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Ring Opening of Naphthenic Molecules Over Metal Containing Mesoporous Y Zeolite Catalyst

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Mesoporous Y zeolite (Meso-Y) with a uniform mesopore was synthesized via pseudomorphic synthesis. The Meso-Y supported Ni-W catalyst (NiW/Meso-Y) was introduced as a catalyst for the selective ring opening of naphthenic rings. The catalytic test for the ring opening of naphthalene as a model compound of multi-ring aromatics was performed using a batch-type reaction system with both sulfided 20 wt% NiW/Meso-Y and NiW/Y catalysts under different reaction conditions. The catalytic results reveal that the Meso-Y supported NiW catalyst experiences a naphthalene conversion similar to the NiW/Y catalyst, but the NiW/Meso-Y catalyst has higher product yields for BTEX (benzene, toluene, ethyl benzene, and xylene) and the middle distillate than those of the NiW/Y catalyst at a low reaction temperature. These results suggest that the mesoporosity of the NiW/Meso-Y catalyst is more advantageous for the ring opening reaction of multi-ring aromatics due to the easier access for the bulky molecules compared to the NiW/Y catalyst.

Keywords: Ring Opening, Multi-Ring Aromatics, BTEX, Mesoporous Zeolite, Heavy Oil Upgrading.

1. INTRODUCTION

The heavy residue upgrading process has attracted significant interest due to the stringent environmental regulations of transportation fuel quality, such as low multi-ring aromatics and sulfur contents in middle distillates. Obtaining higher cetane numbers is also an essential property to improve fuel quality. Aromatic saturation and hydrocracking have been proved as commercial upgrading technologies.[1] However, aromatic saturation or hydrocracking alone is limited due to their low cetane number increase and excessive cracking degree, respectively. A potential route is needed to produce middle distillates with low aromatics and aromatic saturation and selective ring opening. Aromatic saturation of a low-sulfur middle distillate stream is followed by the selective ring opening of partially hydrogenated naphthenic rings without loss of reactant molecular weight because the selective ring opening increases the cetane value in diesel fuel.[2] While the selective ring opening (SRO) of naphthenic molecules is a promising pathway for heavy residue upgrading and it has been studied by many researchers, SRO still presents challenges due to a complex chemistry, product selectivities, operation conditions, composition of the final products, and the catalytic system.[3] In the catalytic system, a bi-functional catalytic system (metallic and acidic functions) is required in the SRO of naphthenic molecules.[4] A suitable acidic function is needed for the ring contraction step and a metallic function for the ring-opening step. Even though noble metals (Pt, Pd, or Ir) supported on an acidic zeolite catalyst are typically used for the SRO reaction, multi-ring aromatics are not easily converted into desired products over microporous zeolites due to the diffusion resistance of bulky molecules.

To overcome that kind of diffusion resistance and deactivation of the catalyst in the microporous zeolites, there have been extensive efforts to synthesize mesoporous zeolites or zeolite nanocrystals.[5] Among the synthetic methods, pseudomorphic synthesis has recently been considered as a useful and convenient method for the synthesis

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of mesoporous zeolite.[6] Mesoporous zeolite with well-controlled intracrystalline mesoporosity was prepared via pseudomorphic synthesis, which is recrystallization of zeolite in the presence of a surfactant.

In this study, we synthesized mesoporous Y (Meso-Y) zeolite materials by pseudomorphic synthesis with different surfactant ratios and prepared a 20 wt% NiW supported Meso-Y catalyst with a uniform mesopore. The ring opening of naphthalene as a model compound of multi-ring aromatics was investigated using a sulfide NiW/Meso-Y catalyst with different reaction conditions.

