One-Pot Synthesis of Active Carbon-Supported Size-Tunable Ni$_2$P Nanoparticle Catalysts for the Pyrolysis Bio-Oil Upgrade

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**ABSTRACT:** Catalytic hydrodeoxygenation (HDO) over Ni$_2$P-based catalysts is a promising technology for the pyrolysis bio-oil upgrading. However, substantial challenges still remain in the realization of the size effect for phosphide catalysts in catalyzing this reaction, and the precise size engineering of these catalysts is difficult. In this work, the Ni$_2$P/active carbon (AC) catalysts with varying nickel phosphide nanoparticle sizes were one-pot prepared via the modified organic liquid chemical reaction method. The Ni$_2$P-based catalysts were tested for HDO of the pyrolysis oil model compound (salicylaldehyde), and the conversion of salicylaldehyde first increases and then decreases with the increase of Ni$_2$P nanoparticle size, demonstrating that the activity for HDO of salicylaldehyde can be controlled by using nickel phosphides of varying nanoparticle sizes. The Ni$_2$P-2/AC catalyst with approximately 5.49 nm Ni$_2$P nanoparticle size exhibited the highest activity with conversion of salicylaldehyde reaching over 99% within 180 min under 220 °C, 2 MPa H$_2$ pressure, and the corresponding yield toward o-cresol was over 97%.

1. INTRODUCTION

Nowadays, the diminishing availability of fossil-based energy resources and the serious environmental pollutions force us to seek and develop alternative fuels to meet the global needs, especially in the area of the transportation sector. Biomass, which radically originated from photosynthesis, is expected to be a renewable alternative to fossil fuels because of its low price, wide distribution, and environment friendliness. One of the most prospective routes of biomass utilization is to convert it into liquid fuels (called pyrolysis oil) via fast pyrolysis technology.4,5 However, the pyrolysis oil has many disadvantages, such as the high oxygenation content, limited thermal stability, high corrosion properties, and low heating value, which hinders the direct utilization of pyrolysis oil as a vehicle fuel in the current infrastructure. In order to convert pyrolysis oil into a liquid vehicle fuel, hydrodeoxygenation (HDO) as an effective catalytic technology is carried out, which can remove oxygen in the pyrolysis oil by reacting its oxygenated molecules with hydrogen using a specific catalyst and obtain high-grade biofuels. Although considerable efforts for the HDO of pyrolysis oil have resulted in impressive progress, the industrial application of this method is impeded by some technical barriers, such as catalyst deactivation, the low yield of the target product, the loss of carbon, and the high hydrogen consumption.1,2 Therefore, it is important to develop effective HDO catalysts for upgrading of pyrolysis oil.

