Aqueous-phase hydrodeoxygenation of lignin monomer eugenol: Influence of Si/Al ratio of HZSM-5 on catalytic performances

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ABSTRACT

Aqueous phase catalytic upgrading of phenolic monomers to hydrocarbons have been explored using Pd/C combined with HZSM-5 zeolite catalysts in the presence of H₂. 2-Methoxyl-4-allylphenol (eugenol), which consists of methyl ether bond, hydroxyl group, aromatic ring and propyl olefin bond, was chosen as a classic lignin model compound. This research focuses on the relationship between the acidity of zeolites and the deoxygenation activities basis on the hydrodeoxygenation (HDO) of eugenol. The results indicated that the decrease of Si/Al ratio resulted in the increase of the acidity of the zeolites, which significantly influenced their catalytic performance for product distributions. Over the HZSM-5 (Si/Al = 12.5) catalyst, the 2-methoxyl-4-propylphenol conversion of 86.5% and the hydrocarbon selectivity of 73.4% were obtained with the HDO of eugenol under 513 K and 5 MPa hydrogen pressure. Owing to the lower selectivity of hydrocarbon with HZSM-5 (Si/Al = 50) as acidic catalyst, the pore treatment was used to enlarge the outer surface of zeolite. After modified by alkali-treatment, much more acid active sites were provided for feasible accessibility of oxygenated reactants. The selectivity of hydrocarbons was improved by the alkaline treatment of HZSM-5 zeolite with 0.3 mol L⁻¹ sodium hydroxide solution.

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1. Introduction

The depletion of fossil fuels as a source for fuels chemicals and energy arouses a strong interest to develop the fraction of energy and chemicals resulting from renewable resources such as biomass [1,2]. A distinctive difference between biomass and fossil feed stocks is the high oxygen content in the former, which leads to a low vapor pressure for many constituents of bio-oil. Therefore, the hydrodeoxygenation (HDO) of multi-alkoxy-substituted phenols to hydrocarbon compounds is the key reaction for the upgrading of lignin-derived bio-oil for the production of high-grade transportation fuels. Moreover, liquid phase processes will likely play a leading role in the bio-oil processing. Although other solvents (e.g. ionic liquids) have been suggested for biomass upgrading, water is the suitable solvent with respect to its low price and dissolving capacity to retain considerable amounts of polar oxygenates from

biomass [3]. The separation of organic products formed during reactions is conducted relatively easily from the water [4]. Furthermore, the solubility of hydrogen in water increases linearly with temperature and pressure, which can be achieved at 2 mL-H₂/g-H₂O with pressure and temperature rising to 3 MPa and 250 °C [5]. Consequently, large attention is focused on the refining of biomass to liquid fuel and other chemicals in aqueous phase by hydrogenation process [6–8].

Meanwhile, development of new water-tolerant catalyst would be rather desired [9]. For reactions in which water participates as a reactant or product, only a few solid acids with acceptable activity, stability and insolubility are applicable. It has been suggested by Mullen et al. [10] and Zhao et al. [11] that zeolites performed well in improving deoxygenation reactions. In particular, HZSM-5 has been suggested as the most suitable zeolite for biomass catalytic hydrodeoxygenation [12]. Additionally, it has been noted that HZSM-5 showed a high rate of dehydration with turnover frequencies of approximately 1600 mol mol⁻¹ [H⁺]⁻¹ h⁻¹, which was two orders of magnitude higher than that of H₃PO₄ (15 mol mol⁻¹ [H⁺]⁻¹ h⁻¹) [13]. An efficient route for upgrading lignin-derived phenolic oil to transportation biofuels is explored by combining Pd/C and HZSM-5 as hydrodeoxygenation catalysts, which achieved an exceedingly high selectivity in removing oxygen-containing

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groups (hydroxyl, methoxy, ketone, alkyl-O-aryl and aryl-O-aryl) of lignin-derived substituted phenolic monomers and dimers in aqueous phase at 473 K. The reaction is accomplished through a series of metal–acid-catalyzed broken down of C–O bonds in phenolic dimers besides hydrogenation and dehydration reactions [14].

