

Enhanced Phenol Hydrodeoxygenation Over a Ni Catalyst Supported on a Mixed Mesoporous ZSM-5 Zeolite and Al₂O₃

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Abstract Developing highly active catalysts for bio-oil hydrodeoxygenation is of great importance in the low cost production of conventional transport alkane fuels. Toward this goal, a Ni catalyst supported on mesoporous ZSM-5 zeolite mixed with 25 wt% y-Al₂O₃ (Ni/Al-HMZSM-5) was designed for hydrodeoxygenation of phenol as model compound. For comparison, the catalytic activities of Ni catalysts on conventional microporous ZSM-5, mesoporous ZSM-5 and γ -Al₂O₃ were also investigated. It was found that almost complete phenol conversion (99.6%) was achieved over the Ni/Al-HMZSM-5 catalyst along with a high cyclohexane selectivity (98.3%) under a relatively mild condition (170 °C, 4 MPa H₂). The open mesopores, stronger acid sites and synergism effect of Brønsted and Lewis acidities are jointly responsible for the excellent hydrodeoxygenation performance. In addition, it was shown that the catalyst was recycled several times with little loss of activity and selectivity.

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Graphical Abstract



 $\label{eq:keywords} \begin{array}{l} \mbox{Weywords} & \mbox{Phenol} \cdot \mbox{Hydrodeoxygenation} \cdot \mbox{Mesoporous} \cdot \\ \mbox{Ni/Al-HMZSM-5} \cdot \mbox{Bio-oils} \end{array}$

1 Introduction

Bio-oils, sustainably produced by pyrolysis or liquefaction of abundant lignocellulosic biomass, have attracted global attention as a promising potential raw material for liquid transportation fuels [1–5]. Lignin is a phenol-based biopolymer, and among lignocellulosic biomass, it shows a high energy density than cellulose and hemicelluloses [6]. Moreover, lignin is a rich source for phenolic bio-oils [7]. However, the direct use of phenolic bio-oils is impossible because of their high oxygen content and the presence of unsaturated and phenolic moieties, which lead to

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low energy density, high viscosity, and low stability [8–10]. Therefore, phenolic bio-oils, consisting of phenolic molecules such as phenol, guaiacol, syringol, and their derivatives, require significant deoxygenation to convert into conventional transport alkane fuels [9, 11]. Phenolic compounds are generally regarded as important model compounds for bio-oils [5], and hydrodeoxygenation is deemed to be the most effective method for bio-oil upgrading [12].

The conventional hydrodeoxygenation studies have focused on NiMo and CoMo sulfide catalysts that are industrial hydrotreating catalysts developed for removal of sulfur, nitrogen and oxygen from petrochemical feedstocks. However, these catalysts may be less suitable for hydrodeoxygenation of bio-oil due to sulfur contamination, coke accumulation, and water-induced catalyst deactivation [13–15]. An alternative approach based on sulfurfree catalysts, liquid acids (e.g., phosphoric acid, acidic ionic liquids) mixed with metals have been developed for hydrodeoxygenation via consecutive hydrogenation and dehydration steps. However, these homogeneous acids add complexity when regenerating the reaction systems, which is energy-consuming [4, 16]. Recently, aluminosilicate zeolites (e.g., ZSM-5, Beta and Y), as typical solid acids, combined with metals have been used to catalyze the hydrodeoxygenation of phenolic compounds to alkanes [17–19]. Additionally, zeolite based catalysts exhibiting high stability, easy separation, and abundant acidic sites, are regarded to be one of the most promising catalysts in the application of bio-oil upgrading. However, conventional zeolite catalysts often suffer from slow diffusions of bulky reactants/ products in their channel systems, as a result of their small pore size (<1.5 nm) [20, 21]. Therefore, the production of relatively bulky bioalkanes is a challenge in the hydrodeoxygenation of phenolic bio-oil over zeolite-based catalysts.

Mesoporous zeolites, with hierarchical porous structures containing both micro- and mesopores, have attracted much attention as a new type of promising catalytic materials [22-24]. The mesoporous zeolite based catalysts have exhibited unique catalytic properties in many reactions because of their efficient mass-transport property compared with the conventional zeolites [25]. For example, mesoporous ZSM-5-supported metal sulfide catalysts (NiMoS/MZSM-5 and CoMoS/MZSM-5) exhibited high activity in the deep hydrogenation of bulky aromatic phenanthrene [26]. The ZSM-5-based catalysts with mesopores, as highly selective Fischer-Tropsch catalysts, gave much higher selectivity to C_5-C_{11} isoparaffins than the conventional ZSM-5-based catalysts [27]. Mesoporous Y zeolite-supported Pd nanoparticles was more active in the hydrodesulfurization of 4,6-dimethyldibenzothiophene than conventional zeolite-based catalysts [24]. Recently, mesoporous ZSM-5-supported Ru or Pt metals were used as highly efficient catalysts for upgrading phenolic biomolecules [28]. However, mesoporous zeolites supported inexpensive Ni catalyst is rarely reported for conversion of biomass, although it is a promising bifunctional catalyst for industrial application due to the high activity for hydrodeoxygenation of biomass and lower cost.

