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Ethylene hydroformylation and carbon monoxide hydrogenation over modified and unmodified silica supported rhodium catalysts

T. Hanaoka[a], H. Arakawa[a], T. Matsuzaki[a], Y. Sugi[b,*], K. Kanno[c], Y. Abe[c]

[a] National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305-8565, Japan
[b] Department of Chemistry, Faculty of Engineering, Gifu University, Gifu 501-1193, Japan
[c] Department of Industrial Chemistry, Faculty of Science and Engineering, Science University of Tokyo, Noda, Chiba 278-8510, Japan

Abstract

Ethylene hydroformylation and carbon monoxide hydrogenation (leading to methanol and C_2-oxygenates) over Rh/SiO_2 catalysts share several important common mechanistic features, namely, CO insertion and metal–carbon (acyl or alkyl) bond hydrogenation. However, these processes are differentiated in that the CO hydrogenation also requires an initial CO dissociation before catalysis can proceed. In this study, the catalytic response to changes in particle size and to the addition of metal additives was studied to elucidate the differences in the two processes. In the hydroformylation process, both hydroformylation and hydrogenation of ethylene occurred concurrently. The desirable hydroformylation was enhanced over fine Rh particles with maximum activity observed at a particle diameter of 3.5 nm and hydrogenation was favored over large particles. CO hydrogenation was favored by larger particles. These results suggest that hydroformylation occurs at the edge and corner Rh sites, but that the key step in CO hydrogenation is different from that in hydroformylation and occurs on the surface. The addition of group II–VIII metal oxides, such as MoO_3, Sc_2O_3, TiO_2, V_2O_5, and Mn_2O_3, which are expected to enhance CO dissociation, leads to increased rates in CO hydrogenation, but only served to slow the hydroformylation process slightly without any effect on the selectivity. Similar comparisons using basic metals, such as the alkali and alkaline earths, which should enhance selectivity for insertion of CO over hydrogenation, increased the selectivity for the hydroformylation over hydrogenation as expected, although catalytic activity was reduced. Similarly, the selectivity toward organic oxygenates (a reflection of the degree of CO insertion) in CO hydrogenation was also increased. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Hydroformylation; CO hydrogenation; Rhodium; Particle size; Additive

1. Introduction

Hydroformylation of alkenes is an important chemical process, and usually carried out using homogeneous catalysts composed of rhodium, cobalt, and other transition metal complexes [1]. Heterogeneous hydroformylation is a promising process from scientific and practical points of view [2–12] although most of the studies on hydroformylation have been carried out under atmospheric pressures. However, high pressure hydroformylation is more interesting both from a commercial and scientific standpoint.

As shown in Fig. 1, CO hydrogenation to form methanol and C_2-oxygenates (C_2–O) shares several features with ethylene hydroformylation, namely, CO insertion and metal–carbon (acyl or alkyl) bond hydrogenation. However, these processes are differentiated in that the CO hydrogenation also requires an initial CO dissociation before catalysis can proceed. Due to the similarity of several key steps, a comparison

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[*] Corresponding author.

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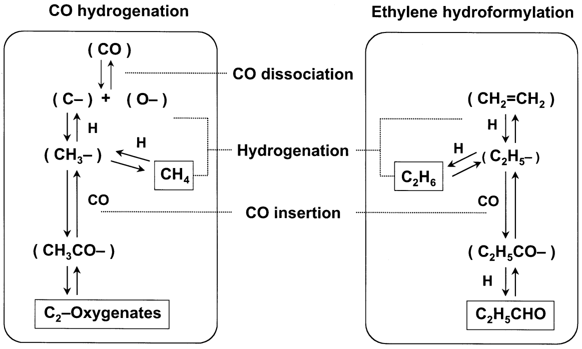

Fig. 1. Mechanistic difference of ethylene hydroformylation and CO hydrogenation.

of ethylene hydroformylation and CO hydrogenation would help define the key mechanistic steps, should elucidate the critical step in CO hydrogenation and potentially lead to improvements in both of these processes.

We have previously described such a study using highly selective catalysts to form oxygenated compounds by CO hydrogenation and by ethylene hydroformylation over cobalt catalysts under high pressure where high dispersion of cobalt is essential for the formation of oxygenated compounds in these reactions [12,13]. We also reported the effects of particle size and modification of Rh/SiO_2 catalyst in the CO hydrogenation under high pressure [14,15]. In this paper, we will examine the effect of particle size and the impact of several metal additives in Rh/SiO_2 catalyzed ethylene hydroformylation and CO hydrogenation under high pressure. The results of this study should help elucidate the critical mechanistic steps in both ethylene hydroformylation and CO hydrogenation to oxygenated compounds using Rh/SiO_2 catalysts.

$$C_2H_4 + CO + H_2 \rightarrow C_2H_5CHO + C_2H_6 \qquad (1)$$

2. Experimental

All catalysts were prepared by an impregnation method. Silica gel (Davison #57) was dried in vacuo at 200°C for 2 h. Rhodium and additive components were impregnated sequentially on silica gel. First, an additive component is impregnated from an aqueous solution, dried in vacuo, and calcined at 400°C under air atmosphere for 5 h. Then, rhodium was impregnated on modified silica gel with aqueous or methanol solution of $RhCl_3 \cdot 3H_2O$ or with a hexane solution of $Rh_4(CO)_{12}$. The resulting catalysts were treated in a hydrogen stream at 400°C for 4 h. Ethylene hydroformylation was carried out in a conventional fixed-bed flow reactor. After in situ reduction of catalyst in hydrogen stream at 400°C, a mixed gas (C_2H_4:CO:H_2:Ar=30:40:20:10 or 30:30:30:10, Ar: standard for analysis) was introduced at room temperature, and then the reaction was started by heating. Products were analyzed by on-line gas chromatographs after 30 min at scheduled temperatures.

