

§1. Preparation and Characterization of Porous Polymer Supported Pt Catalyst

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For the detritiation from tritiated water by the water-hydrogen chemical exchange system, the use of isotope exchange catalyst is thus indispensable. However, as well known, such a catalyst (known as the Kogel catalyst) is difficult to produce and relatively expensive. Therefore, there still is a need to develop a novel inexpensive catalyst with good reproducibility. Although a crucial requirement for an isotope exchange catalyst is appropriate porosity and hydrophobicity, little has been known about the rules governing porosity parameters, such as the pore diameter and the pore volume of the catalyst support. In this study, a novel DVB polymer was chosen as the catalyst support,¹⁾ and the control of the pore size in the range from about 2,000 to 50 nm was examined. The active component Pt was loaded into the obtained DVB polymer, and the activity of H₂ oxidation catalysis was investigated.

Macroporous DVB polymers were prepared from the mixture of 1,3,5-trimethylbenzene (4.2 mL), 2,2,6,6-tetramethylpiperidine 1-oxyl, divinylbenzene (3.0 mL), benzoyl peroxide (0.03 g), acetic anhydride (0.02 mL), and dimethylpolysiloxane (denoted DMS), according to the literature with a slight modification.¹⁾ The DVB polymers obtained using 0.37, 0.35, and 0.31 mL of DMS were denoted as No. 1, No. 2, and No. 3, respectively. The yield of DVB polymer was about 85-80% against the weight of divinylbenzene monomer. Pt loading on the porous DVB polymer was performed by impregnating H₂[PtCl₆]·6H₂O in an ethanol solution using the incipient wetness method. The loading amount of Pt was 1.0 wt%. Pt was reduced at 200 °C in an H₂ (50%)/N₂ (balance) flow before use in the catalytic reaction.

Fig. 1 shows the FE-SEM images of DVB polymers. As clearly seen, polymer No. 1 had a continuous network of wormhole-like macropores with a diameter of about 1,500 nm. Also, it was found that the wall thickness was about 1,000 nm. Observation at higher magnification confirmed that the polymer wall consisted of the aggregation of particles with the particle diameter of about 30 nm. Polymers No. 2 and No. 3 showed interconnected macropores with the sizes of about 300 and 100 nm, respectively, on FE-SEM measurements (Fig. 1). It was also clear that the walls were formed by the aggregation of polymer particles.

The macropore diameter was determined to be 1,661 (No. 1), 299 (No. 2), and 84 nm (No. 3), respectively, by Hg porosimetry. The macropore volume (larger than 50 nm in diameter) was determined to be 1.429, 1.356, and, 1.068 cm³/g, respectively. From these values, the degree of macroporosity was found to depend on the amount of DMS in the starting mixture. The surface area obtained from N₂

sorption study was 610, 581, and 658 m²/g, respectively. Also, it was revealed that DVB polymer possesses a certain amount of micropores (smaller than 2 nm in diameter). The micropore volume of No.1, No.2, and No.3 was 0.263, 0.246, and 0.281 cm³/g, respectively, and was independent of the amount of DVB. This suggested that micropores occurred inside DVB particles; or in other words, in the walls of the macropore structure.

The catalytic activity of Pt/DVB was investigated using an H₂ oxidation reaction. No apparent differences were observed among the Pt/DVB catalysts of polymers No.1, No.2, and No.3. Activation energy was estimated to be about 30 kJ/mol for all Pt/DVB catalysts. On the other hand, TEM study revealed that Pt particles loaded into DVB polymer were distributed mostly in the diameter range of about 2 nm. It, therefore, seems that the Pt particles are existed within the micropores in the polymer walls, not facing the macropores. The control of microporosity thus should be a future step in the development of the Pt/DVB catalyst.

1) Kanamori, K. et al.: Adv. Mater. **18** (2006) 2407.

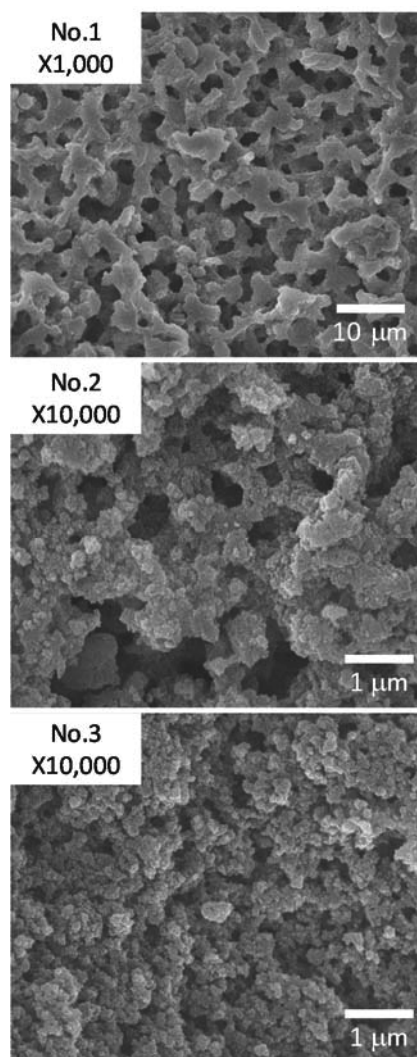


Fig. 1 FE-SEM images of DVP polymers prepared.