



Hydrogenation of naphthalene over noble metal supported on mesoporous zeolite in the absence and presence of sulfur

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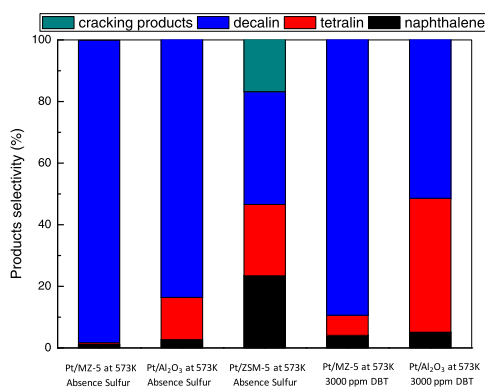
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HIGHLIGHTS

- ▶ Pt catalyst supported on mesoporous ZSM-5 (MZ-5) zeolite was made.
- ▶ Pt/MZ-5 shows better performance in naphthalene deep hydrogenation.
- ▶ Pt/MZ-5 shows good sulfur tolerance in naphthalene deep hydrogenation.
- ▶ Better catalytic performance is attributed to the combine acidity and mesoporosity.

GRAPHICAL ABSTRACT



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ABSTRACT

Deep hydrogenation of aromatics is an important reaction in modern oil refinery. The key of an aromatic hydrogenation unit is high active, sulfur resistant hydrogenation catalyst. In this paper, the catalytic performance of a newly developed hydrogenation catalyst, platinum supported on mesoporous ZSM-5 (Pt/MZ-5), was tested in naphthalene (model compound of light cycle oil) hydrogenation. Pt/ZSM-5 and Pt/Alumina were used as reference. In some experiments, dibenzothiophene (DBT) was added to test the sulfur tolerance of catalysts. In the absence of DBT, Pt/MZ-5 and Pt/Alumina showed much higher hydrogenation activities and decalin selectivity than Pt/ZSM-5. The selectivity to decalin exceeds 97% over Pt/MZ-5 at temperature range between 523 and 573 K. Furthermore, Pt/MZ-5 shows better sulfur resistance than that of Pt/Alumina. In the presence of 3000 ppm dibenzothiophene, the selectivity of decalin over Pt/MZ-5 was only slightly dropped to 89.4% at 573 K, which is much higher than that of Pt/Al₂O₃ (51.4%). The excellent catalytic performance and sulfur tolerance of Pt/MZ-5 were attributed to the combination of high acidity and mesoporous structure in MZ-5.

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1. Introduction

Due to increasingly stringent environmental regulations and fuel specifications, production and use of more environmentally friendly transportation fuels with lower aromatics and sulfur contents have drawn worldwide research interests [1–3]. Deep

hydrogenation can produce cycloalkane from aromatics and thus significantly increase the cetane number (CN) and improve the combustion characteristics. Moreover, it was reported that cycloalkane produced from coal tar and light cycle oil can be used as high thermal (>900 °F) stable jet fuel [3]. For above reasons, deep hydrogenation of aromatics becomes one of the most important unit operations in modern oil-refinery [1–3].

Hydrogenation is an exothermic reaction and thus thermodynamically favored at lower temperature. However, conventional supported Ni–Mo and Co–Mo sulfide catalysts usually active at

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relatively high temperatures (above 573 K), and suffer from thermodynamically limitation for aromatics hydrogenation. Noble metal catalysts are promising candidates for deep hydrogenation of aromatics at lower temperature because of their high hydrogenation activity [1–3]. However, noble metal catalyst is easily poisoned by sulfur containing compounds even at several ppm S levels [4]. Therefore, developing sulfur resistant noble metal catalyst for deep hydrogenation was interested by researchers both for industry and academia [2].

Industrially, the noble metal catalyst was used in supported form. Hence the supports also largely affect the catalytic performance and sulfur tolerance of catalysts. Recent studies showed that the acidic supports can enhanced the catalytic activity and sulfur tolerance in deep hydrogenation of aromatic hydrocarbons, such as HY/USY [5,6], SAPO-11 [7] and Beta [8] zeolite. It was claimed that electron-deficient metal particles were formed in a noble metal/zeolite bifunctional catalyst due to the partial electron transfer from the metal particles to acidic sites of the zeolite supports, and the resulted electron-deficient metal particles has a better resistance to sulfur poisoning [9]. Furthermore, a secondly spillover based hydrogenation pathway in which aromatic hydrocarbons were adsorbed on acidic sites and hydrogenated by the hydrogen from metal particles would occur in zeolite supported catalyst [10]. However, the main drawback of the zeolite support is the solely microporosity, which will result in diffusion limitation [11]. Until now, only zeolite with large micropore such as Y, and Beta can be used as support of an aromatic hydrogenation catalyst.

