

Carburization property of mesoporous silica supported Nb catalyst

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1. Introduction

Developing the catalyst materials for substituting the noble metal catalysts is an urgent issue. Since the early transition metal carbide (ETMC) shows the resemblance in noble metal catalysis, it can be one of the attractive candidates. Usually, ETMC was obtained from corresponding oxide by treating under a hydrocarbon and hydrogen gas at high temperature. The excess carburization process leads to the diminishment of the active site cause of the particle size growth as well as deposited carbon. To avoid the excess carburization treatment, the estimation of carburization degree is important issue. In this study, mesoporous silica supported Nb catalyst was prepared and carburized. The carburization degree was evaluated by using Nb L_{3} -edge XANES analysis and the effect of the support mesoporosity on carburization was also discussed.

2. Experimental

Mesoporous silica SBA-15 and MCM-41 was prepared as in the literature [1, 2]. Peroxonibic acid (PNA) was prepared as in the literature [3] and applied to a preparation of a carbide precursor NbOx/SBA and NbOx/MCM with a Nb loading of 3 wt%. Thus obtained catalyst was carburized in a closed circulating system under CH₄ and H₂ gas mixture by a temperature programmed reaction (TPR) process. In this process, the catalyst was heated up to 1223 K at a linear rate of 10 K·min⁻¹ and kept for a certain period (termed as the temperature maintaining period). The maintaining period was presented in the catalyst notation as NbC/SBA-30 (maintaining period of 30 min). Acquired data was analyzed by a program Athena [4].

Nb L_3 -edge XAFS data were obtained in a partial fluorescence yield (PFY) by silicon drift detector (SDD) and a total electron yield (TEY) modes at BL13 of the SR Center (Ritsumeikan University, proposal No. R1450, R1551) by using InSb(111) double crystal monochromator.

3. Results and Discussion

3.1. Carburization degree of the surface and bulk. Figure 1 shows the Nb L_3 -edge XAFS data. By comparing the edge position and peak profile with the standard sample, the chemical state of Nb species can be determined. As Nb species were reduced from Nb₂O₅ to NbC, the edge energy became smaller both in PFY and TEY modes (Fig. 1 (A)a-c, (B)a-c).

