

Nitriding process of Fe-promoted Nb/SiO₂ catalyst prepared from peroxoniobic acid as Nb precursor

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Introduction

Early transition metal nitride (ETMN) was attractive as a new catalyst material due to the resemblance in physical properties to those of the group 8-10 metals. ETMNs were usually prepared from the corresponding oxides under the NH₃ atmosphere at high temperatures. We have tried to convert ETM oxide into ETMN without using NH₃ gas by the addition of Fe species.

In this study, the Fe added Nb/SiO₂ catalysts were prepared and the nitriding process in a N₂-H₂ mixed gas flow was investigated by *in-situ* XAFS method.

Experimental

Nb/SiO₂ was prepared from peroxoniobic acid and SiO₂ (Aerosil, #200) as a precursor and a support, respectively. Fe was introduced by using Fe(acac)₃. The loading of Nb and Fe were regulated to be 6 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 following two types of TPR process; (1) the sample was heated at a linear rate of 5 K·min⁻¹ to the final temperature (T_{nit}), and (2) the sample was heated to 563 K and maintained for 60 min and heated again to $T_{\text{nit}}=1173$ K. The catalyst prepared from the former and the latter process was denoted as Fe-NbN/SiO₂(1step) and Fe-NbN/SiO₂(2steps), respectively.

Nb K-edge XAFS spectra were collected at BL-10B with Si(311) channel cut monochromator in the 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. The *in-situ* XAFS spectra were collected under a flow of N₂-H₂ during TPR and analyzed by the program REX2000 (Rigaku Co.).

Results and discussion

Nb oxide in Nb/SiO₂ (without Fe addition) was not nitrided by treating with N₂-H₂ gas at 1273 K. By introducing 5-20 mol% Fe into Nb/SiO₂ catalysts and treated with N₂-H₂ gas at 1273 K led to the formation NbN species on SiO₂. Moreover, the T_{nit} could be lowered about 100 K, by using peroxoniobic acid as Nb precursor instead of using NbCl₅.

Figure shows the FT spectra of *in-situ* EXAFS during nitriding process. The Nb-N peak at around 0.18 nm was observed for both catalyst. The intensity of Nb-(N)-Nb peak at around 0.30 nm gradually became stronger during

the temperature maintaining step ($T = 1173$ K). The conversion from Nb-oxide to Nb-nitride was occurred not during TPR process but during temperature keeping process. The growth of Nb-N peak in Fig (b) is faster (at the initial stage of temperature keeping process) than that in Fig (a), which suggests the effectiveness of the 2steps TPR process for nitriding.

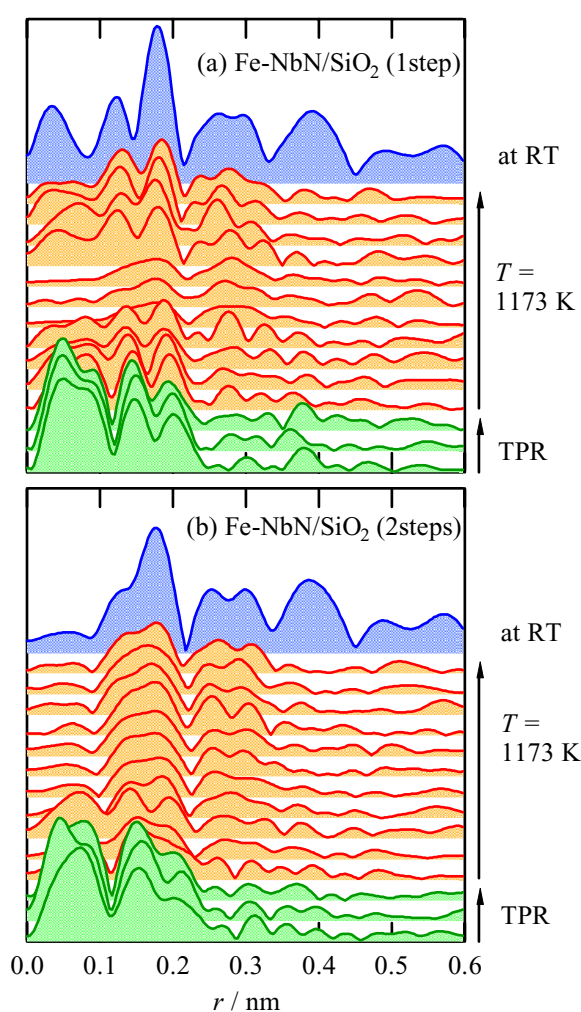


Fig. FT of k^3 -weighted Nb K-edge *in-situ* EXAFS spectra during nitriding process; (a) Fe-NbN/SiO₂ (1step) and (b) Fe-NbN/SiO₂ (2steps).

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