It has been indicated that the acidity of support influences the reaction pathways and product distribution for promoted CoMoS catalysts in HDO reaction of phenolic model compound [15]. According to ZSM-5 zeolite crystal, different Si/Al molar ratios have impact on surface acidity of samples [16]. Zeolites of different Si/Al ratios have been shown to affect cracking reaction of phenolic model compounds [17,18]. H. Ben has investigated influence of Si/Al ratio of ZSM-5 zeolite on the properties of lignin pyrolysis products, indicating that the content of polyaromatic hydrocarbons in pyrolysis oil decreased with an increasing SiO₂/Al₂O₃ molar ratio of zeolite [19]. Rather, the alkali-treatment of the HZSM-5 zeolite is a simple technique that is effective for modifying the porous structure of the zeolite by increasing its mesoporosity and for moderating acid strength [20]. For example, the alkali-treated mordenite zeolites with low Si/Al ratios and with both micro- and mesopores achieved a significant decrease in the oxygen content of the bio-oil produced, which is a crucial improvement for its utilization as a fuel substitute [21]. Currently, the influence of different Si/Al ratio of HZSM-5 zeolites on the properties of hydrodeoxygenation products has rarely been reported.

In this work, hydrocarbons were produced by using HZSM-5 and Pd/C in the catalytic hydrodeoxygenation of lignin phenolic monomers. The effect of Si/Al molar ratio of HZSM-5 was investigated by the combination of the acidic nature of silicon–aluminum oxides and the deoxygenation activities in this reaction. The acidity of ZSM-5 zeolite with various Si/Al ratio was analyzed by NH₃-TPD, which is one of the most commonly methods used for measuring the surface acidity of porous materials such as zeolites, clays or mesoporous silica [22,23]. The deoxygenation performance of HZSM-5 zeolite alkali-treated with sodium hydroxide solution was also discussed.

2. Experimental

2.1. Chemicals and commercial catalysts

The chemicals were purchased from commercial suppliers and used as provided: eugenol (Aladdin, >99% GR assay), ethyl acetate (Aladdin, 99.5% GR assay), ZSM-5 (Catalyst Plant of Nankai University, NKF-5). The Si/Al ratio in the ZSM-5 was 12.5, 25, 50, 75 and 180. Hydrogenation catalyst was Pd/C (Aladdin, loading 5 wt% Pd).

2.2. Catalyst preparation

2.2.1. HZSM-5 preparation

The purchased catalysts were washed by deionized water, dried at 393 K overnight, air-calcined (flow rate: 30 mL min^{−1} g_{cat}^{−1}) at 823 K for 4 h with a heating rate of 3 K min^{−1} to remove template. Prior to testing catalysts, the Na-ZSM-5 was converted to acidic form (H⁺) by three times refluxing in 1 mol L^{−1} NH₄NO₃ at 313 K for 6 h. The solid was filtered, washed, dried at 393 K overnight and calcined in air (60 mL min^{−1}) at 823 K for 4 h (heating rate: 1 K min^{−1}).

2.2.2. Alkaline treatment of HZSM-5

The alkaline treatment to the calcined sample with Si/Al ratio of 50 was performed with NaOH solution at 313 K for 4 h. The extracted catalyst was washed with distilled water at ambient temperature until neutralized. Finally, the catalysts were exchanged with 1 mol L^{−1} ammonium nitrate solution at 313 K for 6 h and

washed with deionized water, repeatedly. After drying at 393 K overnight, the samples in NH₄⁺-form were calcined at 823 K for 4 h to convert them into H⁺-form.

The untreated sample is denoted as HZSM-5-(Si/Al molar ratio) for example HZSM-50 with Si/Al molar ratio labeled behind and the samples treated with 0.3 mol L^{−1} NaOH aqueous solutions are denoted as HZSM-50-0.3 M.

2.3. Catalytic measurements

The eugenol (0.0025 mol) were loaded into a stainless steel autoclave (80 mL) with distilled water (20 mL), Pd/C (0.03 g) and HZSM-5 (0.5 g) at 513 K. The reaction mixture was then placed under 5 MPa H₂ at ambient temperature for 4 h, with a stirring speed of 680 rpm. After the reactor was cooled to room temperature, the gas phase was released and the organic phase was extracted with ethylacetate (3 × 10 mL). Hydrogen and trace amounts of CO₂ and methanol were found in the gas phase, so in this work only the changes in the liquid phase were considered. After reaction, the organic phase and aqueous phase were separated and analyzed by GC–MS (Agilent 7890A/5975C) equipped with a capillary column (HP-5; 30 m × 250 μm) and a flame ionization detector (FID).

