the catalyst was prepared from a corresponding metal carbonyl, chloride, nitrate, or acetate, respectively. All catalysts were treated with hydrogen at 673 K for 2 h just before use. The $Co(CO)/SiO_2$ catalyst was prepared and handled in a nitrogen atmosphere.

Hydroformylation of ethylene was carried out using a fixed-bed type flow reactor with a gas-mixture of Ar (an internal standard): $CO : C_2H_4 : H_2 = 1 : 3 : 3 : 3$ at 1.1 MPa, and 423–503 K. After the reaction had reached a stationary state, the effluent gas was directly introduced to an on-line gas chromatograph system. The selectivity of a product was determined as the ratio of a mole number of ethylene moiety in the product to that of ethylene consumed. The oxo-selectivity was also defined as the total selectivity of oxygenated compounds produced by combination of ethylene and carbon monoxide.

X-ray diffraction measurement of the catalysts was carried out by using a Philips PW-1700 spectrometer employing CuKα radiation.

The distances and the coordination numbers of Co–Co, Co–C, and Co–O bondings in the catalyst were determined by analysis of the CoK–edge EXAFS data obtained using the EXAFS facilities of the Photon Factory in the National Laboratory for High Energy Physics. The EXAFS spectra of the catalysts were measured *in situ* using a quartz cell with CAPTON windows in which the catalysts were prepared under the nitrogen atmosphere. The EXAFS spectra of standard samples of $Co_2(CO)_8$ powder and Co foil were obtained with samples sealed in a polyethylene bag under a nitrogen atmosphere. The phase shift effect was not corrected in the Fourier transform of the EXAFS data.

3. Results and discussion

Table 1 shows the ethylene hydroformylation activity of various catalysts. Principal products were ethane (C_2H_6), propanal (C_2H_5CHO), n-propanol (C_3H_7OH), propanoic acid ($C_2H_5CO_2H$), 2-methyl-2-pentenal ($CH_3C_4H_6CHO$), 2-methyl pentanal ($CH_3C_4H_8CHO$), and 2-methyl-1-pentanol ($CH_3C_5H_{10}OH$). The C_6 oxygenated compounds were produced by aldol condensation and following hydrogenation of propanal.

The $Co(CO)/SiO_2$ catalyst prepared from $Co_2(CO)_8$ exhibited high activity for ethylene conversion and gave hydroformylated products such as propanal. n-propanol, and C_6-oxygenated compounds derived propanal in a selectivity of about 36%. This is the first example of high performance of vapor phase hydroformylation of ethylene over cobalt catalysts. The yields of products of CO hydrogenation such as methane, methanol, or ethanol were much smaller than those of

Table 1
Vapor phase hydroformylation of ethylene on M/SiO_2 catalysts [a]

Catalyst	C_2H_4 conversion/%	Product selectivities/%							oxo selectivity/%	C_3H_7OH/ C_2H_5CHO [b]
		C_2H_6	C_2H_5-CHO	C_3H_7-OH	C_2H_5-CO_2H	$CH_3C_4H_6$-CHO	$CH_3C_4H_8$-CHO	CH_3C_5-$H_{10}OH$		
Rh(Cl)	49.9	67.0	24.9	0.7	1.1	5.8	0.2	0.3	33.0	0.03
Pd(Cl)	91.4	98.1	1.3	0	0.1	0.5	0	0	1.9	0
Ir(Cl)	0.6	87.9	9.0	3.1	0	0	0	0	12.1	0.34
Co(A)	1.7	95.0	2.6	0.4	0	1.5	0.5	0	5.0	0.15
Co(N)	13.7	82.9	10.7	3.5	0	2.6	0.3	0	17.1	0.33
Co(Cl)	3.8	81.3	14.1	3.0	0	1.6	0	0	18.7	0.21
Co(CO)	49.1	64.1	14.1	17.2	0.4	2.7	0.4	0.9	35.9	1.22

[a] Metal loading; 5.0 wt% (Ir(Cl); 5.16 wt%). Reaction conditions; Ar : CO : C_2H_4 : H_2 = 1 : 3 : 3 : 3, 1.1 MPa, 30 ml/min, 463 K, catalyst charge; 1.0 g.

