Hydrogenation of naphthalene on HY/MCM-41 supported sulfided-NiMo catalysts

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Abstract:

A series of mesoporous molecular sieves MCM-41 with different Si/Al molar ratios were synthesized by hydro-thermal method. The influence of aluminum contents on the properties and pore structure of MCM-41 molecular sieves were investigated. The supported Ni-Mo catalysts with MCM-41 and γ-Al_2O_3 as supports were synthesized by impregnating with Ni-Mo-P solution. The activity of the catalysts was characterized by hydrogenation of naphthalene. The influence of Si/Al ratio of MCM-41 on hydrogenation activity of the catalysts was investigated. The results indicated that the relative crystalinity of MCM-41 decreases with the increase of aluminum content in the molecular sieves; however, the hydrogenation activity of the catalysts, especially the ring-opening activity, increases with the increase of aluminum content. The synergistic effect for hydrogenation of naphthalene was found by mixing MCM-41 and HY molecular sieves. At 360°C，the catalysts with HY and MCM-41 mixture as supports has higher activity. The reaction network for hydrogenation of naphthalene includes two parallel pathways; naphthalene was hydrogenated to tetralin, then the isomerization and ring-opening of tetralin occurred, or tetralin was further hydrogenated to decalin, followed by the isomerization and ring-opening of decalin.

Key words: MCM-41 molecular sieve, naphthalene, hydrogenation, activity, reaction mechanis

1. Introduction:

There is an increasing demand for environmentally friendly hydrocarbons and clean-burning high performance fuels, such as distillate fuels like diesel and jet fuels. Distillate fuels typically contain paraffins, naphthenes, and aromatics. For fuels quality parameters such as cetane, gravity and emissions, paraffins are the most desirable components, followed by naphthenes, followed by aromatics. The least desirable are multi-ring aromatic compounds. Owing to more and more strict environmental and clean-fuel legislation, deep hydrodearomaticisation of diesel has been the focus of many recent studies. Many approaches has been applied in the synthesis of catalysts such as using different types of zeolite as supports [1], adding promoters [2], etc.

MCM-41 mesoporous molecular sieve has become one of the world-wide known materials since 1992 for its high surface area and meso-size porosity [3]. MCM-41has shown its advantages in the fields of catalysis, material and organic compounds synthesis [4,5]. Corma et al[6] reported that the activity on one stage mild hydrotreatment of vacuum gasiol on NiMo catalysts supported on MCM-41 molecular sieves, is superior in HDS, HDN and HC reaction, compared to that of catalysts woth the same Ni, Mo content supported on amorphous-alumina or on USY zeolite. T. Halachev[7] reported the catalytic activity of (P)NiMo/Ti-HMS and (P)NiW/Ti-HMS catalysts in the hydrogenation of naphthalene. Condam et al[8] found that cis- and trans-declins easily produced on Pt/MCM-41 compared to Pt/Al_2O_3 and Pt/TiO_2.In this paper, we have synthesized a serial of Al-MCM-41 with difference Si/Al ratios and investigated the performance of hydrogenation of naphthalene on MCM-41 supported sulfided-NiMo catalysts. Based on the relative weak acidity on Al-MCM-41, we also investigated the catalytic performance of modified sulfided-NiMo catalysts supported in mixed Al-MCM-41 with the HY zeolite. For the modified catalysts, the activity and ring-opening products concentration increase with the addition of HY zeolite. These result are benefit from the synergistic effect of combination microporous with mesoporous zeolites.

2. Experimental

2.1 The preparation of MCM-41 with difference Si/Al ratios

Al-MCM-41 with Si/Al ratios of ∞，60，50，40，25 were synthesized following the procedure given in Ref[1] using hexadecyltrimethylammonium bromide(purity ⩾ 99%) as template, sodium silicate solution (SiO_2⩾wt%24.19%) as silica source and pseudobohemite as aluminum source. The sol-gel was crystallized under 120℃ in 24h.The as-synthesized material was calcinated in a N_2 atmosphere at 550℃during 1h followed by a 6h calcinations in the air at the same temperature.

2.2 The preparation and characterization of catalysts

The supports were prepared in the following procedure: molding, desiccantion, ion-exchanging with 1 mol.l^{-1} NH_4NO_3 solution for 3 times and calcinations. The catalysts Al-MCM-41 and catalysts modified by adding HY zeolite (15%) were compared to the reference catalysts (Mo-Ni-P/HY(15%)-Al_2O_3. Mo-Ni-P catalysts were prepared by the incipient wetness impregnation technique with the required amount of an aqueous solution of ammonium heptamolybdate, base nickel cabnate and phosphoric acid to obtain catalysts. By these strategies, we prepared three different kinds of catalysts: (1) sulfided-NiMo supported on different MCM-41(Si/Al= ∞) content(0, 20%, 40%, 60%); (2) Al-MCM-41 supported sulfided-NiMo catalysts with different metal oxides content (20%, 26%, 32%, 40%);(3) sulfided-NiMo supported on mixed support of combination Al-MCM-41 with HY zeolite