2. EXPERIMENTAL DETAILS

2.1. Catalyst Preparation

Meso-Y zeolite materials were synthesized by a modified pseudomorphic synthesis in our lab with different surfactant ratios.[6] In typical synthesis, zeolite HY (1.67 g, CBV720) and hexadecyltrimethylammonium bromide (0.83 g, CTAB) were added to 50 ml of a 0.09 M trimethylammonium hydroxide (TMAOH) and stirred for 30 min at room temperature. The mixture was moved to a Teflon-lined autoclave and hydrothermally treated at 150 °C. After 20 h, the resultant product was filtered and washed with water. The product was dried at 75 °C and calcined at 550 °C. To obtain optimum Meso-Y with both well-developed mesoporosity and retain the microporous zeolitic structure, the molar ratios of TMAOH:CTAB were varied from 0.5 to 3. The 20 wt% NiW supported Meso-Y catalyst was prepared by impregnation of nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) and ammonium metatungstate hydrate ($(NH_4)_6H_2W_{12}O_{40} \cdot H_2O$) in water. Prior to the reaction tests, the catalyst was sulfidated in a tubular furnace by 10 mol% H_2S in hydrogen at 350 °C for 3 h.

2.2. Catalyst Characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku Multiplex (40 kV, 1.6 kW, Cu-Kα radiation). N_2 isotherms were measured by ASAP2020 (Micromeritics). The ammonia temperature programming desorption (NH_3-TPD) was carried out using BELCAT-B.

2.3. Catalytic Performance Tests

The reaction was carried out with a batch-type reactor system (100 ml, Parr Instrument Co.) For the ring opening of naphthalene, the reactor was charged with 30 g of 10 wt% naphthalene in tridecane (TCI) and 0.3 g of a sulfided catalyst. The reactor was purged with nitrogen. After pressurization to the desired pressure (3–5 MPa) by hydrogen the reaction was performed at 350, 375, and 400 °C for 5 h with stirring (500 rpm). The reaction products were analyzed by gas chromatography-mass spectrometry (GC-MS) (HP7890A/5975C, Agilent) with a packed column (DB-5).

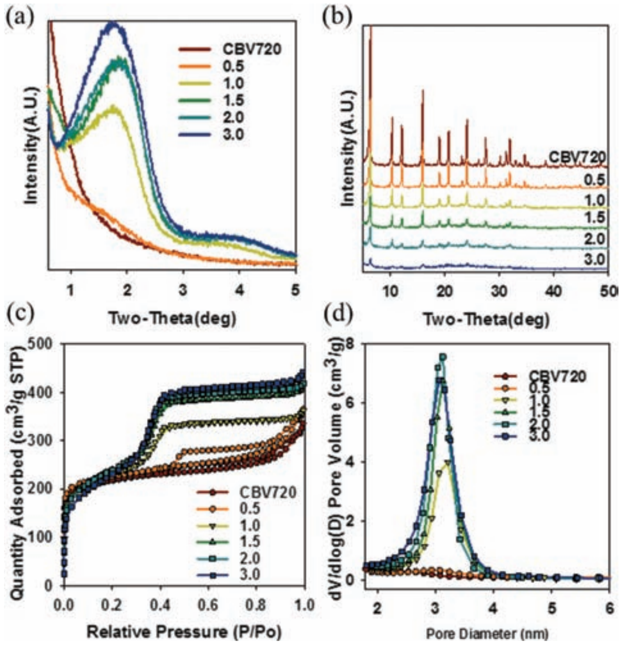

Figure 1. (a) Low and (b) wide angle XRD patterns, (c) N_2 isotherms, and (d) pore size distributions of Meso-Y with different surfactant molar ratios (TMAOH:CTAB).

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns and N_2 physisorption results of the Meso-Y materials prepared by pseudomorphic synthesis with different surfactant ratios. The low angle XRD patterns and pore size distributions revealed that the mesoporosity of the zeolite increased with an increase of the TMAOH:CTAB molar ratio up to 2. The highest surfactant molar ratio (TMAOH:CTAB = 3) had