[b] the ratio of n-propanol to propanal.

products shown in table 1 because of low reaction temperature. It indicates that most of the products in table 1 were directly derived from ethylene.

The activity of this $Co(CO)/SiO_2$ catalyst shown in table 1 continued at least for three days after the small initial drop within one hour. Further examination for a longer period is now under investigation. This $Co(CO)/SiO_2$ catalyst was, however, very air-sensitive, and its hydroformylation activity was lost on exposure to air.

The $Rh(Cl)/SiO_2$ catalyst exhibited as high hydroformylation performance as $Co(CO)/SiO_2$. On the other hand, other catalysts mainly produced ethane. That is, the $Pd(Cl)/SiO_2$ catalyst was very active for hydrogenation of ethylene, and $Ir(Cl)/SiO_2$ was rather inactive and produced mainly ethane. Conventional cobalt catalysts prepared from cobalt nitrate, chloride, and acetate were less active than $Co(CO)/SiO_2$, and produced mainly ethane. The ethylene conversions and the oxo-selectivities of these cobalt catalysts were in the order of $Co(CO) \gg Co(N) > Co(Cl) \gg Co(A)$ and $Co(CO) \gg Co(Cl) \approx Co(N) \gg Co(A)$, respectively.

The oxo-selectivity of $Rh(Cl)/SiO_2$ was decreased from 45% to 23.8% with the increase of the temperature from 443 K to 483 K. However, that of $Co(CO)/SiO_2$

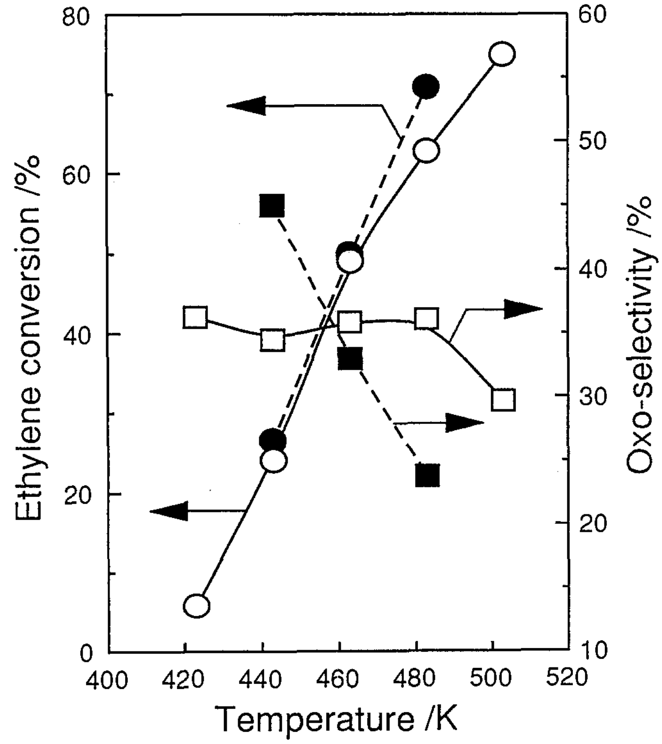


Fig. 1. Effect of reaction temperature on ethylene conversions (○, ●) and oxo-selectivities (□, ■) of vapor phase hydroformylation of ethylene on the $Co(CO)/SiO_2$ (open symbols) and $Rh(Cl)/SiO_2$ (solid symbols) catalysts. Catalysts; metal loading 5.0 wt%. Reaction conditions; $Ar:CO:C_2H_4:H_2 = 1:3:3:3$, 1.1 MPa, 30 ml/min, catalyst charge 1.0 g.

