

XAFS analysis on the supported vanadium carbide catalysts

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1 Introduction

Early transition metal carbides (ETMC) are one of the potential materials to substitute the Pt group metals, since they have the resemblance in catalysis to those of group 8-10 metals [1]. However, high temperature is required to prepare the ETMC, and hence, the aggregation of active site is inevitable. To prevent the aggregation of ETMC, we succeeded to fix the niobium oxide on SiO₂ support and converted into NbC/SiO₂ [2].

It is reported that bulk vanadium oxide is carburized into vanadium carbide at 1253 K [3]. In this report, SiO₂ supported VC catalyst was prepared by carburization of vanadium oxide on SiO₂ (VO_x/SiO₂) as a precursor oxide. The effect of retention time on the carburization degree of vanadium was studied by XAFS.

2 Experimental

Precursor oxide (VO_x/SiO₂) was prepared from peroxovanadic acid and SiO₂ support (Aerosil, #200) by conventional impregnation method. Vanadium loading was regulated as 3 wt%. VO_x/SiO₂ was carburized in a flow reactor under CH₄-H₂ mixed gas stream to produce VC/SiO₂ catalyst. Carburizing process is consisted from two steps; one is temperature-elevating step at a linear rate of 10 K·min⁻¹ to 1073 K, and the second is temperature-retaining step at a 1073 K for a certain period (0 to 90 min).

V *K*-edge XAFS were collected at BL-7C (KEK-PF) and BM23 (ESRF) in a fluorescence mode. Catalyst was transferred into aluminium cell with Kapton windows at the X-ray path. EXAFS analysis was carried out by EXAFS analysis program REX2000 (Rigaku Co.).

3 Results and Discussion

FT spectra of V *K*-edge EXAFS are presented in Fig. 1. Although small peak at around 0.24 nm, which can be assigned to V-(C)-V coordination, was observed for VC/SiO₂-1073K(0min), overall FT profile was resembled to V₂O₅. The vanadium oxide on SiO₂ support was not carburized but reduced partly as only elevating the temperature up to 1073 K under CH₄-H₂ mixed gas stream.

The peak corresponding to V-(C)-V coordination was clearly observed as lengthening the temperature-maintaining time (Fig. 1(b)-(d)). As extended the time of 90 min, FT profile showed the similarity to bulk VC except for the intensity (Fig. 1(d) and (f)). Gas composition analysis revealed that 90 min at 1073 K is enough for carburization of 3 wt% VO_x/SiO₂ into VC/SiO₂. The coordination numbers of V-(C)-V for bulk VC and VC/SiO₂-1073K(90min) were 12.0 and 8.7±0.6,

respectively. It is concluded that the carburization temperature can be lowered down to 1073 K by supporting vanadium species on SiO₂ and the small vanadium carbide cluster can be obtained without visible aggregation by using VO_x/SiO₂ as a carbide precursor.

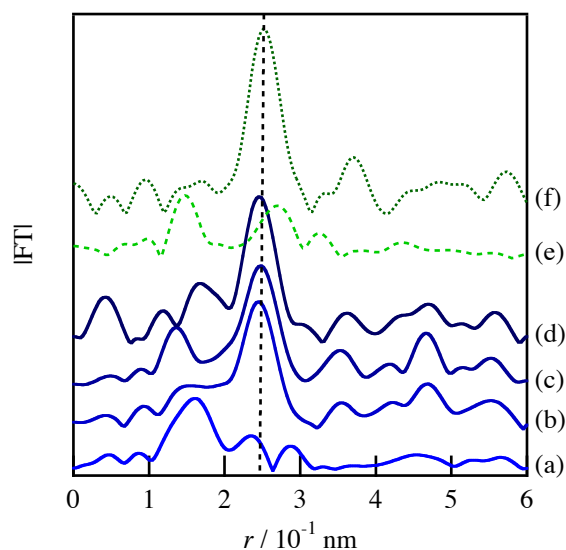


Fig. 1: FT of k^3 -weighted V *K*-edge EXAFS for carburized V catalysts and reference compounds; (a) VC/SiO₂-1073K(0min), (b) VC/SiO₂-1073K(30min), (c) VC/SiO₂-1073K(60min), (d) VC/SiO₂-1073K(90min), (e) V₂O₅ and (f) bulk VC.

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