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Hydrogenation of carbon dioxide over metal catalysts prepared using microemulsion

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Abstract

This paper relates to a novel preparation method of metal supported catalysts using microemulsions. The size distribution of metal particles in the catalysts, thus, prepared was appreciably narrow and the average particle size was much smaller than that of the conventional catalyst prepared from impregnation. It was found that the particle size could be controlled by the conditions of microemulsions regardless of metal content. The Rh, Pd and Pt catalysts prepared from microemulsions were found to exhibit a much higher activity for the hydrogenation of carbon dioxide than those from impregnation.

Keywords: Catalysts preparation; Novel preparation method

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1. Introduction

It is very important to control the metal particle size of supported catalysts, but it is very difficult to do so. Many researchers have studied various methods for the formation of well-controlled metal particles on the carrier. In these methods, the chemical techniques relating to colloidal metal particles have become of considerable interest in recent years [1,2]. Thus, we consider it is significant to apply the microemulsion technique to the catalyst preparation, because monodispersed nanoparticles can be synthesized in microemulsions and their sizes are variable according to the preparation conditions of the microemulsions [3–7]. However, the preparation method for the catalyst based on microemulsions has been scarcely studied, because it is very difficult to deposit the nanoparticles in microemulsions on carriers without formation of large aggregates [8].

This presentation relates to a novel preparation method for noble metal catalysts supported on silica and their catalytic behaviors for the hydrogenation of carbon dioxide.

2. Experimental

2.1. Catalyst preparation

The microemulsions of water-in-oil (w/o) type free from aqueous bulk phase were composed of polyethylene (5) glycol-p-nonylphenyl ether (NP-5) in cyclohexane. The microemulsions were prepared by injecting an aqueous

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metal chloride solution into the concentration of the waterpool of 0.37 mol/dm^3. An NP-5-concentration in cyclohexane was 0.50 mol/dm^3, and water-to-surfactant molar ratios which are denoted by w-values are ca. 5–15. The nanoparticles were formed in the microemulsions by adding hydrazine directly at 25°C. When a diluted ammonium solution was added to the microemulsions containing the nanoparticles, the solution became turbid, but the nanoparticles were not deposited on the wall of the container. After tetraethylorthosilicate was added to the emulsion solution, the solution was heated at 40°C with stirring and then the precipitates containing the nanoparticles were formed. The metal in the supernatant liquid turned out to be less than 0.1% of the added metal by inductively coupled plasma mass spectrometry (Nippon Jahrrell-Ash ICP-575II). Accordingly, the solid precipitates were considered to be loaded with almost all the metal initially added. The precipitates were filtered, thoroughly washed by ethanol, dried at 80°C overnight, and calcined in air at 500°C for 3 h. The catalyst thus obtained was pelleted, crushed, sized to ca. 16–24 mesh, and reduced with H_2 at 450°C for 2 h. From the weight of the catalysts obtained, a part of the charged alkoxides were found not to be converted into the oxides, so the amount of catalyst carriers was calculated from the difference between the weight of the catalyst obtained and the initial amount of the metal. The BET surface areas of the catalysts were 61–65 m^2/g.

In addition, the conventional catalysts were prepared by impregnation of silica-gel with 60 m^2/g surface areas (Cariact-50 offered by Fuji-Davison) with rhodium chloride.

The metal particle was characterized by X-ray diffraction (XRD, Toshiba ADG-302), transmission electron micrography (TEM, Nihon Denshi JEM-2000FX) and CO chemisorption.

2.2. Catalytic hydrogenation of carbon dioxide

The catalytic hydrogenation of carbon dioxide was carried out using a fixed bed flow microreactor at 5.0 MPa. (H_2:CO_2:Ar = 6:3:1). Before each run, the catalyst was reduced in situ at 450°C for 2 h under H_2 flow. The gaseous reactants and products were analyzed by on-line gas chromatography.

