High-Performance Evolution of Ni₂P@Hierarchical HZSM-5 as the Guaiacol Hydrodeoxygenation Catalyst

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1. INTRODUCTION

The rapid consumption of fossil fuels combined with the more and more serious pollution problems has led to increasing focus on global energy and environmental issues, so researching renewable resources is crucial. The bio-oil produced by the biomass fast pyrolysis is attracting more and more attention as an energy substitute to replace traditional fossil energy. It is estimated that the annual biomass potential is available up to 1.08×10¹¹ toe (tons of oil equivalent), almost 10 times the current energy demand in the world. However, there is great diversity in the chemical composition between bio-oil and petroleum, for example, the high oxygen content of bio-oil (45−50 wt %), which hinders the application of bio-oil in the existing equipment. Therefore, bio-oil needs to be upgraded.

Hydrodeoxygenation (HDO) can effectively remove oxygen from bio-oil, which enhances the miscibility of the conventional petroleum fractions and the bio-oil. Recently, metal phosphides are regarded as a promising HDO catalyst for the bio-oil upgrading. It is reported that the activity of Ni₂P on the HDO of bio-oil model compounds is better than that of other metal phosphides, such as CoP, Co₂P, FeP, Fe₂P, WP, and MoP, which is attributed to the special crystal structure of Ni₂P. Generally, the HDO of bio-oil requires metal sites and acidic sites. Metal phosphides are reported to have bifunctional properties, whose acidity is derived from P−OH and unreduced Ni²⁺ on the carrier surface. However, the acidity of Ni₂P is weak; thus, the HDO rate of phenolic compounds is slow. Related studies have confirmed that an acidic carrier is beneficial to the complete deoxygenation of phenolic derivatives; acidic sites can promote dehydration and hydrocracking.

It is well known that the HZSM-5 zeolite is widely used in various catalytic fields because of its unique properties (such as acidity and microporosity). However, the diffusion of reactants in the microporous HZSM-5 zeolite is limited. Moreover, the hierarchical HZSM-5 can improve the diffusion performance of reactants in molecular sieve channels. Based on the above analysis, the hierarchical HZSM-5 zeolite functionalized with Ni₂P is regarded as a promising bifunctional catalyst. However, there are no systematic studies on the synergy between hierarchical HZSM-5 and Ni₂P for HDO.

In this contribution, we proposed a new strategy to synthesize a bifunctional Ni₂P@Hierarchical HZSM-5 catalyst by the modified sol−gel method. The effects of NH₃·H₂O/Ni and Si/Al on the performance of the prepared catalysts for guaiacol HDO (as a model of bio-oil) were investigated in detail to establish the correlation between the catalyst structure and activity.

2. RESULTS AND DISCUSSION

2.1. Characterization of Ni₂P@Hierarchical HZSM-5-X(Y) Catalysts. In the preparation of the catalysts, we extracted silicon from the carrier skeleton as a silicon source and coated Ni₂P on the surface of HZSM-5 by the self-assembly method to obtain Ni₂P@Hierarchical HZSM-5-X(Y) catalysts. The structural properties of Ni₂P@Hierarchical HZSM-5-18(Y) catalysts were acquired from the N₂ adsorption−desorption isotherms, as shown in Table 1. It can be seen that the specific surface areas ranged from 175 to 21337 m² g⁻¹ for all the catalysts, which is beneficial for the reaction of reactants in molecular sieve channels.
246 m$^2$/g at different NH$_3$·H$_2$O/Ni. As NH$_3$·H$_2$O/Ni increased, the specific surface area of the catalyst first increased and then decreased. Ni$_2$P@hierarchical HZSM-5-18(b) had the largest specific surface area. Figure 1a,b shows that all the catalysts prepared by the modified sol–gel method displayed a type IV isotherm (according to the IUPAC classification), indicating that the catalysts had a typical mesoporous structure. The pore size distributions of different catalyst layers are shown in Figure 1c,d. As NH$_3$·H$_2$O/Ni increased, the pore diameter of the catalyst gradually increased. However, the pore diameter of the catalyst gradually decreased with the increase of Si/Al.