In the research of an appropriate catalyst for HDO purpose, various catalysts, including metal sulfides, transition metals, noble metal, metal phosphides, metal carbides, or related compounds, were investigated in the catalytic HDO process.1,4–13 Traditionally, sulfide catalysts such as NiMoS or CoMoS supported on alumina have been used for the HDO of pyrolysis oil. Although conventional sulfide catalysts are very active for oxygen removal, the sulfur source needs to be added to maintain the activity of the catalyst during the reaction, which may cause the contamination of the product.9 An alternative approach based on noble metal catalysts has shown some promise for the upgrading of pyrolysis oil.6 Wildschut et al.11 tested the HDO reaction of pyrolysis oil over Ru/C, Pd/C, and Pt/C catalysts in comparison to metal sulfide-based catalysts, suggesting that the deoxygenation performance of the noble-metal catalysts is better than that of the traditional CoMoS/Al$_2$O$_3$ and NiMoS/Al$_2$O$_3$ catalysts. Unfortunately, the high cost of noble metal catalysts severely hinders their practical applications for bio-oil upgrading. In a more specific scenario, inexpensive Ni$_2$P-based catalysts are promising candidates for various hydrogenation reactions because of their lower cost, good hydrogen transfer properties, and low selectivity for C–C bond hydrogenolysis and decarbonylation.12,13 Recently, nickel phosphide catalysts exhibited superior catalytic activity in HDO reactions for pyrolysis oil and model compounds such as 2-methoxyphenol,14,15 dibenzofuran,16 and 2-methyltetrahydrofuran.13 The performance of the Ni$_2$P-based catalysts is affected by the particle size of the active component and the method of synthesis.17 Several approaches have been developed in the literature for the preparation of Ni$_2$P-based catalysts, including H$_2$ temperature programmed-reduction (TPR) of nickel phosphates, phosphorization of metals or metal oxides with PH$_3$/H$_2$, and decomposition of metal oxides and hypophosphite precursors.
The transmission electron micrographs of the Ni$_2$P-X/AC catalysts (Figure 1A–D) show that the nanoparticles were spherical and uniformly distributed, which suggests that the relative size and dispersity of the metal phosphide nanoparticle are synthesized during the chemical reaction. The sizes of Ni$_2$P nanoparticles Ni$_2$P-1/AC, Ni$_2$P-2/AC, Ni$_2$P-3/AC, and Ni$_2$P-4/AC are 4.47 ± 0.64, 5.49 ± 0.71, 7.04 ± 1.15, and 9.99 ± 2.16 nm, respectively, which indicates that the amounts of oleylamine (OA) and TOP play a key role on the formation of Ni$_2$P nanoparticles. During the process of catalyst synthesis, OA acts as the reductant and thus controls the nucleation rate; meanwhile, TOP is used as the phosphorus source and stabilizing agent, which provides a tunable surface stabilization through coordination on the Ni(0) surface. In the synthesis, for few amount of TOP, a fast reduction of the Ni(II) precursor took place, leading to an important concentration of Ni(0) species which are not efficiently stabilized by the ligands present in solution. Then, a fast aggregation process results in the formation of large size Ni$_2$P nanoparticles over Ni$_2$P-X/AC catalysts. However, when the amount of OA is reduced, a few nuclei are prepared, and the presence of large amounts of TOP, an efficient ligand for Ni(0) species, inhibits their growth, resulting in the formation of small nanoparticles. Thus, the size of Ni$_2$P NPs over Ni$_2$P-4/AC is larger than that of Ni$_2$P-1/AC. In addition, the images of selected-area electron diffraction and lattice fringes (shown in Figure 1B,C) suggest that the spherical Ni$_2$P nanoparticles are single crystalline. Therefore, the size of the Ni$_2$P NPs over the Ni$_2$P-X/AC catalyst can be readily tuned by varying the concentration of OA and TOP, which provides an effective method for precisely controlling their size in a range of 4 to around 10 nm, at which these Ni$_2$P nanoparticles supported on AC with various sizes would have different properties possibly resulting in different reactivities.

Figure 2 illustrates the X-ray diffraction (XRD) patterns of Ni$_2$P-X/AC catalysts with different sizes of Ni$_2$P nanoparticles. From the Figure 2, it can be easily found that a broad diffraction peak at 20.8° is because of the amorphous nature of AC for all of the catalysts. The sharp diffraction signals at 2θ values of 40.7°, 44.6°, 47.4°, and 54.2° can be attributed to the (111), (201), (210), and (300) crystal faces of Ni$_3$P, respectively, which confirms that Ni$_2$P particles were synthesized successfully. Compared with Ni$_2$P-3/AC and...
Ni2P-4/AC, clear diffraction peaks from Ni2P nanoparticles over Ni2P-1/AC and Ni2P-2/AC catalysts could not be detected because of the small dimensions of the Ni2P nanoparticles, which suggests that Ni2P nanoparticles for the Ni2P-1/AC and Ni2P-2/AC catalysts are well dispersed on the surface of the carrier and it is advantageous for metal sites forming high-efficiency synergistic effects with surface acid sites.