In order to overcome the diffusion limitation of zeolite in bulky molecular involved reaction, mesoporous zeolites which have additional intracrystalline or intercrystalline mesoporous besides the microporous structure have been successfully synthesized. Diffusion and catalytic tests have proved that mesoporous zeolite can overcome the mass transfer limitation and exhibit excellent catalytic properties for the conversion of bulky molecules [12–15]. For instance, Ryoo et al. claimed that mesoporous zeolite exhibited better catalytic activity in reactions of bulky molecules, including the protection of benzaldehyde with pentaerythritol, condensation of benzylalcohol with hexanoic acid, and cracking of branched polyethylene [15]. Prins and Sun reported that noble metals supported on mesoporous zeolite had much better performance in the hydrodesulfurization of 4,6-dimethyldibenzothiophene [16].

Our group reported that hierarchical mesoporous zeolites ZSM-5 (MZ-5, synthesized with the mixture of cetyltrimethylammonium bromide and 3-(trimethoxysilyl) propyl octyldimethylammonium chloride as secondary template) shown better performance in dibenzofuran hydrodeoxygenation compared to conventional ZSM-5 and alumina when used as noble metal supports [17]. Here in this paper, the catalytic performance of the newly developed Pt/MZ-5 hydrogenation catalyst was tested in naphthalene (model compound of light cycle oil) hydrogenation. Pt/ZSM-5 and Pt/Alumina were used as reference. In some experiments, dibenzothiophene (DBT) was added to test the sulfur tolerance of catalysts. The results indicated that compared with Pt supported on conventional ZSM-5 and alumina catalysts, the Pt/MZ-5 catalyst exhibited much better hydrogenation activity, decalin selectivity and sulfur tolerance.

2. Experimental

2.1. Materials

Chemicals used in this work including tetrapropylammonium hydroxide (TPAOH, 25 wt.% in water), aluminum isopropoxide (>99%), tetraethylorthosilicate (TEOS, >99%), 3-(trimethoxysilyl) propyl octyldimethyl-ammonium chloride (TPOAC, 42% in

methanol), cetyl trimethylammonium bromide (CTAB, >99%), and chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, >99%), naphthalene (>99%), 2-methyl-2-pentene (2M2P, >99%), dibenzothiophene (>99%) and n-tridecane (>99%). TPOAC was purchased from AEGIS Company, while other chemicals were purchased from Aladdin and used as received without further purification. Commercial Al_2O_3 support was obtained from Shandong Alumina Corporation, China.

2.2. Mesoporous zeolite and catalysts synthesis

MZ-5 was synthesized according to previous publication [17]. Briefly, TEOS, aluminum isopropoxide and TPAOH were firstly stirred to obtain a clear solution, after that pre-calculated amount of TPOAC and CTAB mixture were added under vigorous stirring. The molar ratio of synthesis mixture is $30\text{SiO}_2/1.0\text{Al}_2\text{O}_3/6.0\text{TPAOH}/0.6\text{TPOAC}/0.6\text{CTAB}/2400\text{H}_2\text{O}$. The final mixture was further stirred for 2 h at room temperature to obtain a homogeneous mixture. Then the mixture was transferred to Teflon lined autoclave and heated under static conditions at 423 K for 48 h. After crystallization, the solid product was separated by filtration, washed 4 times with distilled water, then dried at 373 K for 12 h in ambient air, and finally calcined in air at 823 K for 5 h. Conventional ZSM-5 was synthesized at the same conditions with mesoporous ZSM-5 without TPOAC and CTAB. The zeolite samples were ion-exchanged three times with a 0.1 M NH_4NO_3 solution at 363 K for 90 min (liquid/solid ratio of $10\text{ cm}^3/\text{g}$) under stirring, after that the samples were filtered, extensively washed with distilled water and dried at 373 K for 4 h, and calcined at 773 K for 6 h (at a heating rate of 1 K/min).

The supported noble-metal catalysts were prepared by incipient wetness impregnation of the calcined supports (MZ-5, ZSM-5 and alumina) with an appropriate amount of aqueous $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution. The support was added to the aqueous solution containing the Pt precursor at ambient temperature and the suspension kept at this temperature under agitation during 24 h, then dried in an oven at 373 K for 12 h, and calcined at 773 K for 4 h (at a heating rate of 1 K/min). The Pt loading in three catalysts were all 0.5 wt.%.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained with a Bruker D8 Advance X-ray diffractometer, using $\text{Cu K}\alpha$ radiation at room temperature and instrumental settings of 40 kV and 40 mA. Data were recorded in the 2θ range $5\text{--}50^\circ$ with a 0.02° step size.