CO hydrogenation was carried out in a similar manner using synthesis gas (CO:H_2:Ar=45:45:10).

H_2 chemisorption and XRD measurement were applied to determine the dispersion of rhodium particle on silica gel.

3. Results and discussion

3.1. Effects of size of rhodium particle on ethylene hydroformylation and CO hydrogenation

3.1.1. Ethylene hydroformylation

Typical results of ethylene hydroformylation over Rh/SiO_2 catalyst under the conditions of 180°C, 2 MPa, and 100 ml/min are shown in Table 1. Rh/SiO_2 catalyst was prepared from $RhCl_3 \cdot xH_2O$. The particle sizes were calculated from Rh dispersion measured by H_2 chemisorption, but it corresponded well to the values observed by XRD line broadening method. Particle size was changed by Rh loading on silica gel [14]. Hydroformylation to propanal-1 occurred in addition to hydrogenation of ethylene to ethane. Propanal-1, propanol-1, 2-methyl-2-penten-1-al,[1] and ethane were yielded as principal products through the reaction. It is obvious that the selectivity for the hydroformylation as well as the yields of propanal-1 and ethane is highly dependent on Rh particle size. The yield of propanal-1 and its derivatives decreased with increasing Rh particle size, and the selectivity for the hydroformylation was minimized at around 3.0 nm.

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[1] 2-Methyl-2-penten-1-al is formed by aldol condensation of propanal-1 over the catalyst. It is calculated as 2-mole of propanal-1.

Table 1
Effects of particle size on vapor-phase hydroformylation of ethylene over Rh/SiO_2 catalysts[a]

Rh/SiO_2[b] (wt.%)	H_2 adsorbed (μmol/g-cat^{-1})	Particle size[c] (nm)	Yield (μmol/min g-cat^{-1})[d]				Selectivity[e] (%)
			C_2H_5CHO	C_3H_7OH	C_5H_9CHO	C_2H_6	
1	25.0	2.1[f]	22.4 (44.8)	0.2	2.6	42.9 (85.8)	39
5	103	3.0	55.4 (26.9)	0.3	5.4	191 (93.1)	26
5	51.8[g]	7.7	16.8 (16.2)	0.1	0.9	56.5 (54.5)	25
9	139	3.9	33.0 (11.9)	0.1	4.7	627 (226)	6.4
10	169	3.3	36.5 (10.9)	0.1	4.4	630 (187)	5.5
23	50.0	15.4	7.2 (7.2)	0.1	1.0	24.1 (24.1)	28

[a] Reaction conditions: catalyst (Rh, 1–23 wt.%), 1 g; temperature, 180°C; pressure (C_2H_4:CO:H_2:Ar=30:40:20:10), 2.0 MPa; and flow rate, 100 ml/min. Data were taken after 90 min after starting the reaction.

[b] Prepared by impregnation from an aqueous solution of $RhCl_3 \cdot xH_2O$.

[c] Estimated from XRD line broadening.

[d] Values in parentheses are turnover frequencies (10^{-2}/min).

[e] Selectivity for hydroformylation=($C_2H_5CHO+C_3H_7OH+2xC_5H_9CHO$)/($C_2H_6+C_2H_5CHO+C_3H_7OH+2xC_5H_9CHO$).

[f] Estimated from H_2 chemisorption.

[g] SiO_2: cariact-50 (Fuji Silysia Co., Nagoya, Japan).

Fig. 2 shows effects of Rh particle size on the formation of propanal-1 and ethane. Turnover frequencies (TOF) of formation of each product are influenced by Rh particle size. TOF of propanal-1 increased abruptly with Rh particle sizes smaller than 3 nm, whereas it is almost constant for larger particle sizes. This indicates that the hydroformylation is enhanced over highly dispersed Rh/SiO_2 catalysts. These results correspond well with the influences of Rh dispersion on CO insertion in CO hydrogenation as discussed below. Huang et al. [4] also reported that activities for ethylene hydroformylation are a function of Rh dispersion, and that a highly dispersed Rh/SiO_2 catalyst was highly selective for the hydroformylation under atmospheric pressure at 150°C. On the other hand, selectivity for hydrogenation of ethylene displays a maximum selectivity with a Rh particle size of about 4 nm. These observations on the influence of Rh particle size on ethylene hydrogenation were similar to those observed in the hydrogenation of benzene and cyclohexene over Ru/SiO_2 catalyst [16]. A similar tendency with respect to Rh particle size was observed in CO hydrogenation with the optimum particle size for the formation of C_2-oxygenates being 2–4 nm [14].