The X-ray diffraction (XRD) patterns of the prepared catalysts are shown in Figure 2. All samples had four strong diffraction peaks at 40.7, 44.6, 47.3, and 54.1°, corresponding to (111), (201), (210), and (300) of Ni$_2$P (JCPDS 03-0953), respectively. No significant diffraction peaks of Ni, NiO, and other nickel phosphides were found in all samples, indicating that the reduction of Ni–O to Ni$_2$P was relatively sufficient in the oxide precursor. The characteristic peaks of Ni$_2$P for the catalysts prepared by the modified sol–gel method were sharper than those recorded over the catalyst prepared by the impregnation method, which indicated that Ni$_2$P had a higher crystallinity. The relationship between NH$_3$·H$_2$O/Ni and the particle size of Ni$_2$P was investigated by the Scherrer equation (\(D = \frac{K\lambda}{B \cos \theta}\), where \(K\): Scherrer constant, \(\gamma\): X-ray wavelength, \(\theta\): diffraction angle, and \(B\): full width at half-maximum). These

### Table 1. Nominal Compositions and Properties of Ni$_2$P@Hierarchical HZSM-5-X(Y) Catalysts

| sample                     | \(S_{\text{BET}}\) (m$^2$/g) | pore volume (cm$^3$/g) | average pore diameter (nm) |
|---------------------------|-------------------------------|------------------------|-----------------------------|
| HZSM-5-18                 | 362                           | 0.39                   | 4.28                        |
| HZSM-5-85                 | 395                           | 0.36                   | 3.70                        |
| Ni$_2$P@hierarchical HZSM-5-18(a) | 209                           | 0.31                   | 5.08                        |
| Ni$_2$P@hierarchical HZSM-5-18(b) | 246                           | 0.38                   | 6.36                        |
| Ni$_2$P@hierarchical HZSM-5-18(c) | 220                           | 0.47                   | 8.64                        |
| Ni$_2$P@hierarchical HZSM-5-18(d) | 175                           | 0.48                   | 11.10                       |
| Ni$_2$P@hierarchical HZSM-5-18(e) | 188                           | 0.33                   | 7.12                        |
| Ni$_2$P@hierarchical HZSM-5-18(f) | 215                           | 0.76                   | 14.22                       |
| Ni$_2$P@hierarchical HZSM-5-23(b) | 257                           | 0.26                   | 4.00                        |
| Ni$_2$P@hierarchical HZSM-5-50(b) | 263                           | 0.29                   | 4.78                        |
| Ni$_2$P@hierarchical HZSM-5-85(b) | 329                           | 0.30                   | 3.62                        |
| Ni$_2$P@hierarchical HZSM-5-130(b) | 356                           | 0.43                   | 4.82                        |
| Ni$_2$P@hierarchical HZSM-5-85(b)-1 | 247                           | 0.36                   | 5.76                        |
| Ni$_2$P@hierarchical HZSM-5-85(b)-2 | 217                           | 0.31                   | 5.76                        |
| Ni$_2$P@hierarchical HZSM-5-85(b)-3 | 217                           | 0.31                   | 5.72                        |

*Metal/phosphide molar ratio 0.5:1. (a), (b), (c), and (d) are defined as NH$_3$·H$_2$O/Ni = 10, 14, 18, and 22, respectively, molar ratio. (b-) no addition of CTAB, (j) prepared by the impregnation method. 1, 2, and 3 represent the number of cycles of the catalyst, respectively.*

Figure 1. N$_2$ adsorption–desorption isotherms of the (a) Ni$_2$P@hierarchical HZSM-5-18(Y) and (b) Ni$_2$P@hierarchical HZSM-5-X(b) catalysts. Pore size distributions of the (c) Ni$_2$P@hierarchical HZSM-5-18(Y) and (d) Ni$_2$P@hierarchical HZSM-5-X(b) catalysts.
results illustrated that the Ni₃P grain size on Ni₃P@hierarchical HZSM-5 was affected greatly by NH₃·H₂O/Ni. With the increase of NH₃·H₂O/Ni, the particle size of Ni₃P tended to decrease first and then increase. The Ni₃P particle size over the Ni₃P@hierarchical HZSM-5-18(b) was the smallest.

The morphologies of the samples were investigated by scanning electron microscopy (SEM) (shown in Figure 3). Obviously, the silica layer was obtained in all the samples prepared by the modified sol−gel method, and the surface of Ni₃P@hierarchical HZSM-5-18(b) (shown in Figure 3b) was more uniform than that of other catalysts. A uniform layer can expose more active sites, thus improving HDO performance. In the process of uniform silica layer formation, the carrier desilication rate should be moderate. To further testify the distribution of the silica layer and Ni₃P, Figure 3 shows the corresponding energy-dispersive X-ray spectroscopy (EDX) maps. The results showed that the distribution of Si, O, Ni, and P elements was relatively uniform in Ni₃P@hierarchical HZSM-5-18(b).