Fourier transform infrared (FT-IR) spectroscopy was used to reveal the chemical structure of Ni2P-based catalysts (shown in Figure 3). The strong peak at approximately 3400 cm$^{-1}$ was observed in the spectra of Ni2P-X/AC catalysts, which attributed to the O–H stretching vibration. Some peaks appeared at 1630 and 1374 cm$^{-1}$ were C=O stretching vibration and –OH flexural vibration in the –COOH group, respectively. The results suggested that the surface of Ni2P-X/AC catalysts has carboxyl and hydroxyl groups. In addition, the C–H stretching vibrations at 2918 and 2850 cm$^{-1}$ were observed, indicating the presence of the aliphatic chain over Ni2P-X/AC catalysts.

The Raman spectra of the Ni2P-based catalysts were presented in Figure 4, in which the D band at ∼1350 cm$^{-1}$ represents the disordered structure of graphite, whereas the G band at ∼1580 cm$^{-1}$ indicates the structure of the sp$^2$-hybridized carbon atom. The results illustrate that there are structural defects in Ni2P-X/AC catalysts, which may promote the activity of catalysts.

The nature of Ni2P-X/AC catalysts was investigated by scanning electron microscopy (SEM)–energy-dispersive spectrometry (EDS) elemental mapping (shown in Figure 1E). The results suggest that the surface of the prepared catalysts consists of the elemental distribution of P and Ni. TOP is used as the phosphorus source and stabilizing agent, and the reaction of metal salts and TOP can generate the metal–phosphine complexes, which continue to thermal decompose to produce the nickel phosphide nanocrystals. As shown in the EDS mapping of a selected area on the Ni2P-2/AC catalyst, a homogeneous distribution of Ni and P in the same selected area was observed, indicating that Ni2P nanoparticles are dispersed uniformly on the surface of support, which is consistent with XRD results.

2.2. Catalytic HDO Tests. 2.2.1. Effect of Temperature on Catalytic Performance of the Ni2P/AC Catalyst. To evaluate the usefulness of the prepared Ni2P-based catalyst, the activity of Ni2P-X/AC for the HDO of the bio-oil model compound was performed. In the present study, we used SA (2-hydroxy-benzaldehyde) as a representative component of pyrolysis oil to explore the HDO pathways. In this work, transformation of SA into o-cresol can proceed via path (i) hydrogenation/hydrogenolysis or (ii) direct hydrogenolysis of the C=O bond. Figure 5 presents the conversion and yield for SA HDO over Ni2P-2/AC, which were affected by the reaction temperature. The results illustrate that as the reaction temperature increases, the conversion of SA and the yield of o-cresol gradually increased. When the reaction temperature is 260 °C, the yield of the target product of o-cresol is maximized, reaching 97.1% for 2 h, which suggests that the reaction temperature significantly enhanced catalytic activity in regioselective HDO of SA.

2.2.2. Effect of Ni2P NP Size on the Catalytic Performance of Ni2P-Based Catalysts. In order to study the effect of Ni2P NP size on the catalytic performance of Ni2P-based catalysts, the HDO of SA was conducted at 220 °C and 2 MPa H$_2$ pressure. The obvious differences in the catalytic activity can be observed for the Ni2P-X/AC catalysts of varying sizes (shown in Figure 6). As the Ni2P nanoparticles decrease, the conversion first increases and then decreases. Among them, the Ni2P-2/AC catalyst exhibits more reactivity in HDO reaction with conversion of SA reaching over 99% within 180 min, and the yield toward o-cresol was over 97%. Smaller Ni2P...
Ni$_2$P-2/AC were investigated (shown in Figure 7a,b). The pyrolysis oil derived from the phenolic fraction (SA) over Ni$_2$P-2/AC catalyst for the HDO of SA under 2 MPa hydrogen pressure for 2 h. In this work, the interactions between the carbohydrate-derived compounds and literature studies for the pyrolysis oil upgrading focus on the aromatic compounds during the HDO process, a few previous the carbohydrate-derived compounds have an impact on the activity for HDO of SA can be controlled by using nickel phosphides of varying nanoparticle sizes. Thus, the activity for HDO of SA can be controlled by using nickel phosphides of varying nanoparticle sizes.

