

Redox Properties of Mo ions Supported on Zeolites: Mo K-Edge XAFS Study

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Introduction

MoO₃-based catalysts have been applied widely for hydrodesulfurization, hydrocracking, partial oxidation, hydrogenation, metathesis, *etc.* Supported MoO₃ catalysts are typical for olefin metathesis, and a lot of workers had reported many studies about catalytic activity and reaction mechanisms for metathesis reaction. It is widely accepted that metathesis reactivity relates to the reducibility of supported Mo ions, and formation of low-valenced Mo ions (Mo⁵⁺ and/or Mo⁴⁺) by reductive pretreatment is important for metathesis activity. On the other hand, we have reported that Mo species supported on amorphous SiO₂-Al₂O₃ show high activity for propene metathesis without reductive pretreatment. It is summarized in the previous study that poorly-ordered polymolybdate species exist on the support, and support effect of SiO₂-Al₂O₃ is due to the high reducibility of Mo species in contact with propene. For Mo-modified zeolites, remarkable properties and useful activities (e.g., dehydroaromatization of low alkanes) have been reported. Thus, it is important to study differences between the molybdena catalysts supported on amorphous silica-aluminas and zeolites. In this study, we studied the catalytic activity of MoO₃ supported on various zeolite supports without reductive pretreatment, and the difference between silica-alumina and zeolite supports was evaluated by means of Mo K-edge XAFS.

Experimental

Supported molybdena (7.5 wt% as MoO₃) catalysts were prepared by impregnation of each support with an aqueous solution of ammonium heptamolybdate. The supports described in this report were H-BEA (JRC-HBEA-25, Si/Al₂=25), H-MFI (Tosoh HSZ-890-H0A, Si/Al₂=1880), and SAH-1 (amorphous SiO₂-Al₂O₃; JRC-SAH-1, Si/Al₂=4.2). The impregnate 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. FT-EXAFS results were obtained by Fourier transformation of normalized EXAFS (k^3 -weighted) spectra in the range of $\Delta k = 4.0 - 12.5 \text{ \AA}^{-1}$.

Results and discussion

The reactivity of propene methathesis at 473 K was compared between the supported molybdena catalysts. In short, Mo species on H-MFI do not active for metathesis

but assist the formation of higher olefins, and are different from those on SAH-1. To evaluate the structural differences of Mo ions before/after contact with propene at 473 K, Mo K-edge XAFS study was introduced. Fig. 1 shows the XANES spectra of supported MoO₃ catalysts calcined at 773 K. In case of MFI and BEA supports, it is likely that feature of XANES are similar to that of AHM, indicating the formation of polymolybdate species. For SAH-1 support, tetrahedral species may coexist. Fig. 2 shows the FT-EXAFS of those catalysts before/after contact with propene at 423 K. The peaks at *ca.* 1.7 Å should be due to Mo-O scattering. In MoO₃/SAH-1, intensity of the peak becomes low after contact with propene. This feature can also be seen in MoO₃/H-BEA. In MoO₃/H-MFI, however, change of the intensity can scarcely be seen between before and after contact with propene. In addition, intensity of peaks at 3.0-3.5 Å (maybe due to Mo-Mo scattering) in MoO₃/H-MFI is lower than those of other catalysts. It is concluded that local structure of Mo species on H-MFI and its red-ox behavior is quite different from those on H-BEA and SAH-1 supports. Detailed study is now in progress.

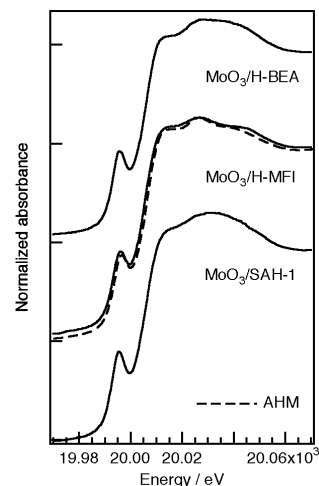


Fig. 1 Mo K-edge XANES of supported MoO₃ catalysts.

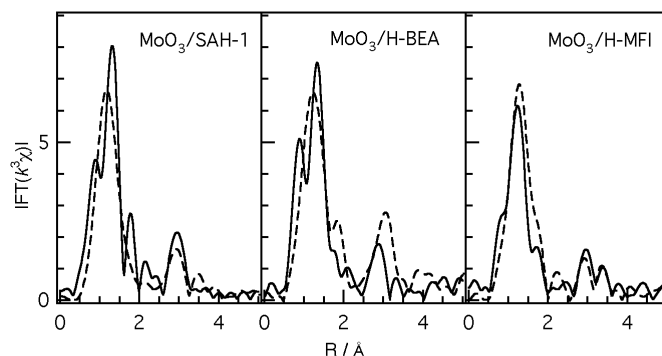


Fig. 2 FT-EXAFS of supported MoO₃ catalysts. (solid line: calcined. dotted line: after contact with propene at 423K)