Scanning electron microscopy (SEM) images were recorded on a JEOL 6300F instrument. Samples were prepared by dusting the zeolite powder onto double sided carbon tape, mounted on a copper stub. The samples were subsequently sputter coated with a thin gold film to reduce charging effects. Transmission electron microscopy (TEM) measurement of MZ-5 was carried out on a JEOL 2010F instrument, operating at 200 kV. TEM analyzes of supported Pt catalysts were carried out on a Hitachi H-7650 microscope, operating at 100 kV. The samples were suspended in ethanol and dispersed on a copper grid coated with lacey carbon film before TEM analysis.

Nitrogen adsorption isotherms were obtained at 77 K on a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. Before measurement, the samples were degassed at 573 K for 6 h. The total surface area was calculated according to the BET method. The mesopore size distribution was obtained by the Barrett–Joyner–Halenda (BJH) analysis of the adsorption branch of the isotherm.

Hydrogen chemisorption was used to determine the Pt dispersion of the supported catalysts on a Micromeritics ASAP 2020C instrument. Before the analyses, the catalyst samples were reduced

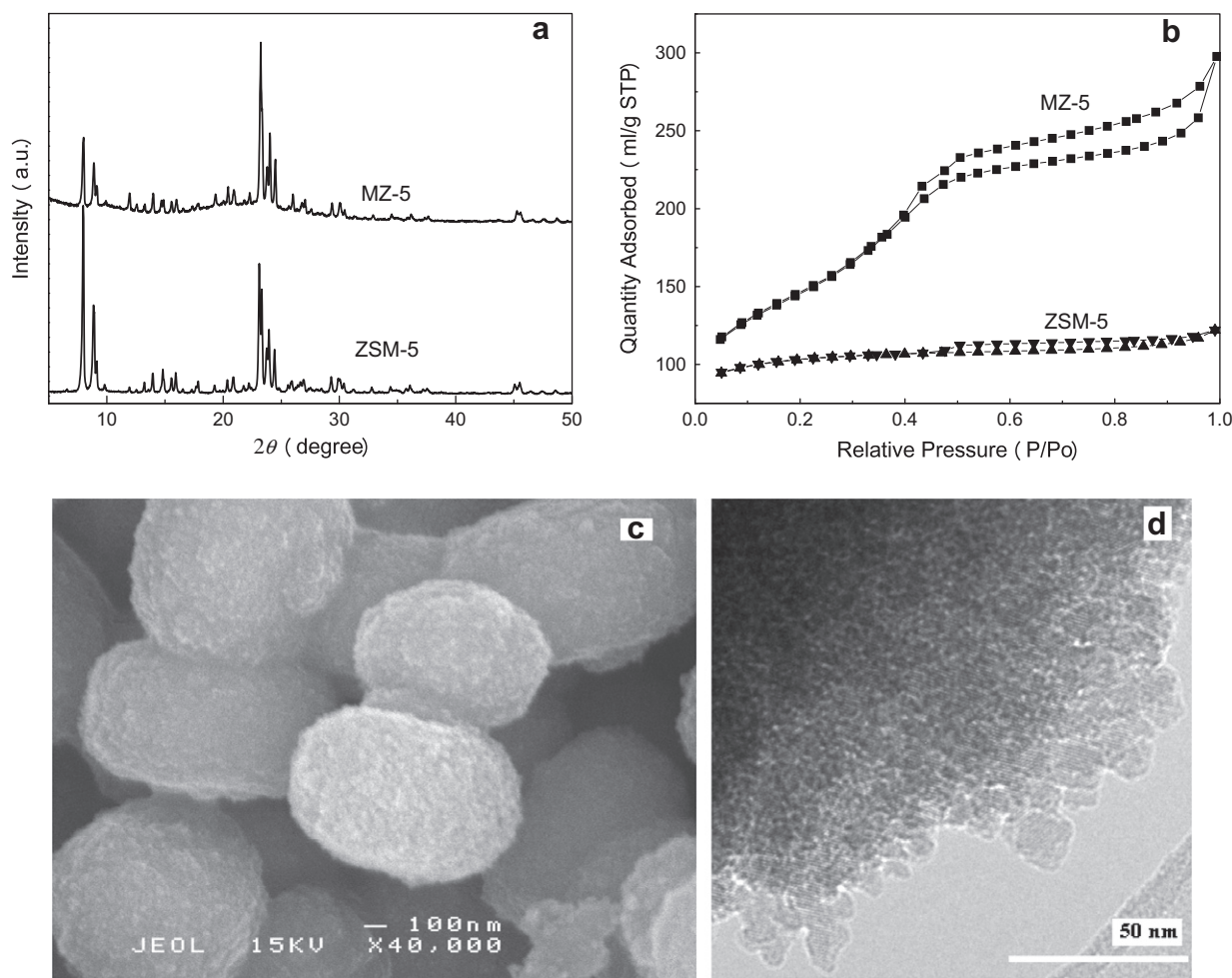


Fig. 1. Characterization results of ZSM-5 and mesoporous ZSM-5 (MZ-5): (a) XRD of MZ-5 and ZSM-5; (b) Nitrogen adsorption/desorption isotherms of MZ-5 and ZSM-5; (c) SEM image of MZ-5; and (d) TEM image of MZ-5.

Table 1

The textural parameters, acidity evaluation and Pt dispersion of various supports.

Support	Surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	D_{meso} (nm)	2M2P conversion (%) ^a	Molar ratio ^b	Pt dispersion (%)
Al_2O_3	240.4	0.39	4.9	21	0	76
ZSM-5	319.4	0.10	NA	55	1.70	32
MZ-5	506.4	0.51	3.6	60	1.47	33

^a Conversion of 2M2P at 423 K.

^b Molar ratio of trans-3M2P to trans- and cis-4M2P.

