



Article Phosphoric Acid Modification of Hβ Zeolite for Guaiacol Hydrodeoxygenation

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Abstract: Regulating the acid property of zeolite is an effective strategy to improve dehydration of intermediate alcohol, which is the rate-determining step in hydrodeoxygenation of lignin-based phenolic compounds. Herein, a commercial H β (SiO₂/Al₂O₃ = 25) was modified by phosphoric acid, and evaluated in the catalytic performance of guaiacol to cyclohexane, combined with Ni/SiO₂ prepared by the ammonia evaporation hydrothermal (AEH) method. Incorporating a small amount of phosphorus had little impact on the morphology, texture properties of H β , but led to dramatic variations in acid property, including the amount of acid sites and the ratio of Brønsted acid sites to Lewis acid sites, as confirmed by NH₃-TPD, Py-IR, FT-IR and ²⁷Al MAS NMR. Phosphorus modification on H β could effectively balance competitive adsorption of guaiacol on Lewis acid sites and intermediate alcohol dehydration on Brønsted acid sites, and then enhanced the catalytic performance of guaiacol hydrodeoxygenation to cyclohexane. By comparison, H β containing 2 wt.% phosphorus reached the highest activity and cyclohexane selectivity.

Keywords: guaiacol; hydrodeoxygenation; cyclohexane; phosphorus modification; zeolite

1. Introduction

Bio-oil from biomass depolymerization is an ideal substitute for conventional fossil fuels due to the increase of crude oil price and environmental pollution. Although its production has been commercialized, the utilization of crude bio-oil has been limited owing to the lack of suitable upgrading techniques. As recently reviewed [1], hydrodeoxygenation (HDO) of bio-oil into hydrocarbon fuels is considered as one of the most promising technologies for bio-oil upgrading, which can produce high-quality renewable fuels. Among the complex composition of bio-oil, lignin-derived phenolic compounds are known to be the most refractory.

Currently, many efforts have been devoted to the HDO of lignin-derived phenolic compounds, such as phenol, anisole, cresol, guaiacol, 4-propylguaiacol and syringol [2–6]. Lercher's group [7] found that a bifunctional combination of Raney Ni and Nafion/SiO₂ could effectively convert bio-derived aromatic monomers into hydrocarbons. In this process, phenolic compound was firstly hydrogenated by Ni species to form intermediate alcohol, and then subsequently hydrodeoxygenated to generate cycloalkane by the synergistic effect of Brønsted acid sites and active Ni sites. It was demonstrated that further dehydration of intermediate alcohol over Brønsted acid sites was the rate-determining step in this cascade reaction. In addition, this group [8] reported that the dehydration rate of intermediate alcohol on HZSM-5 was far greater than that on Nafion/SiO₂. The high performance of HZSM-5 zeolite in alcohol dehydration was ascribed to its large adsorption capacity of alcohol, closely related to the crystalline structure, pore size and acid property.



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). However, competitive adsorption of water molecules on Lewis acid sites decreased most of effective acid sites on HZSM-5, and then reduced the yield of hydrocarbon.

Thereafter, various zeolites with different topologies were used in HDO of phenolic compounds. Hong et al. [9] synthesized various Pt catalysts on different types of zeolites, such as HY, H β and HZSM-5. The selectivity to monocyclic hydrocarbon on HZSM-5 supported Pt catalyst was higher than that over HY and H β zeolite-supported catalysts in the conversion of phenol, which may be ascribed to the shape-selective effect of zeolite. In a batch-type reactor, HDO of guaiacol was also investigated at 250 °C over Pt/HZSM-5, Pt/mesoporous Beta, Pt/HBeta, Pt/MMZBeta, Pt/Al-MCM-48, and Pt/Si-MCM-48 [10]. Among these catalysts, Pt/mesoporous Beta and Pt/HBeta showed excellent catalytic activity due to their sufficiently large pores consisting of 12-rings, consistent with our conclusion [11]. According to our previous work [11], HDO of guaiacol to cyclohexane was achieved at 140 °C on bifunctional catalytic system containing Ni/SiO₂ and H_β zeolite. H_β zeolite was the prospective choice for the conversion of guaiacol to cyclohexane ascribed to its unique pore structure. Furthermore, we also found that the selectivity of cyclohexane was closely associated with the acid properties of H β zeolite. Typically, Ni/SiO₂ combined with H β (SiO₂/Al₂O₃ = 100) exhibited good performance for cyclohexane product with 91.7% yield. An excessively low or high Si/Al ratio was unsuitable for guaiacol HDO. However, Lee et al. [12] reached a different conclusion that a decrease in the Si/Al ratio of Pt/HY increased guaiacol conversion and hydrocarbon yield. In summary, both sufficient large pore and appropriate acid property are essential for HDO of phenolic compounds. To regulate the acid properties of zeolites would further enhance the catalytic activity and product selectivity in HDO reaction.

