Effects of Rh content on catalytic behavior in CO hydrogenation with Rh–silica catalysts prepared using microemulsion

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Rh–silica catalysts having the same physical parameters despite their different Rh contents were prepared using water-in-oil (w/o) microemulsions, and the effects of Rh content on the catalytic behavior were investigated in the hydrogenation of carbon monoxide. It was found that both the product selectivity and the turnover frequency changed dramatically with the Rh content. The selectivity to C_{2+} oxygenated compounds increased with increasing Rh content, while the selectivity to hydrocarbons and the turnover frequency decreased.

Keywords: microemulsion, Rh content, hydrogenation of carbon monoxide, C_{2+} oxygenated compounds

1. Introduction

It is well known that silica-supported rhodium catalysts are effective for the production of C_{2+} oxygenated compounds such as C_2H_5OH, CH_3CHO and CH_3COOH from syngas [1,2], and intensive efforts have been made to investigate their catalytic behavior [3–6]. However, since the catalytic hydrogenation of carbon monoxide is a structure-sensitive reaction, it is important to control the physical parameters of catalysts for the investigation of the effects of the various parameters on the catalytic behavior. Accordingly, new methods are needed for the preparation of metal-supported catalysts, e.g., to enable the control of their metal particle sizes or surface areas.

We have developed a novel preparation method of metal-supported catalysts using water-in-oil (w/o) microemulsions [7,8]. We have demonstrated that the Rh particle size of Rh–SiO_2 catalysts can be controlled by this method in the range of 2–14 nm irrespective of Rh contents, and that the resulting size distribution is sharp [9]. Moreover, we have succeeded in the preparation of Rh–SiO_2 catalysts having the same physical properties despite their different Rh contents. In this study, the effects of Rh content on the catalytic behavior in CO hydrogenation were investigated.

2. Experimental

Silica-supported rhodium catalysts were prepared using a water-in-oil (w/o) microemulsion consisting of cetyltrimethylammonium chloride (CTAC), 1-hexanol and an aqueous solution of $RhCl_3$ (purity min. 99.9%). Nanoparticles of Rh–N_2H_4 complex were synthesized by adding hydrazine hydrate directly into the w/o microemulsion. The concentrations of $RhCl_3$ in water and CTAC in 1-hexanol were 0.38 and 0.50 $mol\,dm^{-3}$, respectively. Tetraethyl orthosilicate (TEOS) as a silica source and diluted NH_3 solution were added to the microemulsion solution containing the Rh complex nanoparticles, and subjected to hydrolysis at 50 °C for 3 min. The silica gel containing Rh complex nanoparticles was filtrated, thoroughly washed with ethanol, dried at 80 °C overnight and calcined under air flow at 500 °C for 2 h to remove the surfactant, CTAC. Finally, the catalysts thus prepared were reduced with H_2 at 450 °C for 2 h. The catalysts were observed by transmission electron microscopy (TEM, Jeol-2000FX). The Rh particle size was determined by the X-ray line-broadening technique and by the pulse method using CO chemisorption on the catalysts. The BET surface area of the catalysts was evaluated by N_2 sorption measurement.

In the resulting catalysts, the Rh particle size calculated from CO uptake was always larger than that determined by the XRD broadening technique. This finding suggests that some of the Rh particles were partly or wholly embedded in the support [8,9]. Accordingly, the ratio of Rh metals in contact with the gas phase to the Rh metals composing the total surface of Rh particles, herein defined as the R value, was calculated by the following equation:

$$R = (\text{Rh metal in contact with the gas phase: determined by CO chemisorption})/(\text{Rh metal composing the total surface of Rh particles: determined by X-ray diffraction analysis}). \quad (1)$$

The catalytic hydrogenation of CO was carried out using a fixed-bed flow microreactor 20 cm in length at 4.0 MPa. An isothermal region 5 cm in length was obtained at the center of the reactor, where the catalyst of 1.0 g was packed. Accordingly, temperature differences of more than 0.5 °C could not be observed throughout the reaction region. Before each run, the catalyst was reduced *in situ* at 450 °C for

2 h under H_2 flow. A gas mixture consisting of H_2/CO/Ar in the ratio 6/3/1 was passed over the catalyst, and the reactants and products were analyzed by on-line gas chromatography. The activity of the catalyst became constant after about 3 h. The reaction data presented in this study were obtained after the activity of the catalyst had became constant.

