

# Nb K- and L<sub>3</sub>-edges XAFS study on the structure of supported Nb carbide catalyst

N Ichikuni\*<sup>1</sup>, F Yanagase<sup>1</sup>, K Mitsuahara<sup>2</sup>, T Hara<sup>1</sup>, S Shimazu<sup>1</sup>

<sup>1</sup> Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, Chiba, Japan

<sup>2</sup> The Research Organization of Science and Technology, Ritsumeikan University, Kusatsu, Japan

E-mail: ichikuni@faculty.chiba-u.jp

**Abstract.** Mesoporous silica SBA-15 supported NbC catalysts were prepared under reduced pressure of CH<sub>4</sub>-H<sub>2</sub> gas in a closed circulating system. Nb K- and L<sub>3</sub>-edges XAFS measurements revealed that small NbC cluster formed on SBA-15 support and gradual carburization process by lengthening the carburization temperature-maintaining period. Carburization degree of Nb species was clearly explained by using threshold energy shift of Nb L<sub>3</sub>-edge XANES profile.

## 1. Introduction

Early transition metal carbide (ETMC) is one of the most attractive candidates for substituting the noble metal catalysts. In general, high temperature is required for preparation of ETMC, and hence, the particle grows larger and has the narrower surface area, which should be improved as applying to the catalyst. We have already reported the preparation of NbC on oxide support [1] and showed the activity toward ethene hydrogenation. However, the activity was not high enough. Development of smaller NbC particles was thought to improve the catalysis.

In this study, the preparation of the NbC nanocluster on mesoporous silica SBA-15 [2] support and characterization by using Nb K- and L<sub>3</sub>-edges XAFS were reported.

## 2. Experimental

### 2.1. Catalyst preparation

SBA-15 was prepared in the same manner as presented in the literature [2]. Peroxonioic acid (PNA) was prepared as in the literature [3] and was used as the Nb precursor for preparation of Nb/SBA catalyst (NbO<sub>x</sub>/SBA). Carburized catalyst NbC/SBA was obtained in a closed circulating system under CH<sub>4</sub> and H<sub>2</sub> gas mixture with the pressure of 26.7 kPa and 26.7 kPa, respectively by a temperature programmed reaction (TPR) process; the catalyst was heated up to 1223 K at a linear rate of 10 K·min<sup>-1</sup> where it was maintained for a certain period (termed as the temperature maintaining period). Nb loading was regulated to 3 wt%. For optimization of temperature maintaining period, the completion of carburization was firstly evaluated by the evolution of CO [4].

For comparison, the silica support (Aerosil, #200) without the mesopore was also employed to the support (NbC/SiO<sub>2</sub>). In this case, the carburization was completed for 30 min at the temperature-maintaining period.



## 2.2. XAFS measurements

Nb  $L_3$ -edge XAFS data were collected in partial fluorescence yield (PFY) by silicon drift detector (SDD) and total electron yield (TEY) modes at BL13 of the SR center (Ritsumeikan University, proposal no. R1450) by using InSb(111) double crystal monochromator. Nb  $K$ -edge XAFS data were taken at PF-AR NW10A (Proposal no. 2014G575) of IMSS-KEK by Si(311) double crystal monochromator in a transmission mode by using two ion-chambers for  $I_0$  and  $I$  filled with Ar50%(N<sub>2</sub> 50%) and Ar100%, respectively. Data analysis was conducted using the Athena [5] for Nb  $L_3$ -edge and EXAFS analysis program REX2000 [6] for Nb  $K$ -edge. Fourier transform (FT)  $k$ -range of  $k^3$ -weighted EXAFS data was 30-150 nm<sup>-1</sup>. Model parameters for Curve-fitting (CF) analysis were extracted from EXAFS oscillations observed for bulk NbC.

