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XAFS characterization of zeolite-supported Re and Mo catalyst for dehydrocondensation of methane towards benzene and naphthalene

Ryuichiro OHNISHI and Masaru ICHIKAWA*
Catalysis Research Center, Hokkaido Univ., Sapporo, 060-0811, Japan

Introduction

The direct conversion of methane to fuels and petrochemical feed-stocks remains a formidable challenge in natural gas chemical industry. HZSM-5 supported Mo has been known to be superb catalyst for this reaction over the others. We discovered novel Re-based catalyst, which gave comparative catalytic performances with Mo catalyst. Here, we will report on XAFS characterization of Mo and Re-based catalysts and other important findings on this reaction1).

Experimental, Results and Discussion

The catalytic tests were carried out at 0.3 MPa of methane with or without CO_2 in a continuous flow system with a quartz reactor. Catalytic performances of the Re catalysts supported with various microporous materials such as HZSM-5, ZRP-1, MCM-22, ZSM-11, H-β, ZSM-12, SAPO-5, ferrierite, and LTL were compared with the corresponding Mo catalysts. The trends of catalytic performances on Re and Mo catalysts impregnated on the different microporous materials are similar with each other in all respects such as product selectivities, and the rates of formation. Moreover, it was demonstrated that regardless metal sorts, e.g., Mo and Re, supporting porous materials having optimum pore sizes of 5.3-5.6 Å (ZSM-5, ZSM-11, ZRP-1 and MCM-22) only provide the effective catalysis of methane dehydrocondensation towards benzene and naphthalene. Accordingly, we propose a templating role of supporting microporous materials for the reaction, which are characteristic of the pore sizes same as the kinetic diameters of benzene and naphthalene molecules.

The catalytic activity declined with time-on-stream even on the best catalyst of Mo or Re at 1023K, 3 atm, and methane specific velocity = 5000 ml/h/g-cat. However, the stability of the catalyst was greatly improved by adding a few % of CO_2 into the feed gas on Re/HZSM-5. The exceeding addition of CO_2 results in decrease of the rate of benzene formation, possibly owing to the oxidation of Re on HZSM-5. Further, the TPO experiments of used catalysts in the methane dehydroaromatization showed that the amount of coke deposition on the catalyst surface was greatly reduced by adding CO or CO_2 to the methane feed. It was revealed that CO_2 is converted to produce double amount of CO under the reaction condition, probably via reaction of $CO_2+CH_x=2CO+x/2H_2$ (x=0-4).

To characterize the active phase of the Re/HZSM-5 responsible for the methane dehydroaromatization to benzene, the Re L_{III}-edge EXAFS studies have been conducted. Fig.1 represents the Fourier transform functions of Re L_{III}-edge EXAFS of Re metal powder as a reference (1) and of 5wt% loading Re/HZSM-5 pre-reduced with hydrogen at 573K for 1h (4), reacted with methane at 973K for 30 min (3) and 24 h (2), respectively. The FT function of 5wt% loading Re/HZSM-5 reduced with hydrogen at 573K for 30min is identical to those of Re powder in every detail. This suggests that after the reduction with hydrogen the Re oxide species is converted to Re particles (Re-Re; R=2.75Å, C.N.=4.0). The FT function of the sample reacted with methane at 973K are also same as those of Re powder. The EXAFS parameters of Re particles were calculated to be R=2.74 and 2.75 Å and C.N.=5.0 and 6.4, for the samples reacted for 30 min and 24 h, respectively. These results imply that the Re oxide species dispersed in HZSM-5 is reduced with hydrogen or methane to metallic Re, which is responsible for the methane dehydroaromatization towards C_2 hydrocarbons, benzene and naphthalene. By contrast, the relatively stable carbide phase of Mo (Mo_2C) has been proposed to be active for the methane dehydroaromatization on Mo/HZSM-5.

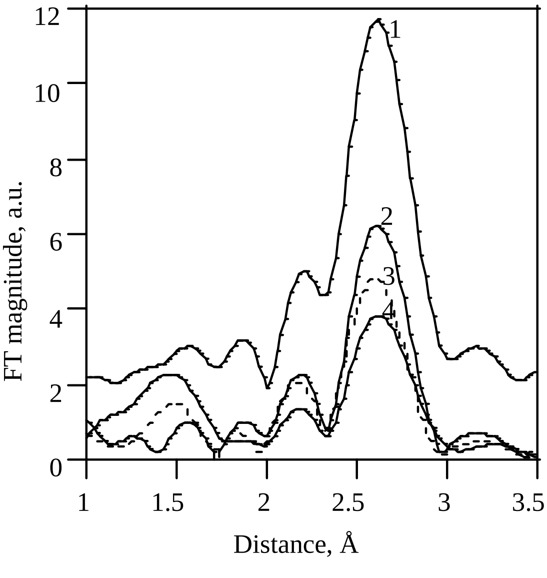

Fig.1. Re L_{III}-edge FT spectra. Signals of (2)-(4) were doubled.

References

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michi@cat.hokudai.ac.jp