3. Results and discussion

3.1. Preparation of Rh–SiO$_2$ catalysts

The Rh particle size, SiO_2 surface area and R value could be controlled independently by the microemulsion method despite the different Rh contents of the catalysts [6,7]. The preparation conditions for the Rh–SiO_2 catalysts are listed in table 1.

The X-ray diffraction patterns of the catalysts are shown in figure 1. The patterns showed a peak corresponding to the (111) plane of Rh metal. Although the intensity of the peak increased with the Rh content, the half-peak widths, which were used to calculate an average particle size by the broadening technique, were almost identical regardless of the Rh contents. The average particle sizes calculated by this technique were 4.5, 4.2 and 4.2 nm at Rh contents of 0.6, 1.1 and 3.5 wt%, respectively.

Figure 2 (a)–(c) shows the TEM photographs of the Rh–SiO_2 catalysts. It can be seen from this figure that the Rh particle size was small and uniform even though the Rh content increased approximately five-fold, and that the size observed from the TEM photograph was in good agreement with that determined by the broadening technique.

The physical properties of the catalysts are listed in table 2, together with the Rh particle size mentioned above. As can be seen, the surface areas and the R values of the catalysts were 420–520 $m^2\,g^{-1}$ and 80–90%, respectively, and could be regarded as almost identical to each other; the Rh particles sizes were also nearly identical. In conclusion, catalysts with the same physical properties could be prepared by the microemulsion method despite their different Rh contents.

3.2. Effects of Rh content on the catalytic behavior

Table 1
Preparation conditions for Rh–SiO_2 catalysts.

$RhCl_3$ aq. (ml)	TEOS (g)	NH_3 aq. (g)	Rh content (wt%)
5.4	95.0	25.0	3.5
4.0	50.0	121	1.1
0.9	25.0	49.0	0.6

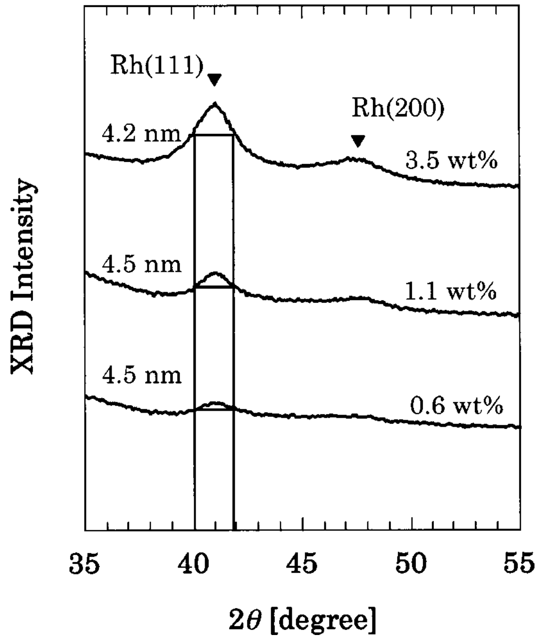

Figure 1. XRD patterns of Rh–SiO_2 catalysts.

