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Study on the removal and depolymerization of lignin from corn stover through the synergistic effect of Brønsted acid, Lewis acid and hydrogenation sites

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ABSTRACT

The effective transformation of lignin is an essential part of realizing the comprehensive utilization of biomass. In this study, a one-pot method for the depolymerization of corn stover lignin used aluminum phosphate (NiAPO-5) zeolite catalyst contained Brønsted acid, Lewis acid and hydrogenation sites was proposed. It was found that the number of Brønsted acid sites was increased after NiAPO-5 was reduced with H_2. The yield of monomers and residue were 35.70% and 38.09% at 235 °C for 3 h, respectively. The result of 2D HSQC NMR showed that the NiAPO-5 (H_2) catalyst significantly affected the cleavage of β-O-4 bonds. The distribution of products and the stability of catalyst revealed that NiAPO-5 (H_2) was an efficient catalyst for the depolymerization of lignin.

1. Introduction

The depolymerization of lignin is of great significance to the efficient utilization of lignocelluloses [1,2]. The key to the depolymerization of lignin is to break the C-O-C and C–C bonds between the phenylpropane structural units and to stabilize the intermediates [3].

Acid depolymerization has always been an effective method to break C-O-C and C–C bonds. Soluble Lewis acid and Brønsted acid were widely used in the depolymerization of lignin and model compounds [4]. Guvenatam et al. studied the depolymerization of lignin by three Lewis acids MCln, M(OAc)n and M(OTf)n, and found that the order of the degree of depolymerization is M(OTf)n > M(OAc)n > MCln. Besides, the choice of metal cation had no obvious influence on the product distribution [5]. Shu et al. used Pd/C and $CrCl_3$ to depolymerize lignin, and found that the higher the metal cation valence, the higher the the liquefaction rate of lignin [6]. Constant etc. believed that the yield of monomers was positively correlated with the hardness of Lewis acid [7]. It was also found that the acidity did not match the ability to break C-O bonds [8]. Therefore, the mechanism of Lewis acid in depolymerizing lignin is not clear.

Homogeneous Brønsted acids such as HCl and H_2SO_4 were also used

to depolymerize lignin, but the products were mainly dimers and oligomers [9]. Deuss et al. found that aldehyde products could inhibit polycondensation when depolymerizing model compounds by HOTF [10]. Onwudili et al. used Pd/C and formic acid to convert kraft lignin and the yield of monomer was 33% [11]. Although there has been a lot of work on the depolymerization of lignin with homogeneous acid, researchers avoid the recovery of homogeneous acid and its corrosiveness to reactor. Solid acids have been extensively studied because they are easy to recover. Yoshikawa et al. developed CeO_2-ZrO_2-Al_2O_3-FeOx catalyst for the depolymerization of alkali lignin, and the yield of monophenol was 17% at 300 °C for 2 h [12]. Zeolites such as H-ZSM-5, H-USY, H-Y, and H-β were also used to depolymerize lignin, but temperatures exceeding 500 °C were required [13].

In order to reduce the reaction conditions and increase the yield of monomers, it is necessary to stabilize the reaction intermediates. Hydrogenation was a commonly used method of stabilization [14–16]. As a hydrogenation metal, Ni is favored for its cheap and excellent hydrogenation ability. Ni loaded on solid acid supports such as SiO_2-ZrO_2 [17], Zeolite [18–21], SiO_2-Al_2O_3 [22] and CeO_2-ZrO_2 [23] had been used in the depolymerization of lignin. Dou et al. realized the conversion of alkali lignin into monomer by Ni/H-beta at 260 °C [24]. Oh et al. also

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realized the conversion of bio-oil with Ni/SBA-15 at 300 °C [25]. Moon et al. found that adding phosphorus to Ni-based catalysts could significantly improve the hydrogenation capacity of Ni. Because there was a ligand and ensemble effect between P and Ni, which made hydrogen easy to dissociate [26]. Gonçalves et al.'s research showed that Ni_2P-based catalysts had better hydrodeoxygenation capabilities for cresol than single-metal Ni-based catalysts [27].

It is worth noting that the generated monophenols will be adsorbed on acid sites when solid acid is used as a catalyst, thereby forming coking and inhibiting the activity of the catalyst. Moreover, the stronger the acidity of the solid acid, the more serious the adsorption [28]. Aluminum phosphate (APO) zeolite is a commonly used solid acid formed by a strictly staggered PO_4 and AlO_4 tetrahedral arrangement. APO zeolite framework is mostly neutral and does not contain exchangeable cations. So, there are only a few weak acid sites on the surface of APO zeolite [29]. APO zeolite has two advantages as the catalyst for the depolymerization of lignin. On the one hand, the weak acid sites in APO zeolite have little effect on the recondensation of lignin reaction intermediates, as the degree of recondensation of lignin intermediates is more serious with increasing acidity [30]. On the other hand, it is possible to introduce charges into the framework through the unequal substitution of the framework atoms to increase the number of weak acid sites, because the depolymerization of lignin requires acid sites [31]. Therefore, the depolymerization of lignin can be promoted by increasing the number of weak acid sites without causing serious recondensation of intermediates.

A large number of studies have been conducted on the depolymerization of model compounds and lignin by Lewis acid, Brønsted acid and hydrogenation. But the role of the three active sites in the one-step depolymerization of lignocellulose has not been reported. Lignocellulose contains original lignin, which will be more easily depolymerized. In addition, the one-step method is simple to operate because it avoids separating the lignin in advance. Therefore, it is very helpful to design the catalyst if the role of Brønsted acid, Lewis acid and hydrogenation sites in the one-step depolymerization of lignocellulose can be studied clearly.

In this study, APO-5 that had the largest pores among APO zeolites was selected. At the same time, nickel with Lewis acidity and hydrogenation ability was incorporated into the APO-5 zeolite to increase the number of acid sites and improve the hydrogenation ability. The synergistic effect of Brønsted acid, Lewis acid and hydrogenation sites was systematically studied.

2. Materials and methods

2.1. The preparation of catalysts

NiAPO-5: The catalyst was synthesized by a solvent-free method. Typically, 1.000 g DPA·H_3PO_4, 0.400 g Boehmite, 0.100 g TEABr, 0.050 g Ni(NO_3)$_2$·$6H_2O$ were mixed and ground for 10 min. The mixture was transferred to a 100 ml autoclave and reacted at 200 °C for 24 h. Then, the sample was calcined at 550 °C for 4 h after being washed with water and dried at 80 °C. The powder obtained here was named Ni1APO-5, which was a doped catalyst. When the doped catalysts Ni2APO-5, Ni3APO-5, and Ni4APO-5 were prepared, the masses of Ni (NO_3)$_2$·$6H_2O$ were 0.100 g, 0.150 g, and 0.200 g, respectively. Ni (NO_3)$_2$·$6H_2O$ was not added when prepared APO-5. Di-n-propylamine phosphate (DPA·H_3PO_4) was prepared by referring to Jin's work [32]. The content of Ni in these catalysts is shown in Table S1.

