Nb and Fe K-edges XAFS study on the structure of supported Fe-NbN catalysts

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Abstract. SiO₂-Supported Fe-NbN catalysts were prepared by temperature programmed reaction (TPR) method from Fe-Nb/SiO₂ oxide precursor under a N₂-H₂ gas stream. As raising the intermediate temperature-maintaining (ITM) step temperature during the TPR, Fe species in the Fe-Nb/SiO₂ catalyst was reduced to zero-valent, confirmed by Fe K-edge XAFS analysis. Although the Fe-Fe coordination number increased by elevating ITM temperature, the size of Fe cluster was still small. The Nb-N coordination number became larger, as higher the ITM temperature. The reduced Fe species effectively assisted the nitridation process of Nb.

1. Introduction
Early transition metal (ETM) nitride is attractive as one of the new catalyst material due to the resemblance in physical and chemical properties to those of group 8-10 metals [1]. It is reported that the nitridation of bulk Nb₂O₅ into NbN requires high temperature as 1470 K [2]. We have already demonstrated that introduction of a Fe species into a SiO₂-supported Nb oxide precursor (Nb/SiO₂) was able to successfully reduce the nitridation temperature of Nb down to 1173 K in temperature programmed reaction (TPR) process [3]. In this case, the conversion from Nb oxide to Nb nitride proceeded around the Fe additive, and hence, the structure of Fe affected the nitridation process [4].

In this study, the intermediate temperature-maintaining (ITM) step was introduced during the TPR process to modify the Fe chemical state. The effect of Fe chemical state on the formation of Nb nitride cluster was also investigated by XAFS analysis.

2. Experimental

2.1. Catalyst preparation
Fe-Nb/SiO₂ was prepared by conventional impregnation method using SiO₂ (Aerosil, #200), ferrocene acetic acid and peroxoniobic acid as precursors. Nb loading amount and a Fe/Nb molar ratio were regulated to 3 wt% and 0.2, respectively. The nitridation of Nb species into NbN was carried out under N₂-H₂ gas stream in a TPR method with a linear rate of 10 K·min⁻¹ up to 1173 K, followed by temperature maintaining for 60 min. Catalysts were denoted with the ITM temperature (K) and time (min) in round brackets as Fe-NbN/SiO₂ (973-60). The catalyst prepared without introducing ITM step was denoted as Fe-NbN/SiO₂ (w/o ITM).
2.2. Characterization

XAFS measurements were performed in a PF (IMSS, KEK, Tsukuba, JAPAN). Nb $K$-edge XAFS spectra were measured at NW10A with a Si(311) double crystal monochromator in transmission mode by using two ion-chambers filled with (50% Ar+50% $N_2$) and (100% Ar) for $I_0$ and $I$, respectively. Fe $K$-edge XAFS spectra were taken in fluorescence mode at BL-12C with a Si(111) double crystal monochromator by using Lytle detector filled with Ar gas. (Proposal No. 2005G214, 2008G638). Curve-fitting (CF) analysis of EXAFS oscillations was carried out by the EXAFS analysis program REX2000 (Rigaku Co.). The $k$ range for the Fourier transforms (FT) of $k^3$-weighted EXAFS data was 40-140 nm$^{-1}$. Model parameters for CF analysis (back scattering amplitude and phase shift) were extracted from EXAFS oscillations observed for bulk NbN and Fe foil.

3. Results and discussion

3.1. Nb $K$-edge XAFS

Nb $K$-edge XANES spectra for the nitrided catalysts and reference compounds are shown in figure 1. The peak at around 19045 eV is distinctly observed in NbN as compared to that in Nb$_2$O$_5$. This peak, noted as γ peak, can be used as fingerprint for the formation of NbN [3]. The γ peak intensity became stronger as introducing ITM step and raising the ITM temperature. It can be said that the ITM step during TPR process is effective for nitridation of Nb in Fe-NbN/SiO$_2$ catalyst.