The effects of the Rh content on the catalytic behavior were investigated using the CO hydrogenation as a test reaction. The turnover frequency (TOF) was calculated as

$$\mathrm{TOF} = \frac{\text{mole of reactant consumed over catalyst per unit time}}{\text{mole of catalyst exposed on surface}} = \frac{Fy_0x}{WC_\mathrm{M}\alpha d_\mathrm{pulse}}, \tag{2}$$

where F is the molar flux, y_0 the molar fraction, x the conversion, W the catalyst weight, C_M wt% of metal, α ($= 0.1108$) is a constant peculiar to Rh metals and d_pulse is the diameter of Rh particles determined by CO chemisorption. The experimental conditions and results are listed in table 3. Interestingly, the selectivity to C_{2+} oxygenated compounds increased dramatically from 11.8 to >40% with increasing Rh content, and the selectivity to CH_4 and the turnover frequency decreased. These changes in the selectivity and activity were attributed to the change in the Rh content, because the physical properties of the catalysts were almost the same, as can be seen from table 2. However, it is possible that the difference in the selectivity was due to the difference in residence time, because the experimental runs in table 3 were carried out at different gas flow rates to keep the CO conversion in each run nearly constant (about 2.0%). Moreover, it is necessary to examine whether these experiments were carried out under a reaction-rate-controlling or a diffusion-rate-controlling condition, because the mass transfer coefficient of the reactant gas is affected by the gas flow rate. Consequently, the effects of the gas flow rate on the selectivity and the rate-controlling conditions were examined. The selectivity and the CO conversion are shown in figure 3. The Thiele modulus ϕ and the effectiveness factor η have the following relationship [10,11], which is listed in table 4:

$$\Phi \equiv \phi^2\eta = \frac{(-r_\mathrm{A})R^2\rho_\mathrm{P}}{9D_\mathrm{eA}C_\mathrm{A}}, \tag{3}$$

where D_eA and C_A represent the effective diffusivity and the concentration of CO, respectively. R and ρ_P repre-

