Characterization of silica-supported Ni catalysts effective for methane decomposition by Ni K-edge XAFS

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The structural change of Ni species during the methane decomposition into hydrogen and carbon over Ni/SiO_2 catalyst was investigated by Ni K-edge XANES/EXAFS. Before the contact of methane with the Ni/SiO_2 catalyst, Ni species were present as Ni metal mainly. The structure of the Ni metal did not change appreciably when the Ni/SiO_2 was actively decomposing methane. In contrast, the formation of nickel carbide species was observed at the deactivation stage of the catalyst.

Keywords: decomposition of methane, silica-supported Ni catalyst, deposited carbon, nickel carbide species.

1. 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. The H_2-O_2 fuel cells such as proton-exchanged membrane cells require elimination of carbon monoxide in H_2 fuel because CO would strongly poison the anode electrocatalysts in the cells. At present, hydrogen was produced mainly through the steam reforming or the partial oxidation of natural gas, where CO was contained inevitably in the formed gas.

Decomposition of methane into hydrogen and carbon is of current interest as an alternative route of production of hydrogen from natural gas. Because no CO was contained in the products formed from the decomposition of methane, the produced hydrogen can be supplied directly to the fuel cells. It is well known that silica-supported Ni (Ni/SiO_2) was one of the effective catalysts for the decomposition of methane (Ishihara, et al., 1995, Otsuka, et al., 2000). However, the complete deactivation of the catalyst was unavoidable.

In the present study, we investigated the structural change of Ni species during the methane decomposition over Ni/SiO_2 catalyst by Ni K-edge XANES/EXAFS. Especially, our attention was focused on the structural change of Ni species during the deactivation of the catalyst.

2. Experimental

Silica-supported Ni(5 wt%) catalyst was prepared by the impregnation of SiO_2 (fumed silica, commercial name: Cab-O-Sil from Cabot Co., 200 $m^2 \cdot g^{-1}$) 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.

The activity and lifetime tests for the catalyst in the decomposition of methane were carried out at atmospheric pressure with a conventional gas-flow system. Prior to the reaction, the catalyst was conditioned by the treatment with hydrogen at 823 K for 1 h. Decomposition of methane was carried out by contacting methane ($P(CH_4)$ = 101.3 kPa, flow rate = 60 $ml \cdot min^{-1}$) with the catalyst (0.040 g). During the reaction, a part of gases in a stream out of the catalyst-bed was sampled out and analyzed by G. C.

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.

3. Results and discussion

Figure 1 shows the one-pass conversion of methane as a function of the time on stream for the methane decomposition over the Ni/SiO_2 catalyst at 803 K. In the reaction, only hydrogen was detected as the gaseous product, and carbons from methane were deposited on the catalyst. The conversions of methane decreased gradually with time on stream in the early period as shown in Fig. 1. The decrease in the conversion was accelerated significantly at ca. 150 min, and finally the catalyst was deactivated completely at 220 min. The value of C/Ni (the amounts of methane decomposed per an atom of Ni) after the complete deactivation of the catalyst was estimated to be 1100. The carbons formed by the methane decomposition grew with filamentous structures on the catalyst as indicated in Fig. 2. It was found that a Ni particle was present on the tip of a carbon filament by SEM and BEI (back-scattering electron image) of the catalyst with deposited carbons.

Figure 3 shows Ni K-edge XANES spectra of Ni/SiO_2

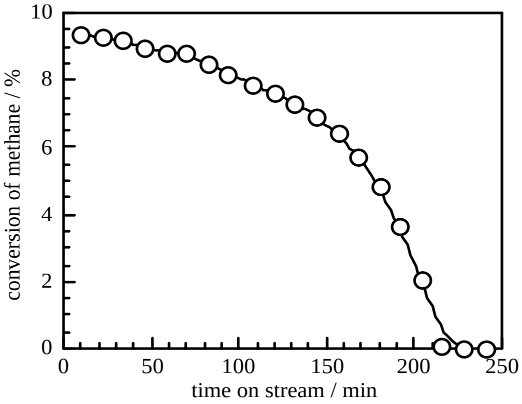


Figure 1
Kinetic curve of the methane conversion in the methane decomposition over Ni/SiO_2 catalyst at 803 K.