To clarify the nitridation degree of Nb, Nb $K$-edge XAFS data were Fourier-transformed as shown in figure 2 (phase shifts are not corrected), and were analyzed by CF method. CF results are summarized in table 1. CN of Nb-Nb and Nb-N for (w/o ITM) catalyst are 7.4 and 3.0, respectively. Although Nb-Nb coordination can be reproduced well with small CN, CN of Nb-N is as small as a half for bulk NbN. Thus, the degree of nitridation does not seem to be enough. On the other hand, by introducing the ITM step during TPR process, CN for Nb-N became close to the number for bulk NbN. As shown in table 1, CN of Nb-N for Fe-NbN/SiO$_2$ (873-60) and Fe-NbN/SiO$_2$ (973-60) are 5.1 and 5.8, respectively. It can be said that as increasing ITM temperature to 973 K, Nb species on SiO$_2$ seemed to be almost fully nitrided.

![Figure 1. Nb $K$-edge XANES spectra for (a) Nb$_2$O$_5$, (b) Fe-NbN/SiO$_2$ (w/o ITM), (c) Fe-NbN/SiO$_2$ (873-60), (d) Fe-NbN/SiO$_2$ (973-60) and (e) NbN.](image1)

![Figure 2. FT of $k^3$-weighted Nb $K$-edge EXAFS oscillations for (a) Fe-NbN/SiO$_2$ (w/o ITM), (b) Fe-NbN/SiO$_2$ (873-60), (c) Fe-NbN/SiO$_2$ (973-60), (d) Nb$_2$O$_5$ and (e) NbN.](image2)
Table 1. Curve-fitting results of Nb K-edge EXAFS for Fe-NbN/SiO<sub>2</sub> catalysts.

| coordination | CN  | r (nm) | dE (eV) | Δσ<sup>2</sup> (10<sup>-4</sup> nm<sup>2</sup>) |
|--------------|-----|--------|---------|----------------------------------|
| NbN (model)  | Nb-N | 6      | 0.220  | 0.0                             |
|              | Nb-Nb| 12     | 0.311  | 0.0 σ=0.006 (nm)                |
| Fe-NbN/SiO<sub>2</sub> | Nb-N | 5.8±1.4 | 0.219±0.002 | 2.3±1.9 0.41±0.40 |
| (973-60)     | Nb-Nb| 10.4±2.0 | 0.314±0.002 | 4.2±1.8 0.26±0.38 |
| Fe-NbN/SiO<sub>2</sub> | Nb-N | 5.1±1.5 | 0.219±0.002 | 3.0±2.2 0.47±0.42 |
| (873-60)     | Nb-Nb| 9.6±2.3 | 0.315±0.003 | 5.7±2.1 0.36±0.49 |
| Fe-NbN/SiO<sub>2</sub> | Nb-N | 3.0±1.3 | 0.221±0.003 | 7.5±3.0 0.33±0.39 |
| (w/o ITM)    | Nb-Nb| 7.4±1.5 | 0.316±0.003 | 6.1±2.4 0.23±0.49 |

* CN: coordination number, r: coordination distance, dE: threshold energy differences, Δσ<sup>2</sup>: the difference between σ<sup>2</sup> for the analyzed value and σ<sup>2</sup> for the model compound.

The particle size of NbN depended on the ITM temperature. CN of Nb-Nb for Fe-NbN/SiO<sub>2</sub> (873-60) and Fe-NbN/SiO<sub>2</sub> (973-60) are 9.6 and 10.4, respectively. In other words, as raising the ITM temperature, NbN cluster size became larger.

3.2. Fe K-edge XAFS

To confirm the effect of the ITM step on the Fe chemical state for Fe-NbN/SiO<sub>2</sub> catalyst, Fe K-edge XAFS data was collected. Figure 3 shows the Fe K-edge XANES spectra. Fe K-edge XAFS for catalysts and model compounds (Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, Fe foil) were obtained in fluorescence mode and in transmission mode, respectively. XANES data in figure 3 were background subtracted and normalized. XANES profiles of Fe oxides and Fe foil are very different, especially for energy region of 7125-7145 eV.