The phosphating process of zeolite is a well-known, relatively inexpensive and seemingly straightforward post-synthetic modification, which is often used to alter its hydrothermal stability and acidity [13]. At present, phosphorus modified zeolite has been widely used in a variety of catalytic processes, including alkylation of aromatic [14,15], catalytic cracking [16], methanol-to-hydrocarbon processing [17], dehydration of bioalcohol [18], and ammonia selective catalytic reduction (SCR) of NO_x [19]. The group of Chen [20] investigated the effect of phosphorus modification on acid properties about HZSM-5/HY composite zeolite. Incorporation of phosphorus increased the amount of strong Brønsted acid sites and decreased the number of Lewis acid sites simultaneously, and then affected the catalytic properties. Corma et al. [21] investigated the catalytic performance of phosphorus modified HZSM-5 in the cracking reaction of N-decane. Phosphorus modification of HZSM-5 improved the selectivity of the olefin product. This catalyst was also used for ethanol dehydration, and obtained a high yield of target product. Obviously, phosphorus modification could effectively tune the acid property of zeolite, such as acid type and acid strength, and then improved the selectivity and yield of target products. However, it has not been explored for the effect of phosphorus modified zeolite on HDO reaction of phenolic compounds.

Herein, a series of P-modified H β zeolites were investigated for HDO reaction of guaiacol to cyclohexane, combined with Ni/SiO₂ prepared by ammonium evaporation hydrothermal (AEH) method [22]. Among these catalysts, H β with 2 wt.% phosphorus exhibited high activity and excellent selectivity of cyclohexane. These P-modified H β zeolites were fully characterized and a structure-performance relationship was deeply discussed with solid evidence. Based on experimental results, the effect of zeolite's acid property was revealed in the HDO reaction.

2. Results and Discussion

2.1. Characterization of Catalysts

2.1.1. Physiochemical Property of P-Modified H_β Zeolites

The physiochemical properties of parent and P-modified H β zeolites are shown in Table 1. According to ICP results, the actual loading of phosphorus on modified H β was similar to its theoretical loading. This suggested that most phosphorus was loaded

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on zeolite, although phosphorus was reported to sublimate during roasting. The N_2 adsorption-desorption isotherms of H β zeolites with different phosphorus loading are shown in Figure 1, and the corresponding textural properties are shown in Table 1. The data of N_2 physisorption indicated that P-modified samples with low phosphorus content offered similar surface area and pore volume as parent one. In this case, phosphorus mainly entered the zeolite's pore. However, when the content of phosphorus increased from 2 wt.% to 5 wt.% over zeolite, the surface area and pore volume of modified samples decreased obviously, which was attributed to the excessive amount of phosphorus species on zeolites. As Bert et al. [23] reported, high concentration of phosphorus was mostly found on or close to the outer surface of zeolites, where particle aggregation occurred. This assumption was verified by SEM images (Figure 2). Obviously, P-modified zeolite existed in the form of crystal particles with obvious dividing lines when the phosphorus loading was no greater than 2 wt.%. However, the particles were conglutinated, as the phosphorus content of zeolite still further increased.

Figure 3 shows the XRD patterns of unmodified $H\beta$ and P-modified $H\beta$ zeolites. Obviously, all samples presented typical characteristic patterns of BEA topology, and no impure peaks appeared. However, the crystallinity of P-modified zeolite decreased significantly as phosphorus loading increased, which was also found in previous literature [24]. It indicated that phosphorus loaded on zeolite would distorted skeleton aluminum, and even caused dealuminization.

Table 1. Physical property of $H\beta$ zeolites with different phosphorus loading.

| | Catalyst | P Loading ^a – | $S_{BET}(m^2 \cdot g^{-1})^{b}$ | | Pore Volume(m ³ ·g ^{−1}) | | |
|---|----------|--------------------------|---------------------------------|----------|---|--------------------------------|---------------------------------|
| | | | Total | External | V _{total} ^c | V _{meso} ^d | V _{micro} ^e |
| 1 | Нβ | 0 | 489 | 139 | 0.41 | 0.26 | 0.15 |
| 2 | 1%P-Hβ | 1.1 | 477 | 133 | 0.41 | 0.27 | 0.14 |
| 3 | 2%Р-Нβ | 1.8 | 466 | 124 | 0.40 | 0.26 | 0.14 |
| 4 | 3%Р-Нβ | 3.0 | 400 | 86 | 0.32 | 0.18 | 0.14 |
| 5 | 5%P-Hβ | 4.6 | 328 | 73 | 0.29 | 0.18 | 0.11 |

^a P Loading: Phosphorus loading of catalyst determined by ICP; ^b S_{BET}: Specific surface area determined by BET; ^c V_{total}: total pore volume; ^d V_{meso}: mesopore volume; ^e V_{micro}: micropore volume.



Figure 1. N₂ adsorption–desorption isotherms of H β zeolites with different phosphorus loading.



Figure 2. SEM images of P-modified Hβ zeolites. (**A**) Hβ, (**B**) 1%P-Hβ, (**C**) 2%P-Hβ, (**D**) 3%P-Hβ and (**E**) 5%P-Hβ.



Figure 3. XRD pattern of various $H\beta$ zeolites.