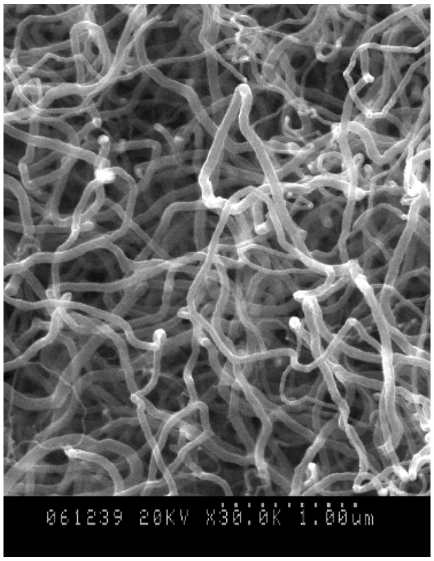
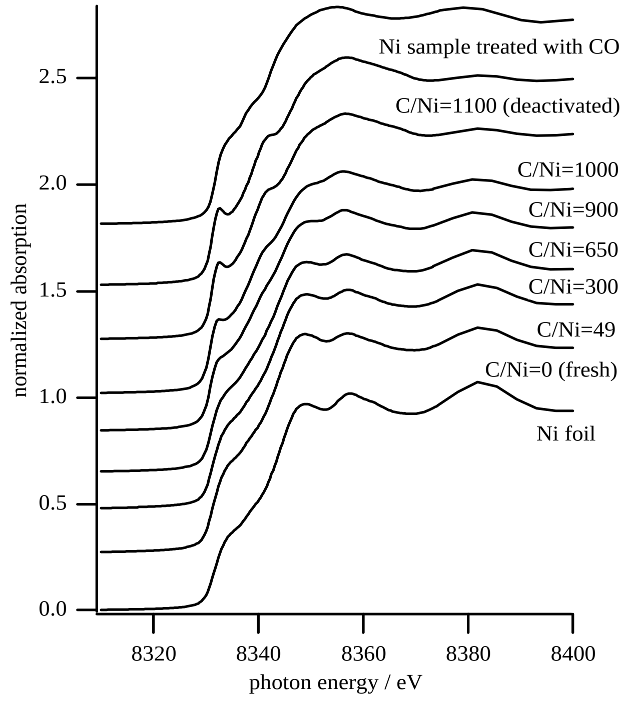


Figure 2
SEM image of the deactivated Ni/SiO_2 catalyst.

catalysts with and without deposited carbons, the Ni sample treated with CO, and Ni foil. The XANES spectrum of the Ni/SiO_2 before the contact with methane (denoted as the fresh catalyst hereafter) 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 = 49 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. 3, 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. This result is consistent with that reported by Hoffer et al.(Hoffer, et al., 1950). 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



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i K-edge XANES spectra of Ni/SiO_2 catalysts with and without eposited carbons, Ni sample treated with CO and Ni foil.

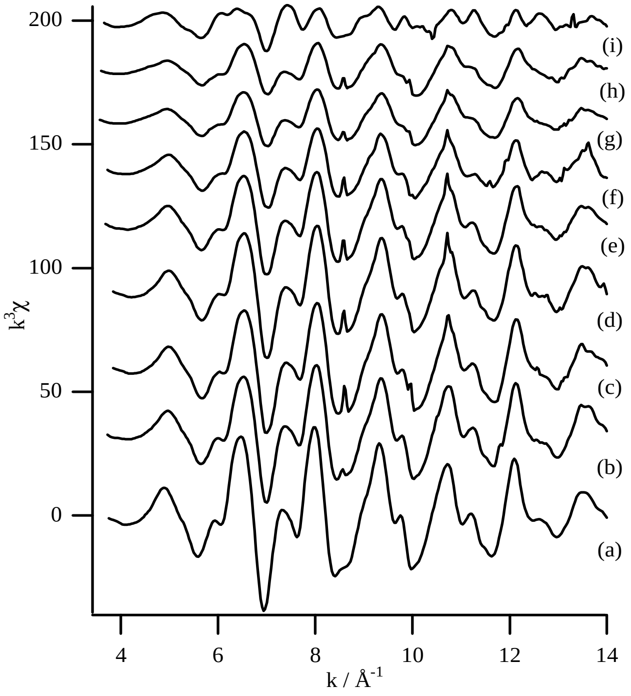

Figure 4
k^3-weighted Ni K-edge EXAFS spectra of Ni/SiO_2 catalysts with and without deposited carbons, Ni sample treated with CO and Ni foil. (a): Ni foil, (b): the fresh catalyst, (c): C/Ni=49, (d): C/Ni=300, (e): C/Ni=650, (f): C/Ni=900, (g): C/Ni=1000, (h): C/Ni=1100 (deactivated catalyst), and (i): the Ni sample treated with CO.