NiAPO-5(H_2): The reduction of the catalyst was carried out in ethanol. The doped catalysts Ni1APO-5, Ni2APO-5, and Ni3APO-5 were, in turn, put into a 50 ml stainless autoclave reactor. Then 2 MPa H_2 was added to the reactor and kept at 300 °C for 3 h under magnetic stirring. After the reaction, the sample was obtained by centrifugation, washed with ethanol and dried at 60 °C under vacuum for 12 h. The powders obtained here were named Ni1APO-5 (H_2), Ni2APO-5 (H_2), and

Ni3APO-5(H_2), respectively.

Ni1/APO-5: The prepared APO-5 and 0.05 g Ni(NO_3)$_2$·$6H_2O$ were ground for 10 min, and calcined at 550 °C for 4 h. The powder obtained here, a supported catalyst, was named Ni1/APO-5. To ensure that the elemental content of the supported catalyst Ni1/APO-5 and the doped catalyst Ni1APO-5 was equal, all prepared APO-5 samples each time was ground to prepare Ni1/APO-5.

Ni1/APO-5(H_2): The Ni1/APO-5 was reduced to obtain Ni1/APO-5 (H_2) by the same method as mentioned above.

Ni/SiO$_2$, Ni/Zeolite: The control catalysts were prepared by loading Ni on SiO$_2$, USY, H-β and ZSM-5 by grinding method. The loading of Ni is 4.12 wt%, which is consistent with the content of Ni in Ni1APO-5(H_2). The calculated amount of Ni(NO_3)$_2$·$6H_2O$ was ground onto the support, and then the sample was calcined at 550 °C for 4 h.

2.2. The depolymerization of lignin

The depolymerization of lignin took place in a 50 ml stainless steel autoclave reactor. Reaction conditions were 2 g corn stover (or organosolv lignin), 0.2 g catalyst, 30 ml methanol, 2 MPa H_2, 235 °C, a reaction time of 3 h, a heating rate of 3.5 °C/min, and a magnetic stirring rate of 700 rpm. After the reaction, the kettle was naturally cooled to room temperature. Then, 0.01 g of acetophenone was added to the reaction system as an internal standard for subsequent GC analysis. 2 ml reaction liquid was collected for GC–MS and GC analysis after filtration. The solid residue consisted of the catalyst and the remaining corn stover, which was washed with ethanol and dried at 80 °C for component analysis. When H_3PO_4 was used as a catalyst, its amount substance was the same as the number of Brønsted acid sites in Ni1APO-5(H_2).

3. Results and discussion

3.1. Characterization of the catalysts

XRD patterns showed that the catalysts matched with the structure of AFI zeolite (Fig. 1a). Ni species existed in the form of Ni^{2+} in the supported Ni1/APO-5, but mainly in the form of Ni^0 in the reduced Ni1/APO-5(H_2). There were no diffraction peaks attributed to Ni species appeared in doped Ni1APO-5, Ni1APO-5 (H_2), Ni2APO-5(H_2) and Ni3APO-5(H_2). However, the diffraction peaks of doped Ni1APO-5, Ni1APO-5 (H_2), Ni2APO-5(H_2) and Ni3APO-5(H_2) were shifted compared to APO-5, while the diffraction peaks of supported Ni1/APO-5 and Ni1/APO-5(H_2) were not shifted (Fig. 1b). It might be that Ni was incorporated into the framework of APO-5. Ni4APO-5(H_2) was not the structure of AFI zeolite, and the diffraction peaks of Ni^0 also appeared, which indicated that Ni could not be excessively doped into APO-5.

XPS was used to prove that Ni was incorporated into the framework of APO-5 (Fig. S1). The peaks at 855.32 and 873.69 eV can be assigned to Ni^{2+}, the peaks at 856.82 and 874.85 eV can be assigned to Ni^{3+}, and the peaks at 861.86 and 881.44 eV can be assigned to statelites (Fig. S1b). The value of Ni^{2+}/Ni^{3+} was calculated based on the peak area (Table S2). The binding energy of Ni_{2p} showed that Ni^{3+} was mainly present in Ni1/APO-5 and Ni1APO-5, while Ni^{2+} was mainly present in Ni1APO-5(H_2) and Ni3APO-5 (H_2). It could be seen that as the content of Ni increases, the value of Ni^{2+}/Ni^{3+} increased, which would generate more Brønsted acid sites (Table S2). The binding energy of Ni_{2p} in Ni1APO-5 was positively shifted compared to that of Ni1/APO-5. The binding energies of Al_{2p}, O_{1s}, and P_{2p} in Ni1APO-5, Ni1APO-5 (H_2) and Ni3APO-5 (H_2) were negatively shifted compared to that of APO-5. However, the binding energies of the elements in Ni1/APO-5 had not shifted. The shift in binding energy usually means electron transfer. When Ni was incorporated into the framework of APO-5, it would interact with the surrounding P, O and Al to maintain the stability of the structure, that was, electron transfer occurred. If Ni species was simply loaded onto the surface of APO-5, there would be no electron transfer. Therefore, the Ni species in NiAPO-5 and NiAPO-5(H_2) were
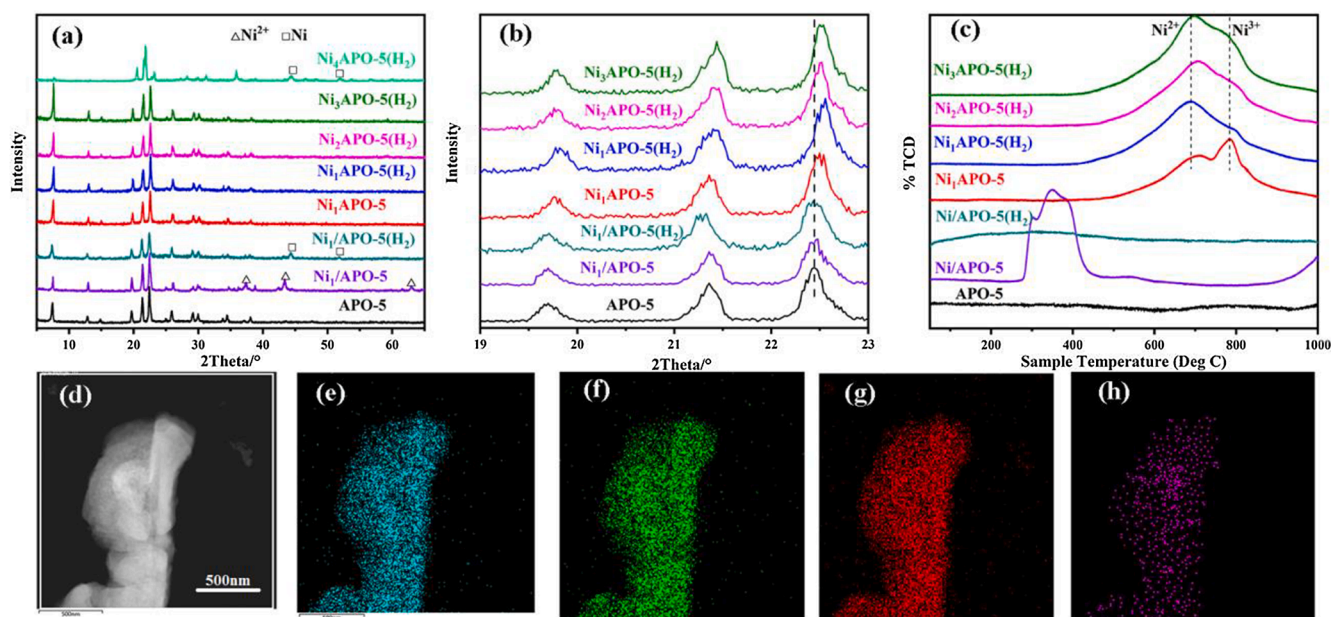
Fig. 1. (a), (b) XRD patterns and (c) H_2-TPR of different catalysts. (d) TEM image of Ni1APO-5 (H_2). Elemental scanning analysis of (e) P, (f) Al, (g) O and (h) Ni.