3. Results and discussion

3.1. Metal particle sizes of catalysts prepared from microemulsions

The XRD patterns of silica-supported Rh catalysts prepared from microemulsions and from impregnation are shown in Fig. 1. The pattern of the catalyst from impregnation showed a sharp peak corresponding to a 111 plane of Rh metal, and the particle size was calculated to be about 11.5 nm by the broadening technique. On the other hand, the catalyst prepared from microemulsions showed no XRD peak of Rh metal, which suggests that the Rh particle sizes were much smaller than those from impregnation. Fig. 2 shows the TEM photograph of the catalyst prepared from microemulsions. It was found that the particle size distribution was narrow, and that the average Rh particle size was 4.5 nm. The Rh particle sizes were also estimated by CO chemisorption. The particle size prepared from microemulsions was 6.7 nm by CO chemisorption, and was larger than 4.5 nm estimated by TEM. This result suggests that some of the Rh particles were buried in the carrier

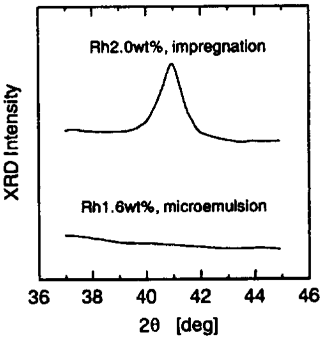

Fig. 1. XRD patterns of silica-supported Rh catalysts prepared from microemulsion and from impregnation.

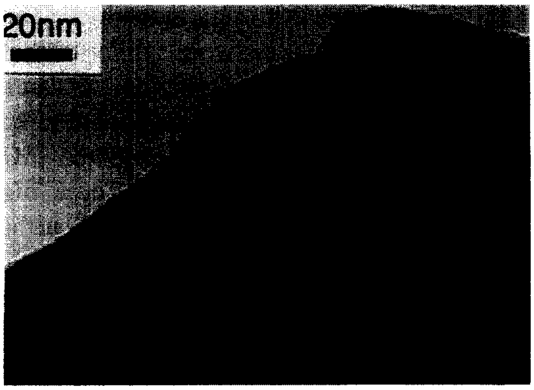

Fig. 2. TEM photograph of the silica-supported Rh catalyst from microemulsion. Rh content, 1.6 wt.-%.

Table 1
Effect of w-values upon Rh diameter in catalysts and their activity for CO_2 hydrogenation

w-value	RH diameter by CO chemisorption (nm)	Rh diameter by TEM (nm)	CO_2 conversion at 180°C (%)
5.0	32.0	3.3	1.7
7.5	27.1	3.7	3.5
15.0	6.7	4.5	18.7

Rh content, 1.6 ± 0.1 wt.-%.

and accordingly were not exposed on the surface. The particle size prepared from impregnation was estimated at 10.7 nm by CO chemisorption, the value of which was in fairly good agreement with 11.5 nm by XRD.

3.2. Effect of preparation conditions of microemulsions

Fig. 3 shows the average diameters and the size histograms of the Rh particles in the catalysts prepared from microemulsions of different *w*-values. It is evident that the average particle diameter increased with the *w*-value under the condition of a constant Rh content. Accordingly, it was suggested that the metal particle sizes of the catalysts could be controlled by adjusting the conditions for the microemulsions where the nanoparticles were synthesized. However, the particle diameters estimated by CO chemisorption were much larger than those by TEM, and decreased with *w*-values in contrast to those observed by TEM, as is shown in Table 1. This result suggests that the coverage of Rh particles by the carrier decreased with *w*-values. It might be due to a low coverage, that is, a high exposure of Rh that the catalyst prepared at a high *w*-value of 15 exhibited a high activity despite of the largest particles, as indicated in Table 1. Here, only methane was detected as a product with all the catalysts.

The effects of the Rh content on the catalytic activity prepared under the condition of a constant *w*-value of 15 were examined for the CO_2 hydrogenation. The Rh particle sizes were almost 4.5 nm by TEM, independent of Rh contents. Assuming that the reaction rate is expressed as $k_{OV}P_{CO_2}P_{H_2}$, the reaction rate constants, k_{OV}, were calculated from the CO_2 conversions. Here, P_{CO_2} and P_{H_2} are the partial pressures of carbon dioxide and of hydrogen, respectively. The k_{OV} is shown as a function of

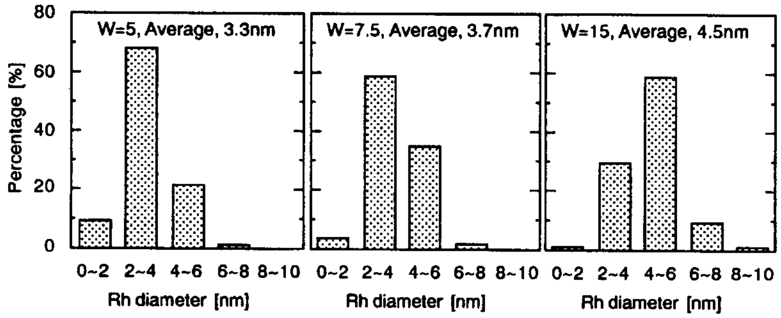

Fig. 3. Distributions of RH diameter of silica-supported catalysts prepared from microemulsions for various *w*-values. Rh content, 1.6 ± 0.1 wt.-%.

