In-situ XAFS studies on nitriding process of Nb/SiO₂ catalyst under N₂/H₂ gas

Nobuyuki ICHIKUNI*1, Hidenori HANEISHI1, Kyoko K. BANDO2, Shogo SHIMAZU1, Takayoshi UEMATSU1

1Chiba University, Inage-ku, Chiba 263-8522, Japan
2National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8569, Japan

Introduction

Transition metal nitrides were usually prepared from the corresponding oxides under the NH₃ atmosphere at high temperatures. But the NH₃ gas is corrosive and expected to reduce the amount at such process. Thus, it should be investigated that the nitriding process can be achieved or not by using only N₂/H₂ gas.

Fe is effective element for dissociation of N₂ and is not expensive. Fe added Nb/SiO₂ catalysts are thought to be nitrided using N₂/H₂ gas flow.

In this study, the Fe added Nb/SiO₂ catalysts were prepared and nitrided in a N₂/H₂ mixed gas flow. In-situ XAFS measurements were performed during the nitriding process.

Experimental

SiO₂(Aerosil #200) supported Fe-Nb₂O₅ precursors were prepared by a co-impregnation method of SiO₂ with NbCl₅ and Fe(NO₃)₃·9H₂O methanol solution. The loading of Nb and Fe were regulated to be 3 wt% and 20 mol% (to Nb atom), respectively. The precursor oxide catalyst was nitrided in N₂/H₂ mixed gas flow to produce Fe-NbN/SiO₂ catalyst by TPR process; the sample was heated at a linear rate of 10 K·min⁻¹ to the final temperature (1193 K), and kept it for a certain time.

Nb K-edge EXAFS spectra were collected at BL-10B with Si(311) channel cut monochromator. It takes about 10 min to collect a EXAFS spectrum. Catalyst sample was pressed into pellets and transferred into the SUS cell with Acrylic windows at the both ends of the X-ray path [1]. The sample can be heated up to 1273 K by infrared gold image furnace. Curve-fitting analyses of EXAFS oscillations in the k-space were carried out by the EXAFS analysis program REX2000 (Rigaku Co.).

Results and discussion

Figure 1 shows the EXAFS Fourier transforms for the catalyst during nitriding process. The main peak during the heating process can be attributed to Nb-O bond. However, new peak appeared besides the Nb-O peak and became higher, which was assigned to be Nb-N bond, during temperature maintaining process (at 1193 K). Moreover, the peak due to Nb-Nb coordination was appeared and gradually grew larger at this step. These results suggested that Nb-oxide bond was only reduced during heating process in N₂/H₂ mixed gas flow, but converted into NbN species at temperature retaining process at 1193 K.

These spectra collected at such high temperature, so the FT intensities were suppressed considerably (Debye-Waller effect). The sample was cooled down to room temperature in the flow of N₂, followed by measurement of the EXAFS spectrum (FT was shown in Fig. 2). It is clearly observed that N₂/H₂ treatment could produce the NbN from the Fe added Nb-oxide. The effects of Fe structure and Fe distribution on the nitriding process should be investigated.

Reference


* ichikuni@faculty.chiba-u.jp