incorporated into the framework of APO-5.

H_2-TPR could further prove that Ni was incorporated into the framework of APO-5 (Fig. 1c). The APO-5 catalyst has no obvious H_2 reduction peak. The supported catalyst Ni1/APO-5 has only one reduction peak at 280–420 °C, which confirms the reduction of Ni species on the catalyst surface. The absence of H_2 reduction peak in Ni1/APO-5 (H_2) indicated that the Ni species on the surface was reduced to Ni^0. The H_2-TPR curve of Ni1APO-5, Ni1APO-5 (H_2), Ni2APO-5(H_2) and Ni3APO-5(H_2) had two obvious reduction peaks in the high-temperature region. The peak at 690 °C is attributed to the reduction of framework Ni^{2+} to Ni^0, and that at 780 °C to the reduction of framework Ni^{3+} to Ni^0. It could be seen that Ni1APO-5 was dominated by Ni^{3+}, while Ni1APO-5 (H_2) by Ni^{2+}, which was consistent with the results of XPS. The framework Ni was more difficult to reduce than supported Ni, so a higher reduction temperature was required for framework Ni. Elemental

scanning analysis of Ni1APO-5 (H_2) showed that Ni species were uniformly dispersed, which would very beneficial to improve its catalytic activity (Fig. 1d-h).

Then the strength and number of total acid sites of the catalyst were studied by NH_3-TPD (Fig. 2a). Table S4 shows the number of total acid sites of different APO-5 catalysts. All catalysts had only one NH_3 absorption peak in the low-temperature region, indicated that these catalysts were dominated by weak acid sites. The number of total acid sites in APO-5 was only 0.032 mmol·g^{-1}, which was related to the strict arrangement of PO_4 and AlO_4. The number of total acid sites in Ni1/APO-5, Ni1/APO-5(H_2) and Ni1APO-5 were 0.782 mmol·g^{-1}, 0.194 mmol·g^{-1} and 1.102 mmol·g^{-1}. It could be seen that the number of total acid sites of the doped catalyst was far more than that of the supported catalyst, which was due to the high dispersion of Ni in the doped catalyst. Surprisingly, the number of total acid sites continued to increase
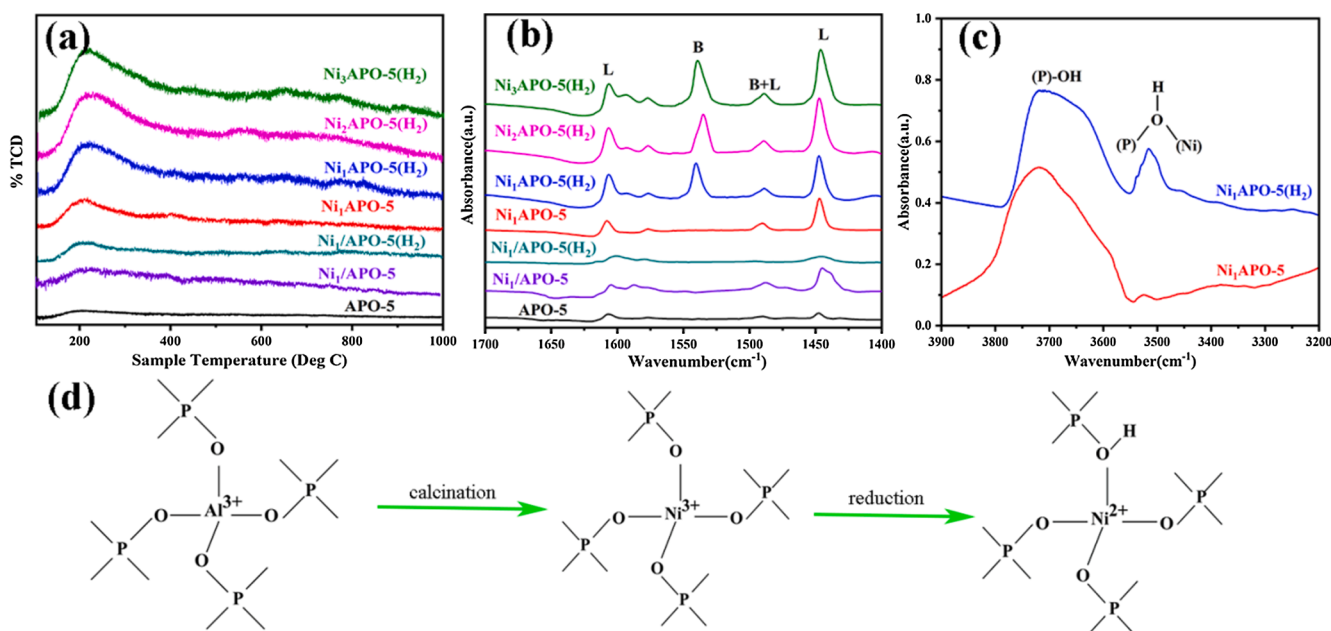

Fig. 2. The results of (a) NH_3-TPD, (b) Py-FTIR and (c) FTIR of different catalysts. (d) The formation process of Brønsed acid sites in NiAPO-5(H_2).

after the catalyst was reduced with H_2, and the number of acid sites of Ni1APO-5(H_2) reached an astonishing 1.955 mmol·g^{-1}. After the amount of Ni was increased, the number of total acid sites further increased and eventually reached a maximum of 2.535 mmol·g^{-1} in Ni3APO-5(H_2).

