Selective Hydrodeoxygenation of 5-Hydroxymethylfurfural to 2,5-Dimethylfuran over Ni Supported on Zirconium Phosphate Catalysts

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ABSTRACT: Crystal α-zirconium phosphate (α-ZrP) was prepared by a hydrothermal method and exfoliated into a layered structure by n-hexylamine (C₆H₁₃NH₂). Ni-based catalyst (Ni/ZrP) was promoted by loading nickel on the layered α-ZrP via ion exchange. The catalyst was performed to catalyze hydrodeoxygenation of 5-hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (DMF), and a 68.1% yield of DMF and 100% conversion of HMF were achieved at 240 °C, 5 MPa H₂, and 20 h. The DMF yield can still retain 52.8% after five cycles. The characteristics of the catalyst were investigated via N₂ adsorption—desorption, X-ray diffraction, field emission scanning electron microscopy, high-resolution transmission electron microscopy, pyridine-adsorbed Fourier transform infrared (FTIR) spectra, FTIR spectra, inductively coupled plasma mass spectrometry, and thermogravimetric analysis—mass spectrometry, as well as Raman spectroscopy. A pathway from HMF to DMF was found with MF as the intermediate product, and DMF production was preferable via the −CH₂OH group hydrogenolysis of HMF over Lewis acidic sites of Ni/ZrP, which is caused by the zirconium vacant orbits.

1. INTRODUCTION

As the world population grows and the economy expands, only fossil fuels have been unable to meet the human survival and development about the huge demand for chemicals and energy. Abundant biomass resources are a promising alternative for the sustainable supply of valuable chemicals (such as alcohols, aldehydes carboxylic acids, and gasoline alkanes) to the chemical industry for the production of drugs, polymeric materials, and fuels.1−5 As an inexpensive and easily available feedstock, lignocellulosic biomass is the most abundant class among the biomass resources. Cellulosic biomass can be converted into liquid biofuels by thermochemical and hydrolysis routes, and lignocellulose can be transformed into a platform material—5-hydroxymethylfurfural (HMF)—by means of chemical catalysis.4 As a versatile platform chemical, HMF can form a number of important C₅ compounds, such as 2,5-dimethylfuran (DMF), 2,5-furandicarboxylic acid, 5-hydroxymethylfuroic acid, 2,5-dihydroxymethylfurfural (DHMF), alkoxyethylfururals, and so forth.5 Among these compounds, DMF (belonging to the second-generation biofuels)5 was proposed as a promising transportation fuel with higher boiling point, higher energy density, and lower solubility in aqueous solutions compared to ethanol.7 Román-Leshkov et al. have converted carbohydrates to DMF for use as a liquid transportation fuel earlier.6 Recently, Zu et al. have utilized Ru/Co₃O₄ to produce DMF from HMF under relatively mild conditions.8 Zirconium phosphate (ZrP), a kind of layered solid acid,10 has been developed to be a class of multifunctional materials in recent years.11,12 α-ZrP (Zr(HPO₄)₂·H₂O) is one of the most important ZrPs that has been prepared by various methods, among which crystalline ZrPs can be prepared by a hydrothermal synthesis method.13,14 Synthetic α-ZrP can be easily intercalated by amines and then exfoliated to prepare polymer nanocomposites.14 More importantly, the ZrP-type materials have been widely used in biomass catalytic conversion. Some studies have been developed to apply α-ZrP with its acid property to produce biomass-derived platform chemicals, such as levulinic acid,16 HMF,17 polyols,18 and so forth. However, using ZrP as the support to load metal species for hydrodeoxygenation (HDO) of HMF to DMF was rarely reported in recent work. Moreover, many studies about
the HDO process are involved in the application of high-price noble metals. The development of non-noble substitutes (base metal) has attracted great attention in both academic and industrial aspects. Because of the different functional groups (such as C=O, CH$_2$−OH, and furan ring) in HMF, HDO of HMF to DMF needs C=O hydrogenation to generate the corresponding −OH groups and subsequent C−OH group deoxygenation, and the hydrogenation of C=O bonds over the non-noble metal catalytic sites can promote a selective production of DMF.