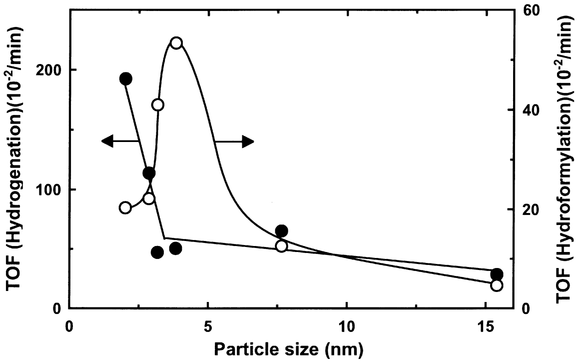

Fig. 2. Effects of Rh particle size on turnover frequencies of hydroformylation and hydrogenation of ethylene. Reaction conditions: catalyst Rh/SiO_2 (Rh, 1–23 wt.%), 1 g; temperature, 180°C; pressure (C_2H_4:CO:H_2:Ar=30:40:20:10), 2 MPa; and flow rate, 100 ml/min. Data were taken at 90 min after starting the reaction.

It is well known that surface structure of metal particle changes with a decrease in particle size. In the case of Rh particle, which have a fcc octahedron structure, the fraction of coordinatively unsaturated Rh atoms at edges and corners relative to the total Rh atoms at the surface increases abruptly at a Rh particle size of 3 nm as shown in Fig. 3 [17,18]. The correlation between particle size and turnover frequency for propanal-1, as shown in Fig. 2, indicates that the hydroformylation preferably occurs at the coordinatively unsaturated Rh atoms located at the edge and corner sites of the particle.

3.1.2. *CO hydrogenation*

Table 2 summarizes the effects of Rh loading on CO hydrogenation over Rh/SiO_2 catalysts. Increased

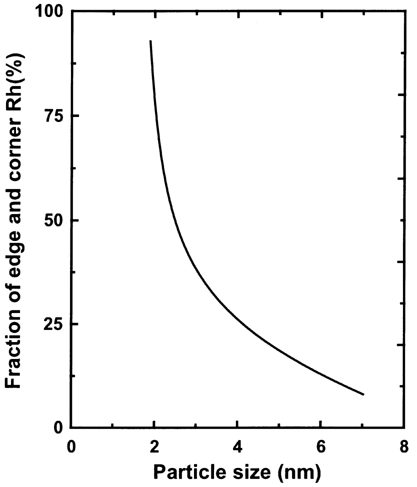

Fig. 3. Relationship between Rh particle size and number of Rh exposed at surface [17].

Rh loading leads to increased CO conversion and significantly alters the product distribution. Since CO hydrogenation occurs only at the surface of Rh particles, the activity and product distribution in CO hydrogenation correlated well to Rh dispersion. TOFs clearly showed the influence of Rh dispersion on the CO hydrogenation activity. With dispersions >0.45, the TOFs were fairly low and did not change significantly with increasing dispersion, but as the dispersion was decreased below about 0.45, the TOFs began to increase markedly, reaching a maximum at a dispersion of about 0.25.

Product distribution was also influenced by Rh dispersion [14]. Methanol (MeOH) was the predominant product at high dispersion of about 0.8, however, the selectivity for MeOH decreased markedly with increased Rh loading (and consequently decreased dispersion). As the dispersion was decreased below about 0.5, the formation of acetaldehyde (AcH) increased abruptly at around 0.5. The formation of acetic acid (AcOH) and ethanol (EtOH) has the maximum selectivities at Rh dispersions between 0.4 and 0.5. CH_4 formation increases steadily with decrease of Rh dispersion. These results indicate that the optimal Rh dispersion for the formation of C_2-oxygenates (C_2–O) in CO hydrogenation over Rh/SiO_2 catalysts is in the range of 0.3–0.5.

CO hydrogenation occurs through multiple steps. Typical steps are CO dissociation, hydrogenation of dissociated species, CO insertion to form higher products, and hydrogenation of these higher products (see Fig. 1). CO dissociation is the initiating step in the formation of both CH_4 and C_2–O (AcH, EtOH, AcOH). The product distribution between CH_4 and the C_2–O

Table 2
Effects of particle size on CO hydrogenation over Rh/SiO_2 catalysts[a]

Rh/SiO_2[b] (wt.%)	Dispersion (H/Rh)	Particle size[c] (nm)	CO conversion (%)	TOF[d] (min^{-1})	Selectivity (%)[e]					
					MeOH*	EtOH*	AcH	AcOH*	C_2–O	CH_4
1.0	0.82	1.4	0.36	2.4	69.1	18.5	0.0	4.4	22.8	2.5
2.0	0.50	2.3	0.45	2.5	39.6	22.8	3.0	16.7	42.5	10.1
4.7	0.44	2.6 (2.8)[f]	1.18	3.4	11.4	19.3	14.0	30.2	63.5	20.9
4.7[g]	0.36	3.1	4.00	12.9	3.4	17.6	33.9	23.8	75.3	16.9
9.0	0.32	3.5 (3.9)[f]	11.55	23.4	1.2	11.6	36.6	21.6	69.7	23.1
14.2	0.23	4.8	16.37	29.9	1.9	9.0	39.7	16.7	65.4	25.7
23.0	0.26	4.3 (4.66)[f]	30.22	29.4	2.0	7.4	36.4	14.3	58.2	31.3
30.0	0.20	5.5	27.85	27.4	2.8	5.7	28.2	17.6	51.6	31.6

