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EXAFS studies on the hydrogen treated NbC/MCM-41 catalyst

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Introduction

It is reported that the carburization of bulk Nb_2O_5 into NbC requires high temperatures as 1370 K [1]. We have demonstrated that the carburizing temperature could be lowered to 1073 K by supporting the Nb species to amorphous silica [2]. Moreover, the smaller particle size of NbC could be prepared by using the highly ordered inorganic mesoporous material MCM-41, possessing the 1.5-5 nm pore, instead of amorphous silica. Excess carburization leads to deposit the carbon on the carbide, and deactivate the catalysis. The high temperature hydrogen treatment was applied to remove the excess carbon on the surface. It is still unknown that such high temperature treatment affects the carbide particle aggregation or not.

In this study, we prepare the NbC/MCM-41 catalysts, and collected an *in-situ* XAFS data to investigate the effect of high temperature hydrogen treatment.

Experimental

The hexagonal mesoporous silica MCM-41 was hydrothermally synthesized using sodium silicate and $[CH_3(CH_2)_{13}N(CH_3)_3]Br$ at 373 K for 144 h. MCM-41 supported Nb_2O_5 precursors were prepared by an impregnation method of MCM-41 with an $NbCl_5$/methanol solution. The precursor oxide catalyst was carburized in a 20% CH_4/H_2 mixed gas flow to produce NbC/MCM-41 catalyst by TPR process; the samples were heated at a linear rate of 10 K·min^{-1} to 1173 K, and kept for 30 min.

Nb K-edge EXAFS spectra were collected at BL-10B of the Photon Factory with Si(311) channel cut monochromator. The sample was pressed into self-supporting disk and transferred into specially designed SUS cell with two Acrylic windows. The sample can be heated up to 1273 K by using infrared gold image furnace. Curve-fitting analyses of EXAFS oscillations in the *k*-space were performed by the EXAFS analysis program REX2000 (Rigaku Co.). Model parameters for curve-fitting analysis (back scattering amplitude and phase shift) were extracted from an EXAFS oscillation observed for bulk NbC (N_1 =12, r_1 =0.315 nm).

Results and discussions

The removal of surface amorphous carbon and/or small crystalline carbon by H_2 treatment (1173 K) was observed by Raman spectroscopy. The activity of catalytic propylamine decomposition was increased by the high temperature H_2 treatment.

Figure 1 shows the FT of the k^3-weighted EXAFS oscillation for NbC/MCM-41 catalyst. Catalysts were treated with 120 ml·min^{-1} flow of H_2 in the *in-situ* XAFS cell and heated for 90 min at 673 K and 1173 K as shown in Fig. 1(b) and 1(c), respectively. Although the high temperature H_2 treatment was carried out *in-situ*, XAFS data shown in Fig. 1 were collected at room temperature under H_2 flow to improve the S/N. Profiles of each spectrum in Fig. 1 are almost the same. Moreover, the coordination number of Nb-(C)-Nb (main peak) was determined to 6.2 for all catalysts. Thus, it can be concluded that by high temperature H_2 treatment did neither cause the aggregation of NbC particle on the MCM-41 surface nor the modification of NbC surface.

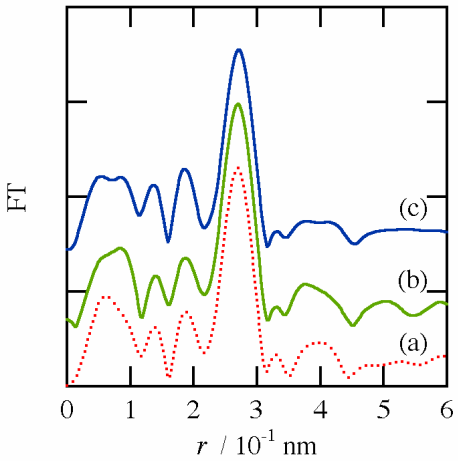

Figure 1. k^3-weighted FT of NbC/MCM-41 catalysts; (a) as prepared, (b) H_2 673 K and (c) H_2 1173 K.

References

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