Materials Science

NW10A/2010G064

XAFS analysis on the supported molybdenum carbide catalysts

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Introduction

Early transition metal carbides (ETMC) are one of the new catalyst material candidates to substituting the Pt group metals, due to the resemblances in physical and chemical properties to those of the group 8-10 metals. ETMC were usually prepared from the corresponding oxides by treating with CH_4-H_2 gas passage at high temperatures, such as 1090 K (MoC) [1]. Lowering the carburizing temperature is strongly expected for the catalytic application of ETMC.

In this study, MoC/SiO_2 catalysts were obtained by carburization of Mo/SiO_2 in a CH_4-H_2 mixed gas flow. The effect of the support porosity on the structure of the MoC was investigated by XAFS analysis.

Experimental

Mo/SiO_2 was prepared from $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ or $MoCl_5$ and SiO_2 support by conventional impregnation method. Non-porous silica (NPS; Aerosil, #200) and mesoporous silica (MCM-41) were used for the support material. The loading of Mo was regulated to 3 wt%. The precursor oxide was carburized in a closed circulating system under CH_4-H_2 mixed gas to produce MoC/SiO_2 catalyst by the following TPR process; the sample was heated to 973 K at the linear rate of 10 $K\cdot min^{-1}$ and maintained for 60 min.

Mo *K*-edge XAFS spectra were collected at AR NW10A with Si(311) double crystal monochromator in a transmission mode. Catalyst was transferred into the aluminium cell with Kapton windows at the both ends of the X-ray path without contacting air. EXAFS analysis was carried out by the program REX2000 (Rigaku Co.).

Results and discussion

FT spectra of Mo *K*-edge EXAFS were shown in Fig. 1. Comparing the profile of carburized catalyst with reference compounds, Mo species on MCM-41 seemed to be fully carburized at 973 K. However, carburization degree and/or the carbide species could not be determined especially for Mo species on NPS support.

To clarify the chemical species of carburized catalyst, Mo *K*-edge XANES were analyzed. XANES data of the catalysts and reference compounds were shown in Fig. 2. XANES data were fitted by using α-MoC_{1-x} and β-Mo_2C in the energy range of 19970-20070 eV. The calculated value was presented in Table. An α-MoC_{1-x} species was mainly produced on MoC/NPS (98 %), whereas two types of carbide species (α-MoC_{1-x} and β-Mo_2C) were almost equally produced on MoC/MCM-41. By using the mesoporous silica as support, the ratio of the stoichiometric molybdenum carbide (β-Mo_2C) can be increased.

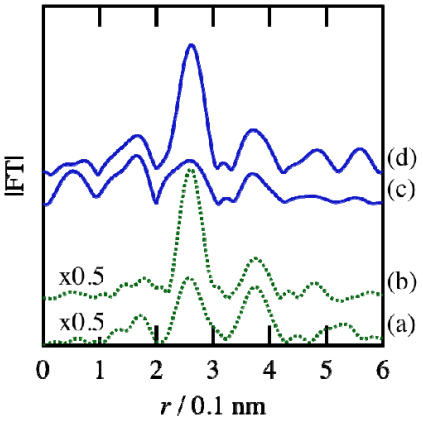

Fig. 1. FT of k^3-weighted Mo *K*-edge EXAFS for carburized Mo catalysts and reference compounds; (a) α-MoC_{1-x}, (b) β-Mo_2C, (c) MoC/NPS, (d) MoC/MCM-41.

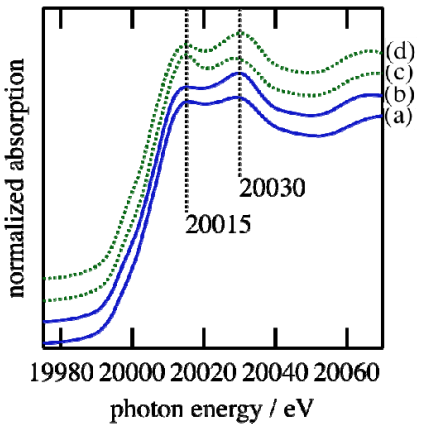

Fig. 2. Mo *K*-edge XANES for carburized Mo catalysts and reference compounds; (a) MoC/NPS, (b) MoC/MCM-41, (c) α-MoC_{1-x}, (d) β-Mo_2C.

Table: Pattern fitting results for carburized catalysts

Catalyst	α-MoC_{1-x}	β-Mo_2C
MoC/NPS	0.98	0.02
MoC/MCM-41	0.56	0.44

Reference

[1] S. T. Oyama, J. C. Schlatter, *Ind. Eng. Chem. Res.* **27**, 1639 (1988).

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