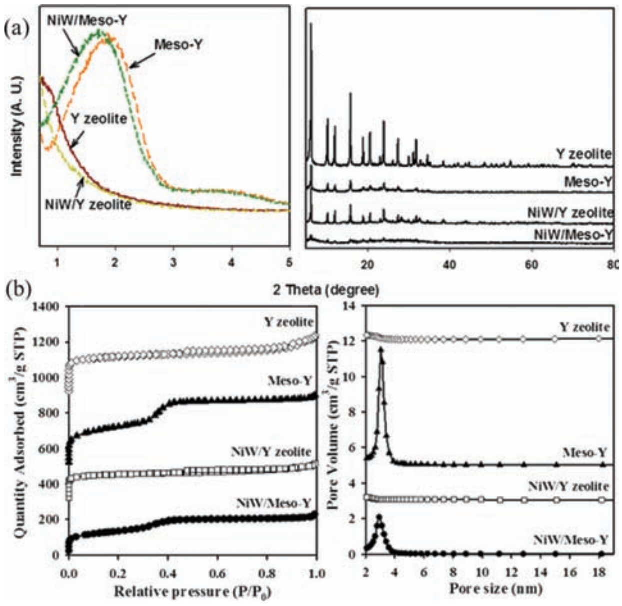

Figure 2. (a) XRD patterns and (b) N_2 isotherms and pore size distributions of zeolite supports and NiW supported catalysts.

Table I. Physicochemical properties of zeolite supports and NiW supported zeolite catalysts.

	Surface area (BET) (m^2/g)			Pore volume (cm^3/g)			
Sample	Total	Micropore	> 2 nm	Total	Micropore	Mesopore	Pore diameter (nm)
Y zeolite	739	527	212	0.49	0.24	0.25	–
Meso-Y	785	224	561	0.59	0.10	0.49	3.21
NiW/Y zeolite	524	393	131	0.31	0.18	0.13	–
NiW/Meso-Y	472	123	349	0.33	0.06	0.28	3.20

a mesoporosity similar to TMAOH:CTAB = 2, but the microporous structure of the HY zeolite almost disappeared as shown in the wide angle XRD patterns. From these analyses, we concluded that the optimum surfactant molar ratio is two to obtain Meso-Y with both well-developed mesoporosity and a retained microporous zeolitic structure. To investigate the effect of the Meso-Y zeolite support on the ring opening reaction of naphthalene, we introduced 20 wt% NiW into the Meso-Y synthesized with TMAOH:CTAB = 2. Figure 2 shows the XRD and N_2 physisorption results for the 20 wt% NiW/Y zeolite and NiW/Meso-Y catalysts. After NiW loading, the low angle XRD patterns were slightly shifted to the left side with similar peak shapes. However, the relative XRD peak intensities of the NiW supported catalysts decreased compared with the zeolite support. In addition, the mesopore volumes and BET specific surface area of the catalysts also decreased after impregnation of NiW metal (Table I). This indicates that the mesopores of the catalysts were filled with NiW metal.

Figure 3 shows the NH_3-TPD profiles to investigate the surface acidic site and the strength of the acidity. NH_3-TPD profiles of two supports show two distinct NH_3 desorption peaks at around 170 °C (weak acid site) and 380 °C (strong acid site) The intensities of the two NH_3-TPD peaks of the Meso-Y support decreased compared with those of the Y zeolite. This means that the surface acidities in the Y zeolite decreased during the pseudomorphic synthesis. After impregnation with metals, the metal loading affected both the weak and the strong acid sites. The weak acidities of the catalysts increased, while the strong acidities significantly decreased by metal loading (Table II). That indicates a big loss in the number of strong acid sites, which might result from direct metal anchoring on proton sites.[7]

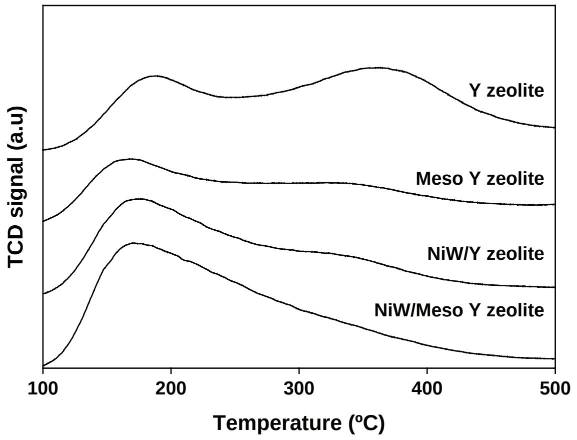

Figure 3. NH_3-TPD profiles of zeolite supports and NiW supported catalysts.