In this work, we prepared a Lewis acid ZrP-supported Ni catalyst to achieve the aim. Briefly, crystal α-ZrP was prepared through a hydrothermal method and exfoliated into a layered structure by n-hexylamine (C$_6$H$_{13}$NH$_2$). Ni/ZrP was manufactured by inserting Ni$^{2+}$ into the layers of amine-intercalated ZrP via ion exchange. After reduction, the Ni/ZrP catalyst was used for catalyzing HDO of HMF to DMF in tetrahydrofuran (THF). The catalyst was investigated by a series of characteristic methods, and the transformation pathway of HMF to DMF was also elucidated.

2. RESULTS AND DISCUSSION

2.1. Catalyst Characterization. The data of Brunauer−Emmett−Teller (BET) and Barrett−Joyner−Halenda (BJH) pore size distribution of pristine α-ZrP and exfoliated α-ZrP are demonstrated in Figure 1 and Table 1, respectively. In Figure 1a, pristine α-ZrP has a BET surface area of 22.5 m$^2$/g and a pore volume of 0.2 cm$^3$/g. In terms of the BJH method, pristine α-ZrP has a pore size of 26.4 nm as displayed in the inset of Figure 1a. Exfoliation of α-ZrP causes the coexistence of mesopores and macropores, as well as the scattered pore size distribution, which leads to the appearance of artificial pores at around 4 nm (see the inset of Figure 1b−d). In addition, exfoliated α-ZrP and freshly reduced Ni/ZrP have been changed with the BET surface area of 26.1 m$^2$/g, pore volume of 0.1 cm$^3$/g, and pore diameter of 14.3 nm compared with those of α-ZrP (Table 1, entries 1 and 2), which is explained by the intercalation of C$_6$H$_{13}$NH$_2$ into Zr(HPO$_4$)$_2$·H$_2$O layers shown in Figure 1b,c.

Comparing Figure 2b with 2c, we can see that the crystal α-ZrP nanoplatelets tend to be transparent and rolled up on the edge of the nanoplatelets, which shows that α-ZrP are

![Figure 1. BET isotherms and corresponding BJH plots of (a) pristine α-ZrP, (b) exfoliated α-ZrP, (c) freshly reduced Ni/ZrP, and (d) spent Ni/ZrP.](image-url)

Table 1. Textural Properties of α-ZrP and Ni/ZrP Based on BET Measurements

| entry | sample       | surface area (m$^2$/g) | pore volume (cm$^3$/g) | pore size (nm) |
|-------|--------------|------------------------|------------------------|---------------|
| 1     | pristine α-ZrP | 22.5                   | 0.17                   | 26.4          |
| 2     | exfoliated α-ZrP | 26.1                   | 0.11                   | 14.3          |
| 3     | freshly reduced Ni/ZrP | 29.3                   | 0.12                   | 16.2          |
| 4     | spent Ni/ZrP | 20.4                   | 0.10                   | 9.1           |

The catalyst characterization includes BET and BJH measurements to evaluate the surface area, pore volume, and pore size distribution. These properties are crucial for understanding the catalytic activity and selectivity of the Ni/ZrP catalyst. The exfoliation process using n-hexylamine leads to a significant increase in surface area and a decrease in pore size, favorable for catalytic reactions.

In Figure 2a−g, we can see scanning electron microscopy (SEM) images of pristine α-ZrP, transmission electron microscopy (TEM) images of α-ZrP, and Ni/ZrP catalysts, as well as the nickel particle size distribution of freshly reduced Ni/ZrP and spent Ni/ZrP. The images demonstrate the structural integrity and particle size distribution of the catalysts, which are essential for catalytic performance.

The cryo-transmission electron microscopy (cryo-TEM) images in Figure 2h−i show the average particle size and thickness of the α-ZrP hexagonal nanoplatelets. The data confirm the overall appearance of pristine α-ZrP and the effectiveness of the Ni/ZrP catalysts in the HDO reaction.
exfoliated by C6H13NH2 successfully. In Figure 2d, we can observe that very tiny particles of NiO/ZrP are evenly dispersed over the surface of α-ZrP, whereas the Ni particles of freshly reduced Ni/ZrP were aggregated into larger particles with the Ni(111) facet, possessing metal stripes with d = 0.2 nm \(^{28}\) (see Figure 2e). Figure 2f shows the TEM image of Ni/ZrP, from which we can observe that the reduced Ni particles have an average size of about 30.3 nm on the α-ZrP layers.

The elemental mapping images (P, Zr, and Ni) of the freshly reduced Ni/ZrP catalyst are shown in Figure 3. We can observe that the P and Zr elements are homogeneously distributed on the ZrP carrier in Figure 3a,b, respectively, whereas the Ni element is distributed with cluster shapes, which is consistent with the Ni species distribution shown in Figure 3c.

