

Dynamic Chemical State Conversion of SiO₂-Supported Ni Catalyst under CO–NO Reaction Conditions by Means of Time-Resolved DXAFS Technique

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1 Introduction

The *in-situ* characterization of SiO₂-supported Ni species has been performed under the reaction gas conditions such as H₂, CO, O₂, and NO by means of the XAFS technique at elevated temperatures [1]. The XAFS analysis revealed that the formed NiO species on SiO₂ was quantitatively reduced to Ni(0) during the heating process under CO. It was also evaluated that the oxidation of the Ni(0) species to NiO occurred under the NO gas condition. Because both redox reactions are completed at 873 K, the dynamic and cyclic conversion of the chemical state is expected for the SiO₂-supported Ni species and the redox cycle proceeds the CO–NO reaction. In this study, the time-resolved DXAFS technique has been applied to observe the dynamic chemical conversion of the Ni species after a rapid injection of the reaction gas to demonstrate the catalytic activity of the SiO₂-supported Ni species.

2 Experiment

The SiO₂-supported Ni catalyst (5 wt%) was prepared by the impregnation method using an aqueous solution of Ni(NO₃)₂·6H₂O. The obtained sample was calcined at 873 K in air for 3 h. An adequate amount of calcined powder was mounted in a SUS tube, and it was located in an observation cell. The 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 sample was reduced by only CO at 873 K as the pretreatment. The mixed gases of CO and NO was rapidly injected to the evacuated cell to start the redox reactions of the Ni catalyst. The successive acquisition of the transmitted intensity with the exposure time of 40 ms were triggered by the gas injection.

3 Results and Discussion

The XANES spectral change was shown in Fig. 1 after the injection of the mixed gas of CO and NO. The early XANES change before 70 s clearly indicated the partial oxidation of the Ni species to NiO. The Ni species was equilibrated without a marked change of the XANES spectrum after 70 s, and then the opposite spectral change to regenerate the initial Ni(0) state was observed after 120 s. These sequential changes indicate that the NO molecule acts as the oxidizing agent to form NiO from Ni(0) and that the formed NiO is reduced by the coexisting CO molecule. When the oxidation rate by NO and the reduction rate by CO are comparable, the observed Ni species is equilibrated as the mixture of NiO and Ni(0).

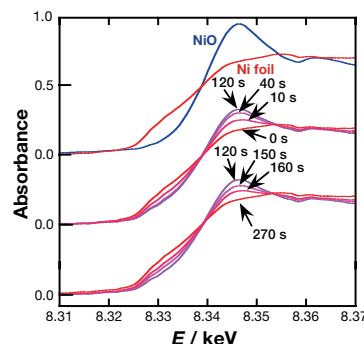


Fig. 1: Dynamic XANES change for the Ni(0) species after a rapid injection of CO–NO gas at 873 K. The partial pressures of CO and NO were equivalent, and the total pressure was 3.4 kPa.

The oxidation of CO and the reduction of NO are simultaneously proceeded under such conditions, indicating the achievement of the catalysis system for the CO–NO reaction by the SiO₂-supported Ni catalyst. The oxidation rate is decreased by the consumption of NO, and thus the Ni(0) species regenerates when the reduction rate by CO exceeds the oxidation rate. The variations of the mixed gas composition showed the similar time-course change of the Ni species as shown in Fig. 2. The major gas decided the final chemical state of the Ni species and the composition of the transient NiO species.

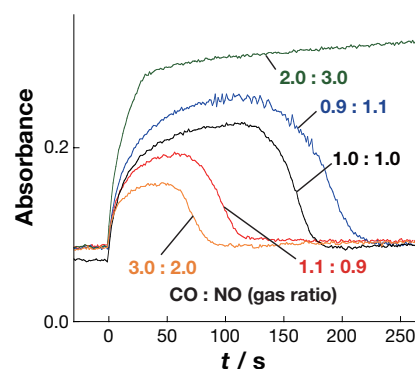


Fig. 2: X-ray absorbance change at the white line peak energy of NiO plotted as a function of time after a rapid injection of the mixed gas at 873 K. The total gas pressure was 3.4 kPa.

Reference

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

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