## 2.3. Adsorption measurement and catalytic reaction

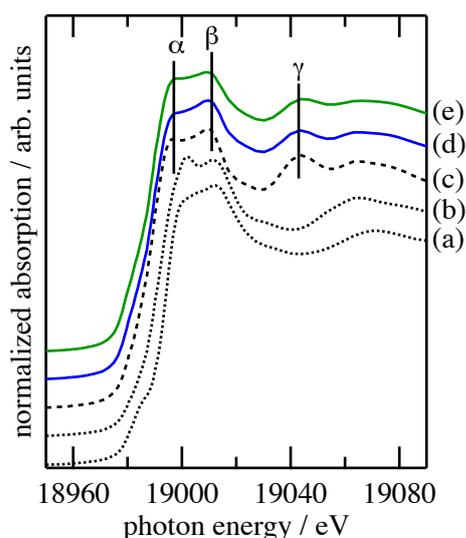
N<sub>2</sub> adsorption isotherms at 77 K of the samples were measured using BELSORP-MAX (BEL Japan, INC). Samples were degassed at 473 K for 2 h before measurement. The specific surface area and pore volume were obtained by Brunauer–Emmett–Teller (BET) method and by Barrett–Joyner–Halenda (BJH) method, respectively.

Ethene hydrogenation was carried out at 273 K in a closed circulating system. The catalyst was treated with 40.0 kPa of H<sub>2</sub> at 1223 K, followed by the evacuation at the same temperature for 15 min, prior to use. The initial pressures of ethene and H<sub>2</sub> were 1.3 kPa and 6.7 kPa, respectively. The catalytic activity of the catalyst was determined from the initial rate of ethane formation.

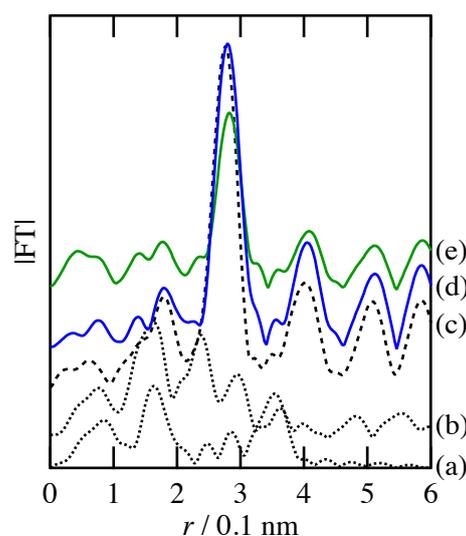
## 3. Results and discussion

### 3.1. Nb $K$ -edge XAFS

Figure 1 showed the Nb  $K$ -edge XANES profiles for the carburized catalysts and reference compounds. Peaks at around 18998, 19011 and 19043 eV are distinctly observed in bulk NbC as compared to those in bulk Nb oxide. Those three peaks, designated as  $\alpha$ -,  $\beta$ - and  $\gamma$ -peaks, respectively, can be utilized as fingerprint for the existence of NbC species. Nb  $K$ -edge XANES profiles of the carburized catalyst (Fig. 1 d, e) are similar to that of bulk NbC. NbC composition of NbC/SiO<sub>2</sub> and NbC/SBA were 97.9% and 90.7%, respectively, by linear combination analysis.



**Figure 1.** Nb  $K$ -edge XANES spectra for (a) bulk Nb<sub>2</sub>O<sub>5</sub>, (b) bulk NbO<sub>2</sub>, (c) bulk NbC, (d) NbC/SBA and (e) NbC/SiO<sub>2</sub>.



**Figure 2.** FT of  $k^3$ -weighted Nb  $K$ -edge EXAFS oscillations for (a) bulk Nb<sub>2</sub>O<sub>5</sub>, (b) bulk NbO<sub>2</sub>, (c) bulk NbC, (d) NbC/SBA and (e) NbC/SiO<sub>2</sub>.

To clarify the local structure around Nb atom, Nb *K*-edge EXAFS data were collected and Fourier-transformed as shown in Fig. 2 (phase shifts are not corrected). FT profiles of NbC/SBA and NbC/SiO<sub>2</sub> were similar to that of bulk NbC except the intensity. CF analysis was conducted for the main peak at around 0.28 nm, which can be attributed to the nearest Nb-(C)-Nb coordination, besides Nb-C (0.223 nm) and Nb-(C)-Nb (0.446 nm) coordination. CF results were summarized in Table 1.