The conventional X-ray diffraction (XRD) patterns of pristine α-ZrP, exfoliated α-ZrP, Ni\(^{2+}\)/ZrP, NiO/ZrP, freshly reduced Ni/ZrP, and spent Ni/ZrP are given in Figure 4I(a–f), respectively. In the case of α-ZrP, the peaks appearing at 2θ = 10.5°, 2θ = 20°, and 2θ = 25° are the characteristic peak of α-ZrP, corresponding to the (002), (110), and (112) planes, respectively.\(^{25}\) After being exfoliated by C\(_6\)H\(_{13}\)NH\(_2\), the reflecte d peaks of (110) and (112) planes have been transferred to 2θ = 7.7° and 11.5° by comparing Figure 4I(a) and 4I(b). In addition, the (002) planes transferred to 2θ = 3.8° can be observed via the analysis of the small angle (2θ = 0.6°-5°) of pristine α-ZrP and exfoliated α-ZrP (Figure 4II). According to Bragg’s law, the d of exfoliated α-ZrP at 2θ = 3.8° has been increased to 2.32 nm compared with that of pristine α-ZrP at 2θ = 10.5° with 0.74 nm. In Figure 4c, the peaks at 2θ = 9.3° and 28.2° show the formation of nickel phosphate

Scheme 1. Structure Unit of Layered α-ZrP\(^*\)

\(^*\)Gray ball: Zr atom, purple ball: P atom, red ball: O atom, and white ball: H atom.
hydrate (PDF-#31-0909), which can prove the cation exchange of $(\text{C}_6\text{H}_{13}\text{NH}_3)_2^{2+}$ with $\text{Ni}^{2+}$. $\text{Ni}(111)$, $\text{Ni}(200)$, and $\text{Ni}(220)$ appear at $2\theta = 44.6^\circ$, $51.4^\circ$, and $75.8^\circ$, respectively, by comparing Figure 4I(d) and 4I(e), which illustrates the reduction of $\text{Ni}$ oxidation species on the ZrP carrier. Additionally, the $\text{Ni}$ particles agglomerate into larger ones with an average particle size of 52 nm (Figure 2h) after the reaction, facilitating that the XRD intensity of the spent catalyst is enhanced (see Figure 4If).

As shown in Figure 5, the weight of $\text{Ni}/\text{ZrP}$ loses 6.7% during the whole heating process, which is caused by the decomposition of $\text{Zr(HPO}_4)_2\cdot\text{H}_2\text{O}$. Three strong ion current signals of $\text{H}_2\text{O}^+$ $(m/z = 18)$ at about 310, 450, and 670 °C also prove the fact that $\text{H}_2\text{O}$ is released from the dehydration of $\text{P}–\text{OH}$ groups in ZrP.

To understand the change in the acidic sites of the ZrP-type catalyst, the pyridine-adsorbed Fourier transform infrared (Py-FTIR) spectra and acid density of pristine $\alpha$-ZrP, exfoliated $\alpha$-ZrP, freshly reduced $\text{Ni}/\text{ZrP}$, and spent $\text{Ni}/\text{ZrP}$ at different desorption temperatures (40, 150, and 240 °C) are shown in Figure 6 and Table 2, respectively. In Figure 6a and Table 2, entry 1, there are two bands at around 1450 and 1540 cm$^{-1}$, which represent the Lewis (L) and Brønsted (B) acidic sites, respectively. The L and B acidic sites are originated from the vacant orbits of $\text{Zr}^{4+}$-contained framework of four-coordination and $\text{P}–\text{OH}$ groups, respectively. In Figure 6b and Table 2, entry 2, the L acid density increases and the B acid density is seriously lost, which are caused by the intercalation of $\text{C}_6\text{H}_{13}\text{NH}_3$ into the $\text{Zr(HPO}_4)_2$ layer. In Figure 6c,d and Table 2, entries 3 and 4, the acidity of the $\text{Ni}/\text{ZrP}$ catalyst is mainly in the form of L acid, along with the L acid density of spent $\text{Ni}/\text{ZrP}$ seriously lost. The L acid densities of all the samples tend to decrease via exfoliation, ion exchange, calcination, and reduction, and they decrease with the increase of evacuation temperature simultaneously (Table 2).

