Novel Preparation of Metal-supported Catalysts by Colloidal Microparticles in a Water-in-oil Microemulsion; Catalytic Hydrogenation of Carbon Dioxide

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A novel catalyst preparation method of employing microemulsions, and the carbon dioxide hydrogenation activities of silica- or zirconia-supported catalysts loaded with colloidal rhodium microparticles in water-in-oil microemulsions are reported; the catalysts thus prepared exhibit much higher activity than those prepared by classical methods.

Recently, the formation of metal and metal oxide microparticles in microemulsions has been widely studied.[1–9] It is generally recognized that the microparticles formed in microemulsions are relatively small and stable, and that their sizes are uniform. With regard to the application of the microparticles to catalysis, many researchers have investigated the catalytic efficiency of the microparticles in the microemulsion phase. However, the application of microparticles produced in microemulsions to the catalysis of vapour-phase reactions has been scarcely investigated. Boutnnet *et al.* investigated the hydrogenation of but-1-ene over platinum, palladium and rhodium catalysts prepared by the deposition on pumice of the colloidal metal particles formed in microemulsion, and they found that these catalysts were no more active than those prepared by the classical method.[10] Here we propose a novel catalyst preparation method of employing microemulsions, and describe the hydrogenation activities of silica- or zirconia-supported catalysts loaded with colloidal rhodium microparticles in water-in-oil (w/o) microemulsions.

Polyethyleneglycol-*p*-nonylphenyl ether ($n = 5$) (NP-5) was employed as a surfactant. The w/o microemulsions composed of NP-5 in cyclohexane were prepared by injecting a fixed amount of aqueous rhodium chloride solutions. The moles of NP-5 per litre of organic phase except for the water pool was 0.50, the concentration of rhodium chloride in the water-pool was 0.37 mol dm^{-3}, and the volume-fraction of the water in the microemulsion (ϕ_w) was 0.11. The microparticles of rhodium compounds were formed in the microemulsion by the direct addition of hydrazine at 25 °C. When a dilute ammonium solution was added to the microemulsion containing the microparticles, the solution became turbid. There was no deposition of microparticles on the container walls. After zirconium *n*-butoxide or tetraethylorthosilicate dissolved in cyclohexane was added to the emulsion solution, the solution was heated at 40 °C with vigorous stirring and pale-yellow precipitates were formed. The precipitates were centrifuged and washed three times with ethanol. Rhodium in the supernatant liquid turned out to be less than 0.1% of the added rhodium, determined by inductively coupled plasma mass spectrometry. Accordingly, all the rhodium initially added was considered to be loaded on the carriers. The precipitates thus obtained were dried at 80 °C overnight, and were calcined in air at 500 °C for 3 h, followed by reduction with H_2 at 450 °C for 2 h. From the mass of the catalysts obtained, some of the charged alkoxides were found not to be converted into the oxides, so the rhodium content of the catalysts was calculated from the initial amount of rhodium and the mass of the catalysts obtained after calcination. The catalysts thus prepared are denoted by [ME] hereafter.

In addition, we prepared three kinds of catalysts to compare with the [ME]. Those were [DEP], [IMP] and [IMP/ME]. The [DEP] catalysts were prepared by deposition of the microparticles suspended in the microemulsion onto a zirconia powder at 70 °C (pH = 9). This zirconia was obtained by calcination of zirconium hydroxide precipitated from aqueous zirconyl nitrate solution. The [IMP] catalysts were prepared by impregnation of two carriers, ZrO_2 obtained from $ZrO(NO_3)_2$ (aq.) and SiO_2 (Cariact-50, Fuji-Davison Co. Ltd) with rhodium chloride. The [IMP/ME] catalysts were prepared by impregnation of the carriers which were obtained by hydrolysis of the alkoxides in the above-mentioned emulsion solution with rhodium chloride.

All the catalysts were sieved and pre-reduced before use. The hydrogenation reaction was carried out using a fixed bed flow microreactor at a pressure of 4.9 MPa ($H_2:CO_2:Ar$, 6:3:1). The effluent gas was directly led off for analysis by gas chromatography. The values of the CO_2 conversion and the product selectivities were obtained at a time on-stream of 1–3 h.