in situ in hydrogen at 733 K for 3 h (at a heating rate of 5 K/min). The system was evacuated at room temperature for 45 min before an initial chemisorption analysis was performed at room temperature to determine the total hydrogen uptake. The system was then evacuated for another 45 min at the same temperature to remove the physically adsorbed hydrogen. Measurements were repeated after hydrogen was reintroduced. The metal dispersions were calculated from the difference between both adsorption isotherms. [18,19]

The acidity difference of ZSM-5 and alumina was evaluated by 2-methyl-2-pentene (2M2P) isomerization according to Ref. [16]. The conversion and molar ratio of trans-3-methyl-2-pentene (trans-3M2P) to trans- and cis-4-methyl-2-pentene (trans- and cis-4M2P) were used as probe of the acidity. The molar ratio of trans-3-methyl-2-pentene (trans-3M2P) obtained by methyl shift to trans- and trans- and cis-4M2P obtained by H shift in isomers

reflects the acidity of solid acids. The higher conversion and molar ratio indicate the stronger acidity.

2.4. Catalytic experiments

A solution of naphthalene (10 wt.%) in n-tridecane was used as feedstock, dibenzothiophene was added in controlled amount for the testing of sulfur tolerance of catalysts. The naphthalene hydrogenation experiments were performed at 473–573 K and 4 MPa total pressures in a continuous-flow, fixed bed reactor. The diameter and length of the reactor were 10 mm and 420 mm, respectively. 1.5 g catalyst with particle size between 250 and 420 μm was used in the experiment, the catalyst bed was in the constant temperature zone of the reactor and embedded between glass wool plugs and quartz beads. A thermocouple was immersed in the catalyst bed to measure the reaction temperature and a back pressure

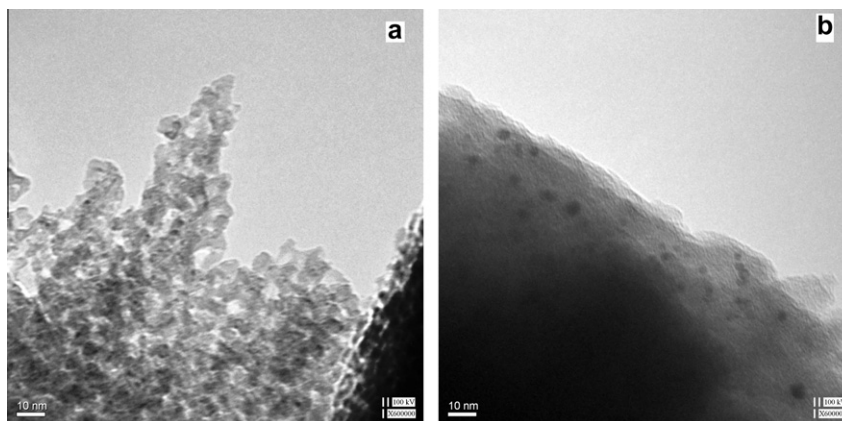
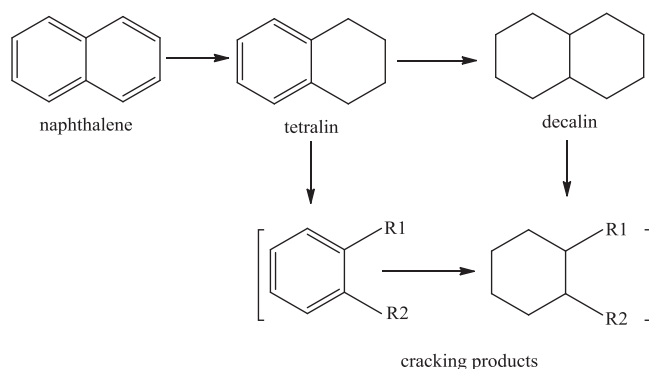


Fig. 2. TEM images of Pt/Al₂O₃ (a) and Pt/ZSM-5 (b).