The elemental composition and valence state of the Ni₃P@hierarchical HZSM-5-85(b) catalyst surface were analyzed by X-ray photoelectron spectroscopy (XPS) (shown in Figure 4). The peaks of Ni 2p₃/2 and P 2p₃/2 of the fresh catalyst are shown in Figure 4b,c, with 856.2 and 852.7 eV corresponding to Ni 2p₃/2 and 134.1 and 129.5 eV corresponding to P 2p₃/2. The peaks of 856.2 and 852.7 eV corresponded to Ni²⁺ and Niδ⁺ (0 < δ < 2), and the peaks of 134.0 and 129.5 eV corresponded to P⁵⁺ and Pδ⁻ (0 < δ < 1), which were compatible with Ni₃P.

The acidity of Ni₃P@hierarchical HZSM-5-X(b) catalysts was compared with that of NH₃-TPD. Figure 5 shows the NH₃-TPD profiles. The area of the NH₃-TPD curve corresponds to the acidity of the sample. The NH₃-TPD profiles of all catalysts had three distinct NH₃ desorption peaks at temperatures of 100–200, 200–500 °C, and above 500 °C,
indicating that there were three types of acid sites on the catalyst surfaces: weak acid sites, medium acid sites, and strong acid sites. From Table 2, the total acidity of the catalysts decreased with the increase of Si/Al.

Table 2. Total Acidity of the Samples by NH₃-TPD

| sample                                | region I (mmol NH₃/g) | region II (mmol NH₃/g) | region III (mmol NH₃/g) | total (mmol NH₃/g) |
|----------------------------------------|-----------------------|------------------------|-------------------------|-------------------|
| Ni₂P@hierarchical HZSM-5-18(b)         | 2.11                  | 0.24                   | 0.74                    | 3.09              |
| Ni₂P@hierarchical HZSM-5-25(b)         | 1.86                  | 0.91                   | 0.19                    | 2.96              |
| Ni₂P@hierarchical HZSM-5-50(b)         | 1.74                  | 0.49                   | 0.58                    | 2.81              |
| Ni₂P@hierarchical HZSM-5-85(b)         | 1.50                  | 0.87                   | 0.31                    | 2.68              |
| Ni₂P@hierarchical HZSM-5-130(b)        | 1.62                  | 0.79                   | 0.16                    | 2.57              |

2.2. Influence of NH₃·H₂O/Ni and Si/Al over the Ni₂P@Hierarchical HZSM-5-X(Y) Catalyst Performance for the HDO of Guaiacol. Scheme 1 shows a possible reaction network for guaiacol. Cyclohexanone and cyclohexanol were detected using gas chromatography–mass spectrometry (GC–MS), but the content of both was extremely low, so they were not included in statistics of product results. The catalytic performance of Ni₂P@Hierarchical HZSM-5-X(Y) catalysts for the HDO of guaiacol from biomass pyrolysis oil was evaluated, and the obtained results are listed in Table 3. The conversion of guaiacol over Ni₂P@Hierarchical HZSM-5-18(Y) catalysts was Ni₂P@Hierarchical HZSM-5-18(b) > Ni₂P@Hierarchical HZSM-5-18(a) > Ni₂P@Hierarchical HZSM-5-18(c) > Ni₂P@Hierarchical HZSM-5-18(d) > Ni₂P@Hierarchical HZSM-5-18(j) in sequence; the results illustrated that the HDO activity of the catalysts increased first and then decreased with the increase of NH₃·H₂O/Ni. The main reason may be due to the fact that the hierarchical structure of the catalysts effectively shortened the paths of contact of the reactant with the active sites. Too little ammonia solution will lead to a slight increase in the mesoporous ratio of the carrier, while excessive ammonia...
solution may cause excessive silicon extraction in the carrier to affect the structure of the original carrier. When NH$_3$·H$_2$O/Ni = 14, the catalyst had the highest HDO activity. The conversion of guaiacol and the yield of cyclohexane over the Ni$_2$P@hierarchical HZSM-5-18(b) catalyst in dodecane reached 32 and 10.4%, respectively. Figure 6a presents the effect of the H$_2$ pressure on the HDO of guaiacol over the Ni$_2$P@hierarchical HZSM-5-18(b) catalyst in dodecane.
catalyst. The conversion of guaiacol was the lowest as 56% when the H₂ pressure was 1 MPa. This may be due to too little dissolution of H₂ in dodecane. When the H₂ pressure was increased to 3 MPa, the hydrogenation reaction over Ni₂P@hierarchical HZSM-5-85(b) had higher catalytic activity, the conversion rate of guaiacol was 85%, and the target product yield of cyclohexane was 60%. Stummann et al.26 had published similar results, showing that under low H₂ pressure the coke deposition on the catalyst was not inhibited and the HDO activity increased with increasing H₂ pressure.

