Chemistry

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In situ XAFS observation of reduction of $Mg_xNi_{1-x}O$ catalyst

Masao KIMURA[1], Noriaki OHTA[2], Hisatsugu KITAGUCHI[1], Kimihito SUZUKI[1], Ken-ichiro FUJIMOTO[1], Yasuhiro NIWA[3], Yasuhiro INADA[3] and Masaharu NOMURA[3]
[1] Adv. Tech. Res. Lab., Nippon Steel Corp., Futtsu, Chiba, 293-8511, Japan
[2] Nippon Steel Technoresearch, Chiba 293-8500, Japan
[3] Photon Factory, KEK, Tsukuba, Ibaraki, 305-0801, Japan

Introduction

Catalytic reforming of CH_4 with CO_2 to produce synthesis gas has gained a growing interest recently, considering chemical utilization of natural gas and CO_2 [1]. Several nickel catalysts for the CO_2 reforming have been developed. It has been reported that nickel magnesia solid solution catalysts ($Mg_xNi_{1-x}O$) reduced at high temperature showed excellent activity and stability for CO_2 reforming of methane [2]. It has been shown that $Mg_xNi_{1-x}O$ catalyst has excellent stability [3]; nickel clusters forms on the catalyst in reduced atmosphere. This reaction is of a great importance to develop $Mg_xNi_{1-x}O$ catalysts. In this study, *in situ* XAFS (X-ray Absorption Fine Structure) technique has been developed to observe structure changes of nickel in catalyst in H_2/He gas at high temperatures.

Experiments

In situ XAFS measurements were carried out using a newly developed reaction cell [4] in a transparent geometry. The cell is made of stainless steel with Kapton-film windows through which an x-ray beam can pass. 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.* 1200 K by rod heaters located above the specimen under a flow of H_2/He gas. The temperature of the specimen was monitored with a thermo-couple located above the specimen holder.

Powders of $Mg_{0.9}Ni_{0.1}O$ (catalyst) and NiO (reference) were mixed with BN powder and packed inside the holder, respectively. The specimens were heated in a 3%H_2/97%He gas 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 temperatures in a range of T=300-1073 K after heating for 600 seconds at each temperature. Figure 1 shows XANES spectra around Ni obtained by *in situ* measurements at T=300 and 1073 K.

In a case of NiO, almost all of nickel atoms change from a state of NiO to that of Ni at T=1073 K. This is consistent with thermodynamical data.

In a case of $Mg_{0.9}Ni_{0.1}O$ catalyst, less than *ca.* 10% of nickel atoms change from a state of NiO to that of Ni at T=1073 K (Fig.1). This shows nickel atoms in $Mg_xNi_{1-x}O$ are hard to be reduced compared with those in NiO, because oxygen atoms in $Mg_{0.9}Ni_{0.1}O$ are tightly bound with magnesium atoms. *In situ* XAFS measurements were carried out at different temperature, and the fraction of reduced nickel in of $Mg_{0.9}Ni_{0.1}O$ catalyst (x=Ni/(Ni+NiO)) at each temperature was obtained from XANES spectrum by curve fitting (Fig.2). The fraction x increases as the temperature increases. The increment becomes sharp at T > 1100 K, but x=12% event at 1150 K.

These results show that nickel particles form in a reduced atmosphere from $Mg_{0.9}Ni_{0.1}O$ catalyst but that only a limited ratio of nickel is reduced. This may prevent the growth of nickel atoms into large particles which are less active in the catalysis reaction.

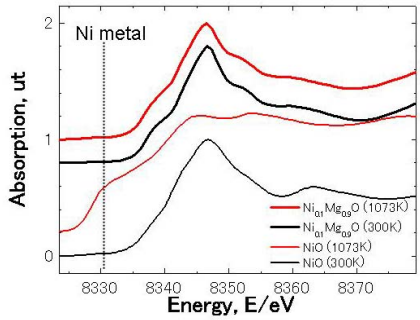

Fig.1 Change of XANES spectra around Ni obtained by *in situ* measurements during heating in H_2/He gas.

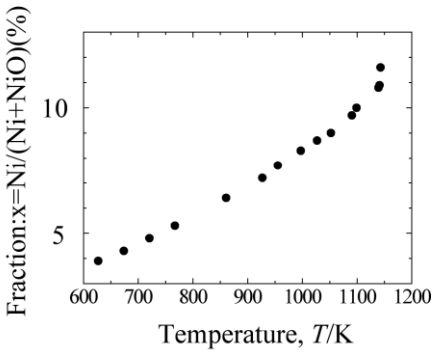

Fig.2 Change of nickel metal among $Mg_{0.9}Ni_{0.1}O$ catalyst as a function of temperature.

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).
[4] M. Kimura et al: PF Act. Rep. #23 Part B, p.155 (2006).