Photon Factory Activity Report 2013 #31 (2014) **B**

BL-12C/2013G596

In-situ XAFS study for reduction by CO of supported NiO catalysts on various SiO_2

Tetsuya Matsuoka, Shohei Yamashita, Misaki Katayama, and Yasuhiro Inada
Graduate School of Life Sciences, Ritsumeikan University,
1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan

1 Introduction

The Ni-based catalysts are widely used for many reactions, such as methane steam reforming, methane dry reforming, and water gas shift reaction. Because the CO gas is contained in these reaction systems, it is important to understand the reaction characteristics between the supported NiO species and CO for the elucidation of the reaction mechanism and the development of new catalysts with improved performance. In this study, the chemical state of the Ni species has been analyzed under the CO atmosphere at elevated temperatures by mean of *in-situ* X-ray absorption fine structure (XAFS) spectroscopy.

2 Experiment

Four kinds of NiO catalysts supported on SiO_2 were prepared using SiO_2 with and without the mesoporous structure. For the former, two kinds of SiO_2 were used with the specific surface area of 190 (SIO-10) and 390 m^2/g (SIO-39). The prepared SBA-15 (720 m^2/g) and MCM-41 (900 m^2/g) were used as the mesoporous SiO_2. The average pore size was 2.1 (SBA-15) and 3.6 nm (MCM-41). The supported NiO catalysts were prepared by the impregnation method using the aqueous solution of nickel nitrate. The obtained powder was calcined in air at 827 K. The formation of NiO was confirmed by the XAFS and X-ray diffraction measurements.

The *in-situ* XAFS experiments were carried out at BL-12C of the Photon Factory (KEK) at the Ni K edge in the transmission mode. The temperature programmed reduction (TPR) by CO was carried out to determine the supported Ni species in the temperature range from room temperature to 1023 K.

3 Results and Discussion

The observed XAFS spectra clearly showed that the calcined NiO species was reduced to metallic Ni(0) during the TPR process. The component Ni species were analyzed by the linear combination fitting of the observed XANES spectrum using the standard samples (NiO and Ni foil). Figure 1 shows the composition change of the NiO species as a function of temperature for four Ni catalysts on various SiO_2.

The supported NiO species was found to be completely reduced at about 850 K for SIO-10 and SIO-39 without the mesoporous structure. A previous *in-situ* XAFS study for the reduction of the supported NiO on SIO-10 by H_2 has revealed that the supported NiO species is quantitatively reduced at about 700 K [1]. The much higher temperature for the reduction of NiO by CO is ascribed to the lower reducing ability of CO than H_2.

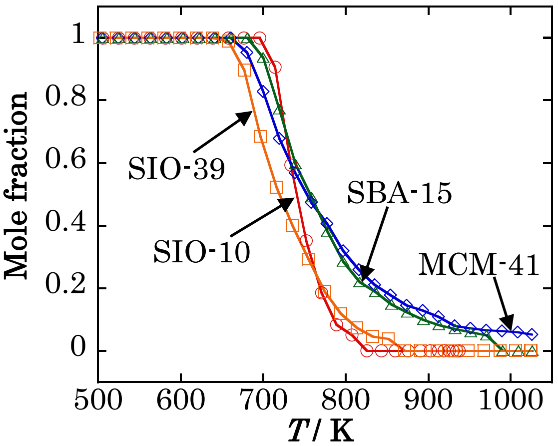

Fig 1. Mole fraction of NiO as a function of temperature during the TPR process by CO on various SiO_2.

It was found that a part of NiO was remained on SBA-15 and MCM-41 at 850 K, at which the reduction was completed on SIO-10 and SIO-39. The mesoporous structure of SiO_2 contributes to resist the reduction. Because the diffusion of CO molecules is disturbed by the mesoporous structure of SiO_2, the NiO species supported in the pores are thermodynamically more stable than those supported outside the pores. Such higher shift of the reduction temperature has been similarly observed for the reduction by H_2.

The almost same reduction temperature between SBA-15 and MCM-41 suggests that the difference in the pore size and structure does not affect to the diffusion of CO. The mole fraction of the remaining NiO at 850 K was estimated to be about 0.2 as seen in Figure 1. This suggests that about 80 percent of the NiO species is supported outside the pores of SBA-15 and MCM-41. Such NiO species are reduced at similar temperature to those on SIO-10 and SIO-39. The remaining 20 percent of the NiO species located inside the pores is thermodynamically stable, and much higher temperature is necessary to complete the reduction. The present *in-situ* XAFS study has revealed that the mixed Ni species may exist at the temperature higher than 850 K under the CO atmosphere.

Reference

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