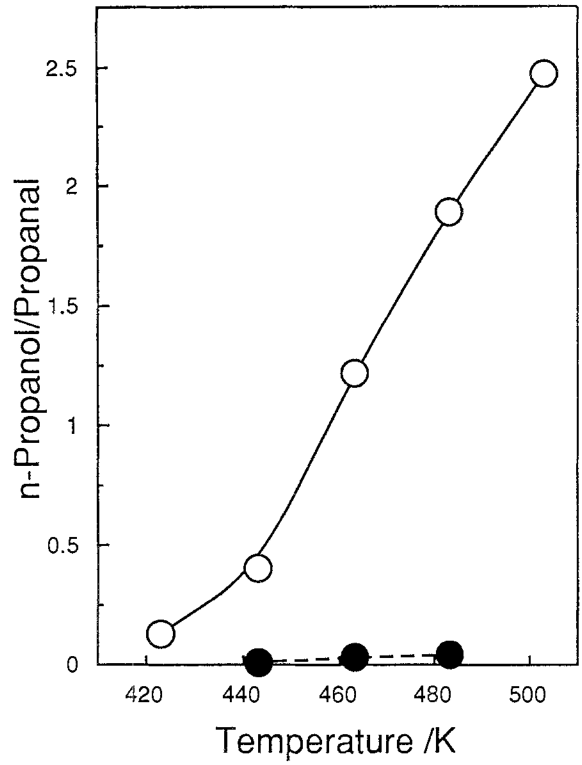


Fig. 2. Effect of reaction temperature on the ratios of n-propanol to propanal of vapor phase hydroformylation of ethylene on the Co(CO)/SiO_2 (open symbols) and Rh(Cl)/SiO_2 (solid symbols) catalysts. Catalysts; metal loading 5.0 wt%. Reaction conditions; Ar : CO : C_2H_4 : H_2 = 1 : 3 : 3 : 3, 1.1 MPa, 30 ml/min, catalyst charge 1.0 g.

was almost constant about 36% in the temperature of 423–483 K as shown in fig. 1.

The ratio of n-propanol to propanal of Co(CO)/SiO_2 was 0.13 at 423 K, and increased with temperature up to 2.47 at 503 K as shown in fig. 2. However, that of Rh(Cl)/SiO_2 was 0.01–0.04 in the temperature of 443–483 K, which was much smaller than that of Co(CO)/SiO_2. It indicates that the primary hydroformylation product of these catalysts is propanal, which is hydrogenated to n-propanol in a secondary reaction. In addition, the activity of aldehyde hydrogenation of Co(CO)/SiO_2 is much higher than that of Rh(Cl)/SiO_2.

Fig. 3 shows the k^3-weighted Fourier transforms of EXAFS data extracted from the absorption spectra of $Co_2(CO)_8$ powder, Co foil, and cobalt catalysts prepared from $Co_2(CO)_8$. The peaks at 2.55×10^{-1} and 2.10×10^{-1} nm in the Fourier transform of $Co_2(CO)_8$ powder are accepted as Co–Co and Co–C bondings, respectively (fig. 3, (a)). The peak at 1.42×10^{-1} nm is accepted as Co–O bondings of the partially oxidized $Co_2(CO)_8$ during the experiment. When