In this work, a facile method was used for synthesizing mesoporous ZSM-5 (MZSM-5) at low cost. To enhance the hydrodeoxygenation activity, the HMZSM-5 zeolite mixed with a 25 wt% fraction of γ -Al₂O₃ (Al-HMZSM-5) was designed as a more effective catalyst support. The phenol hydrodeoxygenation activities of Ni catalysts supported on ZSM-5, MZSM-5, γ -Al₂O₃ and mixed Al-MZSM-5 zeolite materials were compared to try to establish a relationship between activity and catalyst structure. Meanwhile, the physicochemical properties of the catalysts, such as their acidity, surface area, and pore structure, have been evaluated by various techniques.

2 Experimental

2.1 Catalyst Preparation

All reagents used were of analytical grade and were used as-purchased without further purification. Mesoporous ZSM-5 zeolite (MZSM-5) and conventional microporous ZSM-5 were prepared by our previously reported approach [27]. MZSM-5 was synthesized hydrothermally from an aluminosilicate gel with a molar composition of Al₂O₃/50SiO₂/8.9Na₂O/0.02RCC/1950H₂O, where RCC was a random cationic copolymer that contained quaternary ammonium groups and was used as mesoscale template [23]. ZSM-5 was synthesized under the same conditions except for the absence of RCC. Furthermore, H-type zeolites (HZSM-5 and HMZSM-5) were obtained by NH_4^+ ion exchange. The Na-type MZSM-5 and ZSM-5 were treated with 1.0 mol/L NH₄Cl aqueous solution at 80 °C for 5 h under stirring, in a ratio of 1.0 g solid sample to 20 mL NH₄Cl solution. After filtration, washing, drying at 120 °C overnight, and calcination at 450 °C in air for 4 h, the process was repeated again.

 γ -Al₂O₃ powder was obtained by calcining commercial pseudo boehmite in air at 450 °C for 2 h. A mixture of HMZSM-5 and γ -Al₂O₃ (Al-HMZSM-5) was prepared by mixing 25 wt% γ -Al₂O₃ (100–120 mesh) with 75 wt% HMZSM-5 (80–100 mesh) in excess distilled water under vigorous stirring at room temperature, followed by drying in air at 120 °C for 12 h and calcination at 450 °C for 4 h.

Then, supported nickel catalysts (Ni/HZSM-5, Ni/ HMZSM-5, Ni/Al-HMZSM-5 and Ni/ γ -Al₂O₃) were prepared by an incipient wetness impregnation method using aqueous solutions containing required amounts of nickel nitrate (the nominal Ni loading of 10.0 wt%). After impregnation, samples were dried under ambient condition for 12 h, dried in air at 120 $^{\circ}$ C overnight, and thereafter calcined at 400 $^{\circ}$ C for 4 h.

2.2 Catalyst Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-A instrument with CuKa radiation $(\lambda = 0.1542 \text{ nm})$ operated at 50 kV and 30 mA. The scanning range was from 5° to 90°. Nitrogen physisorption was conducted at -196 °C on a Micromeritics ASAP 2020 M apparatus. Sample was degassed for 8 h at 300 °C before measurement. Specific surface area was calculated from the adsorption data using the Brunauer-Emmett-Teller (BET) equation. The pore size distribution was calculated according to the Barrett-Joyner-Halenda (BJH) model using adsorption data. Temperature-programmed desorption of ammonia (NH₃-TPD) was conducted on a Micromeritics ASAP2920 instrument. A 200 mg sample was placed in a quartz tube and pretreated in a helium stream at 450 °C for 2 h. After the sample was cooled to 100 °C, NH₃-He mixed gas (10 vol% NH₃) was passed over the sample for 30 min. After removal of the physically adsorbed NH₃ by flowing helium for 2 h at 100 °C, the total flow rate of gas was fixed at 10 cm³/min, and the sample was heated from 100 °C to 750 °C at a heating rate of 10 °C/min. Scanning electron microscopy (SEM) was performed using a FEI Inspect F50. Transmission electron microscope (TEM) images were collected using a JEM-2100F. Thermogravimetric (TG) analyses of the fresh and spent catalysts were carried out from 40 to 900 °C at 10 °C/min under flowing air (20 mL/min) on a TGADSC1 instrument. The nickel loadings of the calcined catalysts were determined by an inductively coupled plasma atomic emission spectroscopy (ICP-AES), Optima 2000DV.