In order to clarify the role of Pd/C, the hydrodeoxygenation of eugenol was conducted without HZSM-5. Hydrogenation of eugenol lead to 2-methoxy-4-propylphenol as the initial product. Because of the excellent hydrogenation performance of Pd/C, no eugenol as raw material was obtained, as well as in bi-functional system with HZSM-5 of various Si/Al ratio (Table 1). Therefore, the conversion was calculated by regarding 2-methoxy-4-propylphenol as raw materials. And the amount of 2-methoxy-4-propylphenol was not concluded in the products when the calculation of selectivity is performed. The calculations of conversion and selectivity were performed on a carbon atom basis.

Conversion = 100%

$$= \frac{\text{Catoms in (2-methoxy-4-propylphenol)}}{\text{total Catoms in the products besides (2-methoxy-4-propylphenol)}} \times 100\%$$

$$\text{Selectivity} = \frac{\text{Catoms in each product}}{\text{total Catoms in the products}} \times 100\%$$

2.4. Catalytic characterization

The X-ray diffraction (XRD) patterns were measured with a Bruker D8 ADVANCE (Cu Kα = 0.154056 nm) at 40 kV/100 mA on a spinner in the range of 2θ = 5–50° with a step size of 0.01°.

Scanning electron microscopy (SEM) was recorded on a Hitachi S-4800 SEM-microscope (accelerating voltage 5 kV) and dry samples were platinum-coated prior to scanning.

Temperature-programmed desorption (TPD) of ammonia was carried out under flow conditions by Micromeritics 2920TR chemisorption analyzer. The catalysts were activated in Ar at 773 K for 1 h with a heating rate of 10 K min^{−1} from ambient temperature to 773 K. After that, the catalysts were cooled down to 373 K. Ammonia was adsorbed for 2 h by adding 10 vol% to the Ar carrier gas (total flow 40 mL min^{−1}) at 373 K. The sample was purged with Ar (20 mL min^{−1}) for 2 h in order to remove physically adsorbed molecules. The sample was then heated in flowing Ar at a rate of 10 K min^{−1} from 373 K to 873 K for TPD-NH₃ and the species desorbing was detected by TCD detector. For calibration of the method, a standard calibration experiment was performed.

Nitrogen adsorption and desorption experiments were conducted at 77 K using a ASAP 2000-M + C apparatus (Micromeritics). Each samples was degassed under vacuum and 523 K for at least

Table 1Product distributions of hydroxylation eugenol over Pd/C and HZSM-5 as function of Si/Al ratio of HZSM-5^a.

Selectivity of products (C %)	Si/Al ratio of HZSM-5						
	Without HZSM-5	12.5	25.0	50.0	75.0	180.0	50–0.3 M
0.1	9.9	14	3.2	1.6	2.7	19.7
isomers, e.g.	0	0	0	1.6	0	0	0
Isomers, e.g.	0	6.3	6.5	0.3	0	0	4.3
0	4.1	0	0	0	0	0.7
0.1	64.1	53.9	3.8	0.4	0.2	61.5
0	0.2	0.2	3.3	0	0	0
and	0	11.7	8.1	1.1	0	0	0.8
0	3	3.2	0.3	0	0	1.2
99.8	0.8	14.2	86.4	98	97.1	11.8
Conversions of
Conversions of	97.2	86.5	88.3	91.5	85.4	81.1	84.2
Selectivity of Hydrocarbons (C %)	0.1	73.4	63.6	4.4	0.4	0.2	67.1

^a Typical reaction conditions: eugenol (0.0025 mol), HZSM-5 (0.5 g), Pd/C (0.03 g), H₂O (20 mL), 513 K, 5 MPa H₂, 4 h, stirred at 680 rpm.

24 h before adsorption. The surface area was evaluated according to the BET equation in the linear range ($p/p_0 = 0.01–0.25$). The t -plot was applied to evaluate the external surface area and the micropore volume. The mesoporous volume was derived by BJH method.

