

Dynamic Chemical State Change of SiO₂-Supported Ni Species under CO–NO Reaction Conditions As Studied by Time-Resolved DXAFS Technique

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1 Introduction

The characterization of SiO₂-supported Ni species has been systematically performed under the reductive (H₂ and CO) and oxidative (O₂ and NO) reaction gas atmosphere by means of *in-situ* XAFS method at elevated temperature [1]. The XAFS analysis revealed that the NiO species on SiO₂ was quantitatively reduced to metallic Ni(0) and that the reduction reaction completed at *ca.* 750 K. It was also evaluated that the oxidation of the supported Ni(0) species to NiO occurred at *ca.* 800 K under the dilute NO gas flow. The chemical conversion of the Ni species on SiO₂ offers an idea that the oxidation of CO and the reduction of NO (the CO–NO reaction) simultaneously progress under the existence of the SiO₂-supported Ni catalyst at the elevated temperature higher than 800 K. The CO–NO reaction and its achievement without any rare metal catalysts are important to solve the environmental problems due to the toxic emissions produced in the modern society.

The dynamic and cyclic changeover of the chemical state is expected for the SiO₂-supported Ni species, and thus the static observation is not adequate to evaluate the contributions of the Ni species to the CO–NO reaction. In this study, the time-resolved DXAFS experiments have been applied to detect the dynamic chemical state change of the Ni species after a rapid injection of the reaction gas in order to clarify the catalytically active Ni species.

2 Experiment

The SiO₂-supported Ni catalyst was prepared by the impregnation method using an aqueous solution of nitrate salt of Ni. The obtained sample was calcined at 600 °C in air. An adequate amount of sample powder was mounted in a SUS tube, and it was installed in an observation chamber. The time-resolved DXAFS measurements were performed at NW2A (PF-AR, KEK) using a Si(111) bent crystal as the polychromator and a photodiode array detector with a CsI(Tl) phosphor. The reaction gas (CO, NO, and their mixture) was injected to the evacuated sample chamber to start the CO–NO reaction. The successive acquisition of the transmitted intensity with the typical exposure time of 30 ms was synchronized by the gas injection. The time-resolved DXAFS measurements were carried out at 750 °C.

3 Results and Discussion

The XANES spectral change for the reduction of NiO by CO and the oxidation of metallic Ni(0) by NO was shown in Fig. 1. Both of the reactions were clearly proceeded at 750 °C, and the apparent reaction rate was dependent on the injected gas pressure. The typical observation time was *ca.* 120 s for the reduction and *ca.*

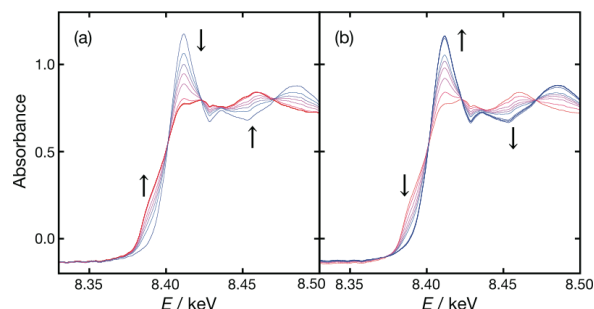


Fig. 1: Dynamic XANES change for the reduction (a) of NiO by CO and the oxidation (b) of metallic Ni(0) by NO after the rapid injection of reaction gas measured at 750 °C.

100 s for the oxidation. The appearance of some isosbestic points indicates no existence of other metastable Ni species between NiO and Ni(0).

The time-course change of the observed X-ray absorbance at the white line peak energy of NiO was given in Fig. 2 for the reduction of NiO by CO, the oxidation of Ni(0) by NO, and the reaction of Ni(0) with the CO and NO gas mixture. The single step reaction was observed for the one-way reactions between NiO and Ni(0), whereas the initial change from Ni(0) to NiO by the oxidation due to NO was returned by the existence of CO with the reducing ability. The two-phase change suggests that the CO–NO reaction is actually undertaken and catalyzed by the SiO₂-supported Ni catalyst.

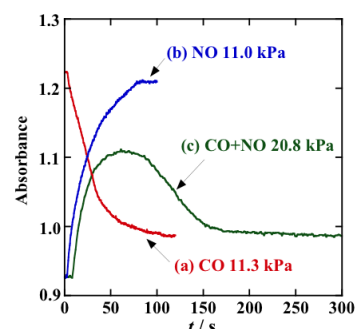


Fig. 2: X-Ray absorbance change for the reduction of NiO by CO, the oxidation of Ni(0) by NO, and the CO–NO reaction of Ni(0).

Reference

[1] T. Matsuoka, *et al.*, *PF Activity Report 2013*, **31B**, 262 (2014).

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