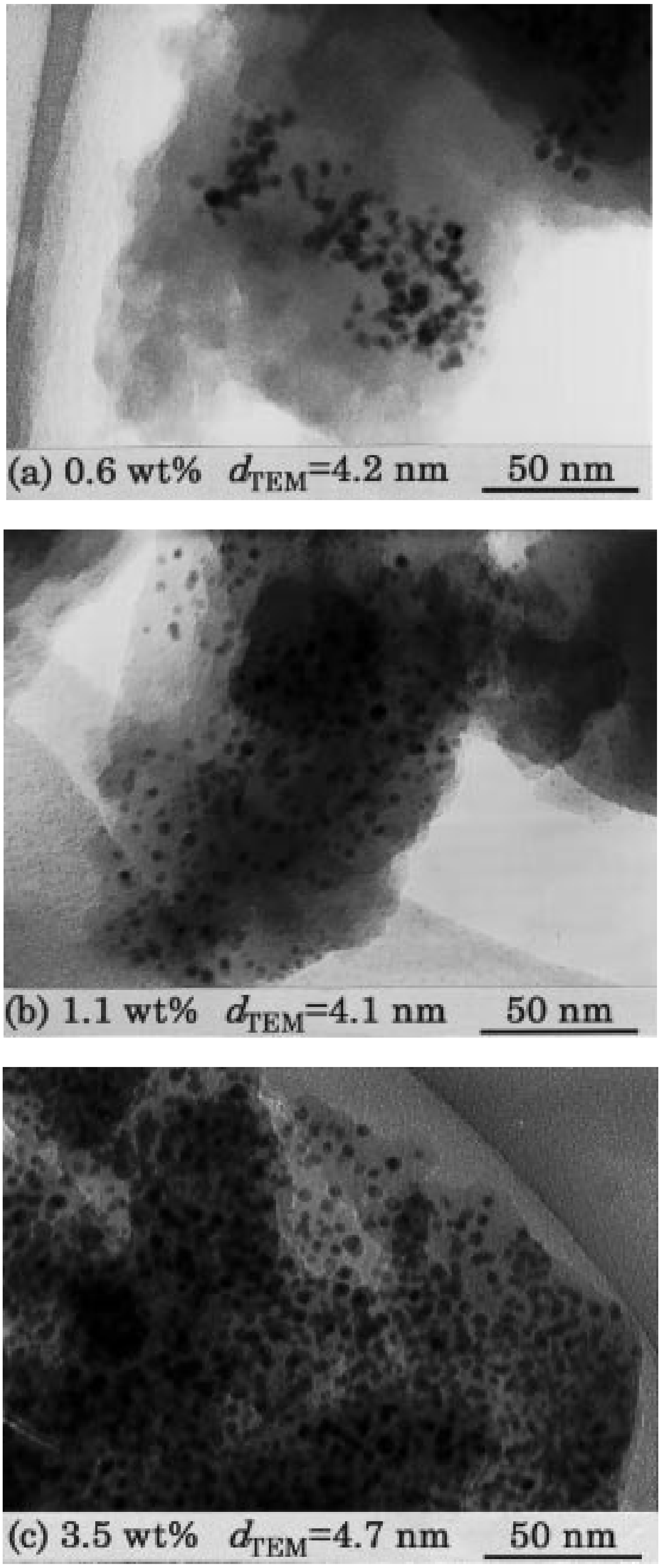

Figure 2. TEM photographs of Rh–SiO_2 catalysts (×500k).

Table 2
Rh content, Rh particle size, BET surface area and R value.

Rh content (wt%)	Rh particle size (nm)	BET surface area (m^2 g-cat^{-1})	R value (%)
3.5	4.2	519	89
1.1	4.5	420	80
0.6	4.5	496	88

sent the radius and the density of the catalyst, respectively. When Φ is less than 0.1, it can be concluded that the reaction is carried out under the reaction-rate-controlling condition [10,11]. As shown in figure 3, the selectivity was almost the same even though the conversion had decreased upon increasing the gas flow rate. Moreover, the values of Φ were less than 0.1, as shown in table 4. These findings indicate that the differences in catalytic behavior demonstrated in table 3 should be ascribed not to the differences in the gas flow rate but to the differences in the Rh content, and that the experiments were carried out under the reaction-rate-controlling condition.

Finally, the distance between the particles was calculated by the following equations:

$$\text{the distance between Rh particles} = \frac{Sw}{n}, \tag{4}$$

$$n = \frac{\text{the number of Rh ions added into the solution}}{\text{the number of Rh atoms the Rh particle consists of}}, \tag{5}$$

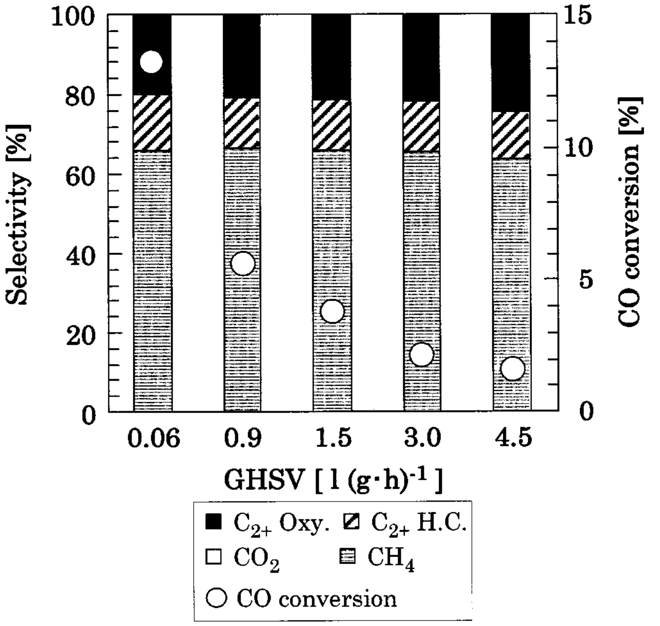

Figure 3. Change in product selectivity with GHSV. Reaction temperature 220 °C, pressure 4×10^3 kPa.

where S and w are the surface area and the weight of catalysts, respectively. n is the number of Rh particles loaded on the SiO_2 support. The distances between the particles estimated from equations (4) and (5) were 220, 150 and 90 nm at Rh contents of 0.6, 1.1 and 3.5 wt%, respectively.

