

***In-Situ* XAFS Study of Redox Reactions by CO and NO for Supported Nickel Catalyst on Silica**

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1. Introduction

The supported rare metal (Rh, Pd, and Pt) catalysts effectively detoxify a harmful emission gas containing CO and NO at an elevated temperature. The evaluations of the reactivity of alternative metal catalysts are very important to reduce the cost for the purification of environment because of the rarity of such metal elements. Nickel is one of promising candidates of the alternative metal catalysts, and the researches to develop new Ni-based catalysts are now widely performed. In addition to the evaluation of their activity and/or selectivity, the characterization of the active species under the reaction conditions is also important to enhance the actual utilization of the Ni-based catalysts. In this study, the chemical state of the supported Ni species has been clarified by means of the *in-situ* X-ray absorption fine structure (XAFS) technique for the Ni catalyst supported on SiO₂ under the dilute CO and NO gas atmosphere in a wide temperature range. The available redox property of the Ni species is essential to construct the Ni-based catalysis system for the CO–NO reaction.

2. Experimental

The supported NiO catalyst (10 wt%) was prepared by the impregnation method using an aqueous solution of nickel nitrate and SiO₂. The obtained sample was calcined at 827 K in air, and the formation of NiO was confirmed by XRD.

The *in-situ* XAFS measurements were carried out at BL-3 of SR Center (Ritsumeikan University) and BL-9C of the Photon Factory (KEK) at the Ni K edge in the transmission mode. The prepared sample was first treated under CO gas flow diluted by He in the temperature range from room temperature to 1023 K. The sample was kept under the dilute CO flow during the cooling process. The atmosphere gas was switched to NO diluted by He, and the temperature was raised up to 973 K. The XAFS measurements were performed during the temperature-programmed reduction/oxidation process by CO/NO, respectively.

3. Results and discussion

Figure 1 shows the XANES spectral change under the CO (a) and NO (b) gas flow. The initial NiO was quantitatively reduced to Ni(0) during the treatment under CO. The final spectrum of Fig. 1(a) is in agreement with that of Ni foil. The reduced Ni(0) species was found to be reversibly oxidized to NiO by the NO gas flow.

The coordination numbers for Ni–Ni of Ni(0) and Ni–O of NiO are plotted in Fig. 2 as a function of temperature. The values were compared to those for the reduction by H₂ and for the oxidation by O₂ reported previously [1]. It was found that the reduction of NiO by CO proceeded at higher temperature because of the lower reducing ability of CO than H₂. The final coordination number of Ni–Ni under CO is smaller than that under H₂, which indicates that the smaller Ni(0) particles are generated at the reduction by CO. The CO adsorption on the formed Ni(0) particle may inhibit the aggregation of the Ni(0) species.

The oxidation temperature of Ni(0) by NO shown in Fig. 2(B) indicates that the NO molecules are reduced by the supported Ni(0) species at temperature range higher than *ca.* 700 K. The present results suggest that the oxidation of CO and the reduction of NO are simultaneously achieved by the mediation of the supported Ni species at such temperature range.

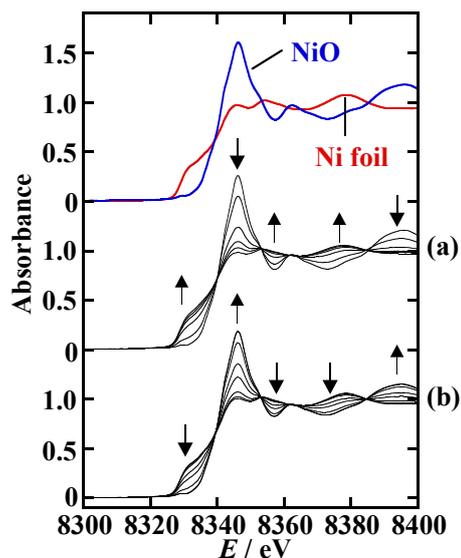


Fig. 1. XANES change during reduction by CO (a) and oxidation by NO (b).

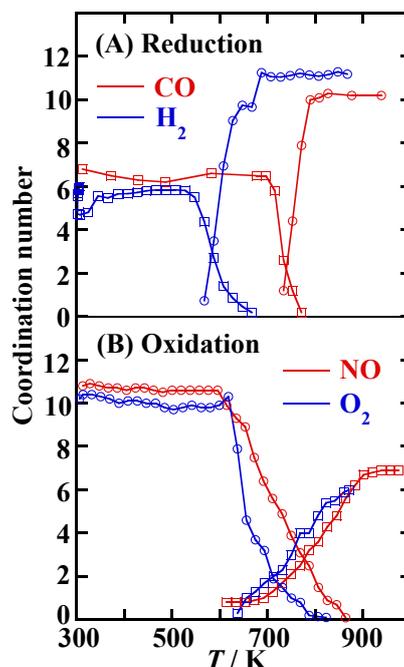


Fig. 2. The coordination number for Ni–Ni of Ni(0) (○) and for Ni–O in NiO (□) during the reduction (A) and oxidation (B) processes.

Reference

[1] S. Yamashita, M. Katayama, and Y. Inada, *J. Phys. Conf. Ser.*, **430**, 012051 (2013).