The FTIR spectra of $\alpha$-ZrP, exfoliated $\alpha$-ZrP, $\text{Ni}^{2+}/\text{ZrP}$, $\text{NiO}/\text{ZrP}$, and freshly reduced $\text{Ni}/\text{ZrP}$ are shown in Figure 7. The peaks at 3594, 3510, and 1620 cm$^{-1}$ are from $\text{H}_2\text{O}$ symmetric and asymmetric stretching and bending vibrations. In Figure 7a, the peak at 532 cm$^{-1}$ ascribes to $\text{Zr}–\text{O}$ group deformation vibration, and the strong band in the range of 965–1120 cm$^{-1}$ is characteristic of $\text{PO}_4$ group stretching vibrations. In Figure 7b, the peak at 2960 is assigned to $–\text{CH}_3$ stretching vibrations, the peaks at 2920 and 2850 are from $–\text{CH}_2$ stretching vibrations, and the band in the range of 1590–1650 cm$^{-1}$ and the peak at 1202 cm$^{-1}$ ascribe to $–\text{NH}$ and $–\text{N}–\text{C}$ stretching vibrations from $\text{C}_6\text{H}_{13}\text{NH}_3$, which demonstrates the exfoliation of pristine $\alpha$-ZrP by $\text{C}_6\text{H}_{13}\text{NH}_3$. In Figure 7c, all the peaks associated with $\text{C}_6\text{H}_{13}\text{NH}_3$ disappear, and an absorption band at 1383 cm$^{-1}$ related to the $\text{NO}_3$ residue was observed during the cation exchange of $\text{C}_6\text{H}_{13}\text{NH}_3^+$ with $\text{Ni}^{2+}$, indicating that almost all

Figure 3. Elemental mapping images of (a) P, (b) Zr, and (c) Ni in the freshly reduced $\text{Ni}/\text{ZrP}$ catalyst.

Figure 4. (I) Conventional XRD patterns of (a) pristine $\alpha$-ZrP, (b) exfoliated $\alpha$-ZrP, (c) $\text{Ni}^{2+}/\text{ZrP}$, (d) $\text{NiO}/\text{ZrP}$, (e) freshly reduced $\text{Ni}/\text{ZrP}$, and (f) spent $\text{Ni}/\text{ZrP}$. (II) Small angle of XRD patterns of (a) pristine $\alpha$-ZrP and (b) exfoliated $\alpha$-ZrP.

Figure 5. TGA–mass spectrometry (MS) curve of freshly reduced $\text{Ni}/\text{ZrP}$ under $\text{N}_2$ flow with the heating rate of 20 °C/min.
C6H13NH3+ is replaced by Ni2+. The NO3− peak becomes broad gradually after catalyst calcination and reduction shown in Figure 7d,e (for specific process, see Scheme 2). There is no P−OH stretching at around 2300 cm−1 associated with B acid, showing the fact that the acidity of Ni/ZrP is mainly in the form of L acid.

2.2. Catalytic Performance. The catalyst was tested in the HDO of HMF to produce DMF. During the reaction process, DHMF and MF were the main intermediates along with different reaction pathways. Meanwhile, the products mainly contained the O-containing intermediates [e.g., 5-methyl-2-furfurylalcohol (MFA) and 2,5-dihydroxymethyltetrahydrofuran (DHMTHF)] and the over-hydrogenated products such as DMTHF and 2,5-hexanediene (HD) from the furan ring opening of DMF. Figure 8 shows the effect of different reaction parameters in the HDO reaction of HMF, such as (a) temperature, (b) time, (c) pressure, and (d) HMF dosage.

**Table 2. L Acid Density of α-ZrP and Ni/ZrP after Evacuation at Different Desorption Temperatures**

| entry | sample            | t (°C) | L acid density (μmol/g) |
|-------|-------------------|--------|-------------------------|
| 1     | α-ZrP             | 40     | 114.8                   |
|       |                   | 150    | 63.1                    |
|       |                   | 240    | 31.9                    |
| 2     | exfoliated α-ZrP  | 40     | 478.2                   |
|       |                   | 150    | 388.8                   |
|       |                   | 240    | 257.0                   |
| 3     | freshly reduced Ni/ZrP | 40 | 192.8                   |
|       |                   | 150    | 88.3                    |
|       |                   | 240    | 59.0                    |
| 4     | spent Ni/ZrP      | 40     | 69.2                    |
|       |                   | 150    | 8.3                     |
|       |                   | 240    | 0.0                     |

**Figure 6.** Py-FTIR spectra of (a) pristine α-ZrP, (b) exfoliated α-ZrP, (c) freshly reduced Ni/ZrP, and (d) spent Ni/ZrP after pyridine desorption at (A) 40, (B) 150, and (C) 240 °C.

