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In-situ XAFS studies on nitriding process of Nb/SiO_2 catalyst under N_2/H_2 gas

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Introduction

Transition metal nitrides were usually prepared from the corresponding oxides under the NH_3 atmosphere at high temperatures. But the NH_3 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 N_2/H_2 gas.

Fe is effective element for dissociation of N_2 and is not expensive. Fe added Nb/SiO_2 catalysts are thought to be nitrided using N_2/H_2 gas flow.

In this study, the Fe added Nb/SiO_2 catalysts were prepared and nitrided in a N_2/H_2 mixed gas flow. *In-situ* XAFS measurements were performed during the nitriding process.

Experimental

SiO_2(Aerosil #200) supported Fe-Nb_2O_5 precursors were prepared by a co-impregnation method of SiO_2 with $NbCl_5$ and $Fe(NO_3)_3 \cdot 9H_2O$ 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 N_2/H_2 mixed gas flow to produce Fe-NbN/SiO_2 catalyst by TPR process; the sample was heated at a linear rate of 10 $K \cdot min^{-1}$ 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 N_2/H_2 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 N_2, followed by measurement of the EXAFS spectrum (FT was shown in Fig. 2). It is clearly observed that N_2/H_2 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.

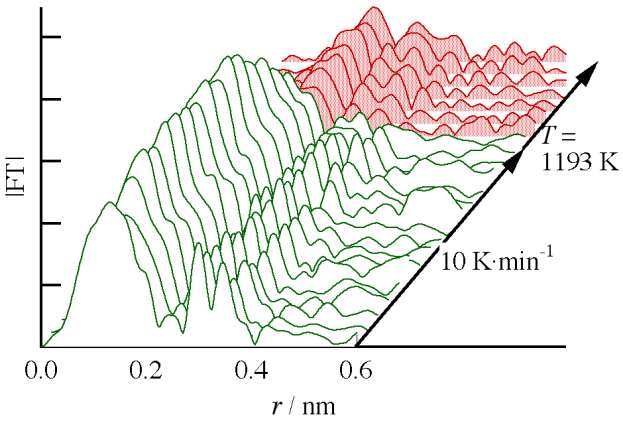

Fig. 1. FT of k^3-weighted Nb K-edge EXAFS for co-imp Fe-Nb/SiO_2 catalyst during nitriding process.

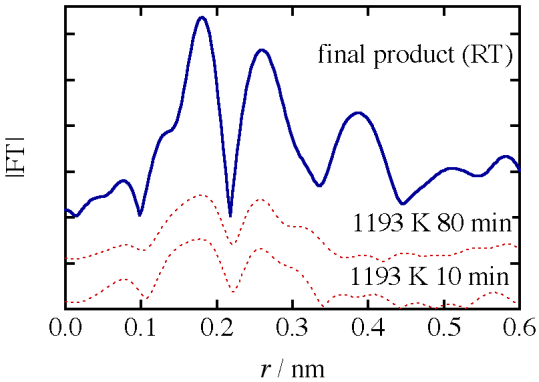

Fig. 2. FT of k^3-weighted Nb K-edge EXAFS for co-imp Fe-Nb/SiO_2 catalyst after the nitriding process.

Reference

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