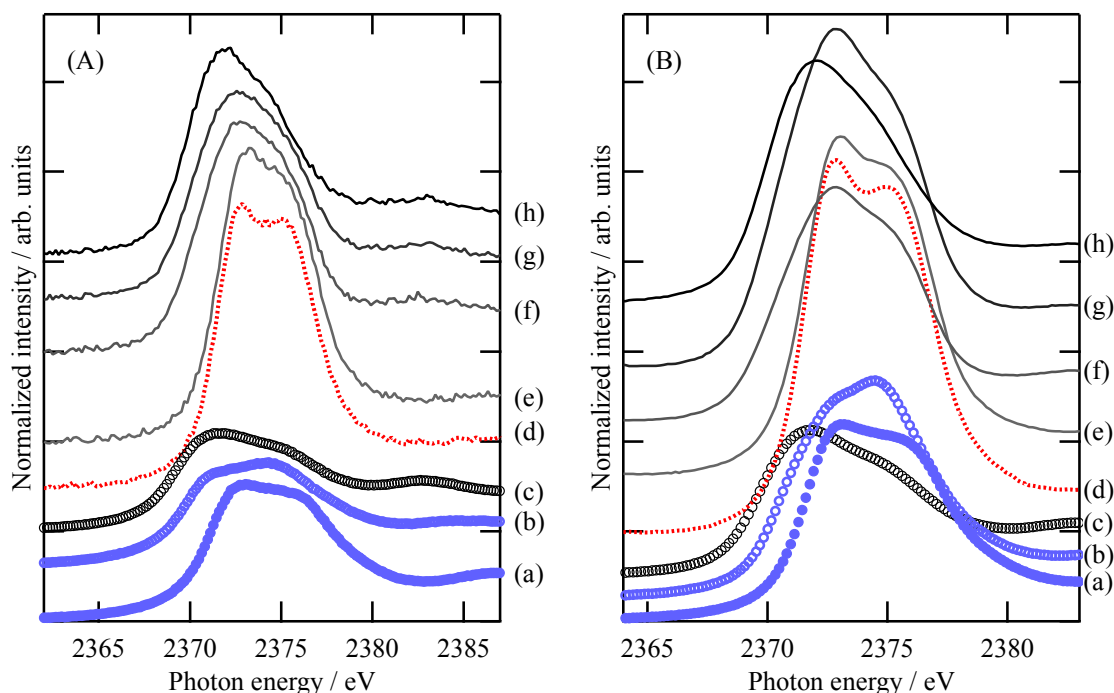


Fig. 1. Nb L_3 -edge XANES spectra in (A) PFY mode and (B) TEY mode; (a) bulk Nb₂O₅, (b) bulk NbO₂, (c) bulk NbC, (d) NbOx/SBA, (e) NbC/SBA-0, (f) NbC/SBA-30, (g) NbC/SBA-180 and (h) NbC/SBA-240.

Interestingly, the observed carburizing tendency was different in PFY and TEY modes. In TEY mode, the edge position was almost the same for the maintaining period of 30, 180, 240 min (Fig. 1(B)f-h). In contrast, the edge position difference was observed among NbC/SBA-30, NbC/SBA-180 and NbC/SBA-240 in PFY mode (Fig. 1(A)f-h). In the latter case, the edge energy was the following order; NbC/SBA-30 < NbC/SBA-180 < NbC/SBA-240. The edge position of NbC/SBA-240 was almost the same as bulk NbC (Fig. 1(A)h, c).

Although the NbC/SBA-180 and NbC/SBA-240 catalysts showed the ethene hydrogenation at 273 K activity, NbC/SBA-30 catalyst did not. The activity of NbC/SBA-180 was higher than that of NbC/SBA-240. The carburization degree must be high to some extent to show the

activity in ethene hydrogenation. However, the excess carburization causes the less activity, which would come from carbon deposition on the NbC surface. It is known that bulk information and the surface information can be obtained by PFY and TEY modes, respectively. From above results, it can be said that the supported Nb oxide species carburized from a surface to an inner part. It is not required the complete carburization to show the catalytic activity. If the carburization was completely done (Fig. 1(A)h), the carbon deposition of the surface seemed to be occurred [5].

3.2. Effect of the support mesoporosity.

Figure 2 shows the Nb L_3 -edge XAFS data in PFY mode. Although carburization maintaining period of 60 min seemed to be enough for MCM-41 support, the longer maintaining period of 120 min was required for the carburization of Nb species on SBA-15 support (Fig. 2d-f).

Average pore size of the MCM-41 and SBA-15 in this experiment was 3.4 and 8.1 nm, respectively. By taking into account of the gas diffusion during the carburization process, Nb species on MCM-41 seemed to require the longer carburization period. This opposite tendency might come from the particle size effect of the Nb species on the support. Using mesoporous support might have a template effect, and limit the particle size less than a pore size. The present results suggest that the carburization property of Nb oxide is strongly affected by its particle size.

References

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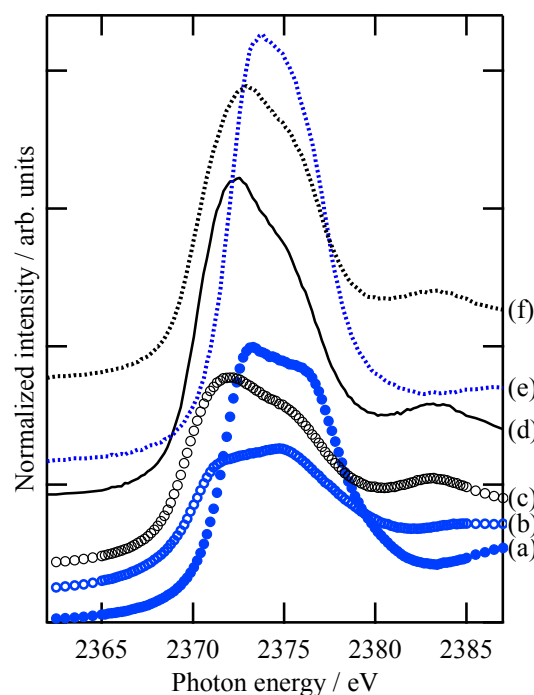


Fig. 2. Nb L_3 -edge XANES spectra in PFY mode; (a) bulk Nb_2O_5 , (b) bulk NbO_2 , (c) bulk NbC, (d) NbC/MCM-60, (e) NbC/SBA-60 and (f) NbC/SBA-120.