

Dynamic Chemical State Conversion of Nickel Species Supported on Silica under CO–NO Reaction Conditions

Shohei Yamashita, Misaki Katayama and Yasuhiro Inada*

College of Life Sciences, Department of Applied Chemistry, Ritsumeikan University, Kusatsu, Japan

*E-mail: yinada@fc.ritsumeik.ac.jp

INTRODUCTION

The supported rare metal (e.g. Pt, Pd and Rh) catalysts are widely used to detoxify a harmful emission gas containing CO and NO. The investigations on the reactivity of the alternative metal catalysts are important for achieving the effective purification to keep the environment. Nickel is one of promising candidates of such alternative metal catalysts, and thus, in this study, the dynamic chemical-state conversion of the Ni species supported on SiO₂ under the CO–NO reaction conditions has been first demonstrated by means of the time-resolved dispersive XAFS (DXAFS) technique [1].

EXPERIMENTAL

The supported NiO catalyst (5 wt%) was prepared by the impregnation method using Ni(NO₃)₂•6H₂O and SiO₂. The obtained powder was calcined at 873 K in air.

The DXAFS measurements were carried out at NW2A station of PF-AR (KEK, Japan). Polychromatic X-rays were obtained with a Si(111) bent crystal (Bragg type) and were detected by a linear photodiode array detector equipped with a scintillator (CsI:Tl). Sample powder was placed in an *in-situ* cell for the DXAFS measurement, and the reaction gas (CO, NO, and their mixture) was rapidly introduced into the evacuated cell at 873 K to follow the chemical-state conversion of the Ni species.

RESULTS and DISCUSSION

The temperature-programmed *in-situ* XAFS analyses have clarified that both the reduction of NiO to Ni(0) by CO and the oxidation of Ni(0) to NiO by NO proceeds at above 873 K. It means that the oxidation of CO and the reduction of NO are potentially driven via the

chemical-state conversion of the supported Ni species under the coexisting condition of CO and NO.

Dynamic X-ray absorbance changes at 873 K after a rapid exposure of the supported Ni(0) catalyst to the mixed gas of CO and NO were shown in Figure 1 together with the XANES spectral change. The initial spectrum of Ni(0) first approached to that of NiO within ca. 50 s, indicating that the oxidation of Ni(0) by NO was predominant rather than the reduction of the formed NiO species by CO, because the oxidation of Ni(0) is faster than the reduction of NiO under the present conditions. The reaction direction was suddenly turned back to return to the initial Ni(0) state. In addition, the amount of the transient NiO species and the length of the transition period were sensitively varied by the injected gas composition, i.e., the larger amount of NiO and the longer transition period were observed under the gas composition with the larger amount of NO. Furthermore, the gas chromatography analysis proved the existence of CO₂ and N₂O in the produced gas. The present XAFS analyses indicate that the oxidation of CO and the reduction of NO are catalytically driven by the reversible chemical-state conversion of the supported Ni species between Ni(0) and NiO.

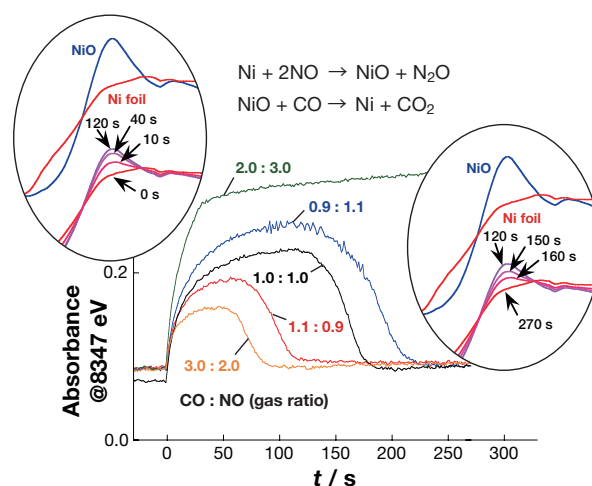


Fig.1 The X-ray absorbance change at 8347 eV is plotted as a function of time after an injection of the mixed gas of CO and NO at 873 K with various compositions. The XANES change is given in insets.

REFERENCES

[1] Y. Inada, A. Suzuki, Y. Niwa and M. Nomura, AIP Conf. Proc., 879 (2006) 1230.