The catalyst was tested by pyridine infrared absorption (Py-FTIR) to clarify the change in the number of total acid sites (Fig. 2b). The absorption peaks Lewis and Brønsted acid sites are at ∼ 1450 cm^{-1} and ∼ 1540 cm^{-1}, respectively. There were only 0.008 mmol·g^{-1} of Lewis acid sites in APO-5, which was attributed to the Al species on the surface. Ni1/APO-5, Ni1/APO-5(H_2) and Ni1APO-5 exhibited Lewis acidity, and the number of Lewis acid sites in Ni1APO-5 was more than that in Ni1/APO-5 and Ni1/APO-5(H_2), which was consistent with the results of NH_3-TPD. It was interesting that a large number of Brønsted acid sites appeared in Ni1APO-5(H_2), Ni2APO-5(H_2) and Ni3APO-5(H_2). It turned out that the change in the number of total acid sites of Ni1APO-5 and Ni1APO-5(H_2) shown by the results of NH_3-TPD was due to the increase of Brønsted acid sites.

The FTIR of the catalyst was carried out to determine the reason for the change in the number of Brønsted acid sites (Fig. 2c). Ni1APO-5 and Ni1APO-5 (H_2) have a broad peak at 3700 cm^{-1}, which indicates P-OH. But Ni1APO-5(H_2) has another peak at 3514 cm^{-1}, attributed to P-O (H)-Ni. P-O (H)-Ni could supply a hydrogen proton, so Ni1APO-5(H_2) had a high content of Brønsted acid sites. Al species existed in the trivalent form in APO-5, and Ni doped in APO-5 could replace Al isomorphically. Ni also existed in trivalent form to maintain electrical neutrality after Ni1APO-5 was calcined at 550 °C, as shown in the results of XPS. When the Ni1APO-5 was reduced with H_2, Ni^{3+} became Ni^{2+}. The near oxygen was protonated to keep the charge neutral. Then, a Brønsted acid site was created (Fig. 2d). Therefore, the number of Brønsted acid sites of Ni1APO-5(H_2), Ni2APO-5(H_2) and Ni3APO-5(H_2) could increase significantly. Then the prepared catalyst was used for the depolymerization of lignin.

3.2. Analysis of products

Fig. 3a and Table S6 show the product distribution after depolymerizing corn stover lignin. Residue refers to unreacted lignin, obtained by analyzing the components of the remaining corn stover. Other products include undepolymerized lignin, oligomer, char and gas products. The

yield of each products were calculated based on the quality of lignin. It could be seen from Fig. 3a that the residue was 64.96% when no catalyst was used, and the yield of monomers was only 6.51%. APO-5 had almost no effect on the depolymerization of lignin due to its low acidity and lack of hydrogenation sites. The yield of monomers did not increase significantly when Ni1/APO-5 and Ni1/APO-5(H_2) were used, while the monomer yield increased slightly when Ni1APO-5 was used, which was attributed to the high dispersion of Ni species in Ni1APO-5. However, the residue was reduced to 45.04%, and the yield of monomers was significantly increased to 30.92% when Ni1APO-5(H_2) was used. The yield of monomers was further improved with the increase of Ni content, reached 35.70% when Ni3APO-5(H_2) was used. At the same time, the retention rate of lignin in the residue also attained the lowest value of 38.09%. For comparison, Raney Ni, Ni/SiO2, Ni/USY, Ni/H-β and Ni/ZSM-5 were used in this reaction (Fig. S7). It can be seen that the effect of NiAPO-5(H_2) catalysts are better than that of control catalysts. The results of NH_3-TPD and Py-FTIR showed that the number of acid sites in the control catalysts were less than that of Ni1APO-5(H_2) (Fig. S4 and Table S4). The large number of acid sites in Ni1APO-5(H_2) was the reason for its excellent catalytic effect. The high yield of monomers can be attributed to the effective removal and depolymerization ability of NiAPO-5(H_2) on lignin. The removal of lignin may be related to Brønsted acid sites, and the depolymerization of lignin may be related to Lewis acid sites and hydrogenation sites.

Firstly, the positive effect of Brønsted acid sites in the removal of lignin was verified. The biggest differences between Ni1APO-5 and Ni1APO-5(H_2) are that the Ni1APO-5(H_2) has a large number of Brønsted acid sites. The Brønsted acid sites in catalyst may promote the removal of lignin, thereby increasing the yield of monomers. The performance of the catalyst was tested with the organosolv lignin as the substrate (Fig. 3b). It could be seen that yield of monomers was 26.93% and 28.28% when Ni1APO-5 and Ni1APO-5(H_2) were used as catalysts, respectively. The advantage of Ni1APO-5(H_2) over Ni1APO-5 did not seem to be obvious when the organosolv lignin was used as the substrate. Ni1APO-5 and Ni1APO-5(H_2) have similar depolymerization ability to lignin, which is related to the similar number of Lewis acid sites and hydrogenation sites. The Brønsted acid site in the catalyst was helpful for the removal of lignin, caused Ni1APO-5(H_2) to perform much better than Ni1APO-5 when corn stover was used as a substrate. However, the early removal of lignin made Brønsted acid useless when the
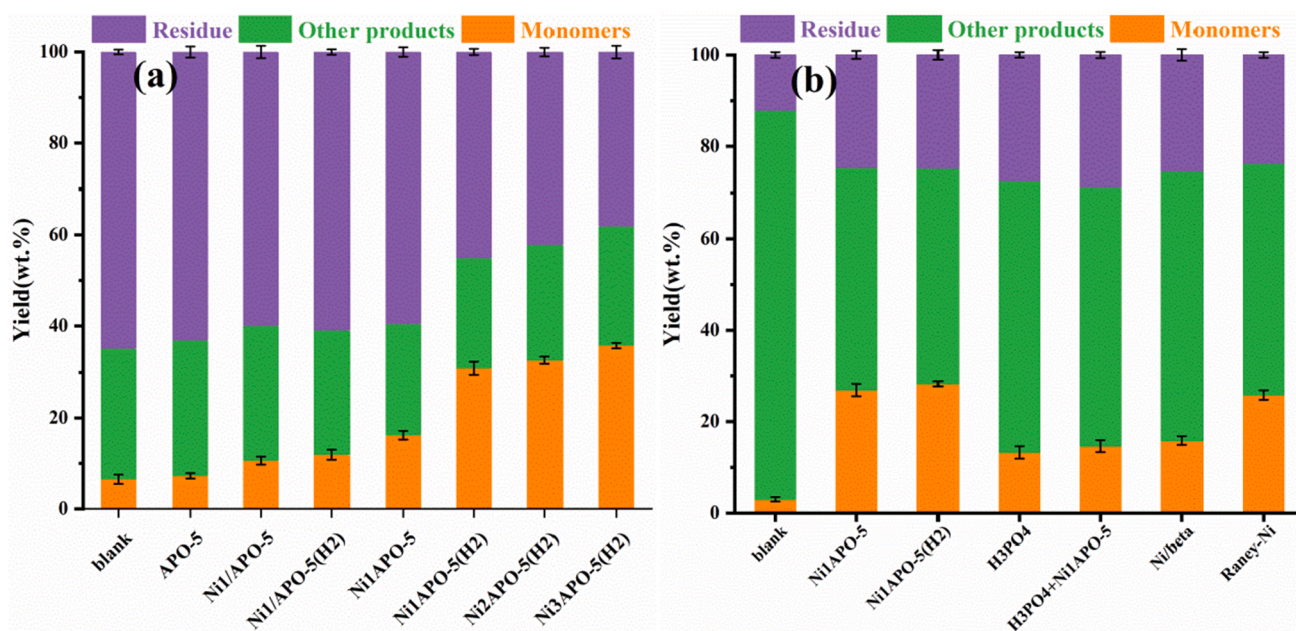