2.3 Catalytic Test

Before use, all catalysts were sieved to form 100 mesh particles and then reduced by H_2 at 460 °C for 4 h. Phenol hydrodeoxygenation was carried out in a 250 mL high-pressure stainless steel reactor equipped with a magnetic stirrer (800 rpm). In a typical experiment, phenol (0.94 g, 0.01 mol) and catalyst (0.5 g) were added to 80 mL water in the reactor. After the reactor was purged three times with hydrogen, the outlet valve was closed to maintain 4.0 MPa of hydrogen pressure. Then the reaction system was heated to 170 °C and kept for a certain period. After the reaction was halted, the reactor was quenched immediately to room temperature in ice water bath and then opened. Ethyl acetate was used to extract the organic mixture and the aqueous phase was also collected. The organic phase and aqueous phase were both analyzed by a gas

chromatograph (GC-126, using a flame ionization detector) with a flexible quartz capillary column coated with SE-54 (30 m×0.32 mm×0.25 μ m). And the reaction products were identified by retention times of their pure compounds at the same condition. And the conversions of phenol and product selectivity were calculated based on the formulas:

 $Conversion = (phenol_{added-mol} - phenol_{remain-mol}) / phenol_{added-mol} \times 100\%$

Selectivity = cyclohexane_{formed-mol}/(phenol_{added-mol} - phenol_{remain-mol}) \times 100%

3 Results and Discussion

3.1 Morphology and Phase

Figure 1 shows the SEM images of the synthesized ZSM-5 and MZSM-5 zeolites and the TEM images of MZSM-5 under different magnifications. As shown in the SEM images (Fig. 1a, b), ZSM-5 sample is composed of relatively uniform spherical aggregates of 18-25 µm in diameter, while the particle shape of MZSM-5 tends towards an cuboidal form with a relatively uniform particle size of 12-17 µm. The light areas in the TEM images of the thinsectioned MZSM-5 (Fig. 1c, d) give direct evidence for the presence of abundant hierarchical mesopores in the sample, and the size range of these mesopores is in good agreement with the pore size distribution derived from N₂ adsorption/desorption which would be discussed below. Uniform crystallographic orientation lattice is also shown in the high magnification TEM image (Fig. 1d), indicating that the presence of a single crystalline pattern. Such structure reveals that the part or the whole framework can be regarded as a single crystal with penetrating mesoporous network inside. As a result, high thermal/hydrothermal stability can be expected. The morphologies of four Ni catalysts were also studied by SEM technique. The SEM images of those samples are shown in Fig. 2. SEM observation of the Ni/Al-HMZSM-5 sample reveals uniform distribution of γ -Al₂O₃ particles among the HMZSM-5 zeolite. Ni/y-Al₂O₃ sample shows irregular morphology and smaller grains.

X-ray powder diffraction data of the catalysts were used to identify crystalline nickel species formed on the support surfaces and the crystallinity of the catalysts. Figure 3 shows the XRD patterns of four Ni catalysts. All the catalysts present the typical diffraction peaks of NiO at $2\theta = 37.3^{\circ}$, 43.5° and 62.9°, indicating the formation of the NiO crystallites on the support surfaces. Notably, NiO diffraction peaks of Ni/Al-HMZSM-5 and Ni/ γ -Al₂O₃ catalysts become weaker or even disappear, indicating the better



Fig. 1 SEM images of **a** ZSM-5 and **b** MZSM-5, and TEM images of MZSM-5 at different **c** and **d** magnifications

dispersion of Ni particles on the supports. Regardless of the diffraction peaks of NiO, both HZSM-5 and HMZSM-5 supports exhibit well-resolved peaks at $2\theta = 7.9^{\circ}$, 8.9° and $22-25^{\circ}$ associated with the MFI structure. The γ -Al₂O₃ sample exhibits typical diffraction lines of Al₂O₃ material at 20 values of 37.5° , 39.4° , 45.8° , 60.8° , 66.9° , and 85.0° , but the intensities of these characteristic diffraction peaks are much weaker. Thus, the mixed Al-HMZSM-5 support still shows typical peaks for the MFI structure, though the intensities of these diffraction peaks are slightly weak-ened, indicating that some structural changes occur in Al-HMZSM-5 when a certain amount of γ -Al₂O₃ was added.