The rhodium particles in the catalysts were characterized by transmission electron microscopy (TEM). Fig. 1 shows a TEM photograph of Rh (1.8 mass%) SiO_2[ME]. The average rhodium-particle size was *ca.* 3.2 nm, and the sizes were appreciably uniform. On the other hand, the rhodium particles of Rh (2.0 mass%) SiO_2 [IMP] could not be discriminated from the carrier, so that the rhodium particle sizes of the [IMP] were estimated to be 10.1 nm from CO uptake. Judging from these

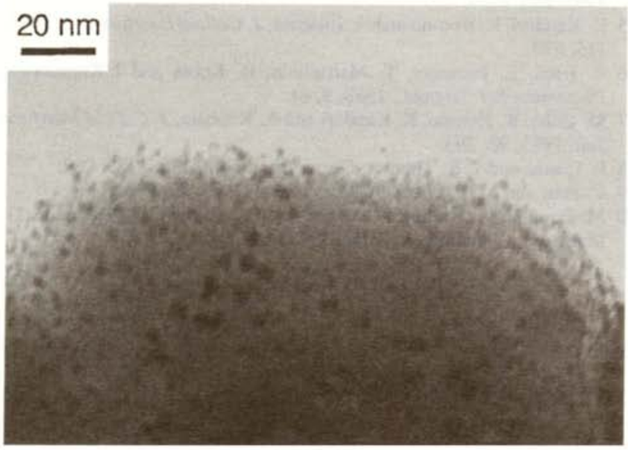

Fig. 1 TEM photograph of Rh (1.6 mass%)/SiO_2[ME]

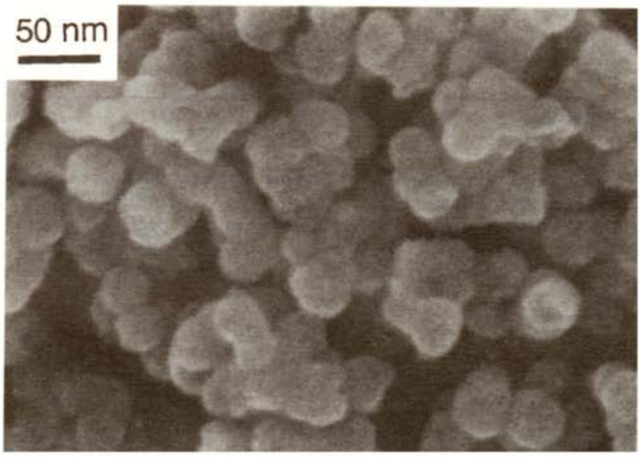

Fig. 2 FE-SEM photograph of Rh (1.6 mass%)/SiO_2[ME]

results, the rhodium particles of the [ME] catalyst might be smaller than the [IMP]. The sizes of the rhodium particles of the [ME] catalyst were calculated to be 4.5 nm from CO uptake. The difference in particle sizes obtained by TEM and CO uptake suggest that all the rhodium particles were not exposed on the catalyst surface, taking into consideration that the carrier was made up later than the microparticles in the preparation of the [ME] catalyst. The microstructure of the catalysts were observed by field emission scattering electron microscopy (FE-SEM). Fig. 2 is a FE-SEM photograph of SiO_2 loaded with Rh (1.8 mass%) [ME], showing that this catalyst consisted of uniform and small silica particles of *ca.* 30 nm. Thus, it is likely that the [ME] catalysts had many pores of *ca.* 30 nm diameter between the silica particles.