[a] Reaction conditions: catalyst (Rh 1–30 wt.%), 1 g; temperature, 280°C; pressure ($CO:H_2:Ar=45:45:10$), 5.0 MPa; and flow rate, 100 ml/min. Data were taken after 20 h after starting the reaction.

[b] Prepared by impregnation from methanol solution of $RhCl_3 \cdot xH_2O$.

[c] Estimated from H_2 chemisorption.

[d] Turnover frequency of CO conversion (1/min).

[e] Based on consumed CO: MeOH*=MeOH+AcOMe; EtOH*=EtOH+AcOEt; AcOH*=AcOH+AcOMe+AcOEt; C_2–O=EtOH*+AcH+AcOH*.

[f] Estimated from XRD line broadening.

[g] Prepared by impregnation from aqueous solution of $RhCl_3 \cdot xH_2O$.

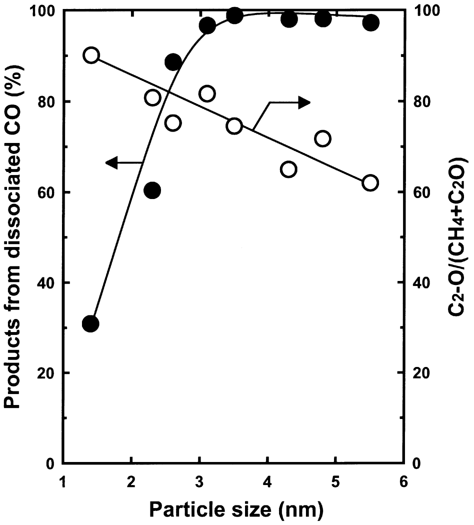

Fig. 4. Effect of Rh particle size on products from dissociated CO in CO hydrogenation over Rh/SiO_2. Reaction conditions: catalyst Rh/SiO_2 (Rh, 1–30 wt.%), 1 g; temperature, 280°C; pressure ($CO:H_2:Ar=45:45:10$), 5.0 MPa; and flow rate, 100 ml/min. Data were taken at 20 h after starting the reaction.

is dictated by the relative rates of CO insertion and the terminating hydrogenation step (or terminating hydrolysis step in the case of acetic acid). Selectivity towards MeOH vs. all other products, including CH_4 and C_2–O, is determined by the relative rate of direct (non-dissociative) CO hydrogenation to methanol and CO dissociation (the initiating step for all other products).

Thus, we can roughly estimate the influences of Rh dispersion on the relative rates of CO dissociation, non-dissociative CO hydrogenation to MeOH, and CO insertion based on the product distribution. The combined CH_4 and C_2–O species, both of which are formed by the hydrogenation of dissociated CO, represent an index for the relative rate of CO dissociation and non-dissociative hydrogenation. Further, the proportion of C_2–O formed vs. methane represents an index for the relative rates of CO insertion and hydrogenolysis of the methyl intermediate formed upon CO dissociation. Fig. 4 represents a plot of Rh particle size vs.:

1. the fraction of C_2–O in all CO dissociation products, calculated as (C_2–O/(CH_4+C_2–O)); and
2. the sum of products through CO dissociation against Rh particle size.

From these plots, we can readily see that the relative rate of CO insertion, to form C_2–O products, decreased increase of particle size. The overall production of products through CO dissociation rapidly increased as the particle size approached 3 nm at which point almost all (ca. 98%) of the CO reacted proceeded via CO dissociation.

Combining these studies (ethylene hydroformylation and CO hydrogenation), one must conclude that highly dispersed Rh/SiO_2 catalysts (i.e., those of small particle size), where there are a large portion of sites at edges and corners, are necessary for high selectivity toward CO insertion. Unfortunately, in the CO hydrogenation to C_2–O, this conflicts with the need for a larger portion of surface Rh atoms to favor CO-dissociation over non-dissociative hydrogenation to MeOH. The consequence of these two conflicting requirements is that the CO hydrogenation process must operate close to an optimum operating particle size of about 3 nm if there is to be a high rate and high selectivity toward C_2–O. The remainder of this study was directed toward clarifying the role of modifiers in the Rh/SiO_2 catalyzed ethylene hydroformylation and CO hydrogenation to oxygenated compounds.