Scheme 1. Reaction pathway of the hydrogenation of naphthalene.

regulator was used to regulate the reaction pressure. Before the hydrogenation experiments, the noble metal catalysts were reduced in situ under H₂ atmosphere at 733 K for 3 h, and then the reactor was cooled down to the reaction temperature. The feedstock was then pumped into the reactor. The H₂/oil (naphthalene plus n-tridecane) volume ratio was constant at 600 and the liquid hourly space velocity (LHSV) was 1.0 h⁻¹ in this study. Experimental data were collected after stable reaction conditions were achieved. The reaction products were collected in a trap with ice-water bath and analyzed off-line with an Agilent GC–MS 7890A-5975C using a 30 m HP-INNOWax column. The naphthalene conversion and product selectivity were determined by GC/MS analysis results.

3. Results and discussion

Fig. 1 gives the characterization results of MZ-5. The XRD patterns presented in Fig. 1a revealed that both conventional ZSM-5 and MZ-5 are highly crystallinity MFI (Mordenite Framework Inverted) structure zeolite. The nitrogen adsorption/desorption isotherms of MZ-5 presented in Fig. 1b exhibited a high adsorbed amount at low P/P_0 and a hysteresis loop at P/P_0 higher than 0.4, which combined the characters of zeolites and mesoporous materials [20]. In comparison, conventional ZSM-5 showed a type I isotherm which is typical for the microporous materials. Moreover, from the pore size distribution curve inserted in Fig. 1b, a uniform pore distribution centered at around 3.6 nm was observed for MZ-5 by BJH analysis. The textural parameters of these three supports were summarized in Table 1. It can be found that the MZ-5 has the highest surface area and pore volume. The BET specific surface area

and mesoporous volume for MZ-5 are 506.4 m² g⁻¹ and 0.51 cm³ g⁻¹, respectively, which are much higher than those of conventional ZSM-5. It can be found in Table 1 that Al₂O₃ also has mesopore channel with 4.9 nm according to BJH analysis.

The SEM image of MZ-5 presented in Fig. 1c indicated that MZ-5 have “rounded boat” morphology which is typical morphology for MFI structured materials. From the high resolution TEM image presented in Fig. 1d the wormhole like mesopore channels and zeolite lattice fringes can be found simultaneously in the MZ-5. The lattice fringes extend throughout the whole crystal, the wormhole like channels in the MZ-5 is quite similar to the mesopore structure in commercial Al₂O₃ (Fig. 2a). These characterization results indicated that the MZ-5 possess both microporous structure and intracrystalline wormhole mesoporous channels.

The 2M2P isomerization reaction was used to evaluate the acidity of three supports [21]. As shown in Table 1, the MZ-5 had similar 2M2P conversion and molar ratio of trans-3M2P to trans- and cis-4M2P with ZSM-5, on the other hand, alumina gave a much lower conversion and molar ratio. This result indicates that MZ-5 possessed similar acidity as conventional ZSM-5, and both much higher than alumina. Based on above results, MZ-5 can be considered as a material that combines the physicochemical characterizations of Al₂O₃ and ZSM-5 with hierarchical porosity and strong acidity.

The supported platinum catalyst was prepared by conventional incipient wetness impregnation method were subjected to XRD, TEM and chemisorptions analysis. No Pt diffraction peaks was found in the XRD patterns, possibly due to the low Pt loading (0.5%). As shown in Table 1, the hydrogen chemisorption results indicated that the Pt dispersion on Al₂O₃ (76%) is much higher than on both MZ-5 (33%) and ZSM-5 (32%). Typical TEM images of Pt/Al₂O₃ and Pt/ZSM-5 were shown in Fig. 2. It can be found that the Pt particle size in Pt/Al₂O₃ (Fig. 2a) and Pt/ZSM-5 (Fig. 2b) was around 1–2 nm and 4 nm, respectively. The lower hydrogen dispersion of Pt on ZSM-5 and MZ-5 was also reported by other researchers [18]. It was reported that in the incipient wetness impregnation process, the electronegative of PtCl₆²⁻ make the Pt has much lower dispersion over the acid zeolite support [18].