3. Results and discussion

3.1. Hydrodeoxygenation of eugenol

Eugenol was selected as a model compound, which is essential for pyrolysis oil stabilization before its hydrogenation/deoxygenation treatment [24]. According to the reaction with only Pd/C as catalyst, eugenol was completely converted

to 2-methoxy-4-propylphenol as the primary product. The main product of reaction is 2-methoxy-4-propyl-cyclohexanol with 2.7% 2-methoxy-4-propylphenol unconverted (Table 1). It is indicated that the hydrogenation of the double bond was facile and selective, while the aromatic ring saturation was partially prevented by improper adsorption on Pd/C as the inhibit of three substituents on aromatic ring.

The hydrodeoxygenation of eugenol by combining Pd/C and HZSM-5 led to a variety of products including methanol, cyclohexanol, cyclohexanone, guaiacol, 3-propyl-cyclohexanone, 4-propyl-cyclohexanone, 2-methoxy-4-propylphenol, 1-methyl-2-propyl-cyclohexane, propyl-cyclohexane and its isomers, such as 1-methyl-3-propyl-cyclopentane. It should be noted that

Scheme 1. Reaction pathways for eugenol to cyclohexane over Pd/C and HZSM-5 in the liquid phase.

2-methoxy-4-propyl-cyclohexanol was not converted when Pd/C alone is used as a catalyst under the reaction conditions (Table 1). However, when Pd/C and HZSM-5 were jointly applied, C–O bond cleavage of aryl-methyl ether bond occurred. It is implied that the acid sites of HZSM-5 is critical to break down the aryl-methyl ether bond. In addition, the presence of dual catalytic functions is indispensable for the overall hydrodeoxygenation. The main component of products is hydrocarbons with 9 or 10 carbon atoms, including propyl cyclohexane and its isomers, such as 1-methyl-3-propyl-cyclopentane. Small amounts of 1-methyl-2-propyl-cyclohexane originated from migration of methyl was detected. The content of propyl-cyclohexane is the highest among products, reaching a selectivity of 53.9%. Another primary product is 2-methoxyl-4-propyl-cyclohexanol, which is less than propyl cyclohexane. This indicates that deoxygenating of 2-methoxyl-4-propyl-cyclohexanol is the dominating reaction under the selected conditions.

3.2. Hydrodeoxygenation reaction pathways

Eugenol is converted to 2-methoxyl-4-propyl-cyclohexanol by allyl hydrogenation and subsequent benzene ring hydrogenation. The conversion of 2-methoxyl-4-propyl-cyclohexanol to propyl-cyclohexanone was so fast that none intermediates was detected. According to the hydrodeoxygenation pathway of guaiacol proposed by Zhao et al., the hydrogenated intermediate 2-methoxy-cyclohexanone is converted to cyclohexanone and methanol via two routes [25]. However, the route of 2-methoxyl-4-propyl-cyclohexanol conversion is speculated to be based on sequential ketone hydrogenation followed by hydrolysis, diol dehydration, and ketone/enol isomerization to propyl-cyclohexanone, as shown in Scheme 1. Regardless of the pathway by which it is formed, propyl-cyclohexanone is gradually converted to propyl-cyclohexanol finally. The hydrodeoxygenation of propyl-cyclohexanol is much faster, thus neither propyl-cyclohexanol nor the propyl-cyclohexene intermediate is observed and

propyl-cyclohexane appears to be the final product. Guaiacol and cyclohexanone resulting from dealkylation were only detected in trace amount.

3.3. Effect of Si/Al ratio of HZSM-5

The acidity and shape selective effect are key properties of molecular sieves [26]. The low-temperature and high-temperature peak in NH_3 -TPD curves of HZSM-5 correspond to weak acid sites and strong Brønsted acid sites, respectively [27]. The density of the Brønsted acid sites, which is the most interesting sites in researching catalytic mechanism has been assigned to the density of framework aluminum ions [28]. The origin of the low-temperature TPD peak caused by weaker sorption remains unrecognizable. The Lewis acid sites presented on HZSM-5 has been correlated to framework sites of zeolite, where Al–O bonds have been transformed by hydrolysis during calcination, or to extra-framework aluminum oxide/hydroxide species [29].