2.1.2. Acid Property of P-Modified H_β Zeolites

The acid properties of parent H β and P-modified H β zeolites were measured by NH₃-TPD and Py-IR. As shown in NH₃-TPD profiles (Figure 4A), all P-modified zeolites exhibited two ammonia desorption peaks, corresponding to weak acid sites in the low–temperature region and strong acid sites in high-temperature region, respectively. Obviously, the number of acid site for P-modified H β changed significantly by modification with phosphorus acid. According to quantitative analysis (Table 2), the amount of total acid site decreased evidently with the increasing amount of phosphorus in P-modified H β , as similar to the amount of weak acid site. However, the amount of strong acid site exhibited a different tendency. Specifically, the amount of strong acid site presented increase at first and then decreased with the increasing content of phosphorus in zeolite. The amount of the strong acid site reached 0.34 mmol/g in 2%P-H β , which was higher than unmodified sample (Table 2, entry 3).



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Figure 4. NH_3 -TPD profiles (A) and Py-IR spectra (B) of H β zeolites with different phosphorus loading.

| Entry | Catalyst | Acid Site(mmol/g) ^a | | D/I | Acid Site(mmol/g) ^b | | |
|-------|----------|--------------------------------|------|------|--------------------------------|------|--------|
| Entry | | В | L | D/L | Total | Weak | Strong |
| 1 | Нβ | 0.27 | 0.23 | 1.17 | 0.97 | 0.68 | 0.29 |
| 2 | 1%P-Hβ | 0.30 | 0.19 | 1.58 | 0.90 | 0.55 | 0.35 |
| 3 | 2%Р-Нβ | 0.29 | 0.18 | 1.61 | 0.91 | 0.57 | 0.34 |
| 4 | 3%Р-Нβ | 0.15 | 0.10 | 1.5 | 0.47 | 0.29 | 0.18 |
| 5 | 5%Р-Нβ | 0.10 | 0.06 | 1.67 | 0.31 | 0.19 | 0.12 |
| | ii n mhn | | | | | | |

Table 2. Acid properties of H_β zeolites with different phosphorus loading.

^a Determined by Py-IR; ^b Determined by NH₃-TPD.

Figure 4B shows the Py-IR profiles of P-modified H β zeolites with different phosphorus content, and the results of quantitative analysis are listed in Table 2. All the examined catalysts presented two pyridine adsorption peaks centered at 1450 cm⁻¹ and 1540 cm⁻¹, corresponding to the Lewis acid site and Brønsted acid site, respectively [25]. Of the examined catalysts, the amount of the Lewis acid site decreased evidently with an increase of phosphorus content in P-modified H β zeolite. Surprisingly, the amount of the Brønsted acid site presented increase at first and then decreased with the increasing content of phosphorus. Meanwhile, the ratio of B/L increased compared with unmodified samples. The Brønsted acid site became the primary acid site. Based on the above analysis, it can be realized that the acid property of zeolite was considerably altered after phosphorus modification, which could be closely related to the structure of P-modified H β .

In order to describe the acid characteristics of P-modified zeolite more accurately, the crystal structure change of zeolite by phosphorus modification was examined using FT-IR, ²⁷Al MAS NMR and ³¹P MAS NMR. Figure 5 displays the FT-IR spectra of P-modified zeolites in hydroxyl-group region. Obviously, there were three characteristic peaks of hydroxyl groups appearing at 3745, 3733 and 3608 cm⁻¹, which were attributed to terminal silanols, (OH)₄ group of zeolite defect sites, and bridging hydroxyls of Si–O(H)-Al, respectively [26]. Of all, the bridging hydroxyl group of Si-O(H)-Al appearing at 3608 cm⁻¹ was assigned to the strong Brønsted acid sites [27]. In the range of low phosphorus content (≤ 2 wt.%), the intensity of (OH)₄ group around 3733 cm⁻¹ decreased obviously as the phosphorus loading increased. Simultaneously, there was a distinct increase in the intensity of the bridging hydroxyl group. It was assumed that monomeric phosphate was mainly formed on zeolite defect site, and then increased the amount of strong Brønsted acid site, consistent with the results of NH₃-TPD and Py-IR. However, when the phosphorus content was higher than 2 wt.%, the peak intensity of bridging hydroxyl group at 3608 cm⁻¹



decreased evidently. That may be ascribed to the generation of condensed polyphosphates on modified samples, which was observed in SEM images (Figure 2).

Figure 5. FT–IR spectra of Hβ zeolites with different phosphorus loading.

²⁷Al MAS NMR spectroscopy was used to characterize the nature of Al species in modified H β zeolites with different phosphorus loading, as shown in Figure 6A. The corresponding concentration of different Al species is compiled in Table 3. As can be observed, the spectrum of parent H β comprised two well–resolved ²⁷Al resonance bands at around 0~-6.0 ppm and 56.1-53.5 ppm. The high chemical shift at 56.1-53.5 ppm was assigned to Altetra-frame, and the low chemical shift at 0~-6.0 ppm was assigned to Al_{non-frame}, which were attributed to the Brønsted acid site and Lewis acid site, respectively. Impregnation of orthophosphoric acid resulted in the decrease of the characteristic line attributed to Alnon-frame and Altetra-frame. These acid sites were converted to highly shielded octahedrally coordinated Al (Al_{octa-dist}) and to tetrahedrally coordinated distorted sites (Altetra-dist) with chemical shift of -12.4 ppm and 38.5 ppm, respectively. These observed resonance peaks of $Al_{octa-dist}$ and $Al_{tetra-dist}$ confirmed the generation of new Al–O–P species. On the basis of reference [28], the Brønsted acid site of Altetra-dist at 38.5 ppm was stronger than that of Altetra-frame at 56.1-53.5 ppm. Obviously, 2% phosphorus loading just converted part of Al_{tetra-frame} into Al_{tetra-dist}, whereas the total amount of tetrahedral aluminum species remained almost constant, indicating the increased strength and similar amount of Brønsted acid site over 2%P-Hβ. This conclusion was consistent with the result of NH₃-TPD and Py-IR. However, when the content of phosphorus increased to 5 wt.%, the proportion of Al_{octa-dist} in Al species increased from 23.9% to 72.1% due to dealumination of zeolite, which led to a decrease in the amount of Brønsted acid site over 5%P-Hβ.

