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Chemical State Analysis of Ni Species Supported on ZnO by Means of *In-Situ* XAFS Technique

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1. Introduction

The Cu catalyst supported on ZnO is known to be active in the synthesis of methanol,[1] and many researches are being conducted on the hydrogenation of CO_2 for the effective utilization of CO_2. It has been reported to be active in hydrogen substitution reactions and CO_2 reduction reactions.[2] The Ni and Co catalysts supported on ZnO show high activity for steam reforming reaction of bioethanol.[3] ZnO is also known as a photocatalyst, driven by visible light, to decompose organic pollutants and to detoxify NO_x.[4] In these photocatalytic reactions, the metal species supported on ZnO play an important role in improving the catalytic activity, which is largely influenced by the oxidation state of the supported metal species.

The XAFS method is a powerful analysis tool for determining the oxidation state of metal species in the solid state, and the hard X-ray XAFS method has the advantage of being able to observe the metal species under reaction conditions. We have systematically analyzed the chemical state of the Ni catalysts supported on silica, alumina, zirconia, etc.[5] In this study, regarding the preparation treatment of the Ni catalyst supported on ZnO, the chemical state of the Ni species has been analyzed by *in-situ* XAFS technique for the temperature-programmed reduction (TPR) process under the diluted H_2 atmosphere. Such basic information will provide a guideline for the development of new catalytic functions.

2. Experimental

An aqueous solution of nickel(II) nitrate hexahydrate was used for the impregnation under the incipient wetness condition to support the $Ni(NO_3)_2$ hydrates on ZnO with the Ni loading of 40 wt%. The powder obtained by drying the mixture at 70 °C in air was used as a measurement sample. *In-situ* XAFS measurement at the Ni K edge was performed at BL-3 of the SR Center for the TPR process under a He-diluted H_2 gas flow (10 vol%) at elevated temperatures to 360 °C.

3. Results and Discussion

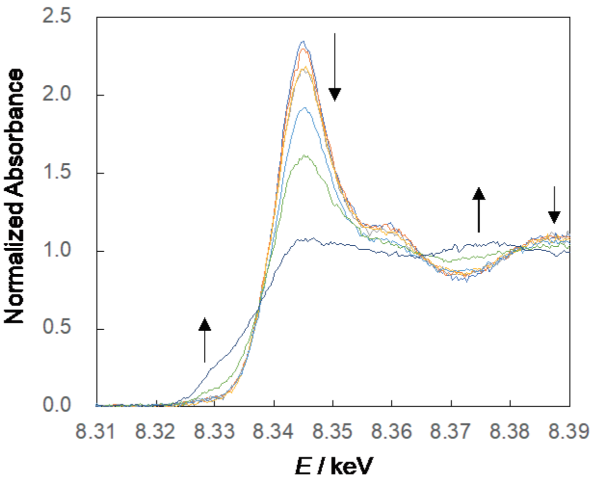

Fig. 1 XANES spectral change for the TPR process of NiO supported on ZnO under a He-diluted H_2 gas flow (10 vol%) measured at 25, 100, 200, 250, 300, 350, and 360 °C.

Figure 1 shows the XANES spectral change for the TPR process. The spectrum at room temperature was consistent with that of $Ni(H_2O)_6(NO_3)_2$ measured independently, indicating that the Ni(II) aqua complex present in the precursor solution was precipitated on ZnO accompanied by nitrate ions. The intense white line observed at 8345 eV was slightly weakened to 200 °C. This decrease in intensity is interpreted as a decrease in symmetry around the Ni(II) center.$^{6)}$ The white line intensity subsequently dropped dramatically, resulting in a low energy shift in the absorption edge. The spectrum at 360 °C was closer to that of Ni metal. Some isosbestic points were clearly observed in the temperature range where the XANES spectrum changed significantly, and it was considered that the conversion from $Ni(H_2O)_6(NO_3)_2$ to metallic Ni proceeded in two components.

The observed XANES spectra were used to estimate the composition of the Ni species. Two characteristic spectra corresponding to $Ni(H_2O)_6(NO_3)_2$ and Ni metal were used as the references for the linear combination fitting (LCF) analysis. The obtained values of mole fraction of the Ni(II) hydrate and metallic Ni(0) are plotted as a function of temperature in Fig. 2. As mentioned above, it was revealed that the Ni(II) hydrate was maintained up to 250 °C and was completely converted to metallic Ni(0) at 360 °C. It should be noted that it is considered that the reduction of ZnO by H_2 was