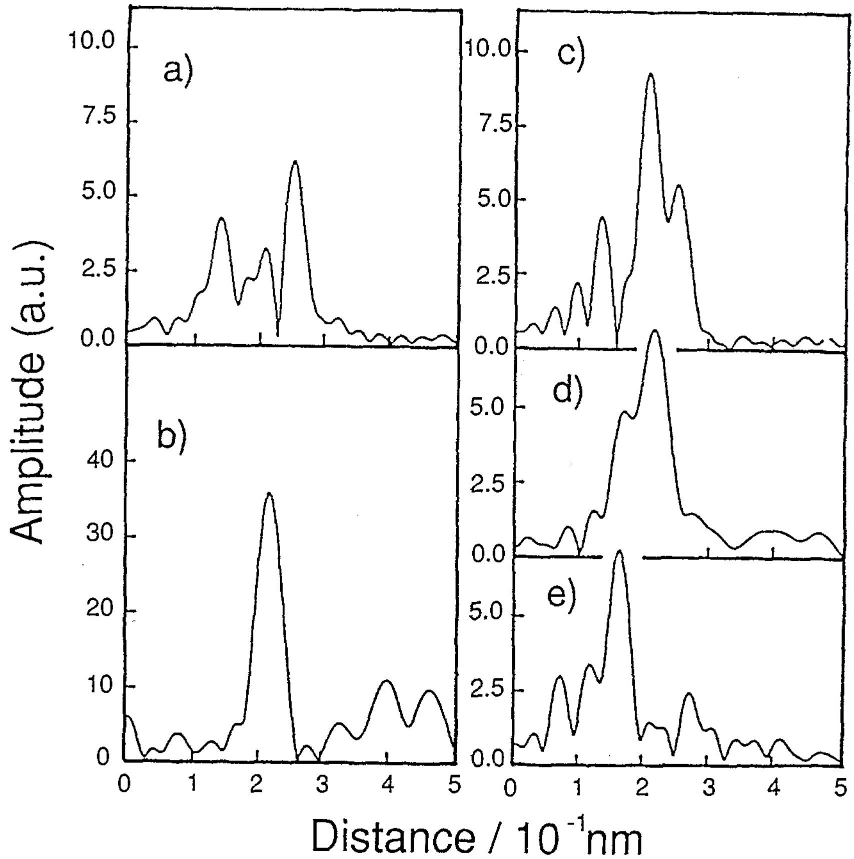


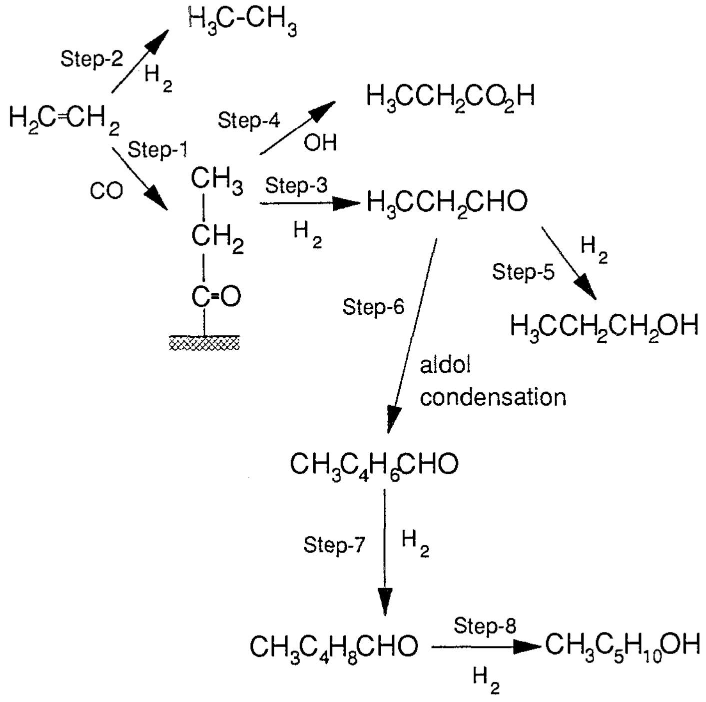
Fig. 3. Fourier transforms of $k^3\chi(k)$ of Co K-edge EXAFS. (a) $Co_2(CO)_8$ powder, (b) Co foil, (c) Co(CO)/SiO_2 just after inpregnation, (d) Co(CO)/SiO_2 after treatment in H_2 at 673 K, and Co(CO)/SiO_2 after exposure to air. Catalyst; metal loading 5 wt%.

$Co_2(CO)_8$ was supported on SiO_2, it turned dark brown and changed to $Co_4(CO)_{12}$ species (fig. 3, (c)) as reported by Iwasawa and Yamada [8].

By the activation of these catalysts at 673 K in H_2, the catalysts changed to black. The peak at 2.14×10^{-1} nm in the Fourier transform is accepted as Co–Co bondings of cobalt metal (fig. 3, (d)). The amplitudes of this peak is much lower than that of cobalt foil (fig. 3, (b)). Coordination numbers of cobalt atom of this catalyst is estimated to 2.6 with the amplitude of this peak. The particle sizes of the cobalt metal on the catalyst is determined about 1 nm under an assumption that the structure of the cobalt metal on the catalysts is similar to that of cobalt foil [9]. The peaks of the 2nd and other higher nearest Co–Co bondings are not observed in the Fourier transforms of the catalyst. This result also shows that the cobalt metal is highly dispersed on the catalysts. The distances of these bondings are shorter than that of cobalt foil (2.16×10^{-1} nm). The difference of the distances of Co–Co bondings of cobalt metal between the catalyst and cobalt foil is larger than experimental errors. This result is another evidence that the cobalt metal particles on the catalysts is highly dispersed [10].