X-ray powder diffraction (XRD) were carried on D/Max-III type spectrometer with Cu Kα radiation, Voltage is 400KV and electrical current 40mA. Surface area,pore volume and average pore diameter were calculated from the adsorption-desorption isotherms of N_2 at 77.35K on a ASPA-2010 adsorption apparatus. The acidity of molecular sieves and catalysts were measured by adsorption-desorption of pyridine. The alumina content in the MCM-41 molecular sieves was measured by chemical-titration method [9].

Reaction system and procedure

2.3 The evaluation of catalytic performance and products identification

The experiments of evaluation of catalytic performance were performed in a fixed bed stainless tubular reactor (10mm internal

diameter and 0.8mlength) in a micro-reactor. The catalysts were pre-sulfided before hydrodearomatization reaction by using CS_2 at 4 MPa under 340℃ for 3h. The reaction condition for hydrodearomatic were 340-370℃, H_2 pressure is 4.0MPa, H_2/Oil ratio is 500,WHSV=$1h^{-1}$. The products were analyzed by a Varian-3400 gas chromatography equipped with a 0.25mm×30m HP CP-1 capillary column and a flame ionization detector and the product identification was carried out by gas chromatography-mass spectrum (GC-MS).

3. Result and discussion:

3.1 The effect of sol-gel Si/Al molar ratio on MCM-41 structure

Fig.1 shows the XRD pattern of pure silica MCM-41 and Table1 depicts the influence of the feed Si/Al ratio on the XRD peak intensity of 100 plane and other properties of MCM-41. A decrease in Si/Al ratio decrease the intensity of the main XRD peak, indicting that increasing Al content of the feed hindered the crystallization process. In Fig.2, the pore diameter distribution of a typical as-synthesized MCM-41 has figured out and the open pore size focus on 2.8-3.0nm.

From table 1 it can be seen with the aluminum added in MCM-41, relative crystalline of molecular sieves decrease, that is because aluminum inserting into Si-O tetrahedron can cause lattice disfigurement and have bad effect to hexagon structure. With the increase of aluminum in MCM-41 the acidity of molecular sieves increase.

3.2 The product identification of hydrodearomatication of naphthalene

The product identification was made by GC and GC-MS analysis. Figure3 shows a typical GC chromatogram of the product. Some products were identified by comparison of GC retention time with those of the standard samples, Other products were identified by GC-MS, which data system searches automatically the associated database spectra of molecules and gives a best fit match.

3.3 The effect of total H_2 pressure on naphthalene conversion and products distribution

To investigate the effect of total H_2 pressure on naphthalene conversion and products distribution. We selected a Catalyst with the formula of MoNi(P)/MCM-41 (20%,Si/Al=∞)-Al_2O_3 and test temperature condition is 370□, the ratio of H_2 and oil is 500,WHSV is $1.0h^{-1}$. From Fig.3 it can be seen that the naphthalene conversion increase with the increase of total H_2 pressure. This is because naphthalene hydrogenation and deep-hydrogenation reaction consume hydrogen which causes the molar of gas decrease. From the equilibrium of the reactions the conclusion can be drawn that increasing H_2 pressure is benefit for naphthalene conversion. Fig 4 shows that the effect of H_2 pressure on the products distribution of naphthalene hydrogenation products

The products can be divided into three parts, which are the tetralin and its isomers, decline and its isomers and ring-opening products. The former two parts is from the hydrogenation pathway and ring-opening products is from the hydrocracking pathway. From Fig.4 it can be seen that naphthalene conversion and the activity of deep-hydrogenation and ring-opening increase with the increase of total H_2 pressure. Increasing total H_2 pressure is good for naphthalene conversion, ring-opening reaction and cetane number improvement.

3.3 The effect of metal content on the naphthalene conversion and products distribution

The MCM-41 is a kind of mesoporous zeolite with high surface area and large pore diameter. This is easy for high concentration active components to disperse on its surface. From Table3 it can be seen that the catalysts activity increase with the increase of metal content. As a result naphthalene conversion increases and deep-hydrogenation products such as decalins and ring-opening increase. But the metal content in the catalysts increases to 40%, the activity of catalyst decrease. The possible reason is that excessive metal may form big particles which deposit on the catalysts. This can block the aperture of catalysts and confine the diffusion of reactant.