3.2 Textural and Acidic Properties

The textural properties of the catalysts were evaluated from nitrogen adsorption–desorption isotherms. Figure 4a shows the N_2 adsorption–desorption isotherms of the catalyst samples. The isotherm curve of Ni/HZSM-5 basically belongs to IUPAC type I, which is a characteristic of microporous materials. Contrary to Ni/HZSM-5, the N_2 adsorption–desorption isotherms of the Ni catalysts supported on HMZSM-5 and Al-HMZSM-5 are of type IV with H1 hysteresis loop. This type of hysteresis is usually found on solids consisting of particles crossed by nearly cylindrical channels. This means that both catalysts are mostly mesoporous. And the capillary condensation of the two catalysts is mainly at the high relative pressure between about 0.7 and 0.9, suggesting a relatively large mesopore size which is shown by pore size distribution results (Fig. 4b). The N₂ adsorption–desorption isotherm of Ni/ γ -Al₂O₃ belongs to type IV with H2-type hysteresis loop, characteristics of solids with "ink-bottle" pores [29].

The Barret–Joyner–Halenda (BJH) formula was employed to determine pore size distribution (PSD) of the catalysts. The BJH pore size distribution of the samples is shown in Fig. 4b. It is important to point out that all the PSDs show a narrow distribution of pores at approximately 4 nm, which should be due to the tensile strength effect (TSE) phenomenon [30]. The pore size distribution curve of the Ni/HZSM-5 further confirms that no mesopore exists in the conventional ZSM-5 sample. In contrast, the PSDs of the Ni/HMZSM-5 and Ni/Al-HMZSM-5 samples are all centered at about 19 nm; however the Ni/Al-HMZSM-5 shows a broader pore size distribution than the former, indicating that addition of γ -Al₂O₃ can increase the amount of pores at about 5–10 nm of Ni/Al-HMZSM-5 catalyst. And the Ni/ γ -Al₂O₃ presents a pore size distribution between 2







Fig. 3 XRD patterns of (*a*) Ni/HZSM-5, (*b*) Ni/HMZSM-5, (*c*) Ni/ Al-HMZSM-5 and (*d*) Ni/γ-Al₂O₃ samples

and 40 nm, with a maximum at 6.5 nm. The much broader pore size distribution of Ni/ γ -Al₂O₃ may be attributed to nonuniform size or shape of the pores in this material, which is in line with the H2-type hysteresis loop of the Ni/ γ -Al₂O₃ (Fig. 4a).

The values of surface area and pore volume of the samples are summarized in Table 1. The actual nickel loadings of the samples determined by ICP are also listed. It can be found that all samples show similar nickel loadings (7.8-8.1 wt%), close to the nominal one (10.0 wt%). As mentioned above, supported nickel catalysts were prepared by the incipient wetness impregnation method. Through standard preparation process, nickel species can be evenly dispersed on the surface of catalysts which contains external surface (Sext) and microporous surface (Smic). Furthermore, for porosity materials, its external surface generally comes from the mesoporous surface. So, it can be deduced that nickel species are dispersed on microporous surface as well as mesoporous surface uniformly under ideal conditions and the amount of nickel species on each kind of surface are related to the surface area. As can be seen, the BET surface of Ni/HMZSM-5 is larger than Ni/HZSM-5 as expected. The micropore areas and volumes calculated by the *t*-plot method for both samples are very similar. Consequently, the external surface area of the Ni/HMZSM-5 sample is greater than that of the Ni/HZSM-5 sample (147 vs. 90 m^2/g). And it should be noticed that the Ni/HMZSM-5 catalyst shows about fourfold larger mesoporous pore



Fig. 4 a Nitrogen adsorption–desorption isotherms and **b** pore size distributions of the catalyst samples. (The isotherms of Ni/HMZSM-5, Ni/Al-HMZSM-5 and Ni/ γ -Al₂O₃ have been offset by 50, 120 and 160 cm³/g along the vertical axis for clarity, respectively.)

volume than its Ni/HZSM-5 counterpart (0.27 vs. 0.07 cm³/g). The Ni/ γ -Al₂O₃ catalyst presents a small BET surface and all of it comes from the external surface due to the absence of micropore of γ -Al₂O₃, while it possesses the largest mesoporous pore volume (0.38 cm³/g). Thus, the BET surface of the mixed catalysts Ni/Al-HMZSM-5

is decreased compared with Ni/HMZSM-5, whereas the external surface area and mesoporous pore volume are increased. It is believed that large external surface area and mesoporous pore volume can facilitate the dispersion of active metal phase and the mass transfer of reactants [24].

