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Disordered mesoporous KIT-1 as a support for hydrodesulfurization catalysts

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MoO_3 and NiO were supported on KIT-1, a new disordered mesoporous molecular sieve. MoO_3 is homogeneously dispersed as a monolayer on the support, whereas NiO tends to form small crystallites in the mesoporous channels. KIT-1 supported MoO_3 and/or NiO catalysts exhibit higher catalytic activities for thiophene hydrodesulfurization than similar MCM-41 and NaY zeolite supported catalysts, because the three-dimensional disordered network of short channels in KIT-1 reduces the risk of blockage in the catalysts and facilitates the transport of reactant and product molecules.

Keywords: disordered mesoporous molecular sieve, KIT-1, KIT-1 supported MoO_3 and/or NiO catalysts, thiophene hydrodesulfurization

1. Introduction

MCM-41 molecular sieves are a new family of amorphous siliceous materials with large surface area and strictly controlled mesoporosity [1]. They are of interest as catalysts or catalyst supports for reactions of bulky molecules. Various MCM-41 based catalysts prepared by incorporating metals, metal oxides, organometallic complexes and heteropoly acids into the mesopores have been reported, showing good catalytic activities for many types of reactions [2–5]. The performance of MCM-41 supported MoO_3 and NiO catalysts for thiophene hydrodesulfurization was studied in our laboratory. It has been found that the activities of the catalysts are strongly affected by blocking of the unidimensional mesoporous channels with undispersed oxide crystallites of the active components [6]. Since MoO_3 is readily dispersed but NiO tends to form small crystallites on the support, Mo/MCM-41 catalysts are more active for thiophene hydrodesulfurization than Ni/MCM-41 and NiMo/MCM-41 catalysts. As compared with NaY zeolite with a three-dimensional pore structure, Mo/MCM-41 catalysts are more active than Mo/NaY catalysts, whereas Ni/MCM-41 catalysts are less active than Ni/NaY catalysts. This shows that the higher surface area and larger pore channels of MCM-41 often make it a superior support in catalytic reactions, but in some cases its unidimensional pore channels may cause transport problems.

Recently, a new disordered mesoporous molecular sieve designated as KIT-1 has been synthesized hydrothermally by Ryoo [7]. KIT-1 is similar to MCM-41 in the respect of high surface area and uniform mesoporous channels, but its pore structure is a three-dimensional network of short worm-like channels instead of a hexagonal packing of straight unidimensional channels. In this paper, KIT-1 supported Ni and/or Mo catalysts were prepared. The dispersion of the metal oxides on KIT-1 was studied by XRD and N_2 adsorption method. The thiophene hydrodesulfurization activities of KIT-1 based catalysts were tested at ambient pressure and compared with those of MCM-41 based catalysts to investigate the effect of the pore structure of the mesoporous supports on catalytic reactivity.

2. Experimental

2.1. Sample preparation

KIT-1 was prepared following the procedure in the literature [7]: 28.1 g sodium metasilicate was mixed with 58.8 ml H_2O to form a clear solution. 21.5 g $C_{16}H_{33}(CH_3)_3NBr$ (CTABr), 43.9 g H_2Na_2EDTA and 9.4 g NaOH were dissolved in 64.5 ml H_2O, and then added dropwise to the sodium silicate solution. The resulting gel mixture with a molar composition of $4SiO_2$:1CTABr:$4Na_4EDTA$:$1Na_2O$:$240H_2O$ was stirred thoroughly and transferred to a stainless steel autoclave, and then heated to 373 K for 24 h. The mixture was cooled to room temperature, and the pH of the mixture was adjusted to 10.5 with 2 mol ℓ^{-1} H_2SO_4. After that it was heated to 373 K again for 24 h. This pH adjustment and subsequent heating to 373 K for 24 h were repeated once more. The product was filtered, washed, dried in air and calcined at 813 K for 1 h in flowing N_2, and then at 813 K for 6 h in flowing air.