Fig. 3. The distribution of products when (a) corn stover and (b) organosolv lignin were used as the substrates.

organosolv lignin was used as a substrate. Therefore, the function of the Brønsted acid site in NiAPO-5(H$_2$) is the removal of lignin.

Then the functions of Lewis acid and hydrogenation sites in the depolymerization of lignin were verified. 2D HSQC NMR was used to detect the broken of the bond in the depolymerization of lignin (Fig. 4, Fig. S8, and Table S8). The product obtained after rotary evaporation of methanol was tested. The results showed that the dominant linkages in the original corn stover lignin were β-O-4 (50.33/100Ar), β-β (5.35/100Ar) and β-5 (3.71/100Ar) bonds. There was only a little change in the content of β-O-4 (45.87/100Ar), β-β (5.92/100Ar) and β-5 (3.94/100Ar) bonds when no catalyst was used, which indicated that the lignin had not been depolymerized (Fig. 4a, b). It could be seen that the signals of -OMe and the three structures of A, B, and C were weakened after Ni1APO-5(H$_2$) was used as the catalyst (Fig. 4c, d). The signal of structure I even disappears. The contents of β-O-4 (10.24/100Ar), β-β (4.45/100Ar), and β-5 (2.81/100Ar) bonds were the lowest. Hence, Ni1APO-5(H$_2$) mainly broke the β-O-4 bond in the depolymerization of lignin.

The model compound PPPD was used to study the active sites in the catalyst that can break the β-O-4 bond (Table 1). It was found that PPPD was depolymerized into 5 monomers after the product was analyzed by GC–MS (Fig. S9). A commercial AlCl$_3$ catalyst was used to test the effect

of Lewis acid sites. The reason why APO-5 was not selected was that the number of Lewis acid sites was too small. NiAPO-5(H$_2$-TPR) was used to test the effect of hydrogenation sites. The result of XRD shows that NiAPO-5(H$_2$-TPR) still has the structure of AFI zeolite (Fig. S4). The results showed that the conversion of PPPD were 25.54% and 35.27% when there were Lewis acid sites or hydrogenation sites in the catalyst, respectively (Entry 2, 4). However, the complete conversion of PPPD was achieved when the Ni1APO-5 with Lewis acid sites and hydrogenation sites was used (Entry 5). The depolymerization of PPPD was the result of the synergistic effect of Lewis acid sites and hydrogenation sites. It was worth noted that the performance of Ni1APO-5(H$_2$) catalyst on the depolymerization of PPPD was similar to that of Ni1APO-5 (Entry 6).

Our previous studies had reported the reaction path of PPPD when it was depolymerized by a catalyst containing Brønsted acid, Lewis acid and hydrogenation sites (Fig. S10) [33]. The first pathway was to product 1, 2, 4, and 5 through reductive cleavage, which was catalyzed by Lewis acid and hydrogenation sites (Route I, Fig. S10). The other pathway was to generate 1 and 3 through acid cleavage, which was conducted by the Brønsted acid site (Route II, Fig. S10). It could be seen that the catalyst used in this experiment mainly undergoes reductive cleavage during the depolymerization of PPPD (Entry 3–5, Table 1).
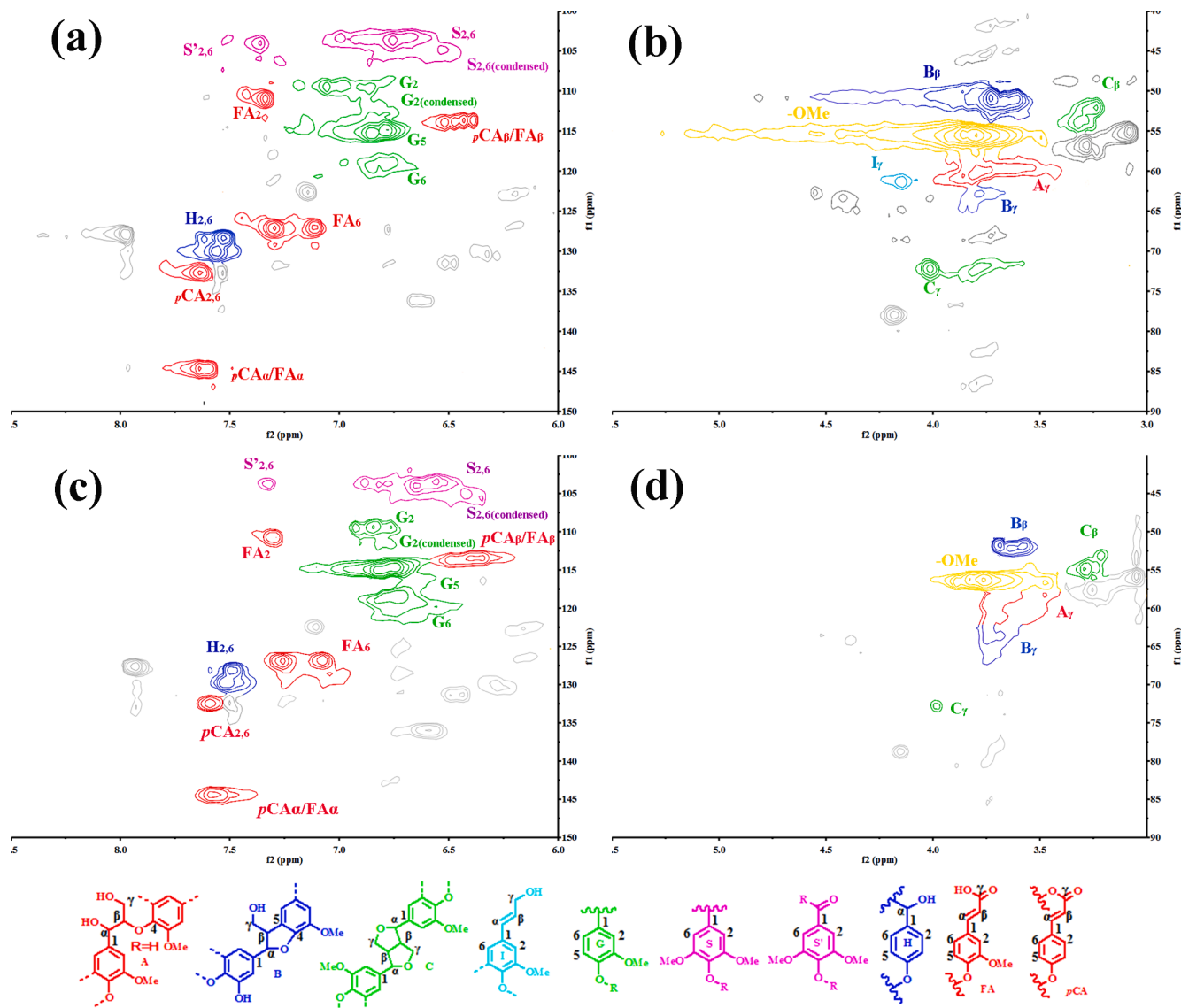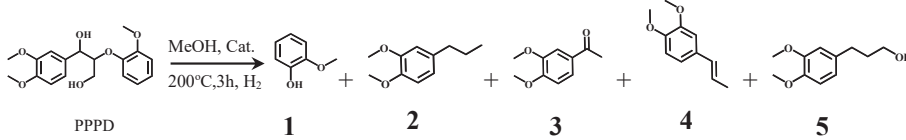