The NiW/Meso-Y was applied in the SRO of naphthalene at 400 °C under various reaction pressures. The naphthalene conversion and yields of middle distillates and BTEX of both the catalysts increased as the reaction pressure increased (Table III). Interestingly, the yields of the middle distillates and BTEX for the NiW/Meso-Y catalyst were similar to these for the NiW/Y zeolite while the total acidity of the NiW/Meso-Y catalyst was about half of that of the NiW/Y zeolite (Table II). That might be due to facile access for the bulky reactant coming from the mesoporosity of the NiW/Meso-Y compared with the NiW/Y zeolite. The yield of saturated products in the NiW/Meso-Y had a higher value than that of the NiW/Y zeolite, which might have been caused by the NiW/Meso-Y having a weaker acidity than the NiW/Y. These results indicate that the SRO of naphthalene strongly depends on the reaction pressure and the higher pressure has a higher conversion and yield of middle distillates and BTEX.

The NiW/Meso-Y was used to investigate the effects of reaction temperature and determine the optimum temperature for SRO for naphthalene. The reaction temperatures were varied from 350 to 400 °C at 50 bar. The naphthalene conversion and yields of middle distillates for NiW/Meso-Y decreased as the reaction temperature increased, but the yields of BTEX and aromatic saturated products increased (Table IV). The NiW/Y zeolite also had a trend similar to the NiW/Meso-Y. However, the NiW/Meso-Y exhibited higher yields of BTEX, tetralin and decalin, and middle distillates than the NiW/Y zeolite at the lowest temperature (350 °C), which might imply that the mesoporosity of

Table II. NH_3-TPD results of zeolite supports and NiW supported zeolite catalysts.

	Amount of desorbed ammonia (mmol/g)		
Sample	170 °C (*l*-peak)	380 °C (*h*-peak)	Total amount of NH_3 (mmol/g)
Y zeolite	0.226	0.741	0.967
Meso-Y	0.147	0.534	0.681
NiW/Y zeolite	0.275	0.453	0.728
NiW/Meso-Y	0.380	—	0.380

Table III. Catalytic performance of catalysts in ring opening of naphthalene with different pressure at 400 °C for 5 h.

Catalyst	Pressure (bar)	Conv. (%)	Product yield (wt%) Middle distillates	Saturated product	BTEX
NiW/Y zeolite	30	75.2	36.1	3.2	10.2
	40	85.4	40.6	3.0	18.0
	50	88.4	41.6	3.8	20.6
NiW/Meso-Y	30	74.5	35.5	11.1	7.7
	40	80.4	38.5	7.0	16.5
	50	89.8	41.3	7.3	20.3

Notes: Conv., naphthalene conversion; Saturated product, total yield of tetralin and decalin; BTEX, total yield of benzene, toluene, ethyl benzene, and xylene.

Table IV. Catalytic performance of catalysts in ring opening of naphthalene with different temperature at 50 bar for 5 h.

Catalyst	Temperature (°C)	Conv. (%)	Product yield (wt%) Middle distillates	Saturated product	BTEX
NiW/Y zeolite	350	93.7	44.0	25.9	7.3
	375	93.2	43.5	14.1	14.1
	400	88.4	41.6	3.8	20.6
NiW/Meso-Y	350	94.4	45.8	30.0	11.4
	375	92.4	43.5	14.7	17.7
	400	89.8	41.3	7.3	20.3

the NiW/Meso-Y catalyst should provide good accessibility of the bulky molecule to catalytic active sites without significant diffusion resistance even at the lowest reaction temperature. In addition, the higher yield of BTEX by the SRO of naphthalene might be due to the mild acidity of the Meso-Y support via pseudomorphic synthesis compared with Y zeolite.

4. CONCLUSION

The optimum Meso-Y was synthesized by the TMAOH:CTAB molar ratio = 2, which yielded both a microporous zeolitic structure and well-developed mesopores. The catalytic tests for SRO of naphthalene over both the NiW/Meso-Y and NiW/Y under different reaction conditions revealed that the NiW/Meso-Y and NiW/Y zeolite had a similar naphthalene conversion. However, the NiW/Meso-Y catalyst had higher product yields for BTEX, aromatic saturated products, and middle distillates than NiW/Y at a low reaction temperature. This suggests that the mesoporosity of NiW/Meso-Y is more advantageous for the SRO of multi-ring aromatics due to easy access for the bulky molecules compared with NiW/Y.

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