MCM-41 was prepared following the procedure in

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another paper [8]: 28.1 g sodium metasilicate was mixed with 124 ml H_2O and 21.5 g CTABr. The pH of the gel mixture was adjusted to 10.5 with 2 mol ℓ^{-1} H_2SO_4. The mixture was crystallized hydrothermally in a stainless steel autoclave at 373 K for 144 h. The product was filtered, washed, dried in air and calcined in the same way as KIT-1.

The NiO(x)/KIT, NiO(x)/MCM and NiO(x)/NaY catalysts were prepared by impregnation of KIT-1, MCM-41 and NaY zeolite with $Ni(NO_3)_2$ solutions of appropriate concentrations, followed by drying at 383 K and calcining at 873 K for 5 h. MoO_3 was introduced into the catalysts through spontaneous dispersion of the oxide at elevated temperature [9]. A mixture of MoO_3 and the molecular sieves was ground and mixed thoroughly, and then calcined at 733 K for 6 h. The Ni,Mo-supported catalysts were prepared by introducing MoO_3 first and then impregnation with $Ni(NO_3)_2$ solution. The weight percentages of NiO and MoO_3 in the catalysts were denoted as x and y, respectively.

2.2. Characterization

X-ray powder diffraction patterns of the samples were obtained on a Rigaku D/MAX-IIA diffractometer using Cu Kα radiation at 40 kV and 20 mA. The N_2 adsorption/desorption isotherms were measured on a Micromeritics ASAP-2000 instrument at liquid N_2 temperature. Specific surface areas of the samples were calculated from the adsorption isotherms by the BET method, and pore size distributions from the desorption isotherms by the BJH method.

2.3. Activity tests

The thiophene hydrodesulfurization activity of the catalysts was tested in a flow microreactor at 673 K and ambient pressure. The catalyst load was 100 mg. A gas mixture of thiophene and H_2 with a molar ratio of thiophene/H_2 = 1/27 was supplied at a flow rate of 10 ml/min. The reaction products were analyzed by means of a gas chromatograph equipped with a flame ionization detector.

3. Results and discussion

Figure 1 depicts XRD patterns of KIT-1 and MCM-41 after calcination. MCM-41 exhibits one very intense line and three distinct weak lines, which can be indexed to (100), (110), (200) and (210) diffractions, respectively. The XRD pattern of KIT-1 is similar to that of MCM-41, but all the diffractions are weakened and broadened, showing that KIT-1 has a more disordered structure than MCM-41. The N_2 adsorption isotherms and pore size distribution curves of KIT-1 and MCM-41 are given in figures 2 and 3, respectively. The shape of the adsorp-

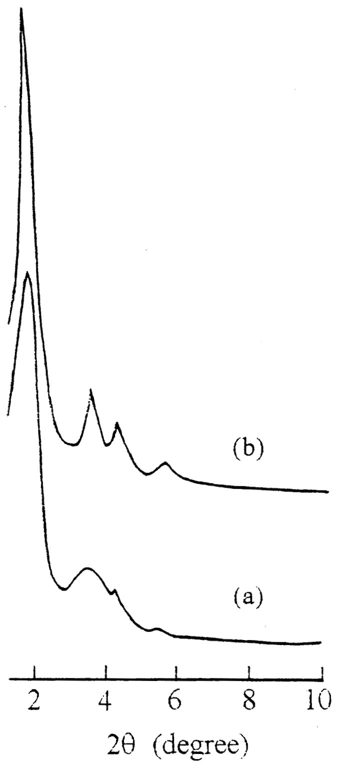

Figure 1. X-ray diffraction patterns of (a) KIT-1 and (b) MCM-41.

