메조포어 분자체 담지 Mo 촉매의 탈황반응 특성에 관한 연구

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A study on the charateristics of thiophene hydrodesulfurization over modified mesoporous materials supported Mo catalysts

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Introduction

Mesoporous molecular sieves are a new family of amorphous siliceous materials with large surface area and strictly controlled mesoporosity. Various mesoporous materials based catalysts prepared by incorprating metals, metal oxides, organometallic complexes and heteropoly acids into the mesopores have been reported, showing good catalytic activities for many types of reaction[1].

Shortly after the discovery of MCM-41, Corma et al.[2] used Al-MCM-41 to support Ni-Mo species in order to prepare catalysts for hydrocracking of vacuum gas oil. They found that Al-MCM-41 supported catalyst were more active in HDS, HDN and hydrocracking than those supported over USY or γ-Al_2O_3. Song and Reddy[3] also investigated the hydrodesulfurization of dibenzothiophene(DBT) over CoMo/Al-MCM-41 at both high and low metal loading. They found that Al-MCM-41 supported catalyst at a high metal loading was substantially more active than its γ-Al_2O_3 supported counterpart in DBT conversion. However they experienced significant deactivations due to the pore blocking by coke deposits and metal oxide crystallites since the mesopores are unidimensional.

In this regard, mesoporous material with three dimensional pore channels would be more promising for the thiophene hydrodesulfurization in view of possible limitation of pore blockage.

In this investigation, the hydrothermal stability of the mesoporous molecular sieves was improved by post salt treatment and the thiophene hydrodesulfurization activities of three dimensional mesopore materials based catalysts were compared with those of MCM-41 based catalyst to investigate the effect of the pore structure of the mesoporous supports on catalytic activity.

Experimental

Three kinds of mesoporous materials were prepared following the procedure in the literature[4-6]. MCM-41 and MCM-48 containing the surfactants as synthesized were added to aqueous solution of $EDTANa_4$(ethylenediaminetetraacetic acid tetrasodium salt, Yakuri, 97%) and NaCl(Junsei, 99.5%). These samples in the salt solutions were heated in an oven for 12days at 373K. The samples after salt treatments were filtered and washed with hot distilled water before cooling and then dried in an oven at 373K and finally calcined in air under static conditions at 813K[7].

Mesoporous materials supported Mo catalysts were prepared by incipient wetness method using the precursor of AHM(ammoniumheptamolybdate, Aldrich, 99.98%). All of the catalysts were dried at 343K in vacuum condition and calcined at 773K for 5hrs.

Presulfidation was made with H_2S/H_2(10 vol% H_2S) mixed gas at 673K for 2hrs, and then reactor was purged with He at 673K for 30min.

The HDS reaction was achieved at a stainless steel micro flow reactor with 0.2 gram catalysts with 150cc/min H_2 and 0.035cc/min thiophene at 673K, 1.5 Mpa for 8hrs. The hydrogen/thiophene mole ratio was 15 and the steady-state was reached after 1hr from the start of the reaction. Reaction products were analyzed using a gas chromatograph(HEWLETT PACKARD 5710A).

The N_2 adsorption/desorption isotherms were measured with a Micromeritics ASAP 2000 instrument at liquid N_2 temperature. Specific surface area of the samples was calculated from the adsorption isotherms by the BET method, and pore size distributions from the desorption isotherms by the BJH method.

X-ray diffraction analysis was achieved using DMAX-Ⅱ instrument of Rigaku, the X-ray source was CuKα radiation and the scanning range and scanning speed were 1.2-10° and 1deg/min, respectively.

Results and discussion

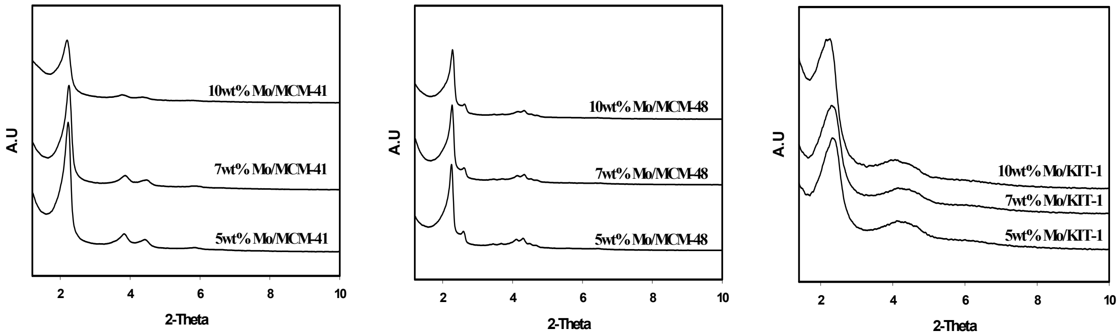

Fig.1. XRD patterns of supported Mo catalysts with different loading (scanning range: 1.2-10°, scanning speed: 1deg/min)

The X-ray diffraction patterns and physical properties of the mesoporous materials supported Mo oxide catalysts are given in Fig.1 and Table 1. The characteristic peaks of mesoporous materials were observed when the molybdenum loading was less than 10wt%. As the metal loading increased, the BET surface area , the pore volume and the average pore diameter of the catalysts decreased. However, the mesoporosity and rather high surface area of the catalysts were retained in all cases. The mesostructure and physical properties of supported Mo catalysts were not affected significantly via post salt treatment during the impregnation.