The NH_3 -TPD results are presented in Figs. 2 and 3. The temperature of the maximum desorption rate (T_{max}) on the TPD curve is not universally comparable characteristics, because it depends on both the nature of the solid sample and the experimental conditions. As a result, although T_{max} values of TPD curves follows the trend of moving towards high temperature with the decreasing of Si/Al ratio, they are not regarded as a comparable characteristics.

On the other hand, one can observe the qualitative properties of interaction with acid sites and calculate the total amount of desorbed ammonia by integrating the TPD curve appropriately after calibrating. As shown in Figs. 1 and 2, the total amount of desorbed ammonia as well as desorbed ammonia amount on weak acid sites and strong acid sites are obtained by integrating the TPD curves. It is implied that the increase of acid quantity followed by a Si/Al ratio decrease.

Moreover, the activation energy of ammonia interacts with weak acid sites on HZSM-5 of various Si/Al ratio and modified zeolite was similar in the range of 40–60 kJ mol^{-1} (Table 2). However,

Table 2
Acidity and activation energy of NH_3 desorption on HZSM-5 with different Si/Al ratio.

Catalyst	Acidity (NH_3 mmol $\text{g}_{\text{cat}}^{-1}$)			Ea (kJ mol^{-1})	
	Total acid sites	Weak acid sites	Strong acid sites	Weak acid sites	Strong acid sites
HZSM5-12.5	3.62	2.16	1.46	51	76
HZSM5-25	2.12	1.21	0.9	43	96
HZSM5-50	1.65	0.9	0.75	55	101
HZSM5-75	1.08	0.59	0.49	44	109
HZSM5-180	0.04	0.02	0.01	50	116
HZSM5-50-0.3M	1.94	1.06	0.89	57	97

Fig. 1. NH_3 -temperature programmed desorption of HZSM-5 with different Si/Al ratio: (a) HZSM5-12.5, (b) HZSM5-25, (c) HZSM5-50, (d) HZSM5-75, (e) HZSM5-180, (f) HZSM5-50-0.3M; experimental data (solid line), fitted data (dotted line).

the activation energy of ammonia desorption on strong acid sites of HZSM-5 is 766 kJ mol^{-1} to 116 kJ mol^{-1} , which approximate to 109 kJ mol^{-1} [30], $114.3\text{--}137.3 \text{ kJ mol}^{-1}$ [27] and kJ mol^{-1} [31] for the heat of adsorption to describe the interaction of ammonia

Fig. 2. NH_3 desorption quantity of HZSM-5 with different Si/Al ratio and alkaline-treated HZSM-5.

with HZSM-5 by computational approaches. To probe the effect of catalyst acidity on conversion of eugenol, the representative phenolic monomer with adjacent hydroxyl and methoxyl functional groups at the aromatic ring, HZSM-5 of various Si/Al ratios ranging from 12.5 to 180 were selected. Scanning electron microscopies of HZSM-5 with various Si/Al ratio shows coffin-like zeolite particles of 3 to $8 \mu\text{m}$ (Fig. 3).

The conversions remain constant when acidic amounts was promoted with decreasing of Si/Al ratio, as shown in Fig. 4. In terms of selectivity, discernible differences can be found among the HZSM-5 catalysts of various Si/Al ratio. When Pd/C and HZSM-5 of higher Si/Al ratio (Si/Al = 50, 75, 180) were jointly used as catalysts for eugenol hydrodeoxygenation, the hydrolysis of the methoxy group and sequential hydrogenation and dehydration of 4-propyl-cyclohexanone are much slower than hydrogenation at the aromatic ring, leading to the accumulation of 2-methoxyl-4-propyl-cyclohexanol as the largest amount product. Because of limited deoxygenation of 2-methoxyl-4-propyl-cyclohexanol, only insignificant amount of the ultimate product, e.g. propyl-cyclohexane were detected. Hence, under the catalytic system consisting of Pd/C and HZSM-5 of Si/Al ratio higher than 50, the acid-catalyzed hydrolysis of the methoxy group severely hinders undergoing of the reaction. On the contrary, the selectivity of hydrocarbons on HZSM5-12.5 is much higher, exceeding 70%. Brønsted acidity estimated from pyridine adsorption decreases when Si/Al ratio increases [32]. Note that the hydrolysis of the methoxy group is much faster over HZSM-5 with a significantly larger concentration of Brønsted acid sites that the dehydration reaction is required [32].