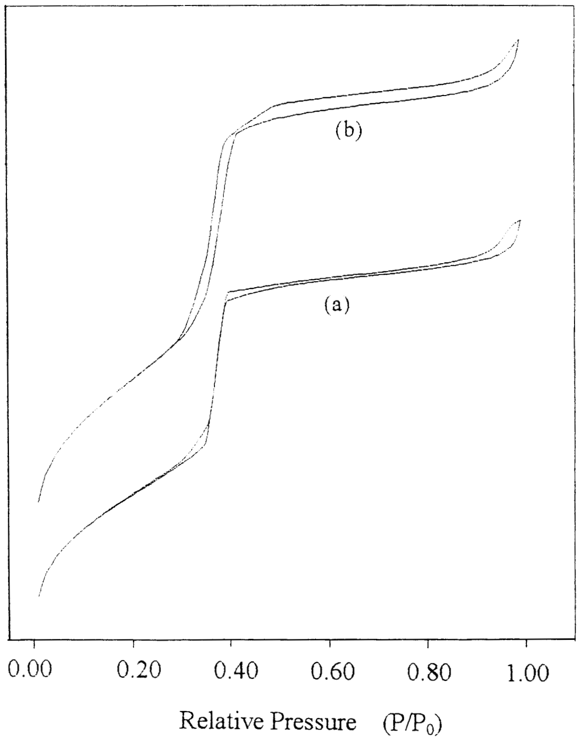

Figure 2. N_2 adsorption and desorption isotherms of (a) KIT-1 and (b) MCM-41.

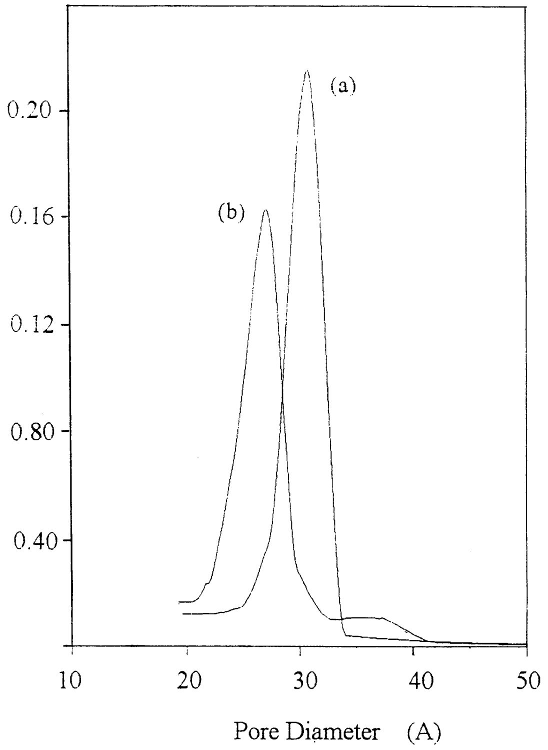

Figure 3. Pore size distribution of (a) KIT-1 and (b) MCM-41.

tion isotherms of these two materials is alike, except that the first hysteresis at low relative pressure characteristic of the mesoporous channels of KIT-1 is smaller, giving evidence of a difference in pore structure between them. The BET surface area of KIT-1 is 1021 m^2/g, which is slightly smaller than the value of 1143 m^2/g for MCM-41. KIT-1 has a uniform mesopore structure as MCM-41. Its most probable pore diameter is around 3.08 nm, which is somewhat larger than the value of 2.69 nm for MCM-41. The peak width at half maximum on the pore size distribution curve of KIT-1 is 0.38 nm, which is smaller than the value of 0.43 nm for MCM-41. The above results are consistent with those in the literature [7], in which it has been proved by a specially designed TEM imaging technique that KIT-1 particles contain a large number of short mesoporous channels connecting in a three-dimensional disordered way instead of a unidimensional hexagonal packing of long linear channels as in MCM-41.

The XRD patterns of the KIT-1 supported metal oxides catalysts are given in figures 4 and 5. The characteristic peaks of MoO_3 and NiO do not show up in the patterns until their contents in the catalysts reach 20 and 6% by weight, respectively. The disappearance of XRD peaks suggests that the metal oxides are to some extent highly dispersed on the surface of the mesoporous channels. Obviously, the dispersion capacity of MoO_3 on KIT-1 tested by XRD is much higher than that of NiO. This result is the same as that observed in the case of MCM-41 [6].