According to the CF results, the *CN*s of peaks at around 0.2 nm which can be attributed Nb-C was almost 6.0 suggesting the Nb species in both catalysts were converted into NbC. At first, we expected that mesoporous silica SBA-15 may have the templating effect that limiting the NbC cluster size, and hence, the NbC cluster size in SBA-15 would be smaller than in SiO<sub>2</sub> support. However, the FT intensity and the *CN* of Nb-(C)-Nb1 of NbC/SBA were larger than those of NbC/SiO<sub>2</sub>, which means that the larger NbC cluster created on SBA-15. The reason of this reversal cluster size order is still unclear, however, the mesopore size of SBA-15 is thought to be one of the factors.

As estimating the NbC cluster size on SBA-15 from the *CN*s of Nb-(C)-Nb1 and Nb-(C)-Nb2, 1.9 nm in diameter was obtained by assuming the corner cutting cubic structure. Table 2 showed textural properties of NbOx/SBA and NbC/SBA by N<sub>2</sub> adsorption measurements. Pore diameter of NbOx/SBA and NbC/SBA were 8.1 and 6.2 nm, respectively. Such large pore size was not able to have the templating effect for such smaller cluster size.

**Table 1.** Curve-fitting results of Nb *K*-edge EXAFS for NbC catalysts.

	coordination	<i>CN</i>	<i>r</i> (nm)	<i>dE</i> (eV)	$\Delta\sigma^2$ (10 <sup>-4</sup> nm <sup>2</sup> )
bulk NbC (model)	Nb-C	6	0.223	0.0	$\sigma = 0.006$ (nm)
	Nb-(C)-Nb1	12	0.315	0.0	$\sigma = 0.006$ (nm)
	Nb-(C)-Nb2	6	0.446	0.0	$\sigma = 0.006$ (nm)
NbC/SBA	Nb-C	6.8±0.9	0.224±0.001	3.13±1.79	0.28±0.16
	Nb-(C)-Nb1	8.2±1.5	0.318±0.001	2.55±2.03	-0.20±0.11
	Nb-(C)-Nb2	3.5±0.7	0.449±0.001	1.12±1.65	-0.27±0.14
NbC/SiO <sub>2</sub>	Nb-C	6.6±0.8	0.222±0.001	1.75±1.68	0.45±0.18
	Nb-(C)-Nb1	6.5±1.1	0.318±0.001	7.04±1.86	0.00±0.24
	Nb-(C)-Nb2	2.2±0.4	0.450±0.001	3.47±1.60	-0.20±0.16

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

### 3.2. Nb *L*<sub>3</sub>-edge XAFS

Nb *L*<sub>3</sub>-edge XAFS measurements were carried out to clarify the chemical state of Nb species in the NbC/SBA catalysts as shown in Fig. 3. The time presented in catalyst notation means the temperature-maintaining period (Figs. 3e-3h). Peak profile and edge position resembles from bulk Nb<sub>2</sub>O<sub>5</sub> to bulk NbC as lengthening the period. As prolonging the period, the band about 2383.1 eV gradually grew clearly same as bulk NbC. The completion of the carburization is expected to be in the 180 to 240 min. Obtained NbC/SBA-180 min and NbC/SBA-240 min catalysts showed the ethene hydrogenation activity at 273 K. However, the latter catalyst showed less activity than the former did. And no ethane was detected on NbC/SBA-30 min catalyst. It can be said that the carburization degree must be high to some extent to show the catalysis. However, the excess carburization reduces the catalysis, which may result from the deposited carbon. Indeed, the enough hydrogen treatment at 1223 K before the reaction improved the catalysis. The 15 min hydrogen treated and 90 min hydrogen treated NbC/SBA catalysts showed the initial rate of ethane was 4.8 and 10.6 mmol·min<sup>-1</sup>·g<sub>Nb</sub><sup>-1</sup>, respectively. This confirmed that deposited carbon on the carburized catalyst surface affected catalysis. To convert the active carbide catalyst, removal process of deposited carbon is necessary.

