

Catalytically Active Mo Species Supported on Zeolites for Methane Dehydroaromatization: Mo K-Edge XAFS Study

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Introduction

MoO₃-modified H-MFI shows high activity for dehydroaromatization of methane, although serious deactivation due to carbon deposition and/or reduction of Mo species can not be avoided during the reaction. In this reaction, many workers have been revealed reduction of Mo species is brought about in contact with methane in the initial step. Reduced Mo ions react methane to form carbide species, Mo₂C, in the second stage. The carbide species is active for dehydroaromatization of methane to form benzene, however, deactivation is brought about by carbon deposition on the catalyst surface at the same time. It is likely the catalytic activity and its deactivation rate depend on the type of silica-alumina supports. Relation between silica-alumina support and active Mo species formed in the reaction is important to clarify the formation process of highly active Mo species and its redox behavior during the reaction. In fact, molybdena species supported on amorphous silica-alumina shows dehydroaromatization activity while it is very lower than that on H-MFI support. By comparing H-MFI with amorphous silica-alumina supports, reduction behavior of Mo ions before/after the reaction can be provided. Characterization of those species by means of Mo K-edge XAFS is appropriate to clarify local structure of Mo ions with different valences. In this report, local structure of supported Mo ions on H-MFI and amorphous silica-alumina (SAH-1) and their redox changes after dehydroaromatization of methane or ethane at 973 K for 3 h are evaluated by 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 (JRC-Z5-90H, Si/Al₂=90), and SAH-1 (JRC-SAH-1, amorphous SiO₂-Al₂O₃ with Si/Al₂=4.2). The impregnate solution was stilled 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 $\Delta k = 4.0 - 12.5 \text{ \AA}^{-1}$.

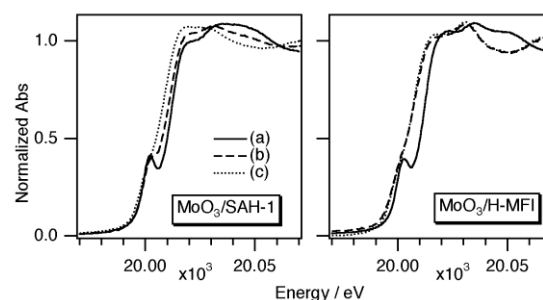


Fig. 1 Mo K-edge XANES of SAH-1(left)- or H-MFI(right)-supported MoO₃(7.5wt%) catalysts: (a) Before reaction, (b) after reaction with CH₄ at 973 K, (c) after reaction with C₂H₄ at 973 K.

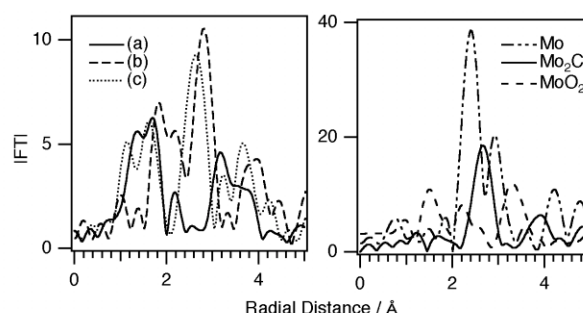


Fig. 2 FT-EXAFS of H-MFI-supported MoO₃ (right) catalysts and reference Mo compounds (right). Denotations of (a)-(c) are as same as those in Fig. 1.

Results and discussion

Fig. 1 shows XANES spectra of MoO₃/SAH-1 and MoO₃/H-MFI before/after catalytic reaction with CH₄ or C₂H₄. For SAH-1 support, reduction of Mo ions proceeds after the reactions, however, reduced level is different between CH₄ and C₂H₄ treatment at 973 K. On the other hand, these spectra are similar to each other in case of MoO₃/H-MFI. This result suggests the various support effect for formation of catalytically active Mo species during the contact with CH₄ or C₂H₄. In fact, MoO₃/H-MFI show high catalytic activity/selectivity for dehydroaromatization of CH₄, as well known. Fig. 2 shows *k*³-weighted FT-EXAFS of MoO₃/H-MFI and reference compounds. After the reaction with CH₄, new FT peak appears definitely at *R* = 2.8 Å, which should not be due to Mo-Mo but Mo-C shell. After C₂H₄ reaction, it is likely that metallic species appears at *R* = 2.6 Å. It suggests that deep reduction of Mo proceeds by C₂H₄ reaction. Detail of the study containing above discussion has several unclear components, and thus now in progress.

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