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EXAFS studies on the SiO_2 supported NbC catalysts prepared by the two-step TPR method

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Introduction

The carbide catalysts were usually prepared from corresponding oxide by TPR (temperature programmed reaction) [1, 2]. The carburization of Nb_2O_5 into NbC requires relatively high temperatures, which may lead to the difficulty of preparation small size NbC. We have already demonstrated that the support effect and the surface carbon could prevent the aggregation of Nb components during carburization for NbC/SiO_2 catalyst [3]. In this study, we prepared the supported NbC catalysts by the two-step TPR method and examined their structures.

Experimental

2wt% Nb_2O_5/SiO_2 catalysts were carburized in a 20% CH_4/H_2 mixed gas flow to produce NbC/SiO_2 by TPR process; The precursors were heated at a linear rate of 10 K·min^{-1} to the final temperature (T_{carb}), which was held until no CO was detected. Catalysts were designated with T_{carb} as NbC(1273). Two-step TPR method was performed as follows; The precursors were carburized at 1073 K as usual method, followed by additional TPR treatment to 1273 K at the same rate, which was designated as NbC(1073-1273).

Nb K-edge EXAFS spectra were collected at BL-10B of the Photon Factory with Si(311) channel cut monochromator. The sample was transferred to Al cells with Kapton windows connected to a closed circulating system without contacting air. Curve-fitting analyses of EXAFS oscillations were conducted 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=12, r=0.315 nm).

Results and discussion

Figure 1 shows the FT of the k^3-weighted EXAFS oscillation. All the catalysts exhibited the almost same profiles as bulk NbC. The curve-fitting results were summarised in table 1. The bond length almost unchanged for all the catalysts. On the other hand, the CN became larger as increasing T_{carb}, suggesting that NbC growth was initially controlled by carburization temperature.

Although the NbC(1073-1273) catalyst carburized at 1273 K, the CN was smaller than that of NbC(1273) and close to NbC(1073). It means that NbC growth was completed at first TPR stage (T_{carb}=1073 K). Moreover, additional TPR process would produce the amorphous and/or graphite carbon around NbC particles and these residual carbons could immobilize the NbC particles during carburization process. NbC surface was stabilized toward oxygen by covered carbon and seemed to have catalytic activity. The design of highly dispersed NbC particle on SiO_2 surface was achieved by use of the two-step TPR method.

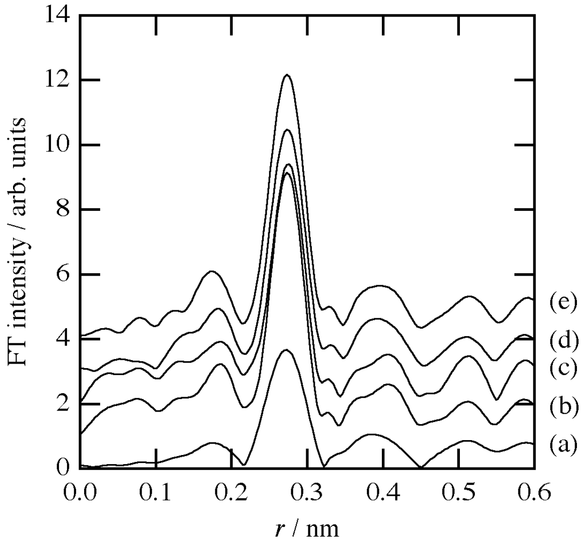

Fig. 1. FT profiles of 2wt% NbC/SiO_2 catalysts; (a) NbC(1073), (b) NbC(1073-1273), (c) NbC(1173), (d) NbC(1223) and (e) NbC(1273).

Table 1: Curve-fitting results for Nb-Nb coordination of 2wt% NbC/SiO_2 catalysts

catalyst	N	r / nm	dE / eV	DW / nm
NbC(1073)	7.3	0.314	-4.00	0.011
NbC(1073-1273)	7.6	0.314	0.819	0.0085
NbC(1173)	7.8	0.313	-1.26	0.0090
NbC(1223)	8.1	0.313	-0.20	0.0090
NbC(1273)	9.0	0.313	-2.37	0.0090

References

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