2.2.3. Effect of the Carbohydrate-Derived Compound on the Catalytic Performance of Ni$_2$P-Based Catalysts. Although the carbohydrate-derived compounds have an impact on the aromatic compounds during the HDO process, a few previous literature studies for the pyrolysis oil upgrading focus on the interactions between the carbohydrate-derived compounds and lignin-derived aromatics in the HDO reaction. In this work, the effects of carbohydrate derivatives (MF) on the HDO of pyrolysis oil derived from the phenolic fraction (SA) over Ni$_2$P-X/AC catalysts were investigated (shown in Figure 7a,b). The presence of MF imposed a great influence on the catalytic activity and stability during the HDO process.27 Nickel acetylacetonate [Ni(acac)$_2$; 99%, Shanghai Dibo Chemicals Technology Co., Ltd.], AC (Xfnano), oleylamine (OAm; 90%, Energy-Chemical), TOP (90%, Energy-Chemical), and tetradecane (C$_{14}$H$_{30}$; 97%, Energy-Chemical), were added in a 100 mL spherical stainless steel reactor (50 mL). Argon (99.9%, Energy-Chemical) was used as the reaction atmosphere. The mixture was adjusted to 1 MPa H$_2$ pressure for 3 h. Furthermore, the influence of the carbohydrate-derived compound (SA) was observed in this work, elucidating that the presence of MF inhibits the HDO of SA. The differences in the reactivity and stability during the HDO process may be attributed to the variation of Ni$_2$P nanoparticle size. Developing size-tunable catalysts and understanding the size effect during the hydrodeoxygenation process will be significant for the pyrolysis bio-oil upgrade.

3. CONCLUSIONS

In conclusion, we report the fabrication of Ni$_2$P/AC catalysts with different Ni$_2$P nanoparticle sizes via the one-pot procedure based on the organic liquid chemical reaction approach. A strong size effect of Ni$_2$P NPs on their catalytic activity and stability in the HDO of SA was observed. Compared with other nickel phosphide catalysts, the Ni$_2$P-2/AC catalyst with approximately 5.49 nm favored the conversion of SA over Ni$_2$P-4/AC catalyst product where the yield reached up to 97.0% under 220 °C, 2 MPa H$_2$ pressure for 3 h. Furthermore, the influence of carbohydrate derivatives (MF) on the HDO of the lignin-derived compound (SA) was observed in this work, elucidating that the presence of MF inhibits the HDO of SA. The differences in the reactivity and stability during the HDO process may be attributed to the variation of Ni$_2$P nanoparticle size. Developing size-tunable catalysts and understanding the size effect during the hydrodeoxygenation process will be significant for the pyrolysis bio-oil upgrade.

4. EXPERIMENTAL SECTION

4.1. One-Pot Synthesis of Ni$_2$P Nanoparticle Catalysts. Ni$_2$P/AC catalysts with various Ni$_2$P nanoparticle sizes were synthesize by the modified organic liquid chemical reaction method.27 Nickel acetylacetonate [Ni(acac)$_2$; 99%, Shanghai Dibo Chemicals Technology Co., Ltd.], AC (Xfnano), oleylamine (OAm; 90%, Energy-Chemical), TOP (90%, Energy-Chemical), and tetradecane (C$_{14}$H$_{30}$; 97%, Energy-Chemical) were added in a 100 mL flask and heated in a nitrogen atmosphere at 120 °C for 20 min under stirring, giving a homogeneous solution. Then, the mixture was continued to heat up to 220 °C in 20 min and the temperature was maintained constant for 3 h, then subsequently cooled. The obtained catalysts were washed with a 1:1 (v/v) mixture of isopropanol and ethanol (99.9%, Kermel), isolated via centrifugation, and dried at 50 °C for 24 h. The specific amounts of the chemicals used to prepare the different Ni$_2$P nanoparticles are gathered in Table 1. According to the inductively coupled plasma atomic emission spectroscopy test, the Ni contents of the Ni$_2$P-1/AC, Ni$_2$P-2/AC, Ni$_2$P-3/AC, and Ni$_2$P-4/AC were 68, 71, 64, and 34%, respectively. The decreasing conversion of SA over Ni$_2$P-X/AC catalysts in the presence of MF [(MF)/(SA) = 1:2 (mol/mol)] indicates that the reactivity of SA was sharply decreased, which may be due to the fact that the reaction of MF on Ni$_2$P-based catalysts was more active at the same active sites of the catalyst where the HDO of SA takes place. Comparison on the results of the presence or absence of MF, signified reduced catalytic activity over the Ni$_2$P-4/AC catalyst was observed, 53% for conversion and 59% for the yield toward o-cresol, which may be ascribed to the poisoning of catalysts by the carbon deposition caused by the polymerization of adsorbed MF.

