Structure Analysis of Metallic Ni Species Supported on Zeolite Prepared by Liquid Phase Reduction

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1. Introduction

The supported Ni species changes its chemical state in response to the environment, and such chemical conversion strongly affects to the catalytic performance. We have systematically investigated the chemical state of the Ni catalysts supported on various supporting materials at elevated temperatures under reductive/oxidative gas flow, and it has been revealed that the redox temperature is dependent on the particle size of the supported Ni species. The reduction of small NiO nanoparticles with the diameter lass than 5 nm proceeds at higher temperature than that of bulk NiO [1]. The formed small Ni nanoparticles, which are known to promote effectively the oxidative coupling of thiophenol [2], are easily oxidized and the NiO nanoparticles are regenerated. The knowledge of the redox properties of much smaller Ni particles is important to enhance the understanding about the chemical conversion behavior of the supported Ni species. Because it is known that the Ni(II) ion is adsorbed in zeolite by the ion-exchange method, the micro pore of zeolite can suppress the aggregation of the supported Ni species. In this study, we have attempted to synthesize the highly dispersed metallic Ni nanoparticles on H-FAU zeolite by using the ion-exchange method and the liquid phase reduction (LPR) technique. The prepared Ni/H-FAU was characterized by the X-ray absorption fine structure (XAFS) method.

2. Experimental

The powder of H-FAU (JRC-Z-HY5.3) was added into an aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$, and the pH value was adjusted to 6.9. After continuous stirring for 24 h at room temperature, the sample power was filtered, washed by water, dried for 24 h at 80 °C, and finally dried in vacuum for 24 h at 130 °C. The obtained powder was refluxed for 6 h at 82 °C in 2-propanol, in which $NaBH_4$ was dissolved. After cooling to room temperature, the sample mixture was sealed in an Al-laminated bag to prevent the oxidation of contained Ni species. All LPR procedures were conducted under a N_2

gas atmosphere. The XAFS measurements of the sealed samples were directly carried out at BL-3 of SR center (Ritsumeikan University) and BL-9C of Photon Factory (KEK) at the Ni-K edge.

3. Results and Discussion

Figure 1 shows the observed XANES spectrum in comparison with those of Ni(II)/H-FAU and Ni foil. It is clearly indicated that the ion-exchanged Ni(II) species is reduced by the LPR method and that the metallic Ni(0) particles are formed on FAU. The composition was analyzed by a linear combination fitting using the XANES spectra, and it was revealed that the mole fraction of the Ni(0) species was 0.73. The Ni–Ni interaction with the interatomic distance of 250 pm is observed in the Fourier transform function given in Fig. 2. The shoulder structure at the shorter distance is due to the Ni–O interaction for the mixed Ni(II) species. The EXAFS analysis clarified the average coordination number of 2.2 for the Ni–Ni interaction. The value is significantly smaller than that (12.0) of bulk metal. The particle size of the supported Ni(0) species was estimated to be 0.4 nm on the basis of the determined coordination number in considering the composition of the Ni(0) species. The fact that there is no peak in the longer distance region supports such small particle size. This study revealed that the small Ni(0) cluster was generated on FAU by the LPR treatment of the ion-exchanged Ni(II) species.

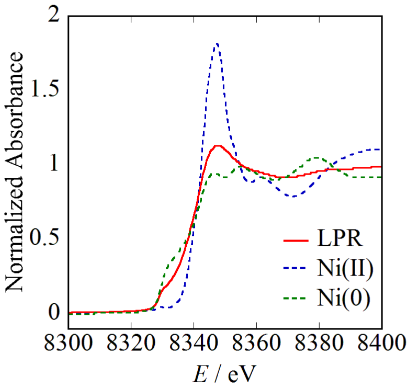

Fig. 1 XANES spectra of the Ni species supported on zeolite.

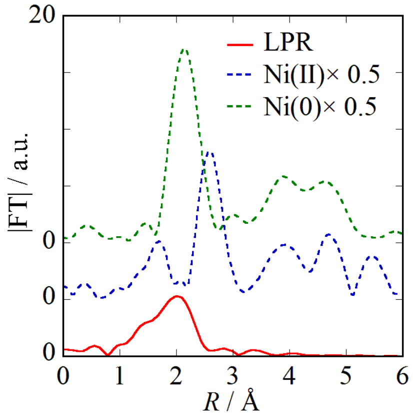

Fig. 2 Fourier transform functions of the Ni species supported on zeolite.

References

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