3.4 The acidic component of supports on the naphthalene conversion and products distribution

From the above results it can be seen that the acidity on the MCM-41 is too weak which causes the number of acidity sites are too small and the acidity strength of catalysts are too weak. This does no good to naphthalene deep-hydrogenation and ring-opening. As a result the main products on NiMo/MCM-Al_2O_3 are tetralins while declins and ring-openings are not as many, which just cause a little increase of centane number. In order to improve the performance in catalytic ring-opening reaction, it is necessary to add the acidic component. HY is a microporous zeolite and its acidy is stronger than MCM-41. So we selected HY molecular sieve as acidic component and added it in the supports. From the Table it can be seen that naphthalene conversion increased with the HY content added to the catalysts increase. The catalysts1 with HY/MCM-41/Al_2O_3 in the support have the high conversion. Catalysts 2 with only HY/MCM-41 have the highest ring-opening content This can be attributed to the interaction of HY acidic component and the synergistic effect for hydrogenation of naphthalene was found by mixing MCM-41 and HY molecular sieves.

Conclusions

1. A series of MCM-41 moliecular sieves with different Si/Al molar ratio were synthesized by hydrothermal method .With the decrease of Si/Al, alumina oxide content and acid sites increased while the relative crystalinity decreased.
2. Total H_2 pressure plays an important role in naphthalene hydrogenation. With pressure increased the activity of deep-hydrogenation and ring-opening increase sharply.
3. The conversion of naphthalene increase with metal oxides active components content on the catalysts with the supports MCM-41 mesoporous zeolites increased
4. Catalysts added HY zeolites naphthalene deep-hydrogenation, especially the ring-opening properties increase.

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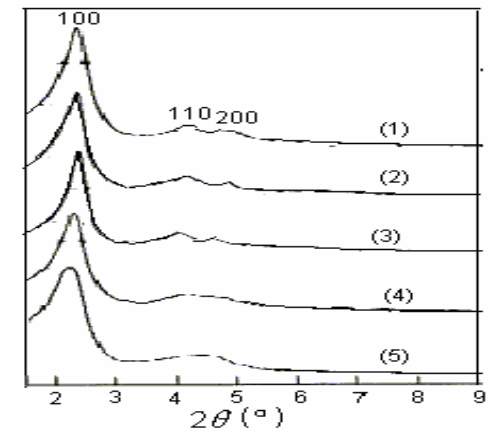

Fig.1 XRD pattern of as-synthesized MCM-41molecular sieves

(1)Si/Al=∞;(2)Si=60;(3) Si=50;(4) Si=40;(50) Si=25

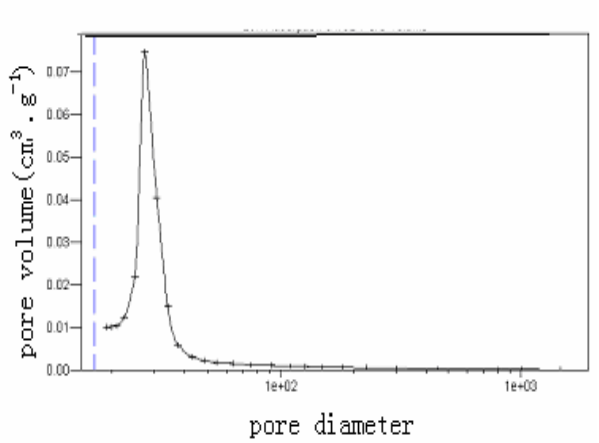

Fig.2 Pore diameter distribution of typical as-synthesized MCM-41

Table1 Effect of Si/Al molar ratio on structure of MCM-41

Si/Al，molar ratio		∞	25	40	50	60
XRD	2θ, °	2.104	2.078	2.231	2.191	2.143
	Relative crystallinity*, %	100	89.8	85.4	82.4	80.7
	d_{100}, nm	4.193	4.245	3.956	4.028	4.114
	Half brand width, nm	0.320	0.320	0.320	0.340	0.340
BET	Surface area, $m^2.g^{-1}$	791	1294	860	794	770
	Pore volumn, $cm^3.g^{-1}$	0.57	1.05	0.68	0.64	0.66
	Pore diameter, nm	2.8	3.2	3.1	2.7	2.9
Acidity, m%		18.4	29.5	26.3	24.7	21.3
$W(Al_2O_3)$, m%		—	3.76	1.62	1.50	1.37

Relative crystallinity: the crystallinity of MCM-41(Si/Al=∞) is 100 while others are realtive to this value