The main compounds found in naphthalene hydrogenation were tetralin, decalin and cracking and ring opening products (alkyl-benzene and alkyl-cyclohexane). Scheme 1 shows the reaction network of naphthalene hydrogenation according to literature and our GC–MS analysis of products [1–3]. The hydrogenation of naphthalene occurs mainly in two steps, hydrogenation of naphthalene into tetralin and subsequent hydrogenation of tetralin into cis- or trans-decalin, as well as the competitive reactions such as cracking and ring openings. The tetralin formation step is generally

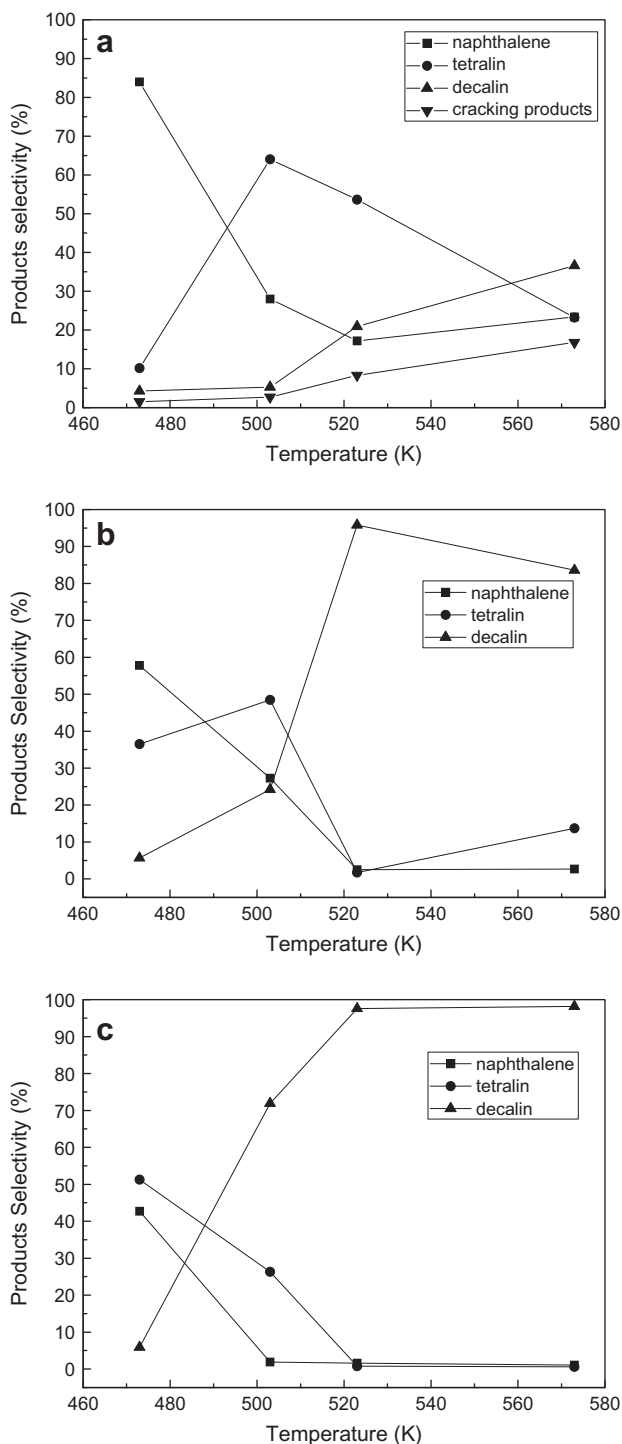


Fig. 3. The product selectivities of naphthalene hydrogenation over Pt/ZSM-5 (a), Pt/Al₂O₃ (b) and Pt/MZ-5 (c).

much easier than the tetralin hydrogenation step. It was reported that the reaction rate for the hydrogenation of naphthalene to tetralin is about 30 times higher than tetralin to decalin [22,23]. From the viewpoint of the increasing CN and particulate matters reduction, decalins (saturated hydrocarbons) (CN: naphthalene is 1, tetralin is 10 and decalin is 36) are more desired products than tetralin in the diesel fuel. Hence decalin selectivity was always used as criterion to evaluate the catalytic performance [7]. And decalin can be used as thermal stable (>900 °F) jet fuel in extreme condition [3]. Hence, the selectivity to decalin is used in our study as the main

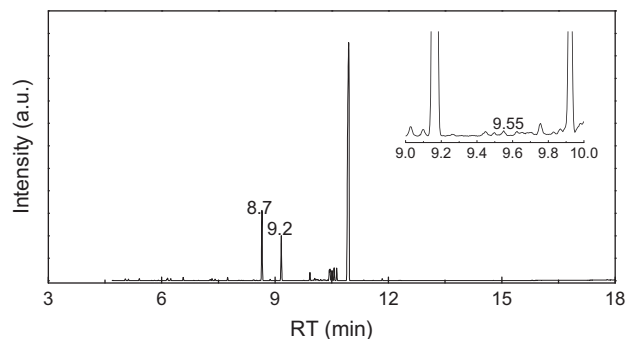


Fig. 4. GC/MS spectrum of naphthalene hydrogenation product over Pt/MZ-5 at 573 K.