In addition, the effect of Si/Al on the HDO of guaiacol over Ni₂P@hierarchical HZSM-5-X(b) catalysts was investigated, and the results are summarized in Table 3. The conversion of guaiacol over Ni₂P@hierarchical HZSM-5-X(b) catalysts was Ni₂P@hierarchical HZSM-5-85(b) > Ni₂P@hierarchical HZSM-5-25(b) > Ni₂P@hierarchical HZSM-5-130(b) > Ni₂P@hierarchical HZSM-5-25(b) > Ni₂P@hierarchical HZSM-5-18(b) in sequence, which indicated that the HDO activity of the catalysts showed a trend of increasing first and then decreasing with the increase of Si/Al. Si/Al of the carrier main chain was critical to the sensitivity of desilication.27 The catalyst had the highest HDO activity when Si/Al = 85. The conversion of guaiacol and the yield of cyclohexene over the Ni₂P@hierarchical HZSM-5-85(b) catalyst in dodecane reached 91.1 and 68.0%, respectively.

Figure 6b shows the conversion of guaiacol and the yield of the cyclohexane target product changing with the reaction time over the Ni₂P@hierarchical HZSM-5-85(b) catalyst. As the reaction time progressed, the conversion of guaiacol and the yield of cyclohexane gradually increased. When the reaction was carried out for 6 h, the conversion of guaiacol was 98%, and the yield of cyclohexane was 78.8%.

2.3. Deactivation Stability Test of the Catalyst. Figure 7a shows the effect of recycling three times with the Ni₂P@hierarchical HZSM-5-85(b) catalyst for the conversion of guaiacol and the yield of cyclohexane. As the number of cycles was increased, the conversion of guaiacol and the yield of cyclohexane decreased significantly. This indicated that the stability of the catalyst was poor, so we analyzed and explained the reasons by the following characterizations.

Table 1 shows that the specific surface area was suddenly decreased from 329 to 247 m²/g after using the Ni₂P@hierarchical HZSM-5-85(b) catalyst once. In addition, the obvious characteristic peaks of Ni₂P were not detected on the XRD patterns of the spent catalysts, as shown in Figure 7b. These indicated that the deactivation of the catalyst was caused by the destruction of the catalyst structure and the loss of Ni₂P after use. Subsequently, we analyzed the solutions after the reaction using inductively coupled plasma spectroscopy, and the results are summarized in Table 4. Both Ni and P elements were detected, which further confirmed the previous viewpoint. In the subsequent experiments, we will prepare a more stable catalyst to improve the performance of the catalysts for the HDO of biomass.

3. CONCLUSIONS

A series of Ni₂P@hierarchical HZSM-5 catalysts with a controllable structure were facilely and eco-friendly synthesized by the modified sol–gel method, which were a bifunctional catalyst with metal sites and acid sites. The results showed that the HDO activity increased first and then decreased with the increase of NH₃·H₂O/Ni and Si/Al. The Ni₂P@hierarchical HZSM-5-85(b) realized efficient conversion of guaiacol to cyclohexane. In the future, we will focus on developing a more stable Ni₂P-based catalyst with a hierarchical structure.

4. EXPERIMENTAL SECTION

4.1. Materials. Nickel(II) acetate tetrahydrate, ammonium phosphate dibasic, hexadecyl trimethyl ammonium bromide, guaiacol, and dodecane were purchased from Shanghai Aladdin Biotechnology Co., Ltd. (China). Ammonia solution (25%) was obtained by Tianjin Fengchuan Chemical Reagent Science and Technology Co., Ltd. (China). HZSM-5 zeolites (Si/Al = 18, 25, 50, 85, and 130, respectively) were supplied by Nankai University Catalyst Co., Ltd. (China). All reagents were of analytical reagent grade and used without further purification. Hydrogen and nitrogen were produced by Tianjin Lufang Gas Co., Ltd. (China).