Table 3. Concentration and distribution of aluminum species in phosphorus modified H β zeolites determined by ²⁷Al MAS NMR.

| Entry | Catalwet | Chemical Shift (ppm) | | | | | |
|--------|----------|----------------------|------|------|-----|------|-------|
| Littiy | Catalyst | 56.1 | 53.5 | 38.5 | 0.0 | -6.0 | -12.4 |
| 1 | Нβ | 15.3 | 54.3 | 0 | 5.9 | 24.5 | 0 |
| 2 | 2%Р-Нβ | 14.4 | 39.5 | 12.6 | 0.3 | 9.2 | 23.9 |
| 3 | 5%Р-Нβ | 3.7 | 6.4 | 17.8 | 0 | 0 | 72.1 |



Figure 6. ²⁷Al MAS NMR spectra (**A**) and ³¹P MAS NMR spectra (**B**) of phosphorus modified Hβ zeolites.

Considering the nature of the phosphorus species on modified zeolite, it was found that ³¹P MAS NMR spectroscopy of 2%P-H β and 5%P-H β , as seen in Figure 6B, showed a broad resonance composed of several superimposed signals from 0 ppm to -40 ppm. The clearest positions were at -0.5, -6.8, -14.1 and -30.2 ppm. The first peak at -0.5 ppm was attributed to the phosphorus species with weak interaction with zeolite [29]. The two peaks at -6.8 and -14.1 ppm were often found in phosphated zeolite and corresponded to terminal phosphate groups and middle phosphate group in polyphosphate chains. The peak at -30.2 ppm was attributed to Al-O-P species [28,30]. Obviously, a large proportion of phosphorus was chemically bonded with Al species in the form of Al-O-P over 2%P-H β , paralleled by the signal increase of the distorted Al species in ²⁷Al MAS NMR. Introduction of phosphorus loading of 5 wt.% led to relatively high intensity of the resonance line at -14.1 and -6.8 ppm, attributed to the presence of polyphosphates bound to octahedrally coordinated aluminum Al_{octa}. Excessive phosphorus caused dealuminization of zeolite, and then decreased the amount of Brønsted acid site, which was also verified by ²⁷Al MAS NMR.

2.1.3. FT-IR Study of Guaiacol Adsorbed on P-Modified Hβ

Firstly, we investigated the adsorption state of guaiacol over 2%P-H β . As reference, we also studied the state of phenol and anisole adsorbed on 2%P-H β , respectively (Figures S1 and S2). Figure 7 showed the IR spectra of guaiacol on 2%P-H β after adsorption at room temperature followed by evacuation at different temperatures. After evacuation at 100 °C, the spectrum of guaiacol adsorbed on 2%P-H β showed three bands at 1616, 1597 and 1502 cm⁻¹ in the low–frequency region, which were similar to γ (C = Cring) of free guaiacol (see Table S1), although there was difference. Meanwhile, the bands of δ (OH) at 1364 cm⁻¹ and δ (CH₃) around 1470–1444 cm⁻¹ were poorly resolved. In the high frequency region, the decrease of the silanol about zeolite at 3740 and 3605 cm⁻¹ was accompanied by the appearance of a band at 3600–3100 cm⁻¹, assigned to Si-OH or Si-O(H)-Al perturbed by an aromatic ring [31]. This indicated that zeolite weakly interacted with basic π –electrons of the aromatic ring of guaiacol by H-bonding at low temperature.

After evacuation at 170 °C, the vibration band of γ (C = Cring) shifted from 1502 cm⁻¹ to 1499 cm⁻¹ and perturbed the δ (CH₃) band around 1470–1444 cm⁻¹ was still observed, but the δ (OH) contribution of guaiacol at 1364 cm⁻¹ disappeared. This could infer that guaiacol adsorbed on 2%P-H β formed methoxyphenate species, according to the red shift of γ (C = Cring) band from 1504 to 1499 cm⁻¹ together with the disappearance of δ (OH) band. Guaiacol was chemisorbed on the Lewis acid site of zeolite to form methoxyphenate species, which was also proposed in the case of guaiacol adsorbed on aluminium oxide [32]. Significantly, guaiacol adsorbed in methoxyphenate species was also observed even at 350 °C, indicating its strong adsorption on catalyst. Meanwhile, it was not difficult to

find that the characteristic peak of Si-O(H)-Al at 3605 cm^{-1} was not recovered completely. Guaiacol molecules may strongly adsorb on the Lewis acid site, which covered its adjacent Si-O(H)-Al group.