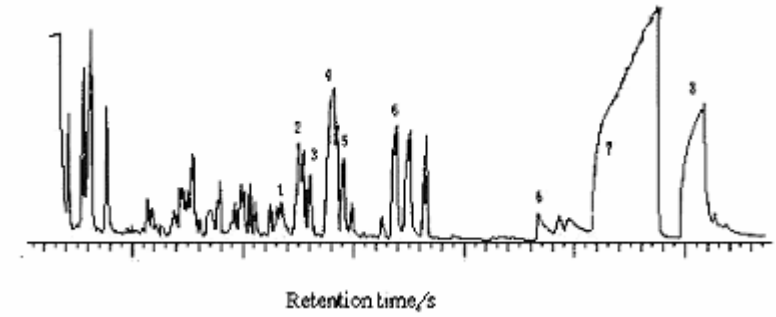

Fig. 3 GS-MS of the products for hydrogenation of naphthalene1-butylcyclohexane; 2-cis-decaline; 3-methylindane and its isomers; 4-trans-decaline; 5-butylbenzene; 6-methylindene and its isomers; 7-tetralin; 8-naphthalene

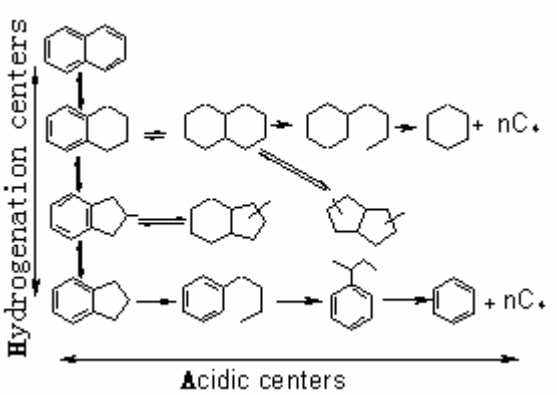

Fig.4 Reaction pathways for hydrogenation of naphthalene sulfurized CoMo catalysts

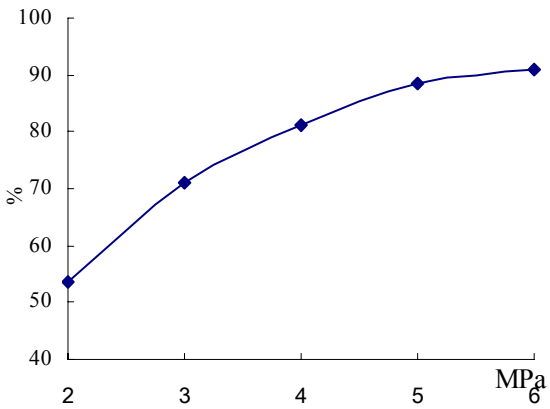

Fig.3 The effect of pressure on the conversion of naphthalene

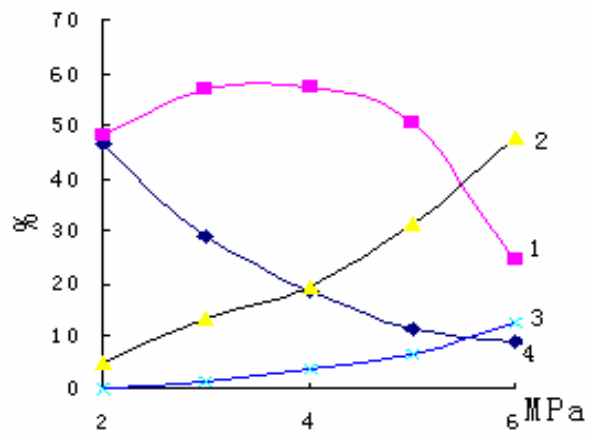

Fig.4 The effect of H_2 pressure on the distribution of products
1—tetralin and its isomers；2—declins and its isomers；3—ring-opening products；4—naphthalene

Table 3 : the effect of metal content on the naphthalene hydrogenation

Metal content，($NiO+MoO_3$)，m%	W(production)，m%				Conversion，%
	Naphthalene	Tetralins	Decalins	Openings	
20	16.96	66.97	9.69	5.34	83.04
26	14.63	63.69	12.23	9.45	85.37
32	9.69	62.06	17.89	9.79	90.31
40	11.84	55.14	23.68	8.45	88.16

Table 4 The properties of catalysts added HY zeolite

Catalysts	T,°C	W(products),%				Conversion, %
		Naphthalene	Tetralins	Declins	Other products	
	340	13.88	24.29	27.00	32.66	86.12
Reference	350	16.81	27.14	30.73	23.37	83.19
	360	18.62	20.13	34.78	22.18	81.38
	340	6.91	60.23	16.05	17.35	93.09
Catalyst 1	350	7.23	49.87	21.21	19.27	92.77
	360	10.24	40.24	19.58	25.32	89.76
	340	9.45	39.52	18.83	29.60	91.55
Catalysts 2	350	11.25	32.10	18.23	35.46	88.75
	360	13.77	24.71	13.97	40.72	86.23

Reference catalyst: Mo-Ni-P/HY(15wt%)-Al_2O_3
Catalyst 1: Mo-Ni-P/MCM-41(45wt%)-HY(15wt%)-Al_2O_3
Catalyst 2: Mo-Ni-P/ HY(20 wt%)- MCM-41