

# XAFS Analysis of Ni(II) Species Supported on Zeolite

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## 1. Introduction

The Ni species on zeolite supported by the ion-exchange method varies its chemical state in response to pH of the aqueous solution of the Ni precursor for the ion-exchange process. In this study, the zeolite-supported Ni catalysts were prepared by the ion-exchange method by changing the pH values from 2 to 12, and the supported species of Ni<sup>2+</sup> has been clarified by means of the X-ray adsorption fine structure (XAFS) technique for the prepared catalysts. Four kinds of zeolite (FAU, MOR, MFI, and LTA) with the different pore structure and the Si/Al ratio have been used as the supporting material of Ni.

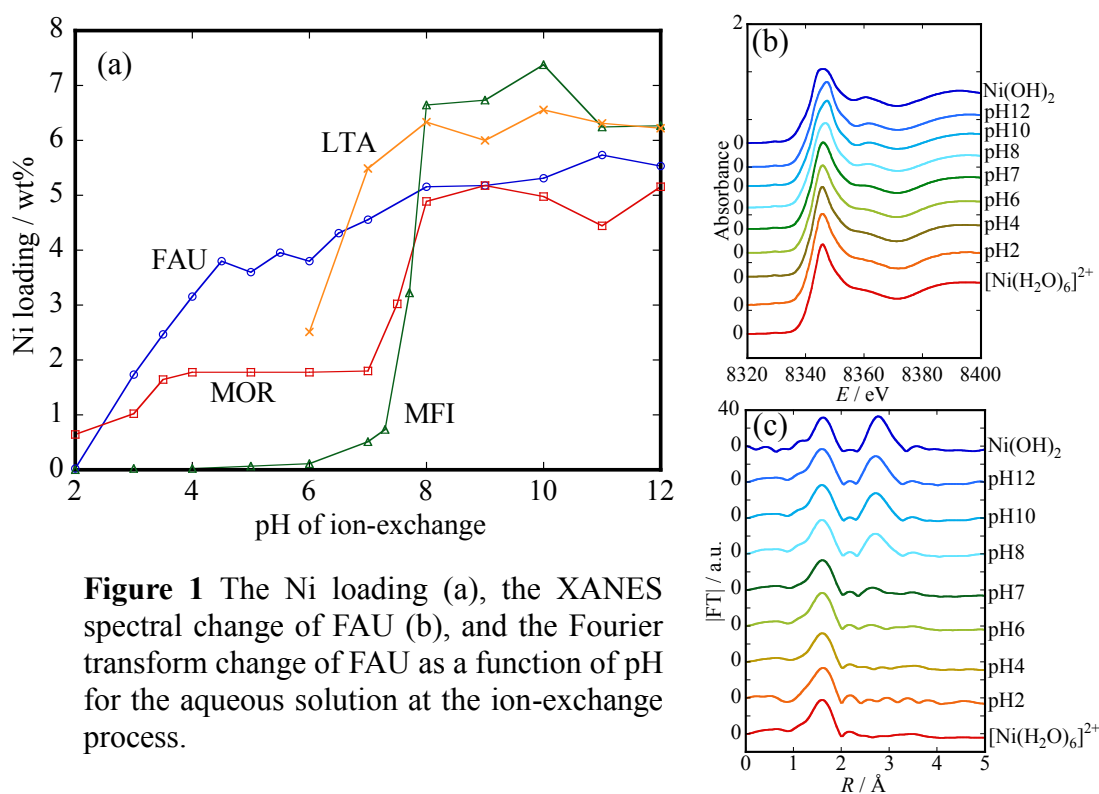
## 2. Experimental

The powder of zeolite was added into an ion-exchanged water and the pH value was initially adjusted to 3.0. After the addition of an aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>, the pH value was controlled in the range from 2 to 12 using an aqueous solutions of NaOH and HNO<sub>3</sub>. After continuous stirring for 3 h by keeping the pH value, the ion-exchanged zeolite powder was filtered, washed by water with the same pH values, and dried for 12 h at 60 °C. The amount of the supported Ni species was determined by the X-ray fluorescence analysis. The XAFS measurements at the Ni K edge were carried out at BL-3 of SR center (Ritsumeikan University) and BL-9C of Photon Factory (KEK).

## 3. Results and Discussion

Figure 1(a) shows the loading of the supported Ni species as a function of pH. In acidic solutions with the pH value less than 7, the Ni loading is the order of FAU > MOR > MFI. The smallest Si/Al ratio of FAU leads to the largest loading because of the most ion-exchange sites. The gradual increase of the Ni loading with increasing pH is explained by the proton

dissociation from zeolite. The saturated Ni loading of 4.6 wt% (FAU) and 1.8 wt% (MOR) correlates with the number of the base sites in zeolite. The XAFS analysis given in Figure 1(b) and (c) indicates that the Ni ion is exchanged with the 6-coordinate octahedral first shell composed of six O atoms, which is identical to the hydrated complex in water. The Ni loading in MFI is unexpectedly small in considering its middle Si/Al ratio between FAU and MOR. The divalent  $\text{Ni}^{2+}$  ion is not strongly adsorbed due to the lack of the adjacent Al sites in the MFI zeolite. At the pH values above 7, the Ni loading was commonly reached to around 6 wt% for all zeolites. Furthermore, the XAFS analysis revealed that the supported species was  $\text{Ni}(\text{OH})_2$ , which is generated by the hydrolysis in aqueous solution. A slight difference of the XANES spectra and the Fourier transforms between the supported  $\text{Ni}(\text{OH})_2$  species and the bulk  $\text{Ni}(\text{OH})_2$  suggests the formation of the layered  $\text{Ni}(\text{OH})_2$  state [1].



**Figure 1** The Ni loading (a), the XANES spectral change of FAU (b), and the Fourier transform change of FAU as a function of pH for the aqueous solution at the ion-exchange process.

## Reference

- [1] Y. Ichiyanagi, H. Kondoh, T. Yokoma, K. Okamoto, K. Nagai, and T. Ohta, *Chem. Phys. Lett.*, **379**, 345 (2003).