Figure 7. IR spectra of guaiacol on (a) KBr and (b–e) 2%P-Hβ after adsorption at RT followed by evacuation at different temperatures ((b) 100 °C, (c) 140 °C, (d) 170 °C and (e) 350 °C). (A) High-frequency region and (B) low-frequency region.

To investigate the effect of phosphorus content on the adsorption property of guaiacol, we compared the guaiacol adsorption on various P-modified H β by FT–IR, as shown in Figure 8. Obviously, the red shift of γ (C = Cring) band to 1498 cm⁻¹ together with the disappearance of δ (OH) band over all samples can be easily observed, indicating that guaiacol strongly adsorbed on Lewis acid site of P-modified zeolite in methoxyphenate species. Simultaneously, the amount of guaiacol adsorbed on P-modified H β was closely related to phosphorous loading. Specifically, the amount of guaiacol adsorbed on zeolite gradually decreased with the increasing phosphorus content, which was consistent with the variation tendency of the Lewis acid site amount on zeolite.



Figure 8. IR spectra of guaiacol adsorption at 350 °C on H_β zeolites with different phosphorus loading.

2.2. Effect of Acid Property on the Catalytic Performance of Guaiacol HDO

In our previous work [11], we found that guaiacol could be converted easily into cyclohexane in the hydrogenation-dehydration pathway on a bifunctional catalyst consisting of Ni/SiO₂ and H β , as shown in Figure 9. In this tandem reaction, the rate–determining step was acid-catalyzed dehydration of 2-methoxycyclohexanol (MCH). To reveal the intrinsic nature of acid site, we investigated the catalytic performance of Al_2O_3 in the reaction of MCH, in which Al_2O_3 contained only Lewis acid site (Table 4, entry 7). Unfortunately, the reactant of MCH was not converted on Al_2O_3 at 140 °C, even in a reaction time up to 5 h. A single Lewis acid site was not effective in dehydration of alcohol at 140 °C. By contrast, the addition of H β into system promoted the conversion of MCH rapidly (Table 4, entry 6). By comparison, we could assume that Brønsted acid site was the main active site for MCH dehydration.



Figure 9. Proposed reaction pathway for guaiacol transformation over Ni/SiO₂ combined with H β [11].

| Entry | Substrate | Catalyst | Reaction Time | Conv. (%) | Main Product |
|-------|------------------|----------------------|------------------|--------------|------------------|
| 1 | GUA | Ni/SiO ₂ | 2 h | 81.8 | MCH |
| 2 | GUA | $Ni/SiO_2 + H\beta$ | 2 h | 72.0 | MCH, cyclohexane |
| 3 | GUA | $Ni/SiO_2 + Al_2O_3$ | 5 h | >99 | MCH |
| 4 | GUA | $Ni/SiO_2 + SiO_2$ | 5 h | >99 | MCH (95.6) |
| 5 | MCH ^b | SiO ₂ | 5 h | - | - |
| 6 | MCH | Нβ | 1 h | >99 | cyclohexanone |
| 7 | MCH | Al_2O_3 | 5 h | - | - |

Table 4. Catalytic performance of different catalysts for the conversion of different substrates ^a.

^a Reaction conditions: 0.05 g Ni/SiO₂, 0.05 g (H β , Al₂O₃ or SiO₂), 0.10 g substrate, 20 mL decaline, 140 °C, 3 MPa H₂; ^b MCH: 2–methoxycyclohexanol.

However, on the bifunctional catalyst containing Ni/SiO₂ and H β , the intermediate product of MCH was not completely transformed over H_β. Meanwhile, guaiacol conversion was prevented by the addition of H β (Table 4, entry 2). That may be attributed to the strong adsorption strength and large adsorption capacity of H^β for guaiacol. According to our previous work [22], the reaction rate of guaiacol hydrogenation over Ni/SiO_2 was positively related to guaiacol concentration in solution. As shown in Figure 8, a large amount of guaiacol strongly adsorbed on the Lewis acid site of H β in methoxyphenate species, which was not desorbed even at evacuation at 350 °C. The large adsorption capacity of H_β for guaiacol markedly decreased the concentration of guaiacol in solution, and then prevented the conversion of guaiacol on Ni/SiO_2 . Simultaneously, guaiacol strongly adsorbed on the Lewis acid site significantly decreased the reaction rate of MCH dehydration on Brønsted acid site. As can be seen from Figure 7, guaiacol adsorbed on the Lewis acid site of H β covered its adjacent Brønsted acid site, which was not recovered even at 350 °C by evacuation. The number of active Brønsted acid sites in MCH dehydration decreased, and then led to low yield of cyclohexane. In brief, the Lewis acid site of zeolite was unfavorable for guaiacol HDO to cyclohexane due to its strong adsorption for guaiacol. In summary, the yield of the product and the reaction rate were closely related to the acid property of zeolite in guaiacol HDO. In particular, as the main active site, the Brønsted acid site of zeolite could effectively catalyze MCH dehydration, and then improved the overall reaction rate of guaiacol HDO. However, the Lewis acid site existed in zeolite was disfavored for guaiacol HDO. Guaiacol adsorbed on Lewis acid site of zeolite covered its adjacent Brønsted acid site, and then reduced the reaction rate of MCH dehydration, and finally showed impeditive functions for cyclohexane yield. Thus, tuning the acid property of the Brønsted acid site and Lewis acid site can effectively reduce the toxicity of guaiacol, improve MCH dehydration and then reach a high yield of the target product.