3.2. Effects of modification of Rh/SiO_2 catalysts on ethylene hydroformylation and CO hydrogenation

3.2.1. Modification of Rh/SiO_2 catalyst with group II–VIII metal oxides

3.2.1.1. Ethylene hydroformylation. Table 3 summarizes ethylene hydroformylation over Rh/SiO_2 catalyst derived from $Rh_4(CO)_{12}$ and modified with group II–VIII metal salts at 180°C under 2 MPa. These metal salts act mainly as oxides over these catalysts as a consequence of the calcination conducted after impregnation. Modification with Sc, Ti, V, Cr, Mn, Fe, Cu, and Zr oxides depressed the activity of both the hydroformylation and hydrogenation reactions, while the addition of Mo oxide enhanced both reactions a little.

Alkaline earth metals depressed the activity for both of hydroformylation and hydrogenation of ethylene, although the selectivity for hydroformylation was essentially unchanged by the modification. ZnO had similar influences as alkaline earth metal oxides, but

Table 3
Effects of II–VIII metal salts on ethylene hydroformylation[a]

Group	Catalyst	Yield (10^{-6} mol/min^{-1} g-cat^{-1})				Selectivity (%)
		C_2H_5CHO	C_3H_7OH	C_5H_9CHO	C_2H_6	
–	$Rh_4(CO)_{12}/SiO_2$	62.1	0.4	8.4	268	23
Iia	$Rh_4(CO)_{12}/MgCl_2/SiO_2$	27.9	0.2	5.0	152	20
Iia	$Rh_4(CO)_{12}/CaCl_2/SiO_2$	36.9	0.3	5.4	147	25
Iia	$Rh_4(CO)_{12}/SrCl_2/SiO_2$	45.6	0.2	5.7	214	21
Iib	$Rh_4(CO)_{12}/ZnCl_2/SiO_2$	47.4	0.6	10.1	145	32
IIIa	$Rh_4(CO)_{12}/ScCl_3/SiO_2$	24.5	0.3	11.5	177	33
IVa	$Rh_4(CO)_{12}/TiCl_4/SiO_2$[b]	19.1	0.8	11.2	184	19
IVa	$Rh_4(CO)_{12}/ZrCl_4/SiO_2$	13.0	0.7	11.1	179	17
Va	$Rh_4(CO)_{12}/VCl_3/SiO_2$	38.2	0.4	10.2	185	24
Via	$Rh_4(CO)_{12}/CrCl_3/SiO_2$	54.1	0.3	6.7	211	24
Via	$Rh_4(CO)_{12}/Mo(CO)_6/SiO_2$	66.4	0.3	7.2	278	23
VIIb	$Rh_4(CO)_{12}/MnCl_2/SiO_2$[c]	25.9	0.2	2.8	134	19
VIII	$Rh_4(CO)_{12}/FeCl_3/SiO_2$	20.3	–	1.7	108	18
Ib	$Rh_4(CO)_{12}/CuCl_2/SiO_2$	51.7	0.2	6.4	228	22

[a] Reaction conditions: Catalyst (Rh, 1 wt.%), 1 g; Rh/additive=1 (mol ratio); temperature, 180°C; pressure (C_2H_4:CO:H_2:Ar=30:30:30:10), 2.0 MPa; and flow rate, 100 ml/min. $Rh_4(CO)_{12}$ was impregnated sequentially from hexane solution on modified SiO_2 with additve. Data were taken at 90 min after starting the reaction.

[b] Ti/Rh=10.0.

[c] Mn/Rh=0.2.

the selectivity was as high as 32%. The selectivity for the hydroformylation was unchanged or decreased by the modification with these metal oxides. The apparent activation energies from Arrhenius plots were not significantly changed by the modifications (Table 4). The changes of activity and selectivity of hydroformylation and ethylene hydrogenation upon modification with these metals could not be explained by a change of reaction mechanism and rate-determining steps. The decrease in activities is likely to be due to the decreased availability of the active sites on the Rh surfaces as the surface becomes covered by the modifier.

Table 4
Activation energy of ethylene hydroformylation over Rh/SiO_2[a]

Catalyst	Activation energy (kcal/mol)	
	C_2H_5CHO[b]	C_2H_6
$Rh_4(CO)_{12}/SiO_2$	19.2	24.3
$Rh_4(CO)_{12}/ZnCl_2/SiO_2$	18.2	23.1
$Rh_4(CO)_{12}/MoCl_3/SiO_2$	17.0	23.2
$Rh_4(CO)_{12}/CaCl_2/SiO_2$	15.0	22.3
$Rh_4(CO)_{12}/TiCl_4/SiO_2$	15.8	22.7
$Rh_4(CO)_{12}/VCl_3/SiO_2$	16.6	23.4
$Rh_4(CO)_{12}/CrCl_3/SiO_2$	15.3	21.8
$Rh_4(CO)_{12}/MnCl_2/SiO_2$	16.4	21.2

[a] Reaction conditions: catalyst (Rh, 1 wt.%), 1 g; Rh/additive=1 (mol ratio); temperature, 140–180°C; pressure (C_2H_4:CO:H_2:Ar=30:30:30:10), 2.0 MPa; and flow rate, 100 ml/min. Data were taken at 90 min after starting the reaction.

[b] Calculated from total C_2H_5CHO yield (C_2H_5CHO+C_3H_7OH+2xC_5H_9CHO).