On exposure to air, the $Co(CO)/SiO_2$ catalyst of fig. 3(d) turned blue. The peak of Co–Co bonding disappeared and a peak of Co–O bonding appeared at 1.59×10^{-1} nm in the Fourier transform of EXAFS as shown in fig. 3(e). It shows that the cobalt metal on $Co(CO)/SiO_2$ is easily oxidized to Co^{2+}. Moreover, these oxidized cobalt catalysts gave no peak in the XRD measurement. This oxidized cobalt catalyst has no activity for ethylene hydroformylation as described above.

The cobalt catalysts derived from cobalt nitrate and chloride gave the similar EXAFS spectra with that of cobalt foil as shown in fig. 4. The peak amplitudes and the distances of nearest Co–Co bondings of these cobalt catalysts were almost same to that of cobalt foil, which means that the cobalt metal particles are much bigger than that of $Co(CO)/SiO_2$. The XRD pattern of $Co(Cl)/SiO_2$ showed that the cobalt metal particles were as large as 20 nm in crystalline size. The $Co(A)/SiO_2$ catalyst gave no Co–Co bonding peak in EXAFS even after treated in H_2 at 673 K. As described previously, a very stable cobalt oxide species, $Co^{2+}–(O–Si)_2$, is formed on SiO_2 when cobalt acetate was used as a precursor [11]. This contributed to the very low activity of this catalyst in the hydroformylation of ethylene.



Scheme 1. Proposed mechanism of the ethylene hydroformylation over $Co(CO)/SiO_2$ catalyst.

Scheme 1 shows the proposed mechanism of ethylene hydroformylation on the Co(CO)/SiO_2 catalyst. An adsorbed ethylene on the catalyst is hydrogenated to ethane (Step-2) or changes to a surface acyl species by CO insertion (Step-1). This surface acyl species is hydrogenated to propanal (Step-3), which changes to n-propanol by hydrogenation (Step-5) or C_6-oxygenated compounds by aldol condensation (Step-6 ~ Step-8). We suppose that a small amount of propanoic acid is directly produced by combination of a surface acyl species and a OH group (Step-4).

In the hydrogenation of carbon monoxide, Pd(Cl)/SiO_2 and Ir(Cl)/SiO_2 catalysts produce mainly methanol, and Co(N)/SiO_2 and Co(Cl)/SiO_2 catalysts give a mixture of hydrocarbons [12]. These results suggest that palladium and iridium catalysts have very low activities for CO insertion to surface alkyl species. On the other hand, those cobalt catalysts are active for CO insertion to surface alkyl species, however, the species are easily converted to hydrocarbons by their strong hydrogenation activity. The Rh(Cl)/SiO_2 catalyst has a strong CO insertion activity and a moderate hydrogenation activity, therefore, it mainly produces C_2-oxygenated compounds such as acetaldehyde and ethanol [13].

As reported previously, the Co(CO)/SiO_2 catalyst is very active for alcohol formation in the hydrogenation of carbon monoxide [14]. As described above, the Co(CO)/SiO_2 catalyst has much higher dispersed cobalt metal particle than other conventional cobalt catalysts. These results indicate that the dispersion of cobalt metal is one of the most important controlling factors of CO insertion.

These results are one of the strong pieces of evidence in support of the mechanism which we have proposed for the syngas reaction on cobalt catalysts: primary oxygenated products are aldehydes, and alcohols are formed via a hydrogenation of corresponding aldehydes [14–16]. That is, the CO insertion to surface acyl group proceeds easily on the Co(CO)/SiO_2 catalyst even at a temperature of 423–503 K. Conventional cobalt catalysts also show this CO insertion activity, although their activities of ethylene hydrogenation are much higher than that of the CO insertion.

Other mechanisms of oxygenates formation in the syngas reaction such as combination of surface alkyl species and adsorbed OH [17], combination of carbene species and hydroxycarbene [18], and condensation of two surface lower alcohol species [19,20] cannot be applicable for these cobalt catalysts.

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