Fig. 4. 2D HSQC NMR spectra of the product when there was no catalyst (a, b) and Ni$_1$APO-5(H$_2$) was used as the catalyst (c, d).

Table 1
The depolymerization of PPPD through catalysts with different active sites.

Entry	Catalysts	Active site	Conv. (mol %)	Yield (mol %)				
				1	2	3	4	5
1	Blank	–	–	–	–	–	–	–
2	AlCl$_3$	L[a]	25.54	17.66	6.96	2.16	–	–
3	Ni1/APO-5(H$_2$)	H[b]	30.12	18.23	8.35	3.67	2.20	1.01
4	Ni1APO-5(H$_2$-TPR)	H[b]	35.27	23.08	10.41	1.64	1.45	1.73
5	Ni1APO-5	L + H	100.00	86.41	33.49	18.45	10.26	2.22
6	Ni1APO-5(H$_2$)	B + L + H	100.00	87.62	34.81	17.50	9.84	2.47
7	H$_3$PO$_4$[d]	B[c]	100.00	90.34	–	33.91	–	–
8	H$_3$PO$_4$ + AlCl$_3$	B + L	100.00	89.28	3.15	28.32	0.58	0.32
9	H$_3$PO$_4$ + Ni1APO-5(H$_2$-TPR)	B + H	100.00	91.37	6.29	31.20	0.21	0.47
10	H$_3$PO$_4$ + AlCl$_3$ + Ni1APO-5(H$_2$-TPR)	B + L + H	100.00	94.58	13.19	35.27	5.26	4.34
11	H$_3$PO$_4$ + Ni1APO-5	B + L + H	100.00	93.26	14.25	36.64	3.64	2.79

[a] L represents the Lewis acid site. [b] H represents the hydrogenation site. [c] B represents the Brønsted acid site. [d] When H$_3$PO$_4$ was used as a catalyst, the amount of its substance was the same as the number of Brønsted acid sites in Ni1APO-5(H$_2$).

Even if Ni1APO-5(H$_2$) contained Brønsted acid site was used, the acid cleavage was still not dominant (Entry 6, Table 1). The reason why the Brønsted acid site in Ni1APO-5(H$_2$) had little effect on the depolymerization of PPPD might be because it was a weak acid site, as shown by the results of NH$_3$-TPD. In order to verify this conjecture, H$_3$PO$_4$ was used as Brønsted acid to depolymerize PPPD. It was found that the products were only **1** and **3**, indicated that only acid cleavage occurred at this time (Entry 7, Table 1). However, it was worth noting that the yields of **3** when H$_3$PO$_4$ was used in combination with any other catalysts were all higher than **2**, **4**, and **5**. It showed that strong Brønsted acid sites could have an advantage when competing with Lewis acid and hydrogenation sites (Entry 8–11, Table 1). The above results indicated that the Brønsted acid site in Ni1APO-5(H$_2$) was not involved in the depolymerization of PPPD because it was a weak acid site. The synergistic effect of Lewis acid and hydrogenation site was sufficient to depolymerize PPPD. This was consistent with the result when the organosolv lignin was used as the substrate. When Ni1APO-5(H$_2$) was used to depolymerize corn stover lignin, weak Brønsted acid sites rarely participated in the reaction of depolymerizing lignin. But it could promote the hydrolysis of cellulose and hemicellulose, thereby improved the removal of lignin. When H$_3$PO$_4$ was used to depolymerize corn stover lignin and organosolv lignin, it could be found that the monomer was mainly G7, and a large amount of cellulose and hemicellulose were hydrolyzed (Fig. S7, Table S6). Homogeneous strong Brønsted acid could not only depolymerize lignin, but also hydrolyze cellulose and hemicellulose. The yield of G7 was very low when Ni1APO-5(H$_2$) was used to depolymerize corn stover lignin, indicated that weak Brønsted acid sites in Ni1APO-5(H$_2$) seldom participate in the depolymerization of lignin. It should be Lewis acid and hydrogenation site to depolymerize lignin.

The removal and depolymerization of lignin are the main reactions in the conversion of corn stover lignin. The Brønsted acid sites in Ni1APO-5(H$_2$) can promote the removal of lignin. Then the removed lignin is depolymerized into monomers under the synergistic effect of Lewis acid and hydrogenation sites. Therefore, the Brønsted acid, Lewis acid and hydrogenation sites are essential for the conversion of corn stover lignin. The increase in the content of Ni can increase these three elements, and the effect on the depolymerization of lignin can be further improved.