3.2.1.2. CO hydrogenation. As shown in Table 5, CO hydrogenation was examined using several modified catalysts which could be compared to the ethylene hydroformylation. As described in the previous literature [15], modification of the Rh/SiO_2 catalyst with Mn_2O_3 and TiO_2 promoted CO hydrogenation. The enhancement with these oxides is believed to arise from an enhanced CO dissociation rate. When compared to similar catalysts used in ethylene hydroformylation, where these oxides were more of a determinant than a promoter, it is clear that they must act on the CO dissociation step as proposed in the earlier publication [15]. It also appears that there are some differences in the CO insertion step between ethylene hydroformylation and CO hydrogenation since Mn modification in CO hydrogenation enhanced the rate to C_2–O, but adversely affected the selectivity for oxygenated compounds in ethylene hydroformylation.

Table 5
Effects of Mn, Ti, and Zr salts on CO hydrogenation[a]

Catalyst	M/Rh	CO conversion	Selectivity (%)[b]					
			MeOH*	EtOH*	AcH	AcOH*	C_2–O[c]	CH_4
$Rh_4(CO)_{12}/SiO_2$		0.4	28.7	15.2	3.9	5.9	25.0	34.3
$Rh_4(CO)_{12}/MnCl_2/SiO_2$	0.2	0.7	21.9	13.2	15.4	6.1	34.7	34.7
$Rh_4(CO)_{12}/MnCl_2/SiO_2$	1.0	0.5	9.2	13.3	15.7	7.2	36.2	42.6
$Rh_4(CO)_{12}/TiC_4/SiO_2$	1.0	1.5	7.3	16.6	7.2	5.2	28.9	46.1
$Rh_4(CO)_{12}/ZrCl_4/SiO_2$	1.0	1.1	16.6	16.7	4.0	7.9	28.6	40.3

[a] Reaction conditions: catalyst (Rh, 1 wt.%), 1 g; Rh/additive=1 (mol ratio); temperature, 260°C; pressure (CO:H_2:Ar=45:45:10), 2.0 MPa; and flow rate, 100 ml/min. $Rh_4(CO)_{12}$ was impregnated sequentially from hexane solution on modified SiO_2 with additve. Reduction of the catalysts: 400°C for 30 min. Data were taken at 30 min after starting the reaction.

[b] Based on consumed CO: MeOH*=MeOH+AcOMe; EtOH*=EtOH+AcOEt; AcOH*=AcOH+AcOMe+AcOEt; C_2–O=EtOH*+AcH+AcOH*.

[c] EtOH+AcH+AcOH.

3.2.2. *Modification of Rh/SiO_2 catalyst with alkali metal salts*

3.2.2.1. Ethylene hydroformylation. Table 6 summarizes the effect of alkali metal salts on ethylene hydroformylation over Rh/SiO_2 catalyst derived from $Rh_4(CO)_{12}$. Unmodified Rh/SiO_2 catalyst gave propanal-1 and its derivatives with 23% of the selectivity for consumed ethylene. The activity of the hydroformylation was slightly decreased by the addition of LiCl, but the rate of the hydrogenation was depressed more significantly. Consequently, the selectivity for the hydroformylation was improved up to 43% of consumed ethylene. Similar improvement in the selectivity for the hydroformylation was observed by the addition of sodium, potassium, and cesium chlorides. The selectivity decreased in the order: Li>Na>K>Cs. The order may reflect the electronegativity of the alkali metal cations.

A three fold increase in LiCl resulted in a decrease of activity for both the reactions, but the selectivity for the hydroformylation was only slightly improved. These results showed that addition of the same amounts of lithium to rhodium was enough for the improvement of the selectivity. The addition of lithium nitrate gave similar results as LiCl. The improvement

Table 6
Effects of alkali metal salts on ethylene hydroformylation[a]

Catalyst	Yield (10^{-6} mol/min g-cat)				Selectivity (%)
	C_2H_5CHO	C_3H_7OH	C_5H_9CHO	C_2H_6	
$Rh_4(CO)_{12}/SiO_2$	62.1	0.4	8.4	268	23
$Rh_4(CO)_{12}/LiCl/SiO_2$	53.9	0.7	7.3	97.2	42
$Rh_4(CO)_{12}/LiCl/SiO_2$[b]	24.9	1.3	3.6	38.8	46
$Rh_4(CO)_{12}/LiCl/SiO_2$[c]	26.5	1.3	3.6	38.8	46
$Rh_4(CO)_{12}/LiNO_3/SiO_2$[d]	26.5	2.0	3.1	37.8	48
$Rh_4(CO)_{12}/NaCl/SiO_2$	43.8	0.4	6.7	110	34
$Rh_4(CO)_{12}/KCl/SiO_2$	30.5	0.3	2.6	73.0	33
$Rh_4(CO)_{12}/CsCl/SiO_2$	23.8	0.2	2.0	78.4	26

[a] Reaction conditions: catalyst (Rh, 1 wt.%), 1 g; Rh/additive=1 (mol ratio); temperature, 180°C; pressure (C_2H_4:CO:H_2:Ar=30:30:30:10), 2.0 MPa; and flow rate, 100 ml/min. $Rh_4(CO)_{12}$ was impregnated sequentially from hexane solution on modified SiO_2 with additive. Data were taken at 90 min after starting the reaction.