4.2. Catalyst Preparation. The HZSM-5-supported Ni₂P nanoparticle [Ni₂P@hierarchical HZSM-5-X(Y)] catalysts
were prepared by the modified sol–gel method. The Ni₄P content of all catalysts was 15 wt %, Ni₄P = 0.5 (molar ratio). Nickel(II) acetate tetrahydrate was mixed with the certain proportion of ammonium phosphate dibasic. The mixture was dissolved in deionized water with the addition of 0.48 g of hexadecyl trimethyl ammonium bromide (CTAB) and stirred until homogeneity. Four mixtures were prepared in the same way. Subsequently, the different proportions of ammonia solution (NH₄H₂O/Ni = a, b, c, and d) were defined as 10, 14, 18, and 22, respectively (molar ratio) were added to the mixture, which was a crucial step in the preparation of the catalyst for the hierarchical structure. After the above solutions were uniformly mixed, 1 g of activated HZSM-5-18 was added separately. The above mixtures were treated for 1 h with ultrasonic and stirring and added to a 100 mL polytetrafluoroethylene-lined hydrothermal synthesis reactor for 6 h at 120 °C. The reacted solutions were stirred, dried to solids in a water bath at 60 °C, and placed in a blast drying oven at 100 °C to be completely dried. The obtained solids were ground into powder and placed in a muffle furnace at 550 °C for 5 h to remove the templating agent (CTAB). Finally, the calcined powder was subjected to temperature-programmed reduction (80 mL/min, 3 °C/min) in a tube furnace at 600 °C for 2 h in the H₂ atmosphere and passivated for at least 4 h under nitrogen conditions at room temperature. The catalysts prepared above were labeled as Ni₄P@hierarchical HZSM-5-18(a), Ni₄P@hierarchical HZSM-5-18(b), Ni₄P@hierarchical HZSM-5-18(c), and Ni₄P@hierarchical HZSM-5-18(d), respectively. In addition, two catalysts Ni₄P@hierarchical HZSM-5-18(X) (NH₄H₂O/Ni = 14, no addition of CTAB) and Ni₄P@hierarchical HZSM-5-18(j) (prepared by the impregnation method) were prepared, which were studied for comparison. The Ni₄P nanoparticles supported on HZSM-5 with varied Si/Al (18, 25, 50, 85, and 130) catalysts were prepared by the same process at NH₄H₂O/Ni = 14 and named as Ni₄P@hierarchical HZSM-5-18(b), Ni₄P@hierarchical HZSM-5-25(b), Ni₄P@hierarchical HZSM-5-50(b), Ni₄P@hierarchical HZSM-5-85(b), and Ni₄P@hierarchical HZSM-5-130(b), respectively.

4.3. Catalytic Performance Test. The HDO reactions were performed in a 100 mL high-pressure reactor (Shanghai Yanzheng, China). The activity of Ni₄P@hierarchical HZSM-5-X(Y) was evaluated by using HDO of guaiacol. The high-pressure reactor was checked for leaks before each reaction. Guaiacol, dodecane, and catalyst were added to the reactor. The air was replaced by purging five times with 3 MPa H₂. Then, the reactor was heated to 300 °C at a stirring speed of 800 rpm. After each reaction, the liquid products were collected while directly removing the gaseous products. The liquid products were analyzed, respectively, by GC (GC1120, China) and GC–MS (Agilent 7890B-5977A, USA). The conversion and the yield were computed by the following definition:

\[ \text{conversion (\%)} = \left(1 - \frac{n_{\text{Gua}}}{n_{\text{Gua,0}}} \right) \times 100\% \] (1)

\[ \text{yield (i, \%)} = \frac{n_{i,t}}{n_{\text{Gua}}} \times 100\% \] (2)

where i represents products cyclohexane, methylcyclopentane, methylcyclohexane, anisole, and phenol in the reaction; \(n_{\text{Gua}}\) and \(n_{\text{Gua,0}}\) represent the content of guaiacol before and after the reaction, respectively; \(n_i\) is the content of product i; and \(t\) is the reaction time.

4.4. Characterization Methods. Specific surface area, pore volume, and pore size analysis were measured by an ASAP 2020M+C specific surface and porosity analyzer. Crystal structure analysis was obtained from XRD using Bruker D8 DISCOVER. Sample morphologies were analyzed by SEM (Hitachi SU8010) coupled with an Oxford MAX-80 energy-dispersive X-ray spectrometer. Surface compositions were measured by XPS using ESCALAB 250Xi. The total acid content of the samples was determined by the chemisorption (NH₃−TPD, AutoChem II 2920).

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**Notes**

The authors declare no competing financial interest.

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