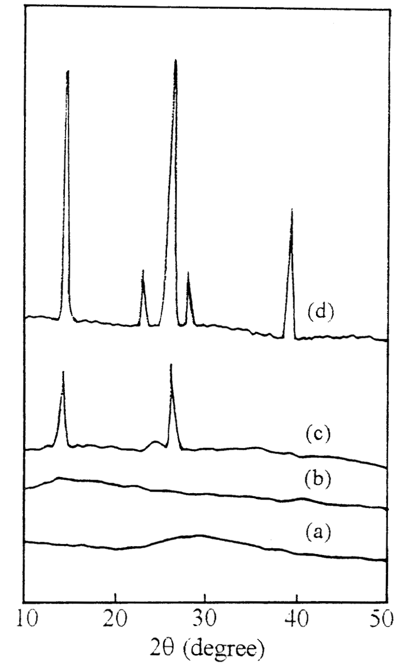

Figure 4. X-ray diffraction patterns of (a) MoO_3(10.0)/KIT, (b) MoO_3(15.0)/KIT, (c) MoO_3(20.0)/KIT and (d) MoO_3.

The textural properties of the KIT based catalysts are listed in table 1. As the loading of the metal oxides is increased, the BET surface area, pore volume and the most probable pore diameter of the catalysts are gradually reduced. However, the mesoporosity and rather

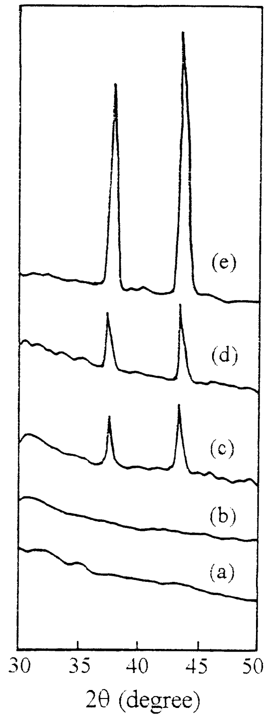

Figure 5. X-ray diffraction patterns of (a) NiO(2.0)/KIT, (b) NiO(4.0)/KIT, (c) NiO(6.0)/KIT, (d) NiO(10.0)/KIT and (e) NiO.

Table 1
Textural properties of the catalysts

Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	PWHM [a] (nm)
KIT-1	1021	1.02	3.08	0.38
MoO_3(10.0)/KIT	746	0.62	3.06	0.38
MoO_3(15.0)/KIT	679	0.55	2.98	0.38
MoO_3(20.0)/KIT	653	0.52	2.87	0.57
NiO(2.0)/KIT	835	0.70	3.08	0.51
NiO(4.0)/KIT	853	0.71	3.08	0.58
NiO(6.0)/KIT	736	0.60	3.08	0.62
NiO(10.0)/KIT	719	0.58	3.06	0.65
NiO(6.0) MoO_3(10.0)/KIT	578	0.46	3.08	0.62

[a] PWHM = peak width at half maximum on the pore size distribution curve.

high surface area of the catalysts are retained in all cases. It is interesting to note that for supported MoO_3 catalysts the peak widths at half maximum on the pore size distribution curves do not change until MoO_3 loading increases to 20%, indicating that the catalysts are as uniform in channel width as the KIT support, despite high oxide loadings. This may suggest that MoO_3 has homogeneously dispersed as a monolayer on the surface of the mesoporous channels of the support. On the other hand, the peaks on the pore size distribution curves of supported NiO catalysts become asymmetrical on the low pore diameter side and their peak widths at half maximum are increased considerably even at very low loadings. This shows that in these catalysts the uniformity of the mesoporous channels is reduced, and a part of the channels is probably blocked by very small NiO crystallites undetectable by XRD. As the NiO loading is increased above 6%, the small NiO crystallites grow to be detectable by XRD, and the increase in peak width becomes more significant. The differences in the dispersion behavior on KIT-1 between the two metal oxides are again similar to those on MCM-41 supports [6].

The steady state hydrodesulfurization activities of the catalysts were measured at 2 h on stream and listed in table 2. The activity of the MoO_3/KIT catalysts increases with the MoO_3 content in the catalysts, and they are about two times as active as the MoO_3/MCM catalysts with the same loadings. At a loading of 10% MoO_3, the activity decreases in the order of $MoO_3/KIT > MoO_3/MCM > MoO_3/NaY$, showing that the three-dimensional branching mesoporous channels of KIT-1 are advantageous to the reaction.

