Enhancement of CO Hydrogenation Activity of Rh/SiO$_2$ with Low Rhodium Content

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The silica-supported Rh catalyst with low Rh content prepared using microemulsion was found to exhibit a very high activity for CO hydrogenation.

It is well known that a silica-supported Rh catalyst is the most effective for the synthesis of C$_2$ oxygenated compounds from syngas although a turnover frequency (TOF) for the CO hydrogenation decreased rapidly as the Rh content of the catalyst became lower than 1 wt%. [1] Therefore, the enhancement of the catalytic activity in the low Rh content is absolutely necessary to industrialize the synthesis process of chemicals from syngas using Rh catalysts, because Rh metal is expensive as well as poor in natural resources.

We have studied a novel preparation method for supported metal catalysts employing water-in-oil (w/o) microemulsion and reported that the silica-supported Rh catalyst prepared by the microemulsion method (denoted by ME) exhibited an extremely high activity for the CO$_2$ hydrogenation.[2-3] In the present study, we investigated the catalyst preparation method using microemulsion to enhance the CO hydrogenation activity of the silica-supported Rh catalyst with low Rh content.

The catalyst A was prepared using a w/o microemulsion consisting of cetyltrimethyl ammonium bromide (CTAB, purity; min. 95%), 1-hexanol and an aqueous solution of rhodium trichloride (purity; min. 99.9%). The concentration of rhodium trichloride solution was 0.19 mol dm^{-3}. A CTAB concentration in 1-hexanol was 0.50 mol dm^{-3}, and a water-to-surfactant molar ratio was 6. By adding directly hydrazine into the microemulsion, the microparticles of rhodium compounds were formed, and subsequently a dilute ammonium solution and tetraethylorthosilicate (TEOS, purity ; min. 95%) as a source of silica support were added to the microemulsion containing the microparticles as described in detail elsewhere.[4] The hydrolysis time for TEOS was 5 min because the hydrolysis reaction was very rapid. The Rh content and the specific surface area of the catalyst A were 0.5 wt% and 80 m^2/g, respectively. The catalysts B (Rh 0.5 wt%) , and C (Rh 2.0 wt%) were prepared by impregnation of silica gel (Cariact-50, 60 m^2/g, offered by Fuji-Sylicia Co Ltd.) with rhodium trichloride solution. The hydrogenation of carbon monoxide was carried out using a fixed bed flow microreactor at 40 atm (H_2:CO:Ar = 6:3:1). Before each run, the catalysts were reduced *in situ* at 450 ℃ for 2 h in H_2 flow.

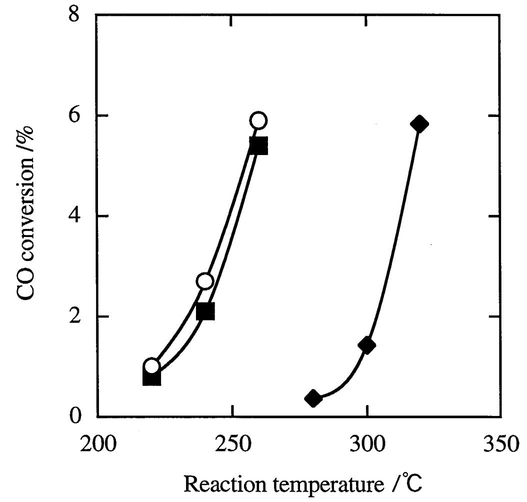

Figure 1. CO hydrogenation over the silica-supported rhodium catalysts.
H_2:CO:Ar = 6:3:1, 40 atm, SV = 2000 $cm^3 g^{-1}h^{-1}$
○; catalyst A (ME 0.5 wt% CTAB), ◆ ; catalyst B (IMP 0.5 wt%), ■; catalyst C (IMP 2.0 wt%).

Figure 1 shows the activities of silica-supported Rh catalysts for CO hydrogenation. The catalyst A prepared using microemulsion exhibited the highest activity although the catalyst A was loaded with a much smaller amount of Rh than the catalyst C prepared by impregnation. The reaction temperature for the catalyst A was shifted down by approximately 60 ℃ in spite of the same Rh content, as compared with that for the catalyst B.Table 1 shows TOF's, TOF for the formation of C$_2$ oxygenated compounds, product selectivities at 260 ℃ , and both of the Rh particle sizes determined from CO chemisorption uptake and measured by TEM. TOF was calculated on the basis of CO chemisorption uptake. As can be seen from Table 1, the

Table 1. TOF, selectivity at 260℃, and Rh particle size of catalysts

Catalyst	TOF / s^{-1}	TOF - C$_2$ Oxy./ s^{-1}	Selectivity / %			Rh particle size determined from CO chemisorption uptake / nm	Rh parcicle size measured by TEM / nm
			CH$_4$	C$_{2+}$ H.C.	C$_2$ Oxy.		
A	0.053	0.0060	74.2	14.5	11.3	7.5	3.4
B[a)]	0.0039	0.0014	55.6	9.7	34.7	2.3	4.3
C	0.014	0.0044	60.5	6.5	31.7	8.5	9.0

a) 300 ℃, C$_2$ Oxy.; ethyl alcohol, methyl acetate, ethyl acetate, acetaldehyde.

