Chemistry

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Local structure analysis for nitride clusters capsulated in zeolite by means of XAFS

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Introduction

The catalysts have to be treated at high temperatures to reduce Mo^{6+} oxide to lower oxidation state. Aggregation of the Mo species is resulted from the high temperature treatment to form large clusters. However, to metal nitrides will be easily synthesized at a low temperature when $Mo(CO)_6$ is used as a precursor. Mo sulfide clusters and Mo oxycarbide species have been synthesized by use of $Mo(CO)_6$ encaged in zeolite pores as a precursor as reported previously. These methods will be applicable to be preparation of molybdenum nitrides catalysts. We investigated the preparation and local structure of Mo nitrides encapsulated in an NaY zeolite.

Experimental

Catalyst preparation

After evacuation at 673 K for 1h ($<1\times10^{-3}$Pa),a zeolite sample (0.1g) was exposed to a vapour of $Mo(CO)_6$ for 16 h at room temperature (RT), followed by evacuation for 10 min at RT to remove physisorbed $Mo(CO)_6$ on the external surface of the zeolite. The amount of immobilized $Mo(CO)_6$ was two molecules per surparcage (SC) of the zeolite according XRF analysis. $Mo(CO)_6$/NaY was nitrided with ammonia of 15 kPa (99.999%). This treatment of ammonia was performed using a closed circulation system. Before the introduction of NH_3, $Mo(CO)_6$/NaY sample was evacuate as the temperature was increased from RT to 523 K at a rate of ca. 8.0 K min^{-1} and kept isothermal at 523 K for 15 min. 15 kPa of ammonia was introduced at 523 K and subsequently, the temperature was ramped to 673 K at rate of 10 K min^{-1} and kept at 673 K for 24 h. After the nitridation, the sample was evacuated at 673 K for 1 h. The Mo nitride catalyst (10wt% Mo) thus prepared is denoted MoN_x/NaY. The amount of H_2 and N_2 produced during the nitrization were analysed by an on-line TCD gas chromatograph (column: active carbon).

XAFS measurement

The Mo K-edge XAFS spectra of the catalysts before and after nitrization were measured at BL10B of KEK-PF in a transmission mode a RT. The synchrotron radiation was monochromatized by a Si(311) monochromator. The EXAFS data were analyzed using a program "Rigaku EXAFS 2000 (REX2000)". The analysis involves pre-edge extrapolation and background removal by a cubic spline method to obtain EXAFS oscillations, which were Fourier transformed from k-space 2.98 - 15 nm^{-1} to R-space.

Result and Discussion

The N/Mo atomic ratio for the sample treated at 673 K was ca. 0.5 after 24 h suggesting the formation of Mo_2N clusters irrespective the initial NH_3 pressure. Figure 1 shows the Fourier transforms (FT) of the k^3-weighted EXAFS oscillations for the MoN_x/NaY (673-24) and $Mo(CO)_6$/NaY. The Fourier transform of the nitrided catalyst showed the first shell around 0.2 nm, indicating the presence of light atoms such as C, N and/or O attached to Mo. Assuming a Mo-Mo shell, the coordination number of the second shell for MoN_x/NaY(673-24) was calculated by EXAFS analysis to be about unity (Table 2), indicating the formation of highly dispersed Mo nitride clusters, possibly dimer clusters in the supercage of NaY. The formation of dimer clusters of Mo oxide, Mo sulfide [1] and Mo oxycarbide [2] have been reported for the oxidation, sulfidation and decomposition of $Mo(CO)_6$ encaged in NaY, respectively.
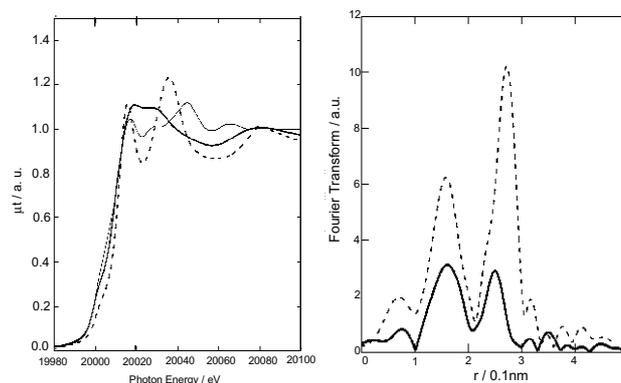

Figure 1 Mo K-edge XANES spectra (right) and Fourier transforms of Mo K-edge EXAFS oscillations (left) for Mo(CO)6/NaY(dashed line), MoNx/NaY nitrided at 673 K for 24 h (thick line), and Mo metal (foil) (thin line)

Conclusion

In summary, it was found that Mo nitride clusters, possibly Mo_2N dimers, encaged in micropores of NaY zeolite were prepared by NH_3 treatments of $Mo(CO)_6$ at 673 K. The Mo nitride clusters were highly dispersed due to a low temperature nitridation reaction.

References

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