[b] LiCl/Rh=2.0.

[c] LiCl/Rh=3.0.

[d] $LiNO_3$/Rh=3.0.

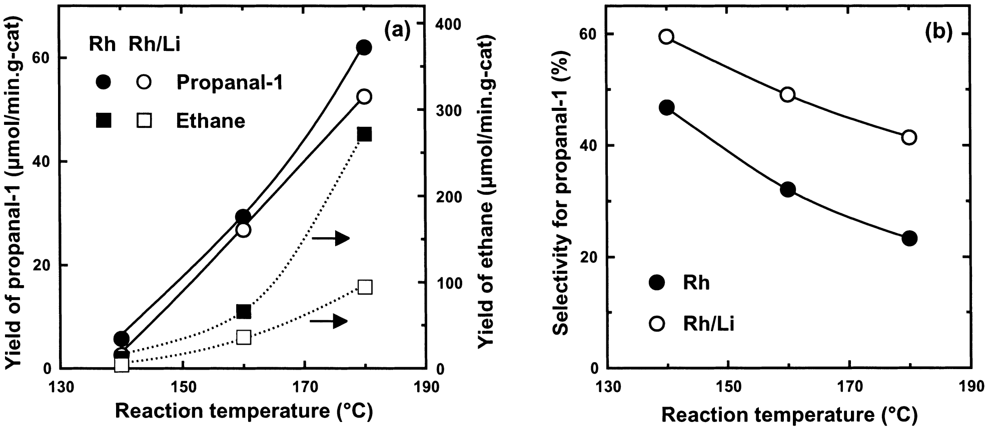

Fig. 5. Effects of reaction temperature on the modification of Rh/SiO_2 with LiCl in hydroformylation and hydrogenation of ethylene. Reaction conditions: catalyst (Rh, 1 wt.%), 1 g; Rh/Li=1 (mol ratio); temperature, 140–180°C; pressure (C_2H_4:CO:H_2:Ar=30:30:30:10), 2.0 MPa; and flow rate, 100 ml/min. Data were taken at 90 min after starting the reaction. Marks: Rh, Rh/SiO_2; Rh/Li, Rh/Li/SiO_2.

should be due to lithium cation, and not due to anion such as chloride and nitrate. These phenomena were also observed in CO hydrogenation over Rh/SiO_2 catalysts [15].

Fig. 5 summarizes the effect of reaction temperature on ethylene hydroformylation over unmodified and lithium-modified Rh/SiO_2 catalysts. Fig. 5a shows the activity of hydroformylation and hydrogenation. The yield of propanal-1 and its derivatives over both catalysts increased with reaction temperature. On the other hand, the formation of ethane over unmodified Rh/SiO_2 catalyst increased more rapidly than that over Li-modified catalysts. Consequently, the selectivity for the hydroformylation decreased with reaction temperature over both catalysts as in Fig. 5b. Decreased consumption of ethylene and an increase in the selectivity for hydroformylation were observed upon the addition of LiCl at every temperature. Improvement of the selectivity upon addition of LiCl was significant at higher temperatures. The apparent activation energies of hydroformylation and hydrogenation calculated from Arrhenius plot are summarized in Table 7. The activities were measured over the catalyst aged at higher temperatures. The change of activation energy of both reactions was small by the addition of alkali metal chlorides. From the results of rates of formation for propanal-1 and ethane, it is not plausible that the addition of the chlorides does not change the rate-determining steps. The addition of LiCl should retard both of hydroformylation and ethylene hydrogenation. However, the retardation of the hydrogenation should be more significant than that of the hydroformylation.

3.2.2.2. CO hydrogenation. CO hydrogenation was carried out over Rh/SiO_2 and Rh/Li/SiO_2 catalysts were used for the hydroformylation (Table 8). The addition of LiCl depressed catalytic activity and the formation of CH_4. Consequently, the selectivity for C_2–O increased by the modification with LiCl. These results

Table 7
Activation energy of ethylene hydroformylation over Rh/SiO_2[a]

Catalyst	Activation energy (kcal/mol)		
	M/Cl[b]	C_2H_5CHO[c]	C_2H_6
$Rh_4(CO)_{12}/SiO_2$	–	19.2	24.3
$Rh_4(CO)_{12}/LiCl/SiO_2$	3	20.2	27.2
$Rh_4(CO)_{12}/LiCl/SiO_2$	1	20.2	24.1
$Rh_4(CO)_{12}/NaCl/SiO_2$	1	20.3	23.5
$Rh_4(CO)_{12}/KCl/SiO_2$	1	19.3	23.4
$Rh_4(CO)_{12}/CsCl/SiO_2$	1	20.0	25.5

[a] Reaction conditions: catalyst (Rh, 1 wt.%), 1 g; Rh/additive=1 (mol ratio); temperature, 140–180°C; pressure (C_2H_4:CO:H_2:Ar=30:30:30:10), 2.0 MPa; and flow rate, 100 ml/min. Data were taken at 90 min after starting the reaction.