**Figure 7.** FTIR spectra of (a) pristine α-ZrP, (b) exfoliated α-ZrP, (c) Ni2+/ZrP, (d) NiO/ZrP, and (e) freshly reduced Ni/ZrP.

C6H13NH3+ is replaced by Ni2+. The NO3− peak becomes broad gradually after catalyst calcination and reduction shown in Figure 7d,e (for specific process, see Scheme 2). There is no P−OH stretching at around 2300 cm−1 associated with B acid, showing the fact that the acidity of Ni/ZrP is mainly in the form of L acid.

2.2. Catalytic Performance. The catalyst was tested in the HDO of HMF to produce DMF. During the reaction process, DHMF and MF were the main intermediates along with different reaction pathways. Meanwhile, the products mainly contained the O-containing intermediates [e.g., 5-methyl-2-furfurylalcohol (MFA) and 2,5-dihydroxymethyltetrahydrofuran (DHMTHF)] and the over-hydrogenated products such as DMTHF and 2,5-hexanediene (HD) from the furan ring opening of DMF. Figure 8 shows the effect of different reaction parameters in the HDO reaction of HMF, such as (a) temperature, (b) time, (c) pressure, and (d) HMF dosage.

**Figure 8a** shows the effect of temperature on the catalytic reaction, and we observed that the HMF conversion changes from 84.8 to 97.2% as the temperature increases from 180 to 260 °C. DMF reaches a higher yield of 63.9% at 240 °C, accompanied with the intermediate: MF (6.3%), over-hydrogenated products: DHMTHF (6.2%) and tetrahydro-5-methyl-2-furanmethanol (MTHFA) (1.3%), and the furan ring-opening product: HD (4.0%). Among them, the HD yield continues to increase caused by furan opening at higher temperature. However, the DMF yield tends to decrease at 260 °C, which is caused by the production of small molecular alkanes from the cracking of chains on the furan ring and coke formation at the higher temperature. Therefore, too high temperature is not favorable for DMF formation.

**Figure 8b** shows the effect of reaction time on HMF conversion under 5 MPa H2 and 240 °C: HMF is almost converted after 8 h, and its yield reaches a maximum yield of 68.1% at 20 h, followed by MF (8.4%), DHMTHF (5.2%), MTHFA (0.2%), and HD (2.9%) formation. Thus, a reasonable control of temperature and pressure with an appropriately prolonged reaction time can suppress the production of byproducts and intermediate products.
Scheme 2. Schematic Diagram of the Catalyst Synthesis Process; (A) Pristine $\alpha$-ZrP, (B) $\alpha$-ZrP Exfoliated by C$_6$H$_{12}$NH$_2$, (C) Ion Exchange of Exfoliated $\alpha$-ZrP with Ni(NO$_3$)$_2$, and (D) Formation of Ni/ZrP via Calcination and Reduction

(A) Pristine $\alpha$-ZrP

(B) Exfoliation

(C) Ion exchange

(D) Calcination and reduction

Figure 8c represents the effect of pressure on HMF conversion, from which we observe that HMF conversion reaches more than 97% when $H_2$ pressure is more than 2 MPa, and the DMF yield and DHMTTHF increase consecutively as the reaction pressure increases. Thus, increasing $H_2$ pressure is conducive for DMF and byproduct (such as DHMTTHF) production.

Figure 8d shows the effect of HMF dosage on catalytic conversion: HMF is almost converted under all HMF dosages, with 250 mg as the optimal dosage, and DMF gains the highest yield under the corresponding reaction conditions. However, the DMF yield decreases and the MF yield increases with an increase of HMF dosage, which is caused by the insufficient Ni/ZrP catalytic activity in this HDO process.

Conclusively, DMF reaches a maximum yield of 68.1%, with HMF converted completely under the reaction condition of 5 MPa $H_2$, 240 °C, and 20 h.

