

## Interaction between Ni Species and Supporting Material for Ni Catalysts Prepared by Impregnation Method

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### 1 Introduction

Dispersion of active species on the supporting material is an important factor to improve the catalytic activity. It has been reported that the drying conditions affect the dispersion for Ni catalysts prepared by the impregnation method [1]. Therefore, the understanding on the chemical state of the Ni species during the drying process leads to contribute to the improvement of the catalytic performance. The purpose of this study is to clarify the interaction between the Ni species and the supporting materials using the *in-situ* X-ray absorption fine structure (XAFS) technique during the drying process for the impregnation preparation.

### 2 Experiment

The Ni catalysts supported on SiO<sub>2</sub> and ZrO<sub>2</sub> were prepared by the impregnation method. The hexahydrate of nickel nitrate was dissolved in deionized water, and the solution was immersed in the supporting material powder under the incipient wetness condition. The samples were dried under the flow of O<sub>2</sub>/He at room temperature for 40 min, and the *in-situ* XAFS measurements were carried out at BL-9C of the Photon Factory (KEK) during the drying process.

### 3 Results and Discussion

The XANES spectral changes of Ni/SiO<sub>2</sub> and Ni/ZrO<sub>2</sub> are given in Fig. 1(A). The observed XANES spectrum and its Fourier transform (FT) function at the beginning of the drying process were in good agreement with those of the aqueous solution of the Ni(II) nitrate, indicating the formation of the octahedral [Ni(OH<sub>2</sub>)<sub>6</sub>]<sup>2+</sup> species on the supporting material. The X-ray absorbance at the white line peak was decreased during the drying process. It is suggested that the symmetry lowering around the Ni ion takes place during the drying process [2] and that such the distortion is generated by the evaporation of water molecules in bulk.

The FT functions also change during the drying process as shown in Fig. 1(B). It was observed that the FT peak intensity decreased during the drying process and that a weak and broad peak was appeared at around 2.5 Å for both samples. The main peak at 1.6 Å is attributed to the interaction with the O atoms existed in the first coordination shell of the Ni(II) ion. The developed new peak can be assigned to the interaction between the Ni atom and the Zr or Si atoms in the supporting material, because the final peak intensity for Ni/ZrO<sub>2</sub> was slightly larger than that for Ni/SiO<sub>2</sub> in response to the enhanced

scattering ability of Zr than Si. The direct observation of the interaction peak between the supported Ni atom and the supporting material indicates that the surface O atom of the supporting oxide binds to the Ni ion. The main Ni–O peak includes such the O atoms.

The EXAFS analysis for the Ni–O interaction peak revealed that the coordination number (*N*) and the bond distance (*R*) were respectively 6 and 2.05 Å for both samples and were almost constant during the drying process. The bound water is replaced with the surface O atom of ZrO<sub>2</sub> or SiO<sub>2</sub> to keep the 6-coordinate structure for the Ni(II) species. The apparent decrease of the FT peak height is due to the increased Debye-Waller factor, indicating the atomic disorder in the first coordination shell due to the interaction at the particle surface of the supporting material. The *N* and *R* value for the Ni–Zr interaction was successfully determined to be 1 and 2.93 Å, respectively.

In summary, the Ni species directly interacting with the supporting material was detected during the drying process. It was suggested that one or more O atoms at the surface of ZrO<sub>2</sub> or SiO<sub>2</sub> were included in the octahedral first-coordination shell of the Ni(II) ion. The succeeding calcination promotes the aggregation of the Ni(II) species to form the NiO particles.

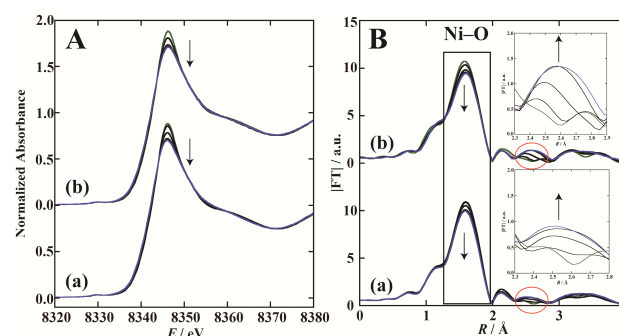


Fig. 1: Ni-K edge XANES spectral change (A) and Fourier transform function (B) for Ni/SiO<sub>2</sub> (a) and Ni/ZrO<sub>2</sub> (b).

### References

- [1] R. Banerjee and P. A. Crozier, *J. Phys. Chem. C*, **116**, 11486 (2012).
- [2] M. Benfatto, J. A. Solera, J. Chaboy, M. G. Proietti, and J. Garcia, *Phys. Rev. B*, **56**, 2447(1997).

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