3.3. The selectivity of the product

In order to clarify the effect of the catalyst on the selectivity of the monomers, the distribution of product at different reaction times was studied. The yield of monomers increased more and more slowly with the extension of the reaction time, and the reaction time of 3 h was the most economical and efficient Fig. 5. According to the distribution of monomers, it could be seen that G4, G6 and H3 were preferentially produced after the reaction starts (Table S7). The yields of G4, G5, G6, H2, H3 and S2 first increased and then decreased with the extension of the reaction time, indicated that these monomers were reaction intermediates. At the same time, the yields of G1, G2, G3, H1 and S1 increased continuously, indicated that these monomers were the final products. Hadai et al. introduced the structure of lignin in herbaceous plants, where FA was connected with arabinose, pCA was connected by β-β bonds, and the units were mainly connected by β-O-4 bonds (Fig. 6) [34]. After the reaction starts, the separation of lignin and hemicellulose occurred, that was, FA was disconnected from arabinose. The β-5 bond was broken, thereby generated G6. In addition, the β-β bond would also be broken to generate H3. The main reaction is the breaking of β-O-4 bonds between monomers to form G4, G5 and S2. The role of Lewis acid site may be to absorb the electron cloud of the β-O-4 bond, thereby promoting its breaking. The role of hydrogenation sites is to stabilize the reaction intermediates. Therefore, the depolymerization of lignin can be achieved under the synergistic effect of Lewis acid and hydrogenation
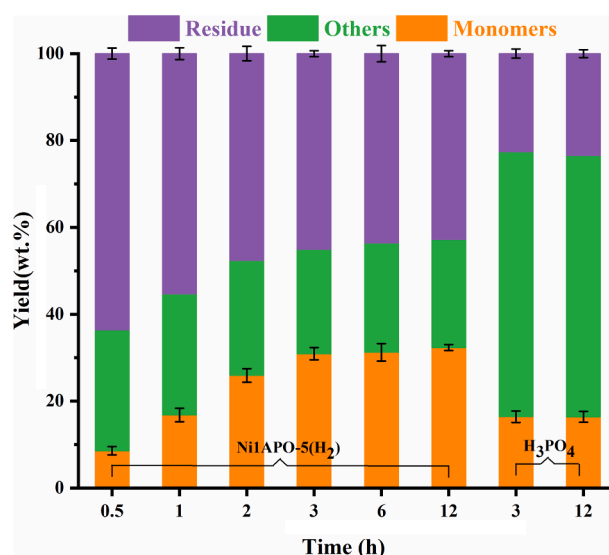

Fig. 5. The effect of reaction time on the distribution of products.
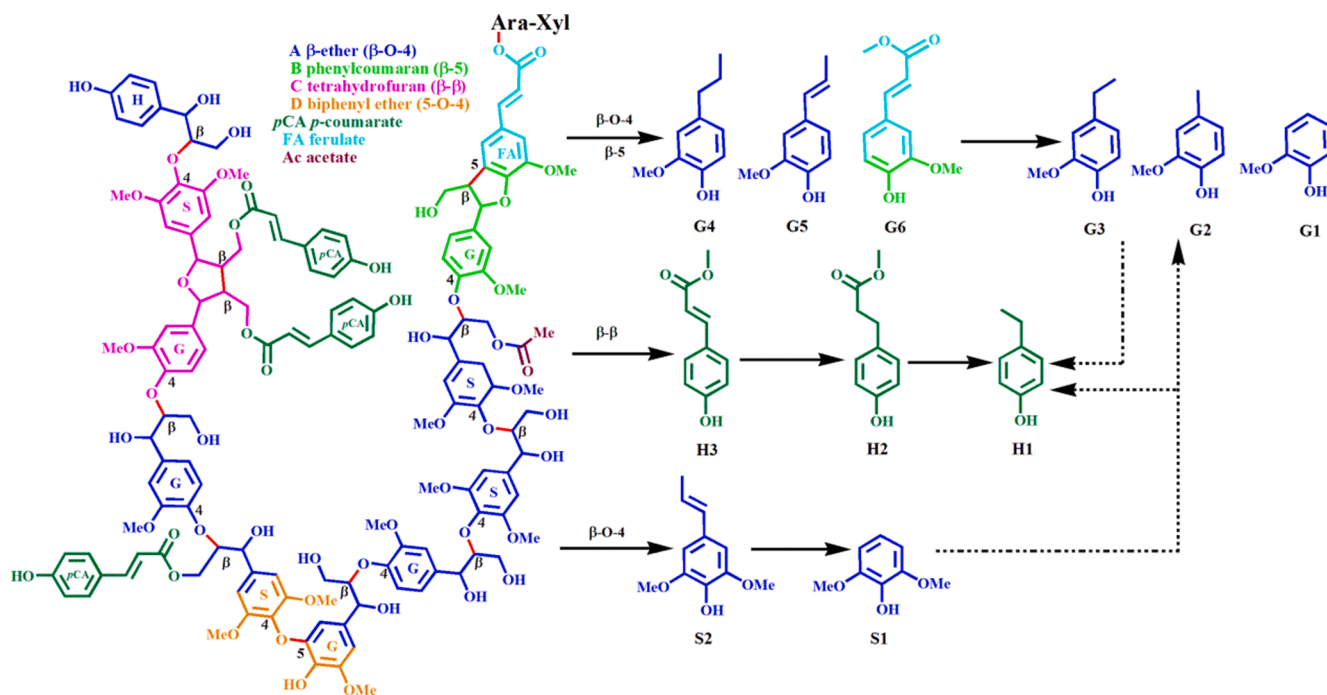
Fig. 6. The reaction pathway from lignin to monomers.

sites. As the reaction time increases, G4, G5, G6, H3, and S2 would undergo the breakage of C–C bonds, forming G1, G2, G3, H1 and S1. In addition, S-type and G-type monomers might also be converted into H-type monomers.