The acidity properties of the catalysts were investigated by the temperature programmed desorption of ammonia (NH₃-TPD) method. The desorption curves deriving from NH₃ over various catalysts are presented in Fig. 5. Based on these curves, the amount and strength distribution of acidic surface sites are analyzed and the results are listed in Table 2. As shown in Fig. 5, two desorption peaks occur for all the catalysts, one peak centers at 188-198 °C and the other at about 454–566 °C, corresponding to the weak and the strong acid sites, respectively. For the Ni/ γ -Al₂O₃ catalyst, these two desorption peaks are broad and center at higher temperature (198 and 566 °C) compared with other catalysts, suggesting that Ni/y-Al₂O₃ catalyst has stronger acidic strength. However, it should be noticed that its acid amounts are very small. The amount and strength distribution of acidic surface sites of the Ni/HZSM-5 and Ni/ HMZSM-5 catalysts are similar due to the fact that same SiO_2/Al_2O_3 ratios (50) in the aluminosilicate gel may lead to the similar acidity properties of these two zeolites. Generally, NH₃-TPD experiment couldn't distinguish the Brønsted and Lewis acid sites on the solid surface in most cases [31, 32]. However, as already reported in previous studies on H-ZSM-5, the higher temperature peak is ascribed to the Brønsted acid sites comprising protonated oxide bridges as Si-OH-Al group, which plays an important role in the cleavage of C-O bonds in phenolics [17, 27]. Thus, the higher temperature peak of Ni/HZSM-5 and Ni/ HMZSM-5 catalysts may be described as the ammonia desorption from Brønsted acid sites. The total amount of acid of Ni/Al-HMZSM-5 reaches a value of 0.492 mmol/g, with the amounts of the two different types of NH₃ adsorption of 0.361 and 0.131 mmol (Table 2), respectively. Interestingly, a shift of desorption peaks toward higher temperature

Sample	Ni content (wt%)	$S_{BET} (m^2/g)^a$	$S_{ext} (m^2/g)^b$	$S_{mic} (m^2/g)^c$	V _{meso} (cm ³ /g) ^d	V _{micro} (cm ³ /g) ^e
Ni/HZSM-5	8.1	287	90	197	0.07	0.08
Ni/HMZSM-5	7.8	332	147	185	0.27	0.07
Ni/Al-HMZSM-5	8.0	314	163	151	0.35	0.05
Ni/γ - Al_2O_3	7.8	165	165	0	0.38	0

and textural properties of the prepared catalyst samples

Table 1 Nickel contents

^aBET surface area

^bExternal surface area, obtained from *t*-plot method

^cMicroporous surface area

^dMesoporous pore volume, obtained from BJH adsorption cumulative volume of pores between 1.7 and 300 nm in diameter

^eMicroporous pore volume, obtained from *t*-plot method



Fig. 5 NH₃-TPD profiles of (*a*) Ni/HZSM-5, (*b*) Ni/HMZSM-5, (*c*) Ni/Al-HMZSM-5 and (*d*) Ni/ γ -Al₂O₃ samples

 Table 2
 The amount and strength distribution of acidic surface sites

 over various catalysts

Sample	Acid amount (mmol/g)				
	Weak	Strong	Total		
Ni/HZSM-5	0.358	0.146	0.505		
Ni/HMZSM-5	0.368	0.138	0.506		
Ni/Al-HMZSM-5	0.361	0.131	0.492		
Ni/γ-Al ₂ O ₃	0.124	0.081	0.205		

is observed for the Ni/Al-HMZSM-5 catalyst, especially for the higher temperature peak (from 456 to 476 °C). It indicates that there occurs an interaction between HMZSM-5 and γ -Al₂O₃ added, thus causing a stronger interaction between NH₃ and the strong acid sites of Ni/Al-HMZSM-5. As mentioned above, the higher temperature peak of HMZSM-5 is ascribed to the ammonia desorption from strong Brønsted acid sites, but for γ -Al₂O₃, it means strong Lewis acid sites. So, the higher temperature of Ni/ Al-HMZSM-5 catalyst may be assigned to the stronger acid sites and synergism effect of Brønsted and Lewis acidities.

