

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

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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 reduced at high temperature showed excellent activity and stability for CO_2 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 CO_2 reforming. 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

Figure 1 shows the main part of a newly developed reaction cell [4]. 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.* 1100 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 $Mg_xNi_{1-x}O$ (catalyst) and NiO (reference) were mixed with BN powder and packed inside the holder, respectively. The specimens were heated in a gas of 3% H_2 /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 temperatures in a range of $T=300$ -1073 K after heating for 600 seconds at a each temperature. Figure 2 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, suggesting that the gas flow around specimen is enough to attain an equilibrium state under the experiments conditions with the *in situ* system.

After experiments, microstructures of the specimen was observed with SEM and TEM. The specimen heated

up to $T=1073$ K 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.

In a case of $Mg_xNi_{1-x}O$ catalyst, less than *ca.* 5% of nickel atoms change from a state of NiO to that of Ni at $T=1073$ K (Fig.2). This shows nickel atoms in $Mg_xNi_{1-x}O$ are hard to be reduced compared with those in NiO, because oxygen atoms in $Mg_xNi_{1-x}O$ are tightly bound with magnesium atoms. This results in that nickel particles formed by reduction stay in small, which is required for a high performance as a catalyst.

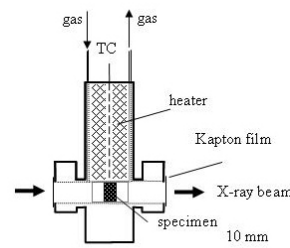


Fig.1 The main part of a newly developed reaction cell.

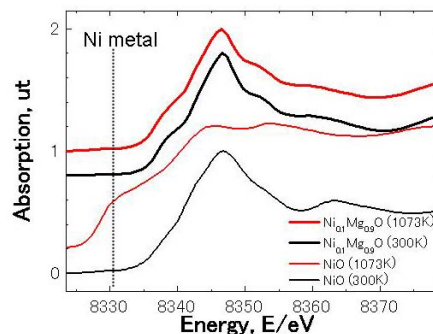


Fig.2 Change of XANES spectra around Ni obtained by *in situ* measurements during heating in H_2/He gas.

References

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