To further clarify the MF distribution, we conducted an HDO experiment of HMF within the initial 5 h under optimal conditions. In Figure 8e, the MF yield trend undergoes an increase first before 2.5 h and then decreases after 2.5 h, whereas the DMF yield continues to increase for 5 h, demonstrating that part of MF has been converted to DMF. The other byproducts, such as DHMTTHF and HD, retain a low yield as the time goes on, showing the existence of MF as the important intermediate.

2.3. Possible Reaction Pathway. The two distinct pathways were associated with the production of DMF from HMF, and MF is produced as an intermediate in the pathways (see Scheme 3). Interestingly, MF is detected during all the batch catalytic experiments in our study. Moreover, it possesses a higher proportion and plays a key role in all of the over-hydrogenated products, which also proves HDO reaction pathway from HMF into DMF via MF. Additionally, the detection of a small amount of DHMTTHF (over-hydrogenated product) explains another HDO pathway from HMF into DMF via DHMDF (as well as MFA, all with low productivity, and the yield cannot be calculated by the minimum detection limit of GC). Meanwhile, the byproducts mainly also contained over-hydrogenated products such as tetrahydro-5-methyl-2-furanmethanol (MTHFM) and DHMTHF and HD generated by DMF furan ring opening and hydration. L acidity of Ni/ZrP favors the mentioned conversion pathway compared with other researchers’ works. For example, Nakagawa and Tomishige have reported that HMF cannot produce MF catalyzed by Ni-Pd/SiO$_2$ without L acid, which may be explained by the fact that the L acid sites on Ni/ZrP would effectively accelerate the cleavage of the $\text{-CH}_2\text{OH}$ bond prior to C=O bond in HMF.

In addition, Saha and Abu-Omar have studied the HDO of HMF over Ni/C without L acids, and Ni/C can be accounted for only 10% HMF conversion with the formation of a trace amount of DMF. Therefore, the insight into the conversion from HMF to DMF confirms the reaction pathway proposed by some teams.

To corroborate this hypothesis, we carried out the controlled HDO reactions over Ni/ZrP by taking intermediate products (MF and DHMDF) as the substrate (see Table 3). When MF was used as the substrate, DMF acquires a yield of 42.6%. On the contrary, when DHMDF was employed as the substrate, the DMF yield is just 6.9%.

According to the obtained experimental results and reported studies, a brief reaction pathway for the HDO of HMF to DMF is proposed in Scheme 4. First, Ni/ZrP is facilely converted into Ni and ZrP with metal and acid functionalities for activating $H_2$ and $\text{-CH}_2\text{OH}$ groups, respectively. The oxygen in the $\text{-CH}_2\text{OH}$ of HMF is activated by the Lewis acidic sites of Zr$^{4+}$ (originated from the vacant orbit of Zr), which is easily hydrodeoxygenated to MF as the primary intermediate because of attacking of H atoms activated by the neighboring Ni metal. Second, the oxygen in the carbonyl group of MF is activated by the Zr$^{4+}$ species, followed by hydrogenolysis via MFA. MFA is a precursor to be converted into DMF, which means that HMF was transformed into MFA directly or indirectly during the hydrogenolysis process. Besides the main pathway, the side products such as MTHFA and HD were observed in these cases, which is responsible for the unwanted furan ring hydrogenation of MFA and furan ring opening and hydration of DMF. In terms of these facts, the reaction pathway mentioned via the MF intermediate was further confirmed.

2.4. Catalyst Stability. To investigate the stability of the prepared catalyst, we selected the reaction condition of 240 °C, 12 h, and 5 MPa $H_2$ pressure as our testing object. After each reaction, the catalyst was filtered, washed three times with ethanol ($0.22 \mu m$ Millipore filter), and dried at 60 °C overnight. The collected catalyst was recalcined at 400 °C under air atmosphere for 3 h and reduced at 400 °C for 2 h.
with a heating rate of 4 °C/min before the next recycling experiments. Figure 9 shows the yield of DMF and Ni content of Ni/ZrP versus Ni/ZrP catalyst usage cycles. It was found that the yield of DMF and Ni content of Ni/ZrP show a positive correlation during the process. We summarize that DMF can retain 52.8% of its original yield with Ni elemental content decreasing from 18.2 to 12% after five consecutive cycles. The continuous leaching Ni species can explain the decreasing activity of Ni/ZrP during the batches of testing experiments. As we know, the Ni species performs a key role in the selective conversion of C=O, C≡C, and C−O bonds of HMF, and leaching Ni also breaks the balanced surface metal−acid sites of the catalyst.

