

## HRTEM and HAADF-STEM Observation of Ni-Nanoparticle-Dispersed Amorphous Silica

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Microporous amorphous silica ( $\text{SiO}_2$ ) membranes have the potential to be used as hydrogen separation membranes [1] because of their high durability at high temperature. These membranes are able to separate hydrogen from other larger gas molecules by a straightforward molecular sieve-like mechanism because they contain nanopores  $\sim 0.3$  nm in diameter throughout the Si-O network. In order to enhance the hydrogen permselectivity, we have developed a composite membrane containing Ni-nanoparticle-dispersed amorphous  $\text{SiO}_2$  using a precursor solution method. Such a membrane can achieve higher  $\text{H}_2$  permeance compared to He and  $\text{N}_2$  at 773 K. One possible explanation for the selective enhancement of  $\text{H}_2$  permeance is the reversible hydrogen adsorption behavior of the Ni nanoparticles in the amorphous material.

In this study, the relationship between the microstructure of Ni nanoparticles dispersed in the Si-O matrix and the membrane's reversible hydrogen adsorption behavior was investigated to elucidate the mechanism of permselectivity.

An Si-Ni-O precursor solution was prepared by dissolving tetraethoxysilane (TEOS:  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 30%  $\text{H}_2\text{O}_2$  aqueous solution in ethanol at 273 K. The amount of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was adjusted to yield Ni/(Si+Ni) atomic ratios from 0.05 to 0.33 [2]. The resulting homogeneous solution was subjected to hydrolysis and polycondensation reactions to cause gelation at 333 K. The precursor powder obtained was pyrolyzed at 873 K for 3 h in air. The resulting powders were then heated in hydrogen at 773 K for 15 h. The powder samples were placed on a carbon grid for characterization by high-resolution electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM). Crystallization of metal nanoparticles was observed using HRTEM, and the size distribution of nanoparticles measured using the HAADF-STEM method. The amount of reversibly adsorbed hydrogen in the prepared powder was measured using an automated gas sorption system. The range of hydrogen pressures for the 773 K-isotherm analysis in this study was 5 to 101 kPa

Figure 1 shows an HRTEM image of the sample with an Ni/(Si+Ni) ratio of 0.33 after heat treatment at 773 K in hydrogen. This confirms that the nanoparticles are spherical. Analysis also confirmed the particle to be metallic Ni. It was found that the sizes of the Ni nanoparticles in the Si-O matrix increase from about 2 to 6 nm with increasing Ni content. Figure 2 shows the pressure dependence of reversibly adsorbed hydrogen at 773 K for a composite powder with Ni/(Si+Ni) close to 0.05. The graph shows that the amount of reversibly adsorbed hydrogen tends to increase with increasing  $\text{H}_2$  pressure. From this figure, the experimentally obtained amount of reversibly adsorbed hydrogen ( $V_r$ ) was calculated as the difference between the amount of adsorbed hydrogen at a hydrogen pressure of 5 kPa and that at a pressure of 101 kPa for each sample. Figure 3 shows a HAADF-STEM image of Ni nanoparticles in the amorphous silica matrix. The bright-contrast Ni nanoparticles were uniformly dispersed throughout the amorphous silica matrix. The composite powders with an Ni/(Si+Ni) ratio of 0.05 had a relatively narrow particle size distribution, with mean particle sizes ( $d$ ) estimated to be 1.75 nm. The total surface area of Ni nanoparticles in the powder

( $A_p$ ) was calculated from  $d$  and the total number of Ni nanoparticles in 1 g of powder. The total amount of adsorbed hydrogen on the Ni nanoparticles was estimated from  $A_p$ , assuming monolayer coverage, and the effective average area occupied by a hydrogen on the surface of an Ni nanoparticle.

The agreement of the estimated and experimentally obtained results suggests that hydrogen is reversibly adsorbed at the interfaces between the Ni nanoparticles and the amorphous Si-O matrix.

#### References

- [1] T. Ioannides et al., Catal. Lett. 36 (1996) 165.
- [2] Y. H. Ikuhara et al., J. Am. Ceram. Soc., 90 (2007) 546.

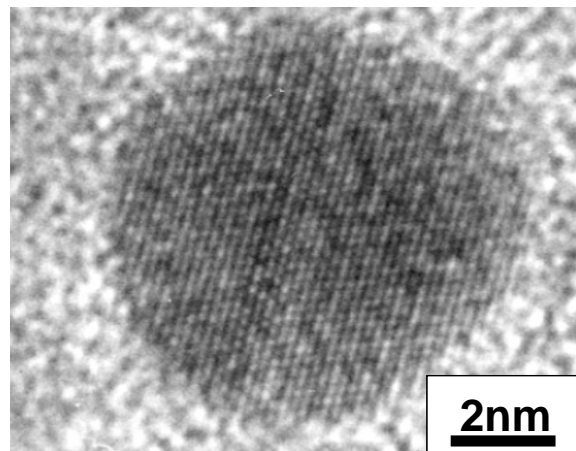


FIG.1 HRTEM image of an Ni-nanoparticle-dispersed amorphous silica powder with Ni/(Si+Ni) = 0.33 heat treated at 773 K in hydrogen.

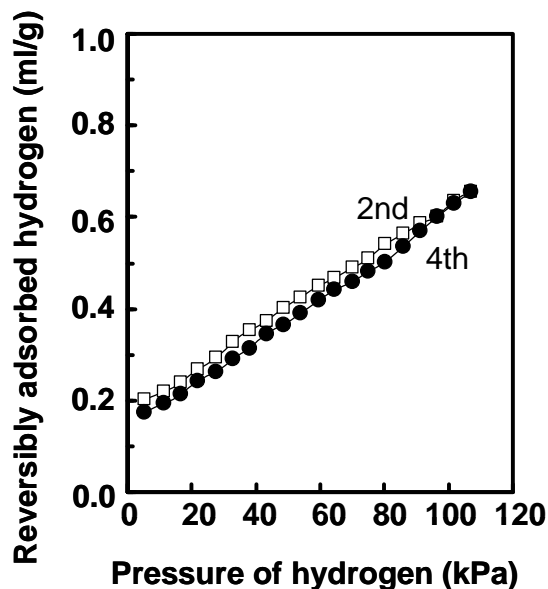


FIG.2. Dependence of the amount of reversibly adsorbed hydrogen on the hydrogen pressure for an Ni-nanoparticle-dispersed amorphous silica with Ni/(Si+Ni) = 0.05.

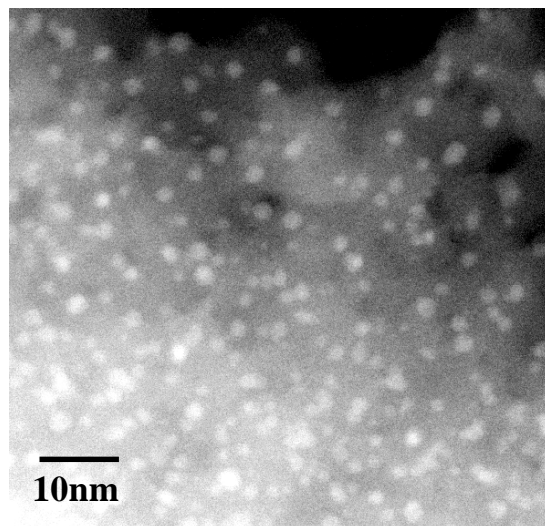


FIG.3. HAADF-STEM image of an Ni-nanoparticle-dispersed amorphous silica powder with Ni/(Si+Ni) = 0.05.