3.3 Hydrodeoxygenation of Phenol

Figure 6 shows the phenol conversion and the products selectivities obtained after 4 h reaction over the four catalysts. And the kinetics of hydrodeoxygenation of phenol over Ni/HMZSM-5 and Ni/Al-HMZSM-5 catalysts is



Fig. 6 Products distribution and phenol conversion after 4 h reaction over different catalysts

showed in Fig. 7. Obviously, in the hydrodeoxygenation of phenol to cyclohexane, cyclohexanone, cyclohexanol, and cyclohexene are formed as intermediates. It implies that phenol hydrodeoxygenation involves the following four reactions (Scheme 1): (i) phenol hydrogenation, (ii) cyclohexanone hydrogenation, (iii) cyclohexanol dehydration, (iv) and final cyclohexene hydrogenation. Similar reaction mechanism was also reported by Zhao et al. [33]. The active hydrogenation sites are on the exposed Ni nanoclusters, while the dehydration is catalyzed by the acid sites that are associated with the catalyst supports.

As shown in Fig. 6, Ni/HZSM-5 exhibits a low catalytic activity of phenol hydrodeoxygenation with phenol conversion of 51.2%, and the selectivity of cyclohexane is only 20.1%. However, a larger amount of cyclohexanol is formed with the total selectivity of 62.5%, indicating that limiting pore aperture in Ni/HZSM-5 retards the mass transfer rate of reactants and/or products under the mild condition, and correspondingly suppresses the overall hydrodeoxygenation reaction. Meanwhile, the Ni/ γ -Al₂O₃ catalyst achieves a high conversion of phenol (89.0%) and gives cyclohexanol as a major product with a selectivity of 99.0%. This phenomenon is attributed to the absence of Brønsted acid sites on γ -Al₂O₃, which are inactive for the dehydration of cyclohexanol, an important step during the hydrodeoxygenation of phenol to cyclohexane [28]. Interestingly, the product of phenol hydrodeoxygenation over the Ni/HMZSM-5 catalyst is dominated by cyclohexane with the selectivity of 85.6%, and the catalyst also gives a higher phenol conversion (83.4%), suggesting that the presence of the mesoporous on the zeolite greatly improves the conversion and selectivity of the reaction. In addition, Ni/ Al-HMZSM-5 exhibits the maximum phenol conversion of 99.6% and the highest cyclohexane selectivity of 98.3%. This means that the mixed catalyst can further enhance phenol to convert into cyclohexane.



Fig. 7 Dependences of phenol conversion and product selectivity on reaction time over a Ni/HMZSM-5 and b Ni/Al-HMZSM-5 catalysts

Based on the abovementioned results of characterization techniques, the excellent phenol conversion and high cyclohexane selectivity of the Ni/Al-HMZSM-5 catalyst can be attributed that larger mesoporous surface area and mesoporous pore volume make nickel species more accessible to the reactants and intermediates and the stronger acid sites and synergism effect of Brønsted and Lewis acidities also improve its catalytic performance.

To further explore the different catalytic performances of Ni/HMZSM-5 and Ni/Al-HMZSM-5 catalysts, the kinetics of hydrodeoxygenation of phenol over the two samples

were studied. For the reaction carried out in the batch autoclave, it was quenched after various reaction times to measure directly the concentrations of intermediates and products (Fig. 7). It can be seen that both the conversion and selective of Ni/Al-HMZSM-5 increase dramatically, while Ni/HMZSM-5 shows a relatively slower rate of growth in the first 2 h. Notably, the hydrodeoxygenation activity of Ni/Al-HMZSM-5 attains about 2.5 times higher conversion than Ni/HMZSM-5 (72.5 vs. 29.5%) after 1 h under the same conditions. It indicates that the hydrodeoxygenation rate of phenol over Ni/Al-HMZSM-5 is much higher than that over Ni/HMZSM-5. Thus it can be seen that addition of γ -Al₂O₂ makes a great contribution to adsorption capability for phenol, cyclohexanone, and cyclohexanol of Ni/ Al-HMZSM-5, which was also mentioned by Zhao et al. [33]. And the hydrogenation reactions of phenol or ketone usually showed positive reaction orders in organic in the previous literature [34], suggesting that the hydrogenation rate on phenol over Ni/Al-HMZSM-5 would be much higher. Moreover, the larger mesoporous surface area and mesoporous pore volume of Ni/Al-HMZSM-5 make nickel species more accessible to the reactants and intermediates thus improving its catalytic performance. Meanwhile, after 3 h, reaction is almost complete over Ni/Al-HMZSM-5, while Ni/HMZSM-5 only attains 72.3% conversion. On the other hand, it is found that cyclohexane dominates the product distribution after 1 h, but the Ni/Al-HMZSM-5 sample maintains about 20% higher selectivity of cyclohexane than Ni/HMZSM-5 during the reaction. Combining the NH₃-TPD results (Fig. 5) and cyclohexane selectivities of these two catalysts, it can be inferred that the stronger acid sites and synergism effect of Brønsted and Lewis acidities over the catalyst are favorable for the dehydration of cyclohexanol during hydrodeoxygenation process, which leads higher selectivity to hydrocarbons. Additionally, the primary products of cyclohexanone and cyclohexanol decrease gradually to quite low selectivity (5-10%) and cyclohexene intermediate is observed with selectivity lower than 10%. Consequently, it can be concluded that Ni/Al-HMZSM-5 is more active compared to Ni/HMZSM-5.