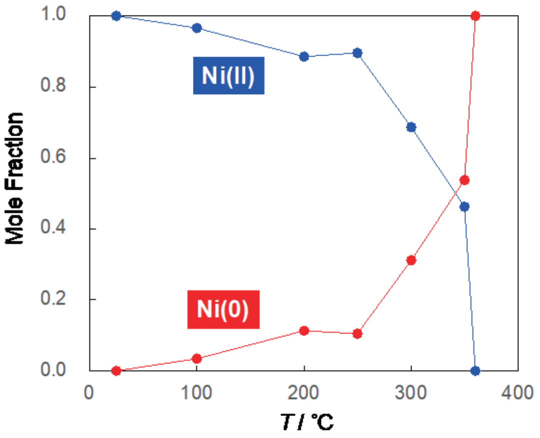

Fig. 2 The values of mole fraction of NiO and Ni metal as a function of temperature estimated by the linear combination fitting of the XANES spectrum.

not progressed, because the absorbance in the pre-edge region was not changed significantly in the temperature range up to 360 °C.

Figure 2 shows that the Ni(0) species increases by about 10 % up to 250 °C. If this change is truly a partial formation of Ni(0), the difference spectrum between 250 °C and 25 °C must be consistent with that between the initial and final spectrum for the present TPR process. Figure 3 shows a comparison of the difference spectra. Both difference spectra have a negative peak at 8345 eV, which corresponds to the decrease in the white line intensity. However, there is a clear difference around 8331 eV. When the Ni(II) hydrate is converted to metallic Ni, the absorbance at 8331 eV must change positively as seen in the difference spectrum. In contrast, no increase in absorbance was observed at 8331 eV at temperatures from 25 °C to 250 °C, only the peak intensity of the white line decreased. This change is not attributable to the conversion of the Ni(II) hydrate to metallic Ni. The Ni(II) ion is octahedrally surrounded by six O atoms in the Ni(II) hydrate, and it is considered that the decrease in symmetry due to the increase in interatomic vibration only reduces the white line intensity.

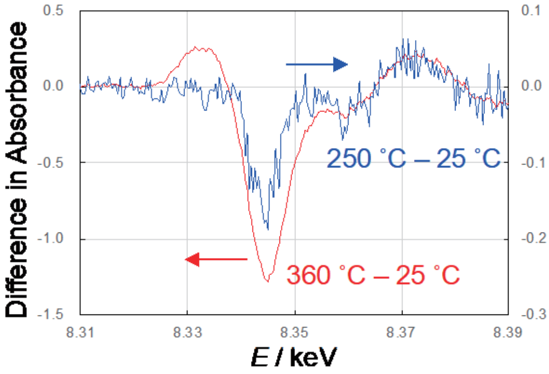

Fig. 3 The difference XANES spectrum between 250 °C and 25 °C (blue) and between 360 °C and 25 °C (red).

Finally, in order to check the validity of the present LCF analysis during the conversion process from Ni(II) to Ni(0), the reproducibility of the observed XANES spectrum at 350 °C is shown in Fig. 4 by comparing with the calculated spectrum using the composition given in Fig. 2. The calculated spectrum with the mole fraction of the Ni(II) hydrate and metallic Ni(0), 0.46 and 0.54, respectively, is well in agreement with the observed one, suggesting that two Ni species are coexisting at 350 °C.

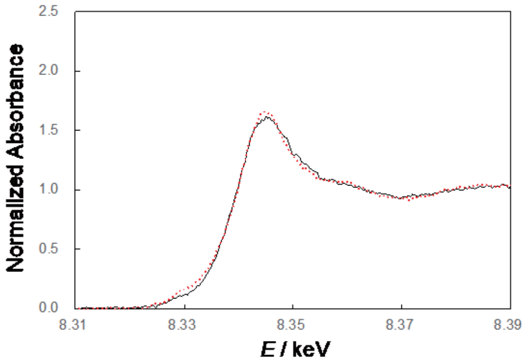

Fig. 4 The observed XANES spectrum (solid line, black) at 350 °C is compared with the calculated spectrum (dotted line, red) depicted using the mole fraction of 0.46 for NiO and 0.54 for Ni metal.

4. Conclusion

In this study, the change in chemical state of the Ni(II) hydrate on ZnO during the TPR process by H_2 has been analyzed using the *in-situ* XAFS method. It has been clarified that $Ni(H_2O)_6(NO_3)_2$ is reduced to metallic Ni at 360 °C without reducing the supporting material ZnO. There was a phenomenon that the white line intensity of Ni(II) decreased in the temperature range lower than 250 °C, and it was not due to the partial reduction but due to the decrease in symmetry around the Ni(II) center. This study has revealed that the detail reaction conditions for the reduction treatment are determined for forming metallic Ni nanoparticles on ZnO. This is important information for performing a catalytic reaction using metallic Ni as an active species on ZnO.

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