2.3. Effect of Phosphorus Loading on Guaiacol HDO over P-Modified Zeolite

To improve the catalytic performance, the acid property of H β was modified by phosphoric acid impregnation. Table 5 shows the catalytic performance of P-modified H β zeolite combined with Ni/SiO₂ for guaiacol HDO. Markedly, phosphorus loading of zeolite had a significant effect on guaiacol conversion and cyclohexane yield. In the case of H β combined with Ni/SiO₂, guaiacol conversion and cyclohexane yield were 72.0% and 15.6% at the reaction time of 2 h, respectively. Increasing phosphorus loading to 2 wt.%, its catalytic system exhibited excellent performance, with guaiacol conversion of 96.2% and cyclohexane yield of 63.1%. However, further increasing phosphorus loading to 5% declined the guaiacol conversion and cyclohexane yield. An excessively low or high phosphorus loading is unsuitable for the production of cyclohexane.

Table 5. Catalytic result of P-modified H β combined with Ni/SiO₂ for guaiacol hydrodeoxygenation ^a.

| Entry | Catalyst | $C_{amy}(9/)$ | Yield (%) | | | |
|-------|--------------------------|---------------|-------------|--------------|------------------|--|
| Linuy | Catalyst | Conv. (76) | Cyclohexane | Cyclohexanol | MCH ^b | |
| 1 | $Ni/SiO_2 + H\beta$ | 72.0 | 15.6 | 1.0 | 41.1 | |
| 2 | $Ni/SiO_2 + 1\%P-H\beta$ | 93.2 | 51.8 | 0.6 | 40.7 | |
| 3 | $Ni/SiO_2 + 2\%P-H\beta$ | 96.2 | 63.1 | 0.5 | 32.5 | |
| 4 | $Ni/SiO_2 + 3\%P-H\beta$ | 90.1 | 20.2 | 1.2 | 67.4 | |
| 5 | $Ni/SiO_2 + 5\%P-H\beta$ | 79.6 | 18.9 | 1.3 | 60.2 | |

^a Reaction conditions: 0.05 g Ni/SiO₂, 0.05 g (x%P-H β , X = 0,1,2,3,5), 0.10 g guaiacol, 20 mL decaline, 140 °C, 3 MPa H₂, 2 h; ^b MCH: 2-methoxycyclohexanol.

According to the above analysis in Section 2.2, the Brønsted acid site of zeolite could effectively catalyze the rate–determining reaction of MCH dehydration, and then improved cyclohexane yield and guaiacol conversion. However, there was no positive correlation between cyclohexane yield and the concentration of Brønsted acid site over modified H β with different phosphorus content (Figure 10A). Despite possessing the highest concentration of the Brønsted acid site, 1%P-H β exhibited lower conversion of guaiacol and cyclohexane yield, compared with 2%P-H β . This was ascribed to the larger amount of the Lewis acid site on 1%P-H β . More guaiacol strongly adsorbed on the Lewis acid site of 1%P-H β poisoned more Brønsted acid site, and then decreased the reaction rate of MCH dehydration. Thus, it is favorable to decrease the amount of the Lewis acid site for guaiacol HDO to cyclohexane.

As shown in Figure 10B, the amount of Lewis acid site of P-modified zeolite was in inverse proportion to its phosphorus content, and 5%P-H β obtained the lowest concentration of the Lewis acid site at 0.06 mmol/g. Based on the result of Figure 8, an increase in phosphorus loading of P-modified H β could decrease its concentration of the Lewis acid site, and then reduced the adsorption content of guaiacol, and finally decreased the blocking effect on MCH dehydration. However, 5%P-H β was not the best choice for guaiacol HDO, although it adsorbed the lowest concentration of guaiacol. That was because the concentration of the Brønsted acid site on P-modified zeolite also changed with the increase of phosphorus content. Specifically, the Brønsted acid site concentration of P-modified H β showed an initial increasing trend and then a remarkable decrease as phosphorus loading increased. The concentration of the Brønsted acid site on 5%P-H β decreased to 0.10 mmol/g, which could not effectively promote the transformation of MCH, and then resulted in low yield of cyclohexane and low conversion of guaiacol. The key to obtain a high yield of cyclohexane is to balance the concentration of the Brønsted acid site and Lewis acid site over P-modified zeolite. As a compromise, 2%P-H β possessed moderate concentration of Brønsted acid site and Lewis acid site, and thus obtained the highest yield of cyclohexane in guaiacol HDO.



Figure 10. The correlation between catalytic activity of guaiacol hydrodeoxygenation and acid property of P-modified H β . (A) Brønsted acid sites and (B) Lewis acid sites. (Reaction conditions: 0.05 g Ni/SiO₂, 0.05 g (x%P-H β , X = 0, 1, 2, 3, 5), 0.10 g GUA, 20 mL decaline, 140 °C, 3 MPa H₂, 2 h).

