

# Characterization of Supported Nickel Species on Alumina

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## 1. Introduction

The Ni catalyst supported on alumina is used to form hydrogen by the CO<sub>2</sub> and steam reforming reactions of methane, and the reactions are very important to solve the energy problems of the modern society. The supported Ni catalysts on alumina show good performance for the conversion, but the efficiency and the lifetime are largely dependent on the preparation method of the catalyst. Such properties are related to the reducibility and stability of the Ni species. Thus, the speciation of the Ni species in the atomic scale is necessary to understand the reduction/oxidation reactivity. In this study, the chemical states of the Ni species have been analyzed by means of the XAFS spectroscopy for Ni catalysts prepared by some different methods, such as the co-precipitation and impregnation method, and under the different temperature conditions for the reduction process. The difference of the generated Ni species is also clarified when the supporting material is changed between  $\alpha$ - and  $\gamma$ -alumina for the impregnation method.

## 2. Experimental

The precipitates were generated from an aqueous solution of Al(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O by adjusting pH to ca. 9 using the aqueous solution of Na<sub>2</sub>CO<sub>3</sub> and were aged for 1 h at 363 K. The precipitates were collected by the filtration, washed by water, dried at 393 K for 12 h, and calcined at 773 K in air for 3 h. The Ni catalyst prepared by the co-precipitation method as described above was thus supported on  $\gamma$ -alumina in considering the calcination temperature, and was reduced under the diluted hydrogen flow (5 vol.% balanced by Ar, 200 cm<sup>3</sup>/min) at three different temperatures of 673 K, 773 K, and 873 K. The aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O was dried over  $\alpha$ -alumina and  $\gamma$ -alumina for the impregnation method. The obtained powders were calcined at 773 K in air for 3 h, and were reduced under the H<sub>2</sub> flow as the same way to that prepared by the co-precipitation method. The reduced Ni species were oxidized under the diluted O<sub>2</sub> flow (5 vol.% balanced by Ar, 200 cm<sup>3</sup>/min) at 773 K to check the reversibility of the redox processes. The XAFS measurements were carried out at BL-3 of SR Center, Ritsumeikan University at the vicinity of the Ni K edge in the transmission mode. The Si(220) double crystal monochromator was used to obtain the monochromatized X-ray. The incident and transmitted X-ray intensity was measured by the ionization chambers flowed by the mixture gas of N<sub>2</sub> and Ar. All powder samples were diluted with the BN powder and formed as the pellet.

### 3. Results and Discussion

The XANES spectra and the Fourier transform functions are shown in Fig. 1 for the Ni catalysts prepared in this study by comparing with those of Ni foil and NiO. The Ni species prepared by the impregnation method on  $\alpha$ -alumina is concluded to be NiO before the reduction as seen in Fig. 1(b), and is quantitatively reduced to the metallic Ni nanoparticles by the reduction at 873 K. The particle radius is estimated to be 42 nm on the basis of the X-ray diffraction pattern, and is almost consistent with the estimation from the Ni–Ni coordination number of 9.7 determined by the EXAFS analysis. The NiO precursor is remained for the samples reduced at lower temperatures. The impregnation method is found to form different Ni species on  $\gamma$ -alumina as seen in Fig. 1(c), and the formed Ni species is similar to that in the Ni catalyst prepared by the co-precipitation method according to the XAFS results shown by Fig. 1(d). The Fourier transform function for the reduced Ni catalyst prepared by the co-precipitation method is similar to that by the impregnation method on  $\gamma$ -alumina. This is reasonable because the  $\gamma$ -alumina is formed at the calcined temperature of 773 K for the co-precipitation method. The XANES spectra for the Ni catalysts on  $\gamma$ -alumina (c and d in Fig. 1) show the characteristics of the divalent Ni species but the peak energy of the white line is clearly higher than that of NiO. The nearest neighboring interaction around the Ni center is slightly longer than that of NiO and the next nearest interaction is largely contracted as shown in Fig. 1B. It is found by the EXAFS analysis that these characteristics are reasonably explained by the formation of nickel aluminate on  $\gamma$ -alumina independent of the preparation method.

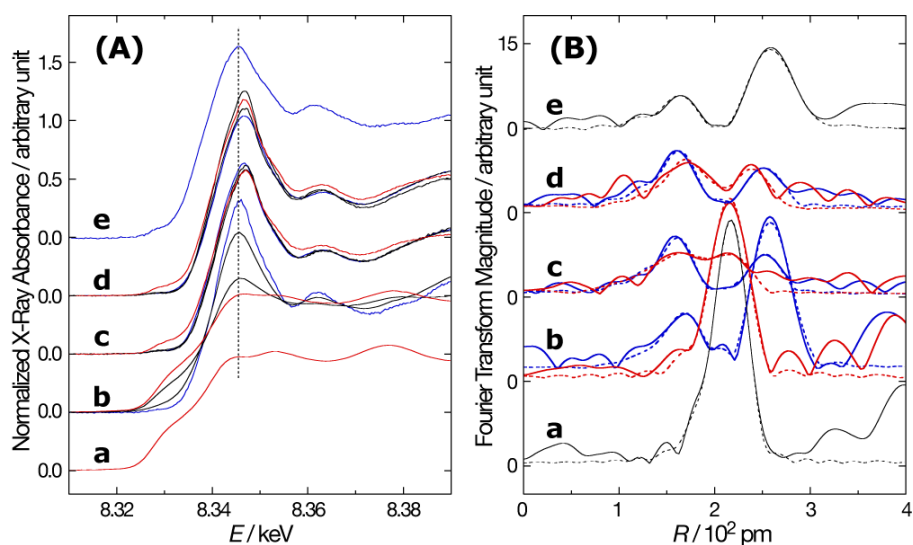


Fig. 1: XANES spectra at the Ni K edge (A) and Fourier transform functions (B) of the Ni catalysts supported on  $\text{Al}_2\text{O}_3$  (b–d) are compared with those of Ni foil (a) and NiO (e). The Ni catalyst is prepared by the impregnation method on  $\alpha$ -alumina (b), the impregnation method on  $\gamma$ -alumina (c), and the co-precipitation method (d). In the panel A, the XANES spectra are given for the calcined samples before reduction (blue) and the reduced samples at 673 (black), 773 (black), and 873 K (red). In the panel B, the functions of the reduced samples (red) are compared with those of the calcined samples (blue). The dotted lines in B represent the fitted function by the curve fitting procedure.