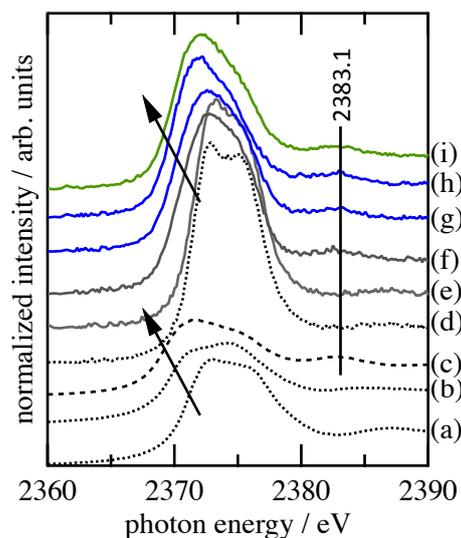
On the other hand, the temperature-maintaining period 30 min was enough for the carburization completion for NbC/SiO<sub>2</sub> catalyst as estimated from the edge energy position (Fig. 3i). Although NbC species on SiO<sub>2</sub> support is smaller than that on SBA support and fully carburized, the initial rate of

ethene hydrogenation was  $1.6 \text{ mmol}\cdot\text{min}^{-1}\cdot\text{g}_{\text{Nb}}^{-1}$ , which was much smaller than that of NbC/SBA showed. Mesoporous structure might affect the rate of carburization and continuing carbon deposition, and thus it is supposed that the catalytic activity was differed between NbC/SBA and NbC/SiO<sub>2</sub>. However, the deposited carbon on NbC surface did not affect the Nb L<sub>3</sub>-edge XAFS data in this condition.

**Table 2.** Textural properties of catalysts

Catalyst	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V^{\text{a}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$D^{\text{b}}$ (nm)
NbO <sub>x</sub> /SBA	764	1.11	8.1
NbC/SBA	389	0.67	6.2

<sup>a</sup> Total pore volume. <sup>b</sup> Pore diameter determined by Barrett-Joyner-Halenda method.



**Figure 3.** Nb L<sub>3</sub>-edge XANES spectra in PFY mode for (a) bulk Nb<sub>2</sub>O<sub>5</sub>, (b) bulk NbO<sub>2</sub>, (c) bulk NbC, (d) NbO<sub>x</sub>/SBA, (e) NbC/SBA-0 min, (f) NbC/SBA-30 min, (g) NbC/SBA-180 min, (h) NbC/SBA-240 min and (i) NbC/SiO<sub>2</sub>.

## Conclusion

NbC was prepared on the support by using peroxoniobic acid, followed by the carburization in a closed circulating system. Completion of carburization can be visualized from the Nb K- and L<sub>3</sub>-edges XAFS analysis. Also the NbC cluster size could be estimated from Nb K-edge XAFS analysis. Although the prolongation of the temperature-maintaining period is seemed to be the effective way to complete the carburization, excess carburization treatment may cause the carbon deposition on the surface and leads to the decrease in the active site.

## Acknowledgment

This study was supported by a Grant-in-Aid for Scientific Research from JSPS (26420784). Nb L<sub>3</sub>-edge XAFS measurements were carried out by using a Project for Creation of Research Platforms and Sharing of Advanced Research Infrastructure (R1450) at BL13 of the SR Center.

## References

- [1] Kodama S, Ichikuni N, Bando K K, Hara T and Shimazu S 2008 *Appl. Catal. A* **343** 25-28
- [2] Zhao D, Huo Q, Feng J, Chmelka B F and Stucky G D, 1998 *J. Am. Chem. Soc.* **120** 6024-6036
- [3] Wakai Y, Hara T, Bando K K, Ichikuni N and Shimazu S 2009 *Top. Catal.* **52** 1517-1524
- [4] Ichikuni N, Sato F, Shimazu S and Uematsu T 2002 *Top. Catal.* **18** 101-104
- [5] Ravel B and Newville M 2005 *J. Synchrotron Rad.* **12** 537-541
- [6] REX 2000 is a commercially available analytical program for XAFS provided by Rigaku Corp.