To present the effect of phosphorus modification visually and clearly reflect the nature of the sequential reaction, we compared the catalytic performance of H β and 2%P-H β with Ni/SiO₂ in a HDO reaction of guaiacol at different reaction time, as shown in Figure 11. Obviously, the intermediate product of 2-methoxycyclohexanol from guaiacol firstly increased and then decreased in the reaction progress. The rapid transformation of 2-methoxycyclohexanol on 2%P-H β significantly accelerated the degradation rate of guaiacol and the cyclohexane formation rate simultaneously. Specifically, the cyclohexane yield was improved from 55.2% to 95.2% over 2%P-H β at low temperature of 140 °C. Compared with representative catalysts as shown in Table 6, 2%P-H β combined with Ni/SiO₂ showed excellent catalytic activity in HDO of guaiacol at low temperature. Phosphorus modification would be a simple and effective method for tuning the acidic property of zeolite, which can be widely used in HDO of lignin-based phenolic compounds.



Figure 11. Effect of reaction time on the catalytic performance of guaiacol hydrodeoxygenation over Ni/SiO₂ combined with parent or P-modified H β (red: 2%P-H β , black: H β ; square, guaiacol conversion; triangle, yield of 2–methoxycylohexanol; circle, yield of cyclohexane).

| Entry | Catalyst | Т (°С) | P _{H2} (MPa) | Conv. (%) | Yiled _{CYH} ^a (%) | Ref. |
|-------|--------------------------|-----------|--------------------------|-----------|--|-----------|
| 1 | Pd/C + zeolite | 275 | 1.5 | 100 | 0.3 | [33] |
| 2 | Pt/zeolite | 250 | 4 | >90 | 45.3 | [10] |
| 3 | Pt/H-MFI-60 | 180 | 5 | 100 | 93 | [34] |
| 4 | Ni/MCM-41 + HZSM-5 | 240 | 5 | 100 | 84.1 | [35] |
| 5 | $Ni/SiO_2 + H\beta$ | 140 | 5 | >99 | 55.2 | This work |
| 6 | $Ni/SiO_2 + 2\%P-H\beta$ | 140 | 5 | >99 | 95.2 | This work |

Table 6. Catalytic activity of representative catalysts for guaiacol hydrodeoxygenation.

^a Yield_{CYH}: Yield of Cyclohexane.

3. Materials and Methods

3.1. Material

The following reagents were provided by various suppliers: guaiacol (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), decalin (TCI development Co., Ltd., Shanghai, China) and H₃PO₄ (Tianli Chemical Reagent Co. Ltd., Tianjin, China). H β (SiO₂/Al₂O₃ = 25) zeolite was purchased from Catalyst Factory of Nankai University (Tianjin, China). It was calcined at 550 °C for 4 h before its use.

3.2. Catalyst Preparation

Ni/SiO₂ was synthesized by the AEH method according to our previous work [22]. A series of P-modified H β zeolites were prepared by impregnation method. Specifically, a certain amount of H₃PO₄ (85 wt.%) was added in deionized water (4.0 g). Subsequently, 1.0 g H β was added slowly into the above acidic solution, followed by ultrasonic treatment for 30 min. Finally, the sample was dried overnight at 100 °C, and finally calcined at 550 °C for 5 h in air. The modified H β with different phosphorus loading was denoted as x%P-H β (x = 1, 2, 3, 5).

3.3. Catalyst Characterization

Phosphorus content of P-modified H β was measured by ICP (Thermo iCAP 6300, ThermoFisher, Waltham, MA, USA). X–ray diffraction (XRD) pattern of P-modified H β was measured by MiniFlex II desktop X–ray diffractometer (Rigaku, Tokyo, Japan), operating at 30 kV and 15 mA with Cu K α radiation. The scanning rate was set as 4°/min. In addition, the SEM image was obtained by field emission scanning electron microscope (JSM 7001–F, JEOL, Tokyo, Japan). The surface area and pore volume of P-modified zeolite were estimated according to N₂ adsorption–desorption isotherms, which were measured on a Micromeritics TriStar 3000 instrument (Micromeritics, Norcross, GA, USA) at –196 °C. To ensure the accuracy of measurement, zeolite powder was firstly degassed at 300 °C for 10 h in a vacuum.

The acid property of P-modified H β was determined by temperature-programmed desorption of ammonia (NH₃-TPD) and pyridine adsorption of Fourier transform infrared spectra (Py-IR). NH₃-TPD was conducted on Auto ChemII2920 chemisorption analyzer (Micromeritics, Norcross, GA, USA). Specifically, 0.10 g sample was initially pretreated at 550 °C for 2 h in flowing Ar (30 mL/min) and then cooled down to 50 °C. Subsequently, NH₃ was introduced into the system at 50 °C for 30 min, followed by swept at 120 °C for 2 h under flowing Ar. Then the sample was heated to 600 °C at a rate of 10 °C/min and the desorbed NH₃ was recorded by TCD. The Py-IR spectrum of samples were performed on a Bruker TENSOR 27 spectrometer (Bruker, Karlsruhe, Germany). Typically, the zeolite powder was pressed into a disk and pretreated at 350 °C for 2 h in a vacuum. Subsequently, it was exposed to pyridine vapor at 35 °C for 30 min and then evacuated at 150 °C for 60 min. The Py-IR spectra of sample was recorded. The concentration of acidic sites was calculated by the procedure reported by Madeira et al. [36].