Table 3
CO hydrogenation over $Rh–SiO_2$ catalysts at 220 °C.

Rh content (wt%)	W/F (g h mol^{-1})	GHSV (l h^{-1} g^{-1})	CO conversion	Selectivity[a] (%)			TOF
				CH_4	C_{2+} HC	C_{2+} Oxy.	($\times 10^{-3}$ s^{-1})
0.6	23.3	1.0	2.5	85.3	4.7	11.8	6.9
1.1	12.0	2.0	1.8	48.8	10.3	20.6	5.8
3.5	5.3	4.5	2.0	37.4	14.0	41.0	3.8

[a] C_{2+} HC: C_{2+} hydrocarbon compounds; C_{2+} Oxy.: C_{2+} oxygenated compounds.

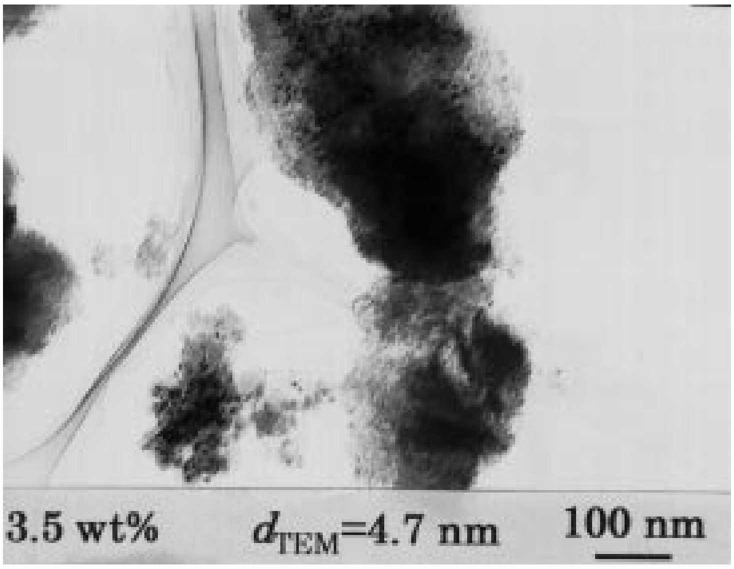

Figure 4. TEM photograph of $Rh–SiO_2$ catalyst (×100k).

Table 4
Effectiveness factor of the CO hydrogenation.

GHSV ($l\,h^{-1}\,g^{-1}$)	CO conversion (%)	$\Phi = \eta\phi^2$ $\times 10^5$
Listed in table 3		
1.0	2.5	4.13
2.0	1.8	5.77
4.5	2.0	14.5
Shown in figure 3		
0.06	13.2	1.28
0.9	5.6	8.13
1.5	3.8	9.20
3.0	2.1	10.2
4.5	1.6	11.6

These values were larger than those observed from TEM photographs. This difference could be ascribed to the fact that the Rh particles were not uniformly loaded on the SiO_2 support, as shown in figure 4; i.e., there were some places with many Rh particles and some places with few Rh particles. However, it can be seen from the TEM photographs that the number of Rh particles increased with Rh content and thus the distance between each particle decreased. Moreover, it is recognized that some of the Rh particles began to touch each other with increasing Rh content. This decrease in the distance might have affected the catalytic behavior.

At present, it remains uncertain why the selectivity to C_{2+} oxygenated compounds was so remarkably enhanced with increasing Rh content.

4. Conclusion

Rh–SiO_2 catalysts having nearly identical Rh particle sizes, surface areas of SiO_2 support and R values could be prepared using the microemulsion method, despite their different Rh contents. The effects of the Rh content on CO hydrogenation were investigated. The product selectivity and the turnover frequency were drastically changed with the Rh content. The selectivity to C_{2+} oxygenated compounds increased from about 12% to more than 40% with increasing Rh content, and the turnover frequency and the selectivity to CH_4 decreased.

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