In conclusion, the presence of hydrocarbons in products as a function of Si/Al ratio of HZSM-5 (Fig. 4) indicated that the promotion of acidic amounts was responsible for the changes of selectivity. Nevertheless, the selectivity to propyl-cyclohexane of Pd/C and HZSM5-50 was rather low comparing to that of HZSM5-12.5 and HZSM5-25. Therefore, HZSM5-50 was post-treated by alkaline afterwards to explore whether better performance could be achieved.

3.4. Effect of alkali treatment

It is reported that desilication by alkaline treatment is, comparing to other methods, a very reasonable and reproducible methodology to prepare mesoporous HZSM-5 zeolite without destroying the structural integrity [33]. First, according to the XRD patterns of HZSM-5 zeolite (Fig. 5) it is shown that no new phase was generated after the alkali-treatment to HZSM-5. The intrinsic lattice structure of HZSM-5 was unchanged, but the relative crystallinity became lower after alkali-treatment. A drastic change in the morphology of the alkali-treated HZSM-5 zeolites was observed from their SEM images, as shown in Fig. 3(g–h). The surface of HZSM-5 became rough after alkali-treatment and particles of HZSM-5 seemed to have been crushed to small pieces and became very irregular.

The study on the variations of the catalyst acidity by NH_3 -TPD showed only slight change in the amounts and properties of acid sites after the alkaline-treatment. Two distinct NH_3 desorption

Fig. 3. SEM micrographs of HZSM-5 with different Si/Al ratio: (a) HZSM5-12.5, (b) HZSM5-25, (c) HZSM5-75, (d) HZSM5-180, (e) HZSM5-50, (g) HZSM5-50-0.3M, (f) and (h) are magnified images of (e) and (g), respectively.

Fig. 4. Conversion of 2-methoxyl-4-propylphenol and selectivity of hydrocarbons over Pd/C and HZSM-5 as function of Si/Al ratio of HZSM-5. Typical reaction conditions: eugenol (0.0025 mol), HZSM-5 (0.5 g), Pd/C (0.03 g), H₂O (20 mL), 513 K, 5 MPa H₂, 4 h, stirred at 680 rpm.

peaks are seen for the untreated sample HZSM-5 in NH₃-TPD profiles as well (Fig. 1). One peak centers at about 480 K and the other at about 690 K, corresponding to the weak and the strong acid sites, respectively. The peak area was proportional to the number of the acid sites on the sample. Compared with the untreated sample, both the strong and the weak acid sites on the alkali-treated sample increased. Such enhancement in the acid sites was accordingly thought to be the result of the desilication during the alkali-treatment to HZSM-5 zeolite. Furthermore, the activation energy of ammonia desorption on strong acid sites of HZSM5-50-0.3M were found to be relatively lower than those on untreated zeolite in spite of the activation energy of ammonia interacts with weak acid sites of HZSM5-50-0.3M being almost the same as that on untreated HZSM-5. Moreover, both the amounts of acid sites and activation energy on strong acid sites are close to the values of HZSM5-25 (Table 2).

The variations in specific surface area and pore volume of HZSM-5 after its alkali-treatment were investigated by N₂

Table 3

Textural properties of untreated and alkaline-treated ZSM-5 zeolites.

Catalyst	BET surface area ^a (m ² g ⁻¹)	External surface area ^b (m ² g ⁻¹)	Mesopore volume ^c (cm ³ g ⁻¹)	Micropore volume ^b (cm ³ g ⁻¹)
HZSM5-50	393	27	0.04	0.16
HZSM5-50-0.3M	457	105	0.16	0.09

^a BET method.^b *t*-Plot method.^c BJH method (adsorption branch).

adsorption and desorption experiments, as shown in Table 3. It is clearly observed that BET surface and mesopore volume appreciably increased from 393 m² g⁻¹ and 0.04 cm³ g⁻¹ to 457 m² g⁻¹ and 0.16 cm³ g⁻¹ after alkali-treatment, respectively. Nevertheless, micropore volume decreased from 0.16 cm³ g⁻¹ of HZSM5-50 to 0.09 cm³ g⁻¹ of HZSM5-50-0.3M. These observations indicated that new mesopores were generated during the alkali-treatment, while the micropores were decreased by the alkali-treatment.