To understand the acid characteristic of zeolite in depth, ²⁷Al MAS NMR, ³¹P MAS NMR and FT-IR spectrometry were used to describe the structural property of P-modified

H β . Specifically, the nature of aluminum species and phosphorus species in P-modified H β were determined by ²⁷Al MAS NMR and ³¹P MAS NMR on an Avance III 600 MHz wide bore spectrometer (Bruker, Switzerland), respectively. The chemical shifts of ²⁷Al and ³¹P were externally referenced to 1 M Al(NO₃)₃(aq) and 85% H₃PO₄(aq), respectively. Moreover, the IR spectrum of P-modified H β were measured on a Vertex 70 FT–IR spectrometer (Bruker, Karlsruhe, Germany) in the range of 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹. Before measurement, the disk of sample was firstly pretreated at 350 °C for 2 h in vacuum. Then the IR spectra of sample was recorded at room temperature.

3.4. FTIR Study of Phenolic Compounds (Phenol, Anisole and Guaiacol) Adsorption on P-Modified $H\beta$ Zeolites

The FTIR spectra of phenolic compounds adsorbed on P-modified H β zeolites were investigated on Bruker TENSOR 27 spectrometer (Bruker, Karlsruhe, Germany). Typically, about 25 mg catalyst was pressed into a disk (2 cm²) and initially evacuated at 350 °C for 2 h. Subsequently, phenolic compounds was introduced by dropping 20 μ L liquid on the disk at room temperature. In order to reach saturated adsorption, the disk was exposed to phenolic compounds in the IR cell at 35 °C for 20 min. Then, the cell was evacuated at 100 °C for 60 min to remove excessive phenolic compounds until the spectrum became constant. Finally, its desorption was carried out at a certain temperature for 20 min and the IR spectrum was recorded at the same time.

3.5. Catalytic Reaction

The catalytic performance of P-modified H β combined with Ni/SiO₂ was evaluated for guaiacol conversion in a 50 mL batch reactor. Prior to each test, the Ni/SiO₂ catalyst was prereduced at 600 °C for 2 h in a flow of 10 vol% H₂-Ar mixed gas (60 mL/min) and then passivated at room temperature for 30 min in a flow of 2 vol% O₂-Ar mixed gas (30 mL/min). Guaiacol (0.10 g), decalin (20 mL), Ni/SiO₂ catalyst (50 mg) and P-modified H β (50 mg) were added into the reactor in sequence. The reaction autoclave was purged by H₂ and then filled with 3 MPa H₂. When reaction temperature reached the selected value, the timing began. Once the reaction finished, the autoclave was cooled down quickly in an ice-water bath.

The liquid products were identified by GC-MS (6890N, Agilent, Santa Clara, CA, USA) and quantified with ethyl benzoate as an internal standard by gas chromatography (GC-2014, Shimadzu chromatogram analysis Co., Ltd., Kyoto, Japan). The conversion of guaiacol and product yield were calculated using the following equation:

$$conversion(\%) = \frac{moles of guaiacol (initial) - moles of guaiacol (final)}{moles of guaiacol (initial)} \times 100\%$$
(1)

yield (%) =
$$\frac{\text{moles of product i}}{\text{moles of guaiacol (initial)}} \times 100\%$$
 (2)

selectivity(%) =
$$\frac{\text{moles of product i}}{\sum \text{moles of product}} \times 100\%$$
 (3)

4. Conclusions

This work has demonstrated a simple and convenient method of modifying zeolite with phosphorus to tune its acidic property. Compared with H β , 2%P-H β showed superior catalytic activity and cyclohexane selectivity in the HDO reaction of guaiacol owing to its appropriate quantity of the Brønsted acid site and Lewis acid site. The increased number of Brønsted acid sites by phosphorus modification accelerated the transformation rate of MCH. Furthermore, phosphorus modification decreased the amount of the Lewis acid site, which greatly reduced the amount of adsorbed guaiacol, and then decreased the poison effect on its adjacent Brønsted acid site. Specifically, 2%P-H β combined with Ni/SiO₂ caused a complete conversion of guaiacol and 95.2% yield of cyclohexane at low

temperature of 140 °C. As expected, such a robust and low-cost phosphorus-modified H β zeolite, especially phosphorus-modified mesoporous H β zeolite [37,38], will have good potential for the HDO reaction in bio–oil upgrading.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3 390/catal11080962/s1, Figure S1: IR spectra of phenol on (a) KBr and (b–f) 2%P-H β after adsorption at RT followed by evacuation at different temperatures, Figure S2: IR spectra of anisole on (a) KBr and (b–f) 2%P-H β after adsorption at RT followed by evacuation at different temperatures, Figure S3: The cyclability of 2%P-H β combined with Ni/SiO₂. Table S1: IR vibrations of pure guaiacol, phenol and anisole and their assignments.

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