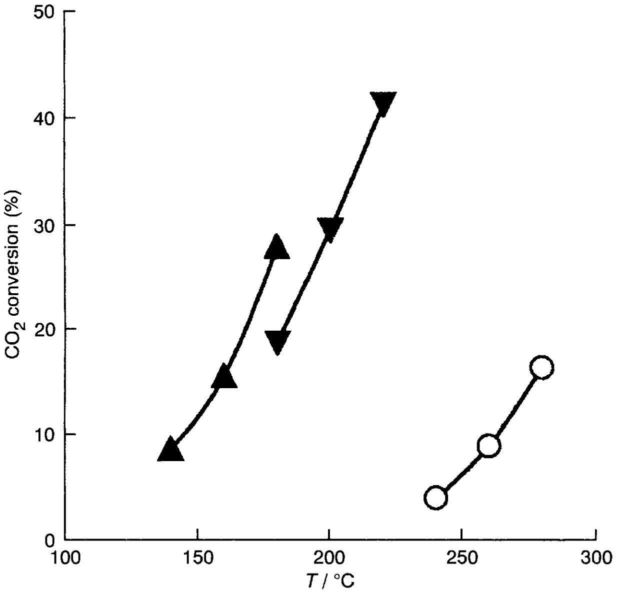

Fig. 3 CO_2 hydrogenation over the silica-supported rhodium catalysts. $H_2:CO_2:Ar = 6:3:1$; 5.1 MPa; W/F, 11.2 g h mol^{-1}. Results obtained after 2 h on-stream. ▲, Rh (2.5 mass%)[ME], 61 $m^2 g^{-1}$; ▼. Rh (1.6 mass%) [ME], 61 $m^2 g^{-1}$; ○, Rh (2.0 mass%) [IMP], 60 $m^2 g^{-1}$.

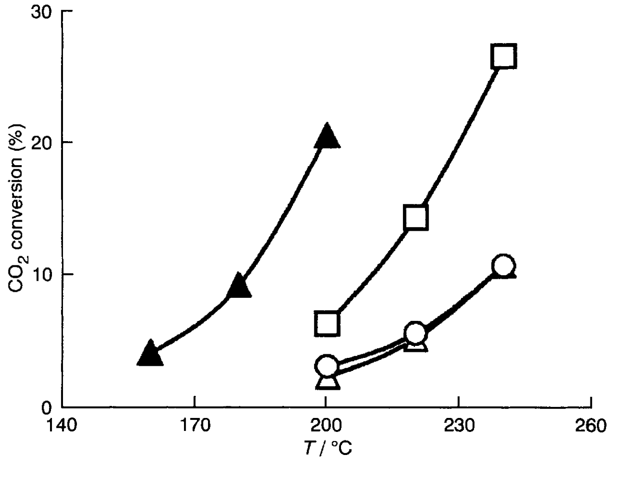

Fig. 4 CO_2 hydrogenation over the zirconia-supported rhodium catalysts. Rhodium content, 1.8 mass%; $H_2:CO_2:Ar = 6:3:1$; 5.1 MPa; W/F, 11.2 g h mol^{-1}. Results obtained after 2 h on-stream. ▲, [ME] 80 $m^2 g^{-1}$; □ [IMP/ME] 64 $m^2 g^{-1}$; ○ [IMP] 89 $m^2 g^{-1}$; △ [DEP] 89 $m^2 g^{-1}$.

Fig. 3 shows the activity of the silica-supported rhodium catalysts for CO_2 hydrogenation. Methane was the only product for all the catalysts. It was noteworthy that the [ME] catalysts exhibited a strikingly high activity, and that the reaction temperatures over the [ME] catalysts were lower by about 100 °C than over the [IMP]. This result indicates that the reaction rates over the [ME] catalyst were about eighty times faster than those over the [IMP]. Although all the rhodium particles were not exposed, it is interesting to note that the [ME] catalyst showed extremely high activity. Such a catalytic performance might be owing to the morphology of rhodium particles.

With regard to the silica-supported catalysts, we were unable to prepare the [IMP/ME] catalyst, because silica gel free from rhodium could not be obtained in the emulsion solution under the above-mentioned conditions. Accordingly, we investigated the rhodium–zirconia catalyst system, as shown in Fig. 4. The rhodium contents were 1.8 mass% per zirconia in all the catalysts. The BET surface areas of the catalysts did not differ greatly. The reaction products were mainly methane over the [ME], [IMP/ME] and [DEP] catalysts, and carbon monoxide over the [IMP] catalysts. The order of the catalytic activity was: [ME] > [IMP/ME] > [IMP] ≈ [DEP]. In agreement with the results reported by Boutnnet *et al.*,[10] the activity of the [DEP] was almost the same as that of the [IMP]. The higher activity of [IMP/ME] than [IMP] may be responsible for the pore structures consisting of uniform zirconia particles, as is the same with silica carriers. (*cf.* Fig. 2). It is evident that the high activity of the [ME] catalyst was caused by the method of catalyst preparation, compared with the activity over the [DEP]. Such a high activity may be attributable to the rhodium particle sizes, the location of the rhodium particles and the interaction between rhodium and carriers, which is now being investigated.

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