The mild desilication of HZSM-5 resulted in a noticeably increased activity of the Pd/C and HZSM5-50-0.3M catalyst as its selectivity of hydrocarbons dramatically exceed the hydrocarbons selectivity of untreated HZSM-5, e.g. 67.1% vs. 4.4% (Fig. 6). Such an increase cannot be explained by the indistinct improvement in

acidity and can be thus assigned to higher porosity of the desilicated catalyst, where active centers are better accessible.

The specific pore size structure of ZSM-5 catalyst is of shape selectivity with an elliptical pore size of 5.4 to 5.6 Angstroms diameter. Only compounds of the approximate molecular size of a C₁₀ molecule are allowed to enter and leave the particular pore size structure [34]. The maximum dimension (kinetic diameter) of eugenol is 8.97 Å diameter evaluated by using Chemskech (ACD Labs) software. The larger molecular diameter than pore size of zeolite catalyst affects the mobility of molecules in catalyst pores. Therefore, the higher molecular weight phenolic compounds could either be unconverted chemicals or catalysis products formed on the outer surface of the catalyst. According to the excellent performance of HZSM5-50-0.3M, the amounts of acid sites that can be accessed by the raw materials and intermediates is dramatically increased through introducing new mesopores by alkali-treatment. However, with respect to a whole, the changing amounts of acid sites obtained by NH₃-TPD was a trend similar to the one observed for the selectivity of hydrocarbons in eugenol hydrodeoxygenation. This indicates that high acidity of catalyst is preferred.

4. Conclusions

In the hydrodeoxygenation of eugenol with catalysts Pd/C and HZSM-5 zeolites, dehydration, hydrolysis, hydrogenation and isomerization proceed together under 513 K and 5 MPa hydrogen pressure. The reaction pathway of eugenol is described to outline the elementary catalytic steps in dual-functional catalyzed hydrodeoxygenation. Eugenol is firstly hydrogenated to 2-methoxy-4-propyl-cyclohexanol, followed by hydrolysis of methoxy group and dehydration of phenolic hydroxyl group to propyl-cyclohexanone. The subsequent series of steps transform propyl-cyclohexanone via hydrodeoxygenation to propyl-cyclohexane and its isomeric compounds as discussed above. The results indicated that the decrease of Si/Al ratio resulted in the increase of the acidity of the zeolites, which contributed to the improved deoxygenation performance of zeolites. Over the HZSM5-12.5 catalyst, the 2-methoxy-4-propylphenol conversion of 86.5% and the hydrocarbon selectivity of 73.4% were obtained. The selectivity of hydrocarbons was lower than 0.5% with HZSM5-75 or HZSM5-180 catalyst, which indicates that the HZSM-5 zeolite with very large Si/Al molar ratio has limited effect on the hydrodeoxygenation of eugenol. The hydrocarbons selectivity increased with decreased Si/Al molar ratio, which suggests that the zeolites with larger amount of acid sites show more effective for the cleavage of methoxyl group and hydration of hydroxyl group. Additionally, the mild desilication of HZSM5-50 catalyst modified the pore structure, especially the relative pore volume of mesopore and micropore, allowed better accessibility of active centers, and consequently feasible deoxygenation was achieved in comparison with the untreated zeolites.

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Fig. 5. XRD patterns of HZSM-5 before and after alkali-treatment: (a) untreated HZSM-5 (HZSM5-50), (b) HZSM-5 zeolite alkali-treated with 0.3 mol L⁻¹ NaOH solution (HZSM5-50-0.3M).

Fig. 6. Selectivity of products over Pd/C and HZSM-5 before and after alkali-treatment with 0.3 mol L⁻¹ NaOH solution. Typical reaction conditions: eugenol (0.0025 mol), HZSM-5 (0.5 g), Pd/C (0.03 g), H₂O (20 mL), 513 K, 5 MPa H₂, 4 h, stirred at 680 rpm.

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