Materials Science

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XAFS analysis on carburization process of Nb/SiO_2 prepared from Nb-sol

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Introduction

Early transition metal carbides (ETMCs) were attracted as new catalyst materials from the resemblance in physical and chemical properties to those of the group 8-10 metals. ETMCs were usually prepared from the corresponding oxides by treating with CH_4-H_2 gas passage at high temperatures, such as 1370 K (NbC) [1]. To apply the ETMC as catalyst, lowering the carburization temperature is expected.

In this study, Nb/SiO_2 catalysts were prepared from peroxoniobic acid (PNA) as precursor. The carburizing process of that into NbC/SiO_2 in a CH_4-H_2 mixed gas flow was investigated by *in situ* XAFS technique.

Experimental

Nb/SiO_2 was prepared from peroxoniobic acid and SiO_2 (Aerosil, #200) as a precursor and a support, respectively. The loading of Nb was regulated to 3 wt%. The precursor oxide catalyst was carburized in CH_4-H_2 mixed gas flow to produce NbC/SiO_2 catalyst by TPR process; the precursor catalyst was heated at a linear rate of 5 $K \cdot min^{-1}$ to the final temperature.

Nb K-edge XAFS spectra were collected at NW10A with Si(311) double crystal monochromator in a transmission mode. It takes about 10 min to collect a EXAFS spectrum. Catalyst was pressed into a self-supporting pellet and transferred into the SUS cell, with Acrylic windows (2 mm thickness) at the both ends of the X-ray path [2]. The *in situ* XAFS spectra were collected under a flow of CH_4-H_2 during TPR and analyzed by the curve-fitting (CF) method with program REX2000 (Rigaku Co.).

Results and discussion

Figure 1 shows the FT of Nb K-edge EXAFS spectra for NbC/SiO_2 catalysts and the reference compounds. Peaks for Nb-C, Nb-Nb (1st), Nb-Nb (2nd) were observed around at 0.18 nm, 0.27 nm, 0.40 nm, respectively. It revealed that the carburization temperature of supported Nb could be lowered to 1073 K by using PNA as Nb precursor.

CF analyses were carried out for Nb-Nb coordination. The coordination number (CN) of Nb-Nb (1st) and Nb-Nb (2nd) for NbC/SiO_2 (1273 K) were 9.3 and 3.3, respectively. CN of those for NbC/SiO_2 (1073 K) were 5.9 and 2.0, respectively. It can be concluded that the highly dispersed NbC species can be created on SiO_2 by lowering the carburizing temperature.

Figure 2 shows Nb K-edge *in situ* XANES spectra during the carburizing process for Nb/SiO_2. The blue lines and the red dotted lines are the temperature raising steps and the temperature maintaining steps at 1173 K, respectively. The 1s-4d transition peaks (at around 18980 eV) are disappeared and new band at around 19050 eV are observed during the temperature raising steps. Above tendency was not observed for the Nb/SiO_2 precursor prepared from $NbCl_5$, which suggests the effectiveness of using PNA as the Nb precursor.

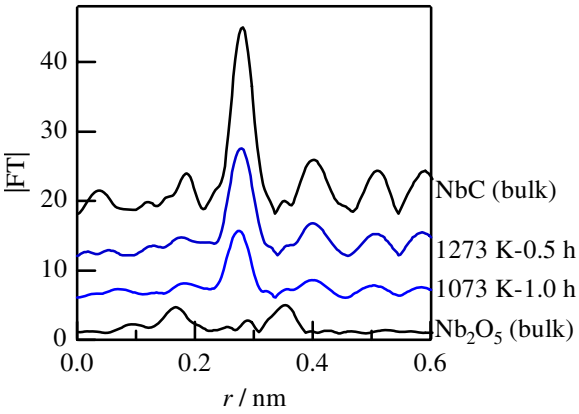

Figure 1. FT of Nb K-edge EXAFS spectra for NbC/SiO_2 catalysts.

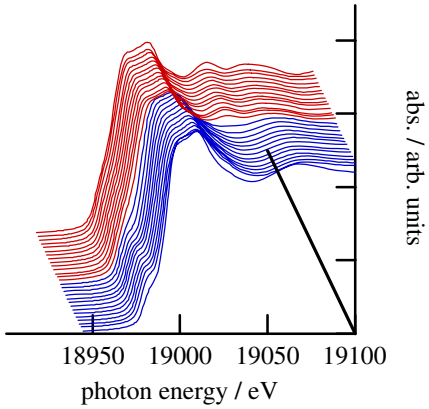

Figure 2. Nb K-edge *in situ* XANES spectra during carburization for NbC/SiO_2 prepared from PNA.

References

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