In addition, we also prepared a series of catalysts with different MZSM- $5/\gamma$ -Al₂O₃ ratios and different Ni loadings for hydrodeoxygenation of phenol. The results showed that Ni/Al-HMZSM-5 catalyst is the most active catalyst compared to others.

Scheme 1 Reaction sequence of aqueous-phase phenol hydrodeoxygenation to cyclohexane on supported Ni catalysts



Table 3	Nickel	contents	and	catalytic	performances	of	the	Ni/Al-
HMZSM	I-5 catal	yst in fou	r run	s (4 h read	ction)			

Run	Ni content (wt.%)	Phenol conversion (%)	Cyclohexane selectivity (%)
1	8.0	99.6	98.3
2	7.1	98.3	97.0
3	6.7	95.5	95.2
4	5.9	79.7	90.5

3.4 Catalyst Recyclability

Table 3 presents the results of the recycling tests of Ni/Al-HMZSM-5 catalyst in the hydrodeoxygenation of phenol. It can be seen that the catalyst can be used thrice while retaining an excellent phenol conversion (99.6% (first), 98.3% (second) and 95.5% (third), respectively) and a high selectivity of cyclohexane (>95.0%); however, a significant drop in conversion of phenol (79.7%) is observed when the catalyst is reused fourthly at the temperature of 170 °C. Generally, sintering, coking, and leaching are regarded as the typical reasons for supported Ni catalyst deactivation [31]. In this study, the calcination and reduction temperatures of the catalysts are both not in excess of 450 °C and the reaction temperature is 170 °C, hence sintering is unlikely. To better understand the catalyst deactivation mechanism, TG and ICP analyses were performed on fresh and used catalysts. The TG curves of the fresh and spent Ni/Al-HMZSM-5 catalysts are illustrated in Fig. 8. Because the two samples were not reduced before thermogravimetric tests, the nickel species in these catalysts were almost NiO. Thus, the weight gain as a result of Ni oxidation (Ni->NiO) during the thermogravimetric analysis may be very small and even can be ignored. It can be seen that there is a weight loss of about 9 wt% for the used catalyst, which may be attributed to the desorption of residual phenol absorbed on the catalyst. Only about 1 wt% coke is formed on the used catalyst during the hydrodeoxygenation reaction (Fig. 8). Thus coke formation may not be the main reason for catalyst deactivation. Moreover, ICP analysis (Table 3) shows that after the first and second runs, 0.9 and 1.3% of Ni have leached from Ni/Al-HMZSM-5, respectively. And nickel content of Ni/ Al-HMZSM-5 catalyst decreases to 5.9 wt% in the fourth run. Thus, the decrease in catalytic performance should be mainly ascribed to the leaching of the Ni species.

4 Conclusions

A mixed catalyst Ni/Al-HMZSM-5 was prepared and exhibits high catalytic activities, excellent selectivity, and extraordinary stability for phenol hydrodeoxygenation



Fig. 8 Thermogravimetry of the fresh and used Ni/Al-HMZSM-5 catalysts: (*a*) fresh catalyst treated by dipping in reaction solution; (*b*) spent catalyst after 4 h reaction at 170 $^{\circ}$ C

under a relatively mild condition (170 °C, 4 MPa H_2). The Ni/Al-HMZSM-5 catalyst has accessible Ni sites and active acidic sites exposed to reactants. Thus, the excellent catalytic properties of Ni/Al-HMZSM-5 are strongly related to the open mesopores, stronger acid sites and synergism effect of Brønsted and Lewis acidities of Ni/Al-HMZSM-5. Moreover, considering most biomass molecules in nature are much larger than the micropore sizes of zeolites and the high costs of noble metal catalysts, this Ni mesoporous catalyst has a good prospect for efficient conversion of biomass to biofuels and biochemicals in the future.