Ni/SiO_2 catalyst.

Figure 4 shows k^3-weighted Ni K-edge EXAFS spectra of the Ni/SiO_2 catalysts with and without deposited carbons, Ni sample treated with CO, and Ni foil. The feature of the EXAFS of the fresh Ni/SiO_2 catalyst was compatible with that of Ni foil, indicating that Ni species on the fresh Ni/SiO_2 were present as Ni metal mainly. In the EXAFS spectra of the Ni/SiO_2 with deposited carbons of C/Ni = 49 and 300, the intensity and pattern of the oscillations were almost consistent with those of the fresh Ni/SiO_2 catalyst, suggesting that the structure of Ni species on the Ni/SiO_2 did not change significantly in the range of C/Ni = 49 to 300. On the other hand, in the range of C/Ni > 650, the intensities of the oscillations of the EXAFS became weaker gradually with the increase in C/Ni, although the patterns of the oscillations were independent of the values of C/Ni. The results implied that the structure of Ni metal was distorted in the deactivation process of the catalyst due to the presence of carbon atoms in Ni metal. However, the EXAFS spectrum of the deactivated catalyst was different from that of the Ni sample treated with CO. Therefore, we consider that the nickel carbide species on the deactivated catalyst is different from Ni_3C.

The structure around Ni atoms can be more clearly visualized by performing Fourier transform of k^3-weighted EXAFS of the Ni/SiO_2 catalyst. Figure 5 shows the Fourier transforms (radial structure function (RSF)) of k^3-weighted Ni K-edge EXAFS of Ni/SiO_2 catalysts with deposited carbons, CO-treated Ni samples, and Ni foil. A peak appearing at 1.8 ~ 2.5 Å, which was due to Ni-Ni bond, was observed for all the RSFs. For the samples with C/Ni > 650, the intensities of the peaks became smaller with the increase in C/Ni, whereas the changes in the intensities of the peaks were not obvious in the range of C/Ni < 300. In addition, the peak at 1.2 ~1.8 Å appeared in the RSFs for the Ni/SiO_2 with carbons of C/Ni > 650. The intensity of the peak became more intense as increasing the amounts of deposited carbons. The peak could be ascribed to the formation of Ni-C bonds which causes the deactivation of the catalysts in the methane decomposition.

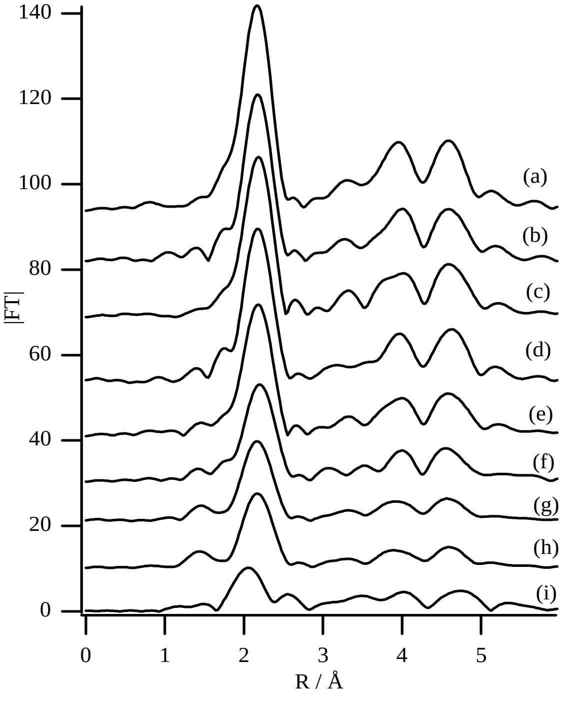

Figure 5

Fourier transforms of k^3-weighted Ni K-edge EXAFS spectra of Ni/SiO_2 catalysts with and without deposited carbons, Ni sample treated with CO and Ni foil. (a)-(i): see the captions for Fig. 4.

From the results mentioned above, we suggest that some nickel carbide species is formed in the deactivation process of the Ni/SiO_2 catalyst. In contrast, the structure of Ni metal is not changed significantly, when Ni/SiO_2 is decomposing methane actively. We confirmed that the EXAFS of the sample with Ni_3C was different from that of the deactivated Ni/SiO_2. Thus, the nickel carbide species in the deactivated Ni/SiO_2 catalyst would be different from Ni_3C. The exact structure of nickel carbide species on the deactivated catalyst can not be described at the moment. Further studies on this structure are in progress.

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