The activity of the NiO/KIT catalysts also increases with the NiO content below 6%, and they are about 5–8 times as active as the NiO/MCM catalysts with the same loadings. At the same NiO loading, the activity decreases in the order of $NiO/KIT \gg NiO/NaY > NiO/MCM$. It is obvious that the merit of KIT-1 as a catalyst support is more predominant for supported NiO catalysts, in which the metal oxide is not homogeneously dispersed as a monolayer on the support but forms small crystalline hindrances in the channels. This is good reason to propose that the mesoporous branching structure of KIT-1 reduces the risk of blockage in the catalysts and facilitates the transport of the reactant and product molecules in the catalytic reaction.

Furthermore, the thiophene hydrodesulfurization activity of NiO(6.0)MoO_3(10.0)/KIT catalyst is higher than MoO_3(10.0)/KIT and NiO(6.0)/KIT catalysts. A synergism between Ni and Mo surface active species on KIT-1 for the reaction is observed distinctly as that on Al_2O_3. However, for the other two supports the activities of the supported mixed oxide catalysts are higher than those of the supported NiO catalysts, but lower than those of the supported MoO_3 catalysts. The positive role of the synergism has been offset by obstruction in the catalysts originated from not well-dispersed NiO crystallites.

In conclusion, the present work demonstrates convincingly that the new disordered mesoporous KIT-1 is a similar but better catalyst support as compared with

Table 2
Thiophene hydrodesulfurization activities of the catalysts

Catalyst	Conversion (%)	Activity ($mmol\ g^{-1}\ h^{-1}$)
MoO_3(10.0)/KIT	16.5	1.57
MoO_3(15.0)/KIT	30.4	2.89
MoO_3(20.0)/KIT	39.2	3.73
NiO(2.0)/KIT	6.8	0.65
NiO(4.0)/KIT	11.2	1.07
NiO(6.0)/KIT	4.6	0.44
NiO(6.0)MoO_3(10.0)/KIT	20.8	1.98
MoO_3(10.0)/MCM	10.3	0.98
MoO_3(15.0)/MCM	16.1	1.54
MoO_3(20.0)/MCM	17.1	1.63
NiO(2.0)/MCM	0.8	0.08
NiO(4.0)/MCM	2.1	0.20
NiO(6.0)/MCM	2.8	0.26
NiO(6.0)MoO_3(10.0)/MCM	8.0	0.76
MoO_3(10.0)/NaY	6.3	0.60
NiO(2.0)/NaY	1.8	0.17
NiO(5.7)/NaY	3.0	0.28
NiO(8.6)MoO_3(10.0)/NaY	4.9	0.47

MCM-41. The unique uniform mesoporosity and branching channel structure of KIT-1 are certain to provide more opportunities for designing good heterogeneous catalysts for numerous reactions.

References

[1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli and J.S. Beck, Nature 359 (1992) 710.

[2] A. Corma, A. Martinez, V. Martinen-Soria and J.B. Monton, J. Catal. 153 (1995) 25.

[3] A. Sinnema, R.J.J. Jansen, K. Pamin and H. van Bekkum, Catal. Lett. 30 (1995) 241.

[4] T. Maschmeyer, F. Rey, G. Sankar and J.M. Thomas, Nature 378 (1995) 159.

[5] C.B. Liu, X.K. Ye and Y. Wu, Catal. Lett. 30 (1996) 263.

[6] J. Cui, Y.H. Yue, Y. Sun, W.Y. Dong and Z. Gao, Stud. Surf. Sci. Catal. 105 (1997) 678.

[7] R. Ryoo, J.M. Kim, C.H. Shin and J.Y. Lee, Stud. Surf. Sci. Catal. 105 (1997) 45.

[8] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins and J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.

[9] Y.C. Xie and Y.Q. Tang, Adv. Catal. 37 (1990) 1.