3.4. The effect of secondary reactions

The signal of condensed lignin could be observed in the 2D HSQC NMR [35]. There was no condensation phenomenon for the original lignin, but severe condensation occurred when no catalyst was added. The content of condensed S (4.65/100Ar) and G (1.03/100Ar) lignin were reduced when Ni1APO-5(H_2) was used (Fig. 8c, Table S8). The GPC curves showed that there were not only monomers, but also a large number of dimers, trimers and oligomers in the product when no catalyst was used (Fig. 7). However, the dimers, trimers and oligomers were significantly reduced when Ni1APO-5(H_2) was used. The average Mw of the product also dropped from 425 g/mol in the blank control to 317 g/mol when Ni1APO-5(H_2) was used (Table S10). The reduction of dimers,
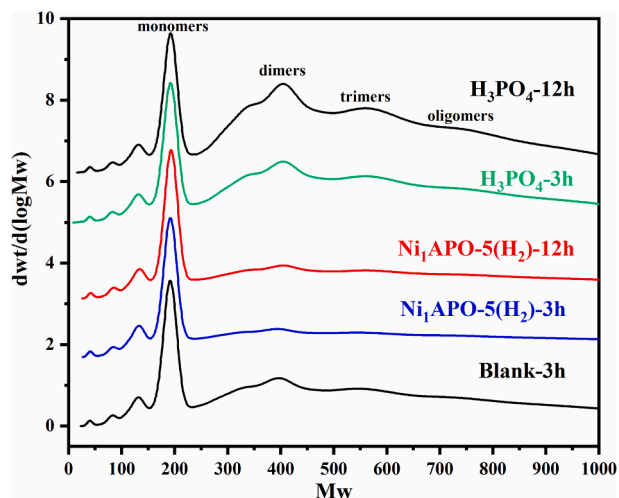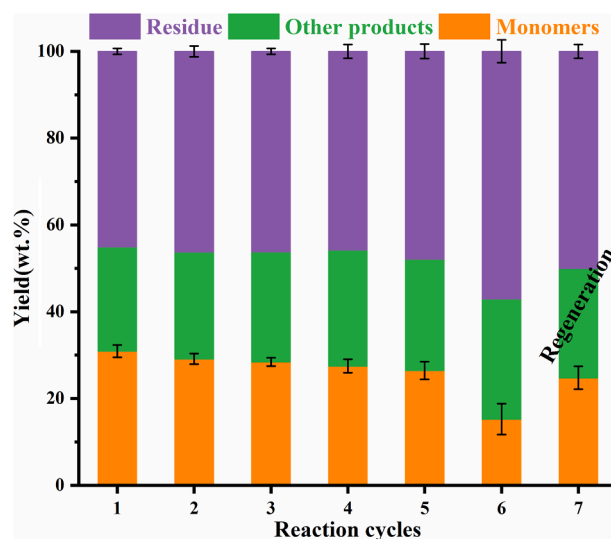

Fig. 8. The catalyst reuses experiment of Ni1APO-5(H_2).

trimers, and oligomers was related to the cleavage of bond and the decrease of polycondensation lignin, which was consistent with the result of 2D HSQC NMR. The good performance of catalyst was not only reflected in the high yield of monomers, but also in the low amounts of polycondensation lignin.

In order to study the repolymerization of monomers, Ni1APO-5(H_2) and H_3PO_4 were used to depolymerize corn stover lignin at different times Fig. 5. The residue was higher when Ni1APO-5(H_2) was used than when H_3PO_4 is used. The ability of heterogeneous weak Brønsted acid to remove lignin is not as good as homogeneous Brønsted acid. The molecular weight of the product after 3 h and 12 h was tested by GPC (Fig. 7). It was found that the Mw of the product increased from 317 g/mol to 353 g/mol when Ni1APO-5(H_2) was used, but the Mw increased from 465 g/mol to 554 g/mol when H_3PO_4 was used (Table S10). The results of 2D HSQC NMR showed that the content of condensed lignin

Fig. 7. The GPC curves of product.

only increased from 2.56% (3 h) to 3.87% (12 h) when Ni1APO-5(H$_2$) was used, while the content of condensed lignin increased from 5.68% (3 h) to 10.28% (12 h) when H$_3$PO$_4$ was used (Table S8). The above results indicated that the weak Brønsted acid sites in Ni1APO-5(H$_2$) did not have a great influence on the repolymerization of monomers, while homogeneous Brønsted acid such as H$_3$PO$_4$ could significantly promote the repolymerization of monomers.

3.5. Catalyst stability studies

The catalyst reuse experiment is crucial in lignin depolymerization. The Ni1APO-5(H$_2$) catalyst was selected for the recycling tests. Fig. 8 and Table S11 show the results of the investigation. The Ni1APO-5(H$_2$) catalyst still maintained high activity after being used for five consecutive times. The Ni^{2+} would be oxidized to Ni^{3+} after P-O (H)-Ni contributed a proton. But Ni^{3+} could be reduced to Ni^{2+} again under the action of methanol and external hydrogen. Therefore, the catalyst could maintain high activity for a long time. However, the yield of monomers dropped significantly during the sixth reaction. The recirculated catalyst was subjected to XRD testing to analyze the cause of catalyst deactivation (Fig. S15a). Although the XRD image of the Ni1APO-5(H$_2$) changed slightly after the fifth reaction, it still maintained the basic structure of AFI zeolite. However, the XRD image of the Ni1APO-5(H$_2$) catalyst changed completely after the sixth reaction. Therefore, the change in the structure of Ni1APO-5(H$_2$) was one of the factors that reduce its activity. The result of ICP showed that the content of Ni in fresh Ni1APO-5(H$_2$) was 4.12 wt%. After six cycles, the content of Ni dropped to 3.81 wt% (Table S1). The loss of active components of the catalyst was also one of the factors for its deactivation. In addition, thermogravimetric analysis showed that the mass loss of the fresh Ni1APO-5(H$_2$) and Ni1APO-5(H$_2$) after six reactions were 5.65 wt% and 9.41 wt%, respectively (Fig. S15b, c). The mass loss at low temperature and high temperature was attributed to adsorbed water and carbon, respectively. The above results indicate that the deactivation of the catalyst may be related to structural changes, loss of active components and carbon deposition. After the sixth use, the catalyst was calcined and reduced again, and its structure and activity were partially restored.

4. Conclusions

The doped Ni^{3+} in NiAPO-5 could be reduced to Ni^{2+} when treated with H$_2$, causing adjacent oxygen in NiAPO-5 to be protonated to offset the charge imbalance. The generated protons would increase the Brønsted acid sites in NiAPO-5(H$_2$). The synergistic effect among Brønsted acid, Lewis acid and hydrogenation sites in the catalyst played a vital role in the efficient conversion of lignin. The catalyst deactivation was related to structural changes, loss of active components and carbon deposition. In summary, this work provided the possibility to realize the high value-added utilization of lignin.

CRediT authorship contribution statement

Baikai Zhang: Conceptualization, Methodology, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Visualization, Project administration, Supervision. **Wenzhi Li:** Conceptualization, Validation, Data curation, Writing - review & editing, Project administration, Funding acquisition. **Tingwei Zhang:** Methodology, Resources. **Xu Li:** Formal analysis, Investigation. **Ajibola T. Ogunbiyi:** Writing - review & editing. **Kun Chen:** Resources, Writing - review & editing. **Changcheng Shen:** Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2021.121509.

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