9A/2000G074

Structural analysis of active species in silica-supported Ni catalyst for methane decomposition

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Introduction

Hydrogen is a clean fuel in the sense that no CO_2 is emitted when it is used in H_2-O_2 fuel cells. Methane decomposition into hydrogen and carbon is of current interest as an alternative route of production of hydrogen from natural gas. Because no CO, which poisons the electro-catalyst in the fuel cells, is contained in the products formed from the decomposition of methane, the produced hydrogen can be supplied directly to the fuel cells.

In the present study, we investigated the structural change of Ni species during the methane decomposition over Ni/SiO_2 catalyst, which is effective for methane decomposition [1], by Ni K-edge XANES/EXAFS.

Experimental

Silica-supported Ni(5 wt%) catalyst was prepared by the impregnation of SiO_2 with an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$, followed by the calcination of the impregnated sample at 873 K in air.

X-ray absorption experiments were carried out on the beam line BL-9A at Photon Factory in Institute of Materials Structure Science for High Energy Accelerator Research Organization, Tsukuba, Japan, with a ring energy of 2.5 GeV and a stored current of 250 – 450 mA. The X-ray absorption spectra of the catalysts were recorded in a fluorescence mode, and those of reference samples were recorded in a transmission mode with a Si(111) two-crystal monochromater.

Results and discussion

Figure 1 shows Ni K-edge XANES spectra of Ni/SiO_2 catalysts before and after the methane decomposition at 773 K, the Ni sample treated with CO at 540 K and Ni foil. The XANES spectrum of the Ni/SiO_2 before the contact with methane (denoted as C/Ni = 0, C/Ni stands for the amount of methane decomposed per one Ni atom in the catalyst) was compatible with that of Ni foil, indicating that Ni species in the fresh catalyst were present as Ni metal mainly. The XANES spectra of Ni/SiO_2 catalysts with deposited carbons of C/Ni = 0 to 650 were similar to that of the fresh Ni/SiO_2 catalyst. In the range of C/Ni = 0 to 650 in the methane decomposition, the activity of the catalyst was kept high. Therefore, we consider that the structure of Ni species did not change appreciably when the Ni/SiO_2 was actively decomposing methane.

On the other hand, in the XANES spectrum of the Ni/SiO_2 catalyst with deposited carbons of C/Ni = 900, two shoulder peaks appeared at 8332 and 8341 eV, and the peaks became more intense with the increase in C/Ni. Furthermore, two peaks at 8349 and 8358 eV, which were observed in the XANES spectra of the fresh Ni/SiO_2 and Ni foil, became fainter with the increase in C/Ni > 900. These results suggest that the structure of Ni species changed significantly in the range of C/Ni > 900 in the methane decomposition. In Fig. 1, a XANES spectrum of the Ni sample which had been prepared by the treatment of Ni metal powder with CO at 540 K for 100 h was also shown. XRD pattern of this Ni sample indicated that the sample consisted of Ni metal and Ni_3C. The treatment of Ni metal with CO caused the change of XANES spectrum, i.e., a new shoulder peak appeared around at 8340 eV and two peaks, which were observed at 8349 and 8358 eV, became faint. These changes of the XANES spectra from Ni metal to the CO-treated Ni metal must be caused by the formation of Ni-C bonds in Ni species. The changes of the XANES spectra observed at the deactivated stage (C/Ni > 900) of the catalyst were similar to that caused by the treatment with CO. Therefore, we suggest that some nickel carbide species is formed in the deactivation process of the Ni/SiO_2 catalyst.

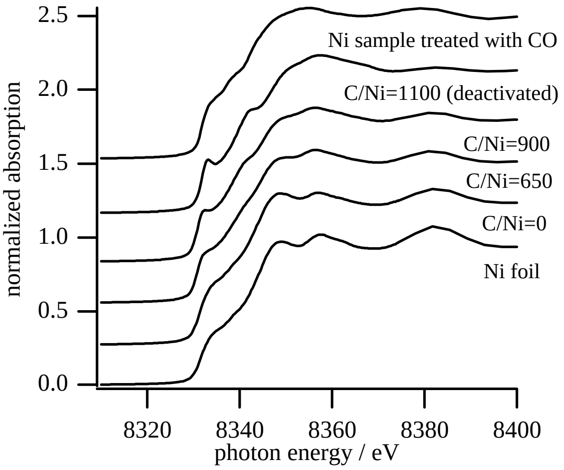

Fig.1 Ni K-edge XANES spectra of Ni/SiO_2 catalysts during the methane decomposition at 773 K and reference samples.

References

[1] T. Ishihara et al., Chem. Lett. 93 (1995).

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