The Raman spectra of the freshly reduced Ni/ZrP (a) and spent Ni/ZrP (b) are demonstrated in Figure 10. Comparing Figure 10a with 10b, we can see that the significant bands at 1375 cm⁻¹ from C−C skeleton modes associated with chemical structures consist of condensed benzene rings and the G peak at around 1590 cm⁻¹ from disordered graphite. Therefore, the coke deposition can explain the activity decline of the catalyst to some extent. Besides, the position between 22° and 35° of the peak in the low angle region corresponds to the (002) peak of graphite, caused by the stacking of the graphitic basal planes of char crystallites (see Figure 4d). As the reaction proceeds, the pore volume and pore size of the catalyst become smaller, thereby resulting in the decreased BET surface area (see Figure 1d and Table 1, entry 4).

In order to observe the coke deposition more intuitively, the TEM images of the spent Ni/ZrP before and after recalcination at 400 °C under air atmosphere are shown in Figure 11. Figure 11a,b depicts the layers of dark spots, which were resulted from coke deposition, while the spots disappear after the catalyst is recalcined, shown in Figure 11 c,d. Thereupon, Ni/ZrP recalcination we mentioned is an effective way to dispel the coke. In a word, the catalytic activity loss of Ni/ZrP can be summarized as follows: (i) Ni particle size increases; (ii) Ni species is lost, which breaks the balance of metal−acid; and (iii) formation of coke after the catalytic reaction. However, based on Figure 8, the main deactivation of the Ni/ZrP catalyst is deduced by Ni leaching.
suppressing Ni leaching to enhance the catalytic stability are in progress.

3. CONCLUSIONS

Pristine α-ZrP was synthesized via a hydrothermal technology, followed by exfoliation with C6H4N2H to expand the surface area and porosity. Ni/ZrP was prepared by ion exchange of exfoliated α-ZrP and Ni(NO3)2·6H2O followed by calcination and reduction at elevated temperatures. Ni/ZrP is characterized by a series of techniques, and its catalytic performance was tested in the HDO of HMF to DMF. We proposed a conversion path from HMF to DMF with MF as the main intermediate and found that the synergistic effect of metallic Ni and L acidic sites created from the zirconium vacant orbits on α-ZrP is favorable for the hydrogenolysis of C=OH groups of HMF. Ni/ZrP has a better performance on HDO of HMF to DMF with the target product yield of 68.1% in the first run and presents the stability by retaining its original activity of 52.8% after five runs.

4. EXPERIMENTAL SECTION

4.1. Materials. All chemical reagents were used directly without further purification. Dichlorooxozirconium (ZrOCl2·8H2O, AR, ≥98%), C6H4N2H2 (AR, ≥99%), THF solvent (AR, ≥99%) and nickel nitrate (Ni(NO3)2·6H2O, AR, ≥98%) were purchased from Shanghai Macklin Biochemical Co., Ltd. Phosphoric acid (H3PO4) solution (85 wt %) was purchased from Shanghai Macklin Biochemical Co., Ltd. Dichlorooxozirconium (ZrOCl2·8H2O, AR, ≥98%) was bought from J&K Scientific Ltd. DMF (C3H6O2, AR, ≥99%) was purchased from J&K Scientific Ltd. MFA (C6H8O2, AR, ≥97%) was bought from Energy Chemical Co., Ltd. Ethanol absolute (AR, ≥99.7%) was purchased from Tianjin Yongda Chemical Reagent Co., Ltd.

4.2. Catalysts Preparation. 4.2.1. Preparation of Pristine α-ZrP. According to the literature,14 4.0 g of ZrOCl2·8H2O was mixed with 40.0 mL (3.0 M) of H3PO4 solution and sealed into a Teflon-lined pressure vessel and heated at 200 °C for 24 h. After the reaction, the solid was filtered with deionized (DI) water through a 0.22 μm Millipore filter (Jinteng, China) until the filtrate was neutral. The product was dried at 60 °C overnight to obtain 2.4 g of pristine α-ZrP.

4.2.2. Exfoliation of Pristine α-ZrP. Referring to the literature,50 pristine α-ZrP was interstratified by C6H4N2H2. Briefly, 0.839 g of C6H4N2H2 was dissolved in 20 mL of water, and then 1.0 g of solid α-ZrP was added into the mixture. The mixture was stirred for 24 h at room temperature. The solid phase was centrifuged at 10 000 rpm for 10 min (RCF 10610, 10610TG16-WS, Hunan Xiangyi Centrifuge Co. Ltd., China) in DI water twice and then centrifuged in acetone to remove extra water and C6H4N2H2. The sample was dried at 60 °C to obtain the exfoliated α-ZrP.

