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EXAFS studies on the MCM-41 supported NbC catalysts

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Introduction

Highly ordered inorganic mesoporous material MCM-41, possessing the 2-4 nm pore, has the specific surface area more than 1000 $m^2 \cdot g^{-1}$. Thus, it seemed to be good support for catalyst to maintain the higher dispersion. However, the mesoporous structure was easily destructed by some treatment, especially immersing to solvent and thermal treatment. Moreover, the carburization of bulk Nb_2O_5 into NbC requires relatively high temperature as 1370 K [1]. Although the carburising temperature could be reduced to 1073 K by use of silica support [2], it is still high from calcination temperature. So it seems that it was difficult to prepare NbC/MCM-41 catalyst with highly ordered mesoporous structure.

In this study, we tried to prepare the MCM-41 supported NbC catalysts, and characterized by use of XAFS measurement.

Experimental

Nb_2O_5/SiO_2 precursors were prepared by an impregnation method of SiO_2 (Aerosil #200) or MCM-41 with a $NbCl_5$/methanol solution. The calcined precursor oxide catalyst was carburized in a 20% CH_4/H_2 mixed gas flow to produce NbC/SiO_2 catalyst by TPR process; The samples were heated at a linear rate of 10 $K \cdot min^{-1}$ to 1273 K, which was held until no CO was detected. Catalysts were designated with a kind of silica as NbC/200 or NbC/MCM-41.

Nb K-edge EXAFS spectra were collected at BL-10B of the Photon Factory with Si(311) channel cut monochromator. The sample was transferred into Al cells with Kapton windows. 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 and N_2 = 6, r_2 = 0.446 nm).

Results and discussions

Figure 1 shows the FT of the k^3-weighted EXAFS oscillation. NbC/200 catalyst exhibits the almost same profile as bulk NbC. Although the magnitude of the FT for NbC/MCM-41 is very weak, the profile resembles to the bulk one. The curve-fitting results were summarised in Table 1. Although the FT profiles of the catalysts resembled as bulk NbC, the CN was drastically diminished. As the case of 1st Nb-Nb coordination, CN for NbC/200 and NbC/MCM-41 were 9.5 and 5.4, respectively, suggesting the smaller NbC particles could be constructed on the MCM-41.

From X-ray diffraction analysis and transmission electron microscope observation, the specific hexagonal mesoporous structure of the MCM-41 was maintained for NbC/MCM-41. The design of highly dispersed NbC particle on MCM-41 surface with highly ordered mesoporous structure was achieved by use of the $NbCl_5$ as Nb precursor and the TPR method for carburization.

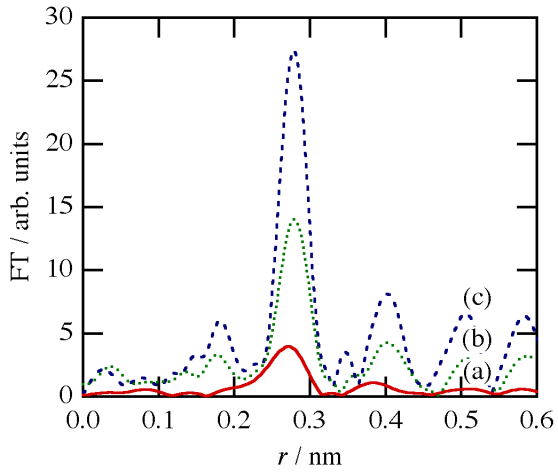

Figure 1. k^3-weighted FT of NbC catalysts; (a) NbC/MCM-41, (b) NbC/200 and (c) bulk NbC.

Table 1: Curve-fitting results for Nb-Nb coordination of supported NbC catalysts

catalyst	N	*r* / nm	d*E* / eV	DW / nm
NbC/MCM-41	5.4	0.311	-6.88	0.0097
	2.0	0.438	-12.6	0.0094
NbC/200	9.5	0.316	2.12	0.0075
	3.1	0.447	1.79	0.0057
bulk NbC (model)	12.0	0.315	0.00	0.006
	6.0	0.446	0.00	0.006

References

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