

Mo K-Edge XAFS Study of Supported Mo ions on Silica-Alumina for Metathesis Catalysts

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Introduction

Molybdenum-containing heterogeneous catalysts for olefin metathesis have been a great interest since Banks et al. had reported the first observation. For the Mo metathesis catalyst, reductive pretreatment (with H₂ or CO) generally needs to reduce Mo⁶⁺ ions to form reduced ions as the active species. However, we reported recently that molybdena supported on amorphous silica-alumina exhibit high activity for propene metathesis, which is a typical metathesis reaction, even at room temperature without reductive pretreatment. To obtain detailed structural information about the active molybdena species for metathesis, Mo K-edge XANES was applied to characterize the active molybdena species.

Experimental

Supported molybdena catalyst samples were prepared by impregnation of each metal oxide support with an aqueous solution of ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄•4H₂O). The oxide supports used in this study were SiO₂, γ-Al₂O₃, H-ZSM-5, H-MOR, and amorphous SiO₂-Al₂O₃ containing 28.6 wt% (JRC-SAH-1, denoted as SAH-1) and 13.8 wt% (JRC-SAL-2, denoted as SAL-2) Al₂O₃. The impregnating solution was stirred at room temperature and evaporated at 343 K for 6 hours, and then, the paste was dried for overnight and calcined at 773 K for 6 hours. Mo K-edge XAFS spectra were measured at BL-10B of KEK-PF in a transmission mode at room temperature.

Results and discussion

In our previous study, it is concluded that 7.5 wt% MoO₃/SAH-1 catalyst shows the maximum reactivity for propene metathesis at 293 and 473 K without any reductive pretreatment. In this catalyst, pre-reduction with H₂ at 773 K brought about low activity for metathesis. This feature was also seen in zeolite-supported MoO₃ catalysts. In general, reductive pretreatment gives reduced Mo ions as active species for metathesis. Thus we attempted to apply XAFS spectroscopy to elucidate structural details. Mo K-edge XANES spectra on MoO₃/SAH-1 catalysts were shown in Fig. 1. Before reaction, the spectral feature is almost similar to Mo-polyanions such as AHM (ammonium heptamolybdate) or ADM (ammonium dimolybdate). These polymolybdates has distorted octahedral and/or T_d tetrahedra. It suggests that poorly-ordered Mo polyanion species are dominant

on silica-alumina. After reaction, structural change can slightly be seen in XANES. From the results of EXAFS shown in Fig. 2, structural change of Mo ambient can clearly be seen. By the metathesis reaction, FT peak intensity at ca. 1.3 Å becomes low. This indicates the decrease of mean coordination number of oxygen ions around Mo ions. The peak intensity at 3.0 Å due to Mo-Mo scattering is almost independent on the reaction. Thus it is concluded that slight reduction of polymolybdate species was brought about in contact with propene. This redox performance is due to unique property because this phenomenon can hardly be seen in non-silica-alumina-support catalysts.

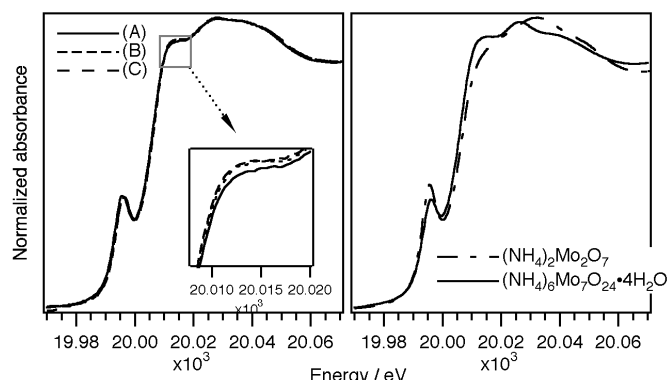


Fig. 1 Mo K-edge XANES spectra (left) of 7.5 wt% MoO₃/SAH-1 catalysts.; before reaction (A), after reaction at 293 K (B), and after reaction at 473 K (C). The spectra of reference polymolybdate compounds are also shown (right).

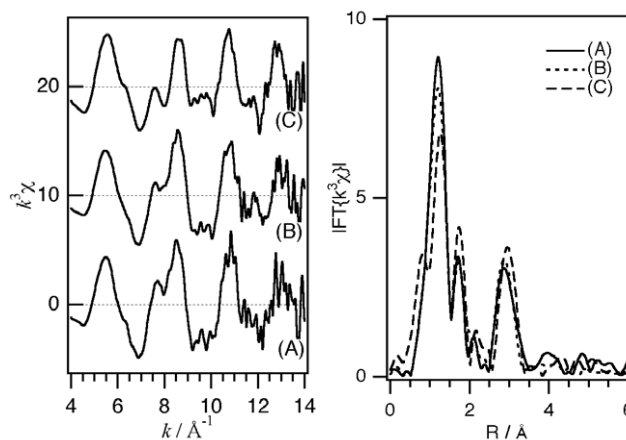


Fig. 2 k³-weighted EXAFS (left) and FT-EXAFS (right) at Mo K-edge on 7.5 wt% MoO₃/SAH-1 catalysts.; before reaction (A), after reaction at 293 K (B), and after reaction at 473 K (C).