Table 1. Physical properties of supported Mo catalysts

	S_{BET}(m^2/g)^a	APD(Å)^b	PV(ml/g)^C		S_{BET}(m^2/g)^a	APD(Å)^b	PV(ml/g)^C
MCM-41	1206	32	1.26	7wt% Mo/MCM-41	919	31	0.88
MCM-48	1258	31	1.41	7wt% Mo/MCM-48	1100	28	1.16
KIT-1	1216	30	1.21	7wt% Mo/KIT-1	1005	29	0.94
5wt% Mo/MCM-41	973	31	0.94	10wt% Mo/MCM-41	808	32	0.77
5wt% Mo/MCM-48	1155	29	1.25	10wt% Mo/MCM-48	1063	29	1.12
5wt% Mo/KIT-1	1060	29	1.00	10wt% Mo/KIT-1	979	29	0.92

a: BET surface area
b: average pore diameter
c: pore volume

Fig.2 shows the HDS activity of MCM-41, MCM-48 and KIT-1 supported Mo catalysts with time on stream. Mo/MCM-41, Mo/MCM-48 and Mo/KIT-1 catalysts showed similar activity tendency from start of reaction to 5hr. But the activity of Mo/MCM-41 catalysts decreased rapidly after 5hr. It is believed that the cause of rapid deactivation of MCM-41 supported Mo catalysts would be the blocking of the unidimensional pore channels with coke deposits.

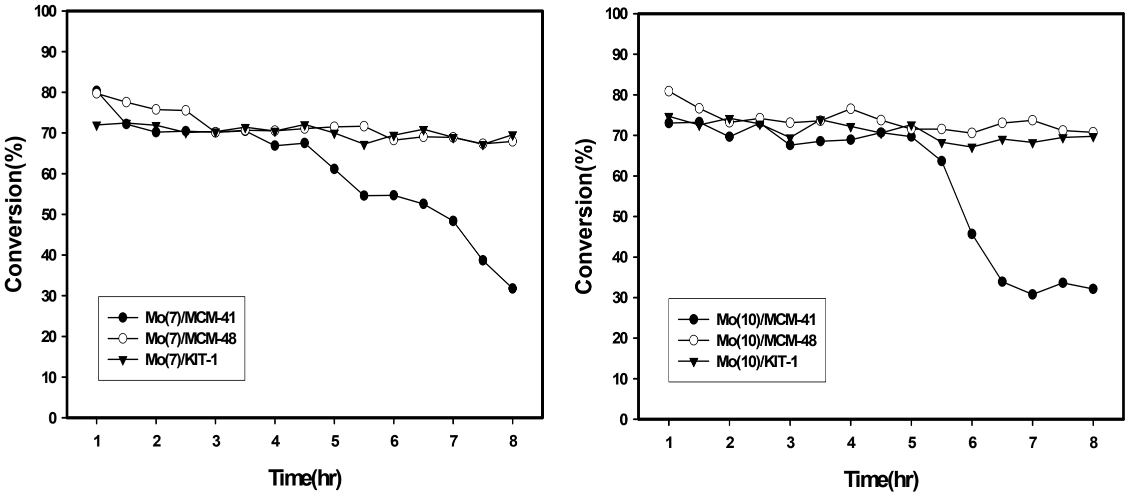

Fig.2. HDS activity over supported Mo catalysts with time on stream (reaction temperature:673K, reaction time:8hrs, H_2/thiophene=15, W/F=5.71g-cat · min/cc thiophene)

On the other hand, Mo/MCM-48 and Mo/KIT-1 having the three dimensional pore channels showed higher stability upto 8hr. The pore structure of these catalysts could reduce the risk of blockage in the catalysts and facilitate the transport of reactant and product molecules.

References

1. J. C. Vartuli, S. S. Shih, C. T. Kresge and J. S. Beck, *Stud. Surf. Sci. Catal.,* 117 (**1998**) 13
2. A. Corma, A. Martinez, V. Martinez-Soria and J. B. Monton, *J. Catal.*, 153 (**1995**) 25
3. Chunshan Song and Kondam Madhusudan Reddy, *Appl. Catal. A: Gen.*, 176 (**1999**) 1
4. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 359 (**1992**) 710
5. A.Monnier, F. Schuth, Q. Huo, D. Kumar, D. Margolese, R. E. Maxwell, G. D. Stucky, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke, B. F. Chmelka, *Science*, 261 (1993) 1299
6. Ryong Ryoo, J. M. Kim, C. H. Ko and C. H. Shin, *J. Phys. Chem.*, 100 (**1996**) 17718
7. Shinae Jun, Ji Man Kim, Ryong Ryoo, Young Soo Ahn, Moon Hee Han, *Micropor. Mesopor. Mat.,* 41 (**2000**) 119

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