![Figure 3](image)

**Figure 3.** Fe K-edge XANES spectra for (a) Fe<sub>2</sub>O<sub>3</sub>, (b) Fe<sub>3</sub>O<sub>4</sub>, (c) Fe-NbN/SiO<sub>2</sub> (w/o ITM), (d) Fe-NbN/SiO<sub>2</sub> (873-60), (e) Fe-NbN/SiO<sub>2</sub> (973-60) and (f) Fe foil.

![Figure 4](image)

**Figure 4.** FT of <i>k</i><sup>3</sup>-weighted Fe K-edge EXAFS oscillations for (a) Fe-NbN/SiO<sub>2</sub> (w/o ITM), (b) Fe-NbN/SiO<sub>2</sub> (873-60), (c) Fe-NbN/SiO<sub>2</sub> (973-60) and (d) Fe foil.
Table 2. Curve-fitting results of Fe $K$-edge EXAFS for Fe-NbN/SiO$_2$ catalysts.

| coordination         | CN | $r$ (nm) | $dE$ (eV) | $\Delta \sigma^2$ ($10^{-4}$ nm$^2$) |
|----------------------|----|----------|-----------|-------------------------------------|
| Fe foil (model)      | Fe-Fe | 8       | 0.248     | 0.0                                |
| Fe-NbN/SiO$_2$ (973-60) | Fe-Fe | 5.4±0.2 | 0.248±0.001 | -3.6±0.4 | -0.08±0.06 |
| Fe-NbN/SiO$_2$ (873-60) | Fe-Fe | 4.3±0.2 | 0.248±0.001 | -3.4±0.5 | -0.04±0.05 |
| Fe-NbN/SiO$_2$ (w/o ITM) | Fe-Fe | 3.9±0.2 | 0.248±0.001 | -8.9±0.8 | -0.08±0.06 |

*CN: coordination number, $r$: coordination distance, $dE$: threshold energy differences, $\Delta \sigma^2$: the difference between $\sigma^2$ for the analyzed value and $\sigma^2$ for the model compound.

As compared with the ITM step introduced catalyst, Fe species in without ITM step catalyst seemed to be the mixture of Fe oxide and Fe metal. While the XANES profile of the ITM step introduced catalyst showed the resemblance in that of Fe foil. The ITM step during TPR process seemed to be effective for reduction of Fe in Fe-NbN/SiO$_2$ catalyst.

Figure 4 shows the FT of $k^3$-weighted Fe $K$-edge EXAFS oscillations. Peak at around 0.22 nm (phase shift uncorrected) can be attributed Fe-Fe coordination. CF results for Fe-Fe coordination are summarized in table 2. CN of Fe-Fe for the without ITM step catalyst is 3.9 and the small peak can be observed at around 0.16 nm. The Fe species in the without ITM step catalyst was not fully reduced and included oxide form as revealed from the XANES profile and the FT profile.

CN of Fe-Fe for Fe-NbN/SiO$_2$ (873-60) and Fe-NbN/SiO$_2$ (973-60) are 4.3 and 5.4, respectively. Although the CN of Fe-Fe became larger as raising the ITM temperature, the number was still smaller than that of the bulk Fe (8.0). Consequently the Fe cluster size on Fe-NbN/SiO$_2$ (973-60) was still small.

By comparing the Fe $K$-edge XANES of 7140-7160 eV region, it can be said that the profile for Fe-NbN/SiO$_2$ (973-60) catalyst is more similar to Fe metal than that for Fe-NbN/SiO$_2$ (873-60) is. From XANES analysis, the increment of CN from Fe-NbN/SiO$_2$ (873-60) to Fe-NbN/SiO$_2$ (973-60) might come from not only Fe particle size growth but also the reduction degree of Fe.

It was revealed that by introducing the ITM step to TPR process is effective way to promote the nitridation of Nb and also the reduction of Fe. The reduced Fe species effectively assisted the nitridation process of Nb. In other words, the nitridation process of Nb oxide into NbN is affected by the state of Fe additive.

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