[b] Additive/Rh ratio.

[c] Calculated from total C_2H_5CHO yield ($C_2H_5CHO+C_3H_7OH+2xC_5H_9CHO$).

Table 8
Effects of alkali metal salts on CO hydrogenation[a]

Catalyst	CO conversion	Selectivity (%)[b]					
		MeOH*	EtOH*	AcH	AcOH*	C_2–O[c]	CH_4
$Rh_4(CO)_{12}/SiO_2$	0.4	28.7	15.2	3.9	5.9	25.0	34.3
$Rh_4(CO)_{12}/LiCl/SiO_2$[d]	0.3	30.9	14.4	7.0	11.0	32.4	19.9

[a] Reaction conditions: catalyst (Rh, 1 wt.%), 1 g; Rh/additive=l (mol ratio); temperature, 260°C; pressure (CO:H_2:Ar=45:45:10), 2.0 MPa; and flow rate, 100 ml/min. $Rh_4(CO)_{12}$ was impregnated sequentially from hexane solution on modified SiO_2 with additive. Reduction of the catalysts: 400°C for 30 min. Data were taken at 30 min after starting the reaction.

[b] Based on consumed CO: MeOH*=MeOH+AcOMe; EtOH*=EtOH+AcOEt; AcOH*=AcOH+AcOMe+AcOEt; C_2–O=EtOH*+AcH+AcOH*.

[c] EtOH*+AcH+AcOH*.

[d] Li/Rh=3.

of CO hydrogenation and ethylene hydroformylation show that both reactions have the common characters for rate-determining steps. Further investigations should be essential to conclude the rate-determining steps.

3.2.3. Mechanistic aspects of ethylene hydroformylation and CO hydrogenation over modified Rh/SiO_2 catalysts

Fig. 1, shown earlier, demonstrates the mechanistic difference between ethylene hydroformylation and CO hydrogenation. The biggest difference is that a CO dissociation step is involved in CO hydrogenation, but not in ethylene hydroformylation. As previously discussed, transition metal oxides such as Sc, Ti, V, Cr, Mn, and Zr oxides enhance CO dissociation step in CO hydrogenation, and formed hydrocarbons in high selectivity [15]. However, no such influences with these oxides were observed in ethylene hydroformylation. These differences are due to the absence of CO dissociation step in the hydroformylation.

In CO hydrogenation, the modification of Rh/SiO_2 catalyst with lithium enhanced the formation of C_2-oxygenates and retarded the hydrogenation to methane although catalytic activity was decreased. Similar phenomena were also observed in ethylene hydroformylation where the selectivity for hydrogenation to ethane decreased and the selectivity for propanal-1 increased. These similarities are due to the facts that both reactions involve common steps, CO insertion to alkyl species to form acyl species and hydrogenation of alkyl species to form alkane. Lithium modification influences both CO insertion and the hydrogenation, but the hydrogenation path is retarded more effectively than the CO insertion in both CO hydrogenation and ethylene hydroformylation.

4. Conclusion

The effects of particle size and additives on ethylene hydroformylation were studied over Rh/SiO_2 catalysts. Hydroformylation and hydrogenation of ethylene occurred concurrently to produce propanal-1, its derivatives, and ethane. The effect of particle size in both reactions was quite different. Whereas the hydroformylation rate was enhanced over fine Rh particles, the rate of the hydrogenation processes was maximum at around 3.5 nm. These results suggest that the active sites for hydroformylation and hydrogenation have different characteristics.

When these findings were compared to CO hydrogenation, similar trends were observed. Large particles led to better CO dissociation, and therefore better rates, but selectivity for C_2–O, a measure of the relative CO insertion rate for the dissociated CO, an enhanced CO insertion (over hydrogenation) was again observed over highly dispersed Rh/SiO_2 catalysts.

Some additives intended to alter catalytic activity and the selectivity toward hydroformylation in the ethylene hydroformylation were also examined. The addition of alkali metals reduced overall catalytic activity, but influenced the hydrogenation to ethane to a larger extent. As a consequence, there was an increase in the selectivity for hydroformylation.

With Rh/SiO_2 catalyst, the CO insertion steps in ethylene hydroformylation and CO hydrogenation, believed to control the selectivity for hydroformylation and C_2–O, respectively, are believed to have common characteristics. Upon the addition of alkali metals, a similar shift toward higher selectivity for C_2–O would be expected and is indeed observed.

On the other hand, the activity and the selectivity in ethylene hydroformylation were not influenced much by the addition of group II–VIII metal oxides such as MoO_3, Sc_2O_3, TiO_2, V_2O_5, and Mn_2O_3. The same additives enhance the overall activity in CO hydrogenation. Since these additives are believed to affect CO dissociation, a process absent in ethylene hydroformylation, the lack of any positive influence upon ethylene hydroformylation was expected.

Our observations are limited to the effect of Rh dispersion and the modification of Rh/SiO_2 catalysts on catalytic behavior of ethylene hydroformylation and CO hydrogenation, and further investigations from the points of view of analysis are important to understand fully the differences of ethylene hydroformylation and CO hydrogenation.

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