![Figure 5. Effect of reaction temperature on the catalytic performance of the Ni$_2$P-based catalyst for the HDO of SA under 2 MPa hydrogen pressure for 2 h.](image)

![Figure 6. Effect of Ni$_2$P NP size on the catalytic performance of the Ni$_2$P-based catalyst for the HDO of SA.](image)
and Ni2P-4/AC catalysts were 4.7, 4.9, 4.9, and 4.9 wt %, respectively.

4.2. Characterizations. Transmission electron microscopy (TEM) analysis was carried out using JEM-2100F. XRD was performed by a D/MAX-2500 diffractometer with Cu Kα radiation (\(\lambda = 1.54184 \text{ Å}\)) operating at 40 kV and 40 mA in the range of 5°–90°. The FT-IR spectrum was determined by Bio-Rad FTS6000. Raman spectroscopy was recorded using an argon ion laser at 514.5 nm wavelength (Renishaw inVia reflex Raman microscope, Renishaw plc, U.K.) to analyze the graphitic structure of samples.

4.3. Catalytic Ability Test of Ni2P-Based Catalysts. The catalyst was applied in the model reaction of biofuel upgrade: the HDO of SA in the presence or absence of MF. In a typical reaction procedure, SA (8.19 mmol), MF (0–8.19 mmol), tetrahydrofuran (40 mL), and a solid catalyst (0.10 g) were added to the stainless steel autoclave reactor (∼100 mL). In this work, MF was used to investigate the influence of carbohydrate derivatives on the HDO of SA. The molar ratio of MF to SA was adjusted from 0 to 1.0 (mol/mol). After checking the leakage and displacing air, hydrogen of 2 MPa pressure was pumped into the reactor, then carried out at 140–260 °C under stirring at 800 rpm. After the reaction, the solid catalyst was separated and the liquid product was obtained at room temperature. The liquid products were analyzed by a gas chromatograph–mass spectrometer (GC/MS, Thermo Science Trace 1300, US) with a DB-SMS capillary column (30 m × 0.32 mm × 0.5 μm) and further quantified using a GC with an FFAP capillary column (30 m × 0.32 mm × 0.5 μm) equipped with a flame ionized detector (GC/FID, Pgeneral GC-1100, China) using dodecane as an internal standard.

| Table 1. Amounts of Chemicals Used for Synthesizing Various Sizes of Ni2P Nanoparticles |
|-----------------------------------|------|------|------|------|------|
| catalysts | Ni (acac)₂ (g) | OAm (mL) | TOP (mL) | tetradecane (mL) | AC (g) |
| Ni2P-1/AC | 0.5 | 2.5 | 7.5 | 40 | 2.28 |
| Ni2P-2/AC | 0.5 | 4.0 | 6.0 | 40 | 2.28 |
| Ni2P-3/AC | 0.5 | 7.0 | 3.0 | 40 | 2.28 |
| Ni2P-4/AC | 0.5 | 8.5 | 1.5 | 40 | 2.28 |

Figure 7. Effects of MF on the HDO of SA: (a) and (b) over Ni2P-2/AC and (c) and (d) over Ni2P-X/AC with different particle sizes.

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ACS Omega 2019, 4, 2075–2080.

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