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In-situ XAFS Study on Catalysts for Methane Dehydroaromatization Reaction

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Introduction

We have reported that rhenium or molybdenum supported on HZSM-5 zeolite are very effective for methane conversion towards hydrogen and aromatics such as benzene[1-3]. The active species for this reaction has been proposed as molybdenum carbide and rhenium metal particles dispersed in zeolite, by our EXAFS characterization. In this report, first trial of *in-situ* XAFS characterization of Re/HZSM-5 catalyst at 973 K is described.

Experimental

Reaction

The 10 mg of 2 wt. % Re/HZSM-5 catalyst sample was set inside of *in-situ* XAFS cell designed for this research. First the cell was purged by helium for 1 hour to eliminate oxygen, then the atmosphere was exchanged to hydrogen. The temperature was raised by 10 K/min to 623 K and kept for 2 hours to reduce the catalyst. After reduction, the atmosphere was exchanged to methane at the same temperature, followed by raising the temperature to 973 K.

XAFS measurements

Before (298 K) and after (623 K) H_2 reduction, EXAFS spectrum of Re/HZSM-5 was measured. Under H_2 reduction and CH_4 reaction condition, L_I, L_{II} and L_{III} XANES were measured successively to pursue structure change. At 973 K under reaction, Re L_{III} EXAFS was measured under *in-situ* condition. After reaction for 3 hours, the temperature was reduced to 298 K, where L_{III} EXAFS of Re/HZSM-5 was measured, which is corresponded to *ex-situ* condition to compare with. *In-situ* conditions were confirmed by mass spectroscopy measured simultaneously, monitoring mass number 1 to 150 for once a minute.

Result and Discussion

First, before reduction at room temperature, L_I / L_{II} / L_{III} XANES spectra of Re/HZSM-5 catalyst were measured. L_I XANES has characteristic pre-edge and post-edges which are similar to that of tetrahedral $NH_4[ReO_4,]^-$, which is precursor of this catalyst. Fourier Transform of L_{III} EXAFS only shows Re=O double bond.

Time-resolved L_I XANES spectra are shown in Fig. 1. First before 429 K, pre-edge peak is gradually decreased. Soon after the pre-edge decrease is completed, bulk reduction of rhenium proceeded directly to metal without showing the VI or VI oxidation states at 541 K. In reaching 623 K, the reaction has already completed, and under two-hour reduction at 623 K, the spectra stand still. L_{II} / L_{III} XANES show that the white line is decreased and shifted to lower photon energy, which means unoccupied d orbital is gradually filled with electrons to produce rhenium metal along with the reduction. After measuring steady-state XANES spectra, L_{III} EXAFS spectrum was measured at 623 K in hydrogen stream. Fourier transforms shows that the Re=O double bond (1.69 Å) was completely reduced to produce only Re-Re single bond (2.76 Å), which supports XANES results.

The mass spectra, measured under CH_4 reaction, from 623 K to 973 K, shows that over 900 K, m/e 78 is observed, which proves that methane dehydroaromatization occurred and the XAFS measurements are conducted under *in-situ* condition. Successive L_I / L_{II} / L_{III} XANES in this period show no spectral change, which indicates that no bulk carbidation or oxidation was occurred under methane reaction. Furthermore, L_I XANES measured for 2 hours at 973 K under benzene evolution did not show any spectral change as well, showing that the rhenium metal structure is preserved under reaction.

In keeping this catalyst at 973 K for 1 hour, XANES spectra have no change, while the mass spectra shows gradual decrease of benzene evolution, where L_{III} EXAFS spectra are measured for three times at 973 K successively, followed by XANES measurements. Fourier transforms shows no height or spectral change, this may show that “sintering” of particle, which cause decrease of reaction sites, did not occur. Thus we concluded that the deactivation reaction is not caused by sintering effect.

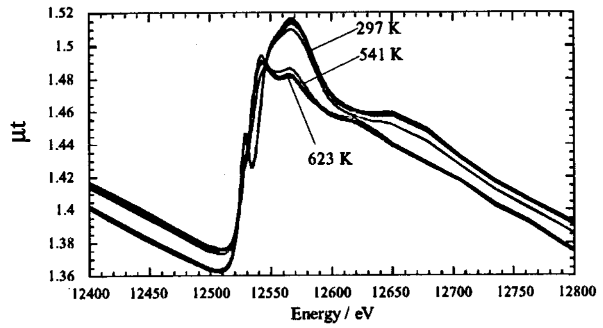

Fig.1. Successive change of Re L_I XANES in raising temperature from 297K to 623 K under H_2 flow

References

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