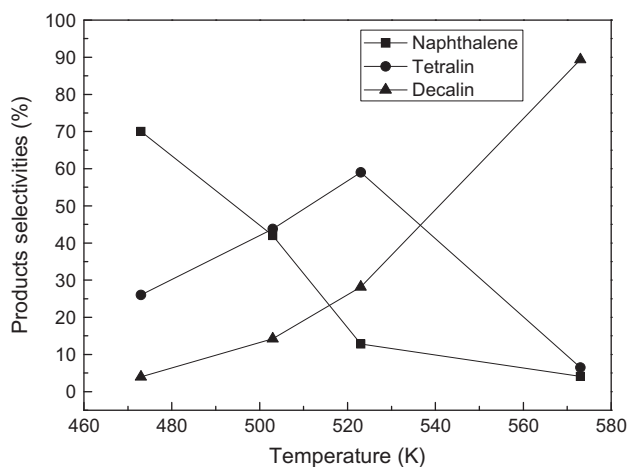


Fig. 5. The influence of temperature of sulfur resistance of Pt/MZ-5.

criterion to evaluate the catalytic performance of catalyst's naphthalene hydrogenation ability.

Fig. 3 shows the products selectivity for naphthalene hydrogenation over three catalysts at different temperature. As shown in Fig. 3a, the Pt/ZSM-5 exhibits poor hydrogenation activity between 473 K and 573 K, the highest naphthalene conversion is only about 83% at 523 K, and the main product is tetralin. The maximum decalin selectivity is only 36.6% (at 573 K). High selectivity of the cracking products (16.8% at 573 K) was also found over Pt/ZSM-5. It is clearly that the Pt/ZSM-5 shows low naphthalene conversion, low decalin selectivity and high selectivity to cracking products.

The Pt/Al₂O₃ shows much higher hydrogenation activity (Fig. 3b), the naphthalene conversion reaches 97% with decalin as the main product between 523 and 573 K, and no cracking products are found in the products. The decalin selectivity reaches a maximum value of 95.8% at 523 K. When the reaction temperature increased to 573 K, it is decreased to 83.6%, while the tetralin selectivity increased from 1.7% to 13.7%, though the reaction kept the similar high naphthalene conversion as at 523 K.

Fig. 3c presents the product selectivity in naphthalene hydrogenation over Pt/MZ-5. Compare with Pt/ZSM-5 and Pt/Al₂O₃, the Pt/MZ-5 shows much higher decalin selectivity. Complete naphthalene conversion is achieved at 503 K, which is 20 K lower than that of Pt/Al₂O₃. The main product is decalin over Pt/MZ-5 between 503 and 573 K, and the decalin selectivity exceeds 97% when reaction temperature was 523 K and 573 K, and very little cracking product is detected in the products as for the Pt/Al₂O₃. Fig. 4 presents a typical GC/MS spectrum of naphthalene hydrogenation products over Pt/MZ-5 at 573 K. The peaks at 8.7 and 9.2 are trans- and cis-decalin,

Table 2The conversion and the products selectivity over Pt/Al₂O₃ and Pt/MZ-5 absence and presence of sulfur at 573 K.

Catalyst	Dibenzothiophene content in feed	Naphthalene conversion (%)	Products selectivity		
			Naphthalene (%)	Tetralin (%)	Decalin (%)
Pt/MZ-5	0	98.9	1.1	0.7	98.2
Pt/MZ-5	300 ppm	98.8	1.2	1.4	97.4
Pt/MZ-5	3000 ppm	95.9	4.1	6.5	89.4
Pt/Al ₂ O ₃	0	97.3	2.7	13.7	83.6
Pt/Al ₂ O ₃	300 ppm	94.2	5.8	11.0	83.2
Pt/Al ₂ O ₃	3000 ppm	94.9	5.1	43.5	51.4

respectively. Tetralin (RT 9.55 min) can be found only when the spectrum was enlarged 100 times. Other peaks in the spectrum are solvent n-tridecane and its isomerization/cracking products.