4.2.3. Preparation of NiO/ZrP and Ni/ZrP. A solution was prepared by dissolving 4.5 g of Ni(NO3)2·6H2O in 50 mL of DI water. An amine intercalation sample (0.5 g) was added to this solution, and the mixture was refluxed for 24 h at 80 °C. In this step, Ni2+ was loaded on the layers of α-ZrP via ion exchange. The solid Ni2+/ZrP was recovered from the solution by centrifugation, washed extensively with DI water, and dried at 60 °C overnight. Last, the solid was calcined under air atmosphere at 500 °C for 4 h in a muffle furnace (FO310C, Yamato Scientific Co., Ltd., Tokyo, Japan), denoted as NiO/ZrP.

Prior to the experiment, NiO/ZrP was reduced in flowing H2 (30 mL/min, purity ≥ 99.9%) at a heating rate of 4 °C/min to 400 °C for 2 h to obtain freshly reduced Ni/ZrP.

4.3. Catalyst Characterization. XRD (X’Pert-ProMPD, PANalytical Company, Almelo, Netherlands) operated at 40 kV and 40 mA with Cu Ka radiation (λ = 0.154 nm) was performed to compare the crystallinity of pristine α-ZrP, exfoliated α-ZrP, NiO/ZrP, freshly reduced Ni/ZrP, and spent Ni/ZrP at room temperature.

The specific surface area of samples was measured by the BET equation, and the pore size distribution was investigated by the BJH method depending on N2 adsorption–desorption at −196 °C (IQ-2, Quantachrome Instruments, Boynton Beach, FL).

The structural and morphological information of pristine α-ZrP was obtained by using a cold field emission scanning electron microscope (S-4800, Hitachi, Tokyo, Japan). Pristine α-ZrP, exfoliated α-ZrP, and freshly reduced Ni/ZrP were observed by a high-resolution transmission electron micro-

Table 3. Controlled Experiments for DMF Production from Intermediates HDO

| entry | substrate | conversion (%) | product yields (%) |
|-------|-----------|----------------|--------------------|
|       |           |                | DMF                | DHMTHF | MTHFA | HD   | MFA |
| 1     | MF        | 96.8           | 42.6              | 3.8    | 0.5   | 1.5  |     |
| 2     | DHMTHF    | 96.3           | 6.9               | 3.7    | 0.2   | 8.4  | 0.7 |

“Experimental conditions: 1.98 × 10−3 mol substrate, 0.1 g catalyst, 240 °C, 5 MPa H2, 12 h, rotating speed: 500 rpm, and 40 mL THF.”
scope (JEM-2100, JEOL Ltd., Tokyo, Japan) equipped with an energy-dispersive X-ray spectrometer (Thermo Scientific UltraDry, Waltham, MA) to compare their microstructure. All samples were dispersed in ethanol absolute and ultra-sonicated 10 min for TEM analysis.

Coke deposition on the catalyst was analyzed by a Raman microscope equipped with the 523 nm excitation wavelength laser diode and back-scattering configuration (Lab RAM HR800-LS55, Horiba Jobin-Yvon, Paris, France), and the spectral resolution was about 0.7 cm\(^{-1}\).

The Ni elemental content (wt %) of freshly reduced Ni/ZrP and used Ni/ZrP was measured by an inductively coupled plasma mass spectrometer (Agilent 7900, Agilent Technologies, Santa Clara, CA). All the samples were digested with 1 mL (30 wt %) of H\(_2\)O\(_2\) and 2 mL (65 wt %) of HNO\(_3\) at 100 °C for 12 h and diluted to the desired concentration for test.

The thermal stability and composition of the prepared catalyst are investigated by thermogravimetric analysis (TGA; Linseis STA PT1600, Selb, Germany) under N\(_2\) flow (purity \(\geq 99.9\%\)) with a heating rate of 20 °C/min up to 1100 °C. H\(_2\)O released from the catalyst decomposition is monitored via the
mass spectrometer (Pfeiffer Omnistar, Assassin, Germany). In order to investigate whether the B and L acidity was present in the catalysts, the Py-FTIR ( Nicolet 6700, Nicolet Instrument Company, PA) spectrum at an average of