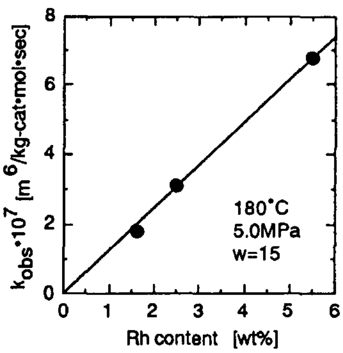

Fig. 4. Effect of Rh content on reaction rate constant in Rh/SiO_2 catalysts prepared from microemulsion.

the Rh content in Fig. 4. The k_{OV} was almost proportional to the Rh content. The catalyst with a Rh content of 5.5 wt.-% had a high CO_2 conversion of 12.0% at 140°C.

3.3. Comparison of catalytic performance between the microemulsion and impregnation methods

The catalytic activities and selectivities of silica-supported Rh, Pd and Pt catalysts were compared for the hydrogenation of carbon dioxide to investigate the difference in performance between the microemulsion and impregnation methods. The *w*-value in the microemulsions was 15 where most of the Rh particles were exposed on the surface. The results are summarized in Table 2. The major product was methane with Rh catalyst, and carbon monoxide with Pd and Pt. The product distributions with the catalysts from microemulsions were similar to those with the catalysts from impregnation. As can be seen from Table 2, the preparation method had a marked effect on the activity and the [ME] catalysts were much more active. These high activities were not responsible for the surface areas, because there was not a significant difference in the surface areas. According to TEM, the particle diameters of the Pd and Pt catalysts [ME] were 6–7 nm, the values of which were smaller than those by the catalysts [IMP] (Pd; 12.0 nm, Pt; 11.8 nm by XRD). The size distribution of the Pd and Pt catalysts [ME] was broader than that of the Rh catalyst [ME]. The particle diameters calculated from CO chemisorption were extremely large (about 24 nm), which shows that the Pd and Pt catalysts [ME] had a low exposure of the metals.

4. Conclusion

We described a novel preparation method for the supported metal catalysts by use of nanoparticles synthesized in microemulsions. The important characteristics of the catalysts thus prepared were as follows.

1. The metal particle size of the catalysts were much smaller than those of catalysts prepared from impregnation, and the size distribution was considerably narrow.

Table 2
CO_2 hydrogenation over various metalc atalysts supported on silica

Catalyst	Content (wt.-%)	*T* (°C)	Conversion (%)	Selectivity (C-mol-%)		
				CH_4	MeOH	CO
Rh [ME]	1.6	180	18.7	100.0		
		200	29.5	100.0		
		220	41.4	100.0		
Rh [IMP]	2.0	240	4.2	93.3	1.5	5.2
Pd [ME]	2.1	250	9.6	2.2	7.7	90.1
Pd [IMP]	2.0	250	0.8	1.4	8.2	90.4
Pt [ME]	0.5	250	4.2	0.2		99.8
Pt [IMP]	0.5	250	0.9			100.0

Reaction condition: *P*, 5.0 MPa; SV, 2000 l/kg h.
[ME]: prepared from microemulsion; [IMP]: prepared from impregnation.

2. It was suggested that the metal particle sizes could be controlled by the water-to-surfactant molar ratio (*w*-value) in microemulsion, although there was a problem that an appreciable part of the particles of the catalyst prepared at a low *w*-value were covered with the carrier.
3. The silica-supported Rh, Pd and Pt catalysts prepared from microemulsions at a high *w*-value of 15 were found to exhibit a much higher activity for the hydrogenation of carbon dioxide than those prepared from impregnation. This result was considered to be due to the smaller metal particle size prepared from microemulsions.

Acknowledgements

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