As illustrated above, both the Pt/Al₂O₃ and Pt/MZ-5 exhibit excellent catalytic activity for the saturated hydrogenation of naphthalene to decalin. Since sulfur tolerance is an important aspect of practical application of the naphthalene hydrogenation, hence the dibenzothiophene was added into the feed to examine the catalyst's sulfur tolerance. The reaction temperature has a large influence on the hydrogenation activity and sulfur tolerance of catalyst. As shown in Fig. 5, the decalin selectivity significantly increased from 28.2% at 523 K to 89.4% over Pt/MZ-5 at 573 K in the presence of 3000 ppm dibenzothiophene condition. Hence, reaction temperature 573 K was selected to investigate the catalyst's sulfur tolerance in the present study. Table 2 presents the naphthalene conversion and product selectivity over Pt/MZ-5 and Pt/Al₂O₃ in the presence of DBT. After addition of 300 ppm dibenzothiophene, the conversion of naphthalene and the decalin selectivity were only slightly decreased of for both catalysts, that means both Pt/Al₂O₃ and Pt/MZ-5 had a certain sulfur tolerance. While when the dibenzothiophene addition increased to 3000 ppm, though the naphthalene conversion only slightly decreased over the two catalysts, the decalin selectivity was both dropped down. Especially over the Pt/Al₂O₃, as the decalin selectivity decreased from 83.6% to 51.4%, while for Pt/MZ-5 it only decreased from 98.2% to 89.4%. These results indicate that the Pt/MZ-5 have better sulfur tolerance.

The catalytic characteristics of three catalysts can be easily linked with their structure and acidity properties. The molecular sizes of compounds in naphthalene hydrogenation have molecular size between 0.50 and 0.71 nm. The molecules can penetrate and diffuse easily in the channel of Al₂O₃ (4.9 nm) and mesopores of MZ-5 (3.6 nm). But the channel of 10-member ring of ZSM-5 will bring serve diffusion resistance. On Pt/ZSM-5, poorer hydrogenation capacity is attributed to the diffusion limitation of naphthalene and tetralin in the microporous structure of ZSM-5 while the strong acidity and the low metal dispersion gives rise to the cracking of hydrogenation products. Such a result is in accordance with the previous report of Pawelec et al. [23]. Both the Pt/Al₂O₃ and Pt/MZ-5 have mesopore structure, which favors the reactants and the products diffusion, promotes the hydrogenation activity and suppress the products cracking, hence exhibits much higher catalytic activity for the saturated hydrogenation of naphthalene to decalin. The diffusional issue can also be used to explain that no cracking products found over Pt/MZ-5 though it have comparable acidity of Pt/ZSM-5. Interestingly, Pt/MZ-5 has similar mesopore structure and lower Pt dispersion than Pt/Al₂O₃, but the deep hydrogenation ability and sulfur tolerance of Pt/MZ-5 is much better than that of Pt/Al₂O₃. This is related to the strong acidity, mesoporous/microporous bimodal structure and high hydrodesulfurization performance of Pt/MZ-5. In Pt/MZ-5, electron-deficient Pt particles with good hydrogenation performance and sulfur tolerance would be formed by partial electron transfer from Pt particles to acidic sites. In Pt/MZ-5 and Pt/Al₂O₃, spillover based hydrogenation pathway will

play an important role. However, the hydrogen spillover in Pt/MZ-5 was different from Pt/Al₂O₃. The MZ-5 support has microporous and mesoporous bimodal structure, and the precursor solution of Pt may not only stay on the outer surface but also enter the mesoporous channels as well as the microporous channels during the preparation of Pt particles [16]. Because of the small pore diameter, some Pt active centers in the microporous channels cannot be reached by dibenzothiophene. Hence, the Pt sites located in the mesopores that are poisoned by adsorbed sulfur may possibly be partially recovered by spillover hydrogen coming from the micropores [24,25], that means more sulfur tolerance over Pt/MZ-5. Moreover, naphthalene hydrogenation in the presence of DBT can be considered as a competitive process of HDA and HDS. It has been reported that Pt/mesoporous ZSM-5 has better catalytic performance in hydrodesulfurization than Pt/Al₂O₃ [16]. The higher HDS activities also prompt the sulfur tolerance of Pt/MZ-5. Based on above discussion, mesoporous structure and high acidity are two preconditions for a support used in naphthalene hydrogenation.

4. Conclusion

Compared to Pt/ZSM-5 and Pt/Al₂O₃, Pt/MZ-5 exhibited better activity and good sulfur tolerance in the deep hydrogenation of aromatics. The better catalytic performance is attributed to the combination of the properties of zeolites and mesopores materials. This study proves that mesoporous zeolites are ideal candidates of supports for deep hydrogenation reactions when dealing with bulky molecules.

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