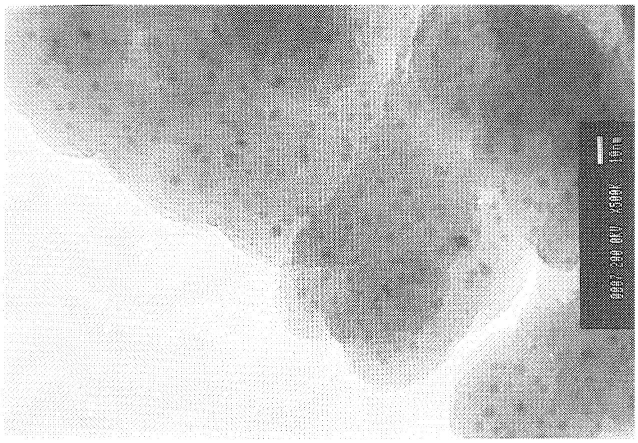

Figure 2. TEM photograph of the catalyst A prepared by the microemulsion.
Microemulsion system; CTAB/1-hexanol/$RhCl_3$aq, w value; 6, Rh content 0.5 wt%, average particle size 3.4 nm.

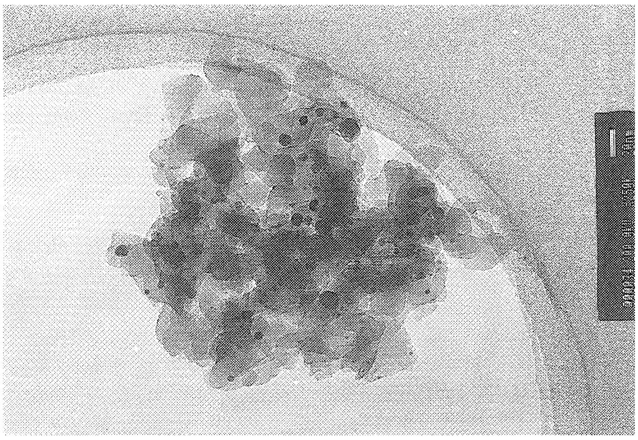

Figure 3. TEM photograph of the catalyst C prepared by the impregnation method.
Rh content 2.0 wt%, average particle size 9.0 nm.

TOF for the catalyst A was extremely higher than that of the impregnated catalysts (B, C). The TOF for the formation of C_2 oxygenated compounds such as ethyl alcohol, methyl acetate, ethyl acetate, and acetaldehyde over the catalyst A was also higher than those over the impregnated catalysts. The Rh particle size of the catalyst C measured by TEM was in good accordance with that determined by CO chemisorption, while the Rh particle size of the catalyst B was larger than that determined by CO chemisorption. This result suggests that very small Rh particles were formed in the catalyst B because of low Rh content and couldn't be detected by TEM.

In the case of the ME catalyst, the Rh particle size determined by CO chemisorption was larger than that measured by TEM, which suggests that some of the Rh particles of the catalyst were partly buried in the support. Therefore, it is surprising that the catalyst A exhibited an extremely high activity although some of Rh particles were buried in the support.

Figure 2 shows the TEM photograph of the catalyst A. Rh particles were very uniform and the average size was 3.4 nm. On the other hand, Figure 3 shows that the Rh particles of the catalyst C are composed of small and large ones with broad distribution. It was reported that the TOF for CO hydrogenation was extremely high over the impregnated Rh/SiO_2 catalysts with Rh sizes in the range from 3 to 4 nm.[1] Accordingly, it is attributed to the optimum control of the Rh particle size that the catalyst A exhibited an extremely high activity for CO hydrogenation.

In conclusion, the Rh catalyst prepared using the microemulsion consisting of CTAB, 1-hexanol and an aqueous solution of rhodium trichloride exhibited an extremely high activity in spite of Rh content as low as 0.5 wt% because the Rh particle size could be controlled at the optimum by the microemulsion method.

References and Notes

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