

In-situ XAFS observation of reduction of nickel oxides

Masao KIMURA^{*1}, Akane SUZUKI², Noriaki OHTA³, Yasuhiro NIWA², Yasuhiro INADA²,
and Masaharu NOMURA²

¹Adv. Tech. Res. Lab., Nippon Steel Corp., Futtsu, Chiba, 293-8511, Japan

²Photon Factory, KEK, Tsukuba, Ibaraki, 305-0801, Japan

³Nippon Steel Technoresearch, Chiba 293-8500, Japan

Introduction

Catalytic reforming of CH₄ with CO₂ to produce synthesis gas has gained a growing interest recently, considering chemical utilization of natural gas and CO₂ [1]. Several nickel catalysts for the CO₂ reforming have been developed. It has been reported that nickel magnesia solid solution catalysts reduced at high temperature showed excellent activity and stability for CO₂ reforming of methane [2]. It has been shown that NiO/MgO catalyst has excellent stability [3]. Reduction reaction of nickel oxide and metal oxide including nickel is of a great importance to research and develop nickel catalysts for the CO₂ reforming. In this study, *in-situ* XAFS (X-ray Absorption Fine Structure) technique has been developed to observe structure changes of nickel oxide in H₂/He gas at high temperatures.

Experiments

Figure 1 shows the main part of a newly developed reaction cell. The cell is made of stainless steel with Kapton-film windows which X-ray beam can pass through. Powder specimen was kept inside a holder in a shape of cylinder. The thickness of specimen is about 4 mm.

The holder was sealed in the center of the cell. The specimen was heated up to *ca.* 1073 K by rod heaters located above the specimen under a flow of H₂/He gas. The temperature of the specimen was monitored with a thermo-couple located above the specimen holder.

NiO powder was mixed with BN powder to obtain XAFS spectra with high quality and packed inside the holder. The specimen was heated in a gas of 3%H₂/97%He with a flow rate of 200 ml/min. XAFS spectra at Ni K-edge were measured in a transmission geometry at BL-12C and NW2A at PF, KEK, Tsukuba, Japan.

Results and Discussion

XAFS spectra were observed at different times: *t* after the temperature reached a specific temperature. No difference was observed among spectra of *t* = 5, 10, 20 and 40 min. at all temperatures.

Figure 2 shows the radial distribution function (RDF) around Ni obtained by *in situ* measurements at *t* = 5 min. RDF before heating shows that the specimen is in the state of NiO. As the temperature increases, peak intensities corresponding to NiO decrease and those of Ni metal increase. Near *T* = 983K, peaks corresponding to Ni

metal were clearly observed in RDF. At *T* = 1073K, only peaks corresponding to Ni metal were observed in RDF.

After experiments, microstructures of the specimen were observed with SEM and TEM. The specimen heated up to *T* = 1073K contains fine grains of Ni metal with a size less than 1.0 μm in diameter among BN grains. There was no clear indication of reaction between Ni and BN grains.

It can be concluded that the reduction of NiO to Ni in a flow of H₂/He gas can be clearly observed by the new system. The reduction reaction completes at *T* = *ca.* 1073 K. Mixture of NiO with BN has no detectable effects on reduction reaction.

This system is being applied to Ni base catalyst. Combination of this system with quick-XAFS may be powerful to observe dynamics of reduction of Ni base catalyst and formation of Ni nano particles.

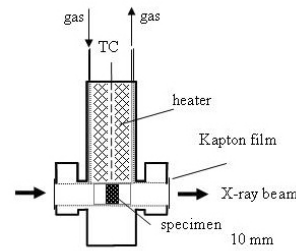


Fig. 1 The main part of a newly developed reaction cell.

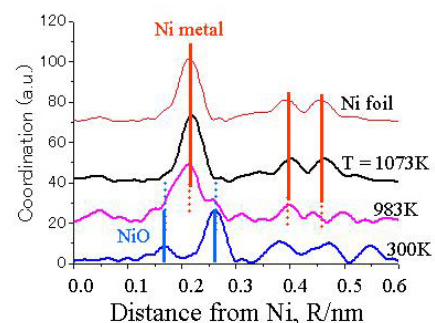


Fig. 2 Change of RDF around Ni obtained by *in situ* measurements during heating in H₂/He gas.

References

- [1] B. Delmon, Appl. Catal., **B1**, 139 (1992).
- [2] K. Fujimoto et al, Energy Conversion and Managements, **33**, 529 (1992).
- [3] Y. H. Hu and E. Ruckenstein, J. Catal., **163**, 306 (1996).

*kimura@re.nsc.co.jp