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References

- 1. Stöcker M (2008) Angew Chem Int Ed 47:9200-9211
- 2. Espro C, Gumina B, Paone E, Mauriello F (2017) Catalysts 7(3):78
- Wan X, Zhou C, Chen J, Deng W, Zhang Q, Yang Y, Wang Y (2014) ACS Catal 4:2175–2185
- Gamliel DP, Bollas GM, Valla JA (2017) Energy Technol 5:172–182
- 5. Corma A, Iborra S, Velty A (2007) Chem Rev 107:2411–2502
- 6. Huber GW, Iborra S, Corma A (2006) Chem Rev 106:4044-4098
- Zakzeski J, Bruijnincx PCA, Jongerius AL, Weckhuysen BM (2010) Chem Rev 110:3552–3599
- 8. Liu DJ, Chen EYX (2014) ACS Catal 4:1302–1310
- 9. Liu SS, Sun KQ, Xu BQ (2014) ACS Catal 4:2226-2230
- Xia QN, Cuan Q, Liu XH, Gong XQ, Lu GZ, Wang YQ (2014) Angew Chem Int Ed 53:9755–9760

- Mohan D, Pittman CU, Steele PH (2006) Energy Fuels 20:848–889
- 12. Czernik S, Bridgwater AV (2004) Energy Fuels 18:590-598
- Jongerius AL, Jastrzebski R, Bruijnincx PCA, Weckhuyse BM (2012) J Catal 285:315–323
- Ryymin EM, Honkela ML, Viljava TR, Krause AOI (2009) Appl Catal A 358:42–48
- Ryymin EM, Honkela ML, Viljava TR, Krause AOI (2010) Appl Catal A 389: 114–121
- Yan N, Yuan Y, Dykeman R, Kou Y, Dyson PJ (2010) Angew Chem Int Ed 49:5549–5553
- Zhang W, Chen J, Liu R, Wang S, Chen L, Li K (2014) ACS Sustain Chem Eng 2:683–691
- 18. Zhao C, Lercher JA (2012) Angew Chem Int Ed 51:5935-5940
- Hong DY, Miller SJ, Agrawal PK, Jones CW (2010) Chem Commun 46:1038–1040
- Liu JY, Wang JG, Li N, Zhao H, Zhou HJ, Sun PC, Chen TH (2012) Langmuir 28:8600–8607
- 21. Li Y, Sun C, Fan W, Wang Y, Lan A, Han P, Li X, Dou T (2015) J Mater Sci 50:5059–5067
- 22. Wang Y, Lancelot C, Lamonier C, Richard F, Leng K, Sun Y, Rives A (2015) ChemCatChem 7(23):3936–3944

- 23. Tang TD, Zhang L, Fu WQ, Ma YL, Xu J, Jiang J, Fang GY, Xiao FS (2013) J Am Chem Soc 135:11437–11440
- Fu WQ, Zhang L, Tang TD, Ke QP, Wang S, Hu JB, Fang GY, Li JX, Xiao FS (2011) J Am Chem Soc 133:15346–15349
- 25. Neumann GT, Hicks JC (2013) Cryst Growth Des 13:1535-1542
- 26. Fu WQ, Zhang L, Wu DF, Xiang M, Zhuo Q, Huang K, Tao ZD, Tang TD (2015) J Catal 330:423–433
- 27. Kang J, Cheng K, Zhang L, Zhang Q, Ding J, Hua W, Lou Y, Zhai Q, Wang Y (2011) Angew Chem Int Ed 50:5200–5203
- Wang L, Zhang J, Yi XF, Zheng AM, Deng F, Chen CY, Ji YY, Liu FJ, Meng XJ, Xiao FS (2015) ACS Catal 5:2727–2734
- 29. Storck S, Bretinger H, Maier WF (1998) Appl Catal A 174:137–146
- Groen JC, Peffer LAA, Pérez-Ramírez J (2003) Micropor Mesopor Mat 60:1–17
- 31. Zheng A, Li S, Liu SB, Deng F (2016) Acc Chem Res 49:655-663
- Zheng A, Huang SJ, Liu SB, Deng F (2011) Phys Chem Chem Phys 13:14889–14901
- 33. Zhao C, Kasakov S, He J, Lercher JA (2012) J Catal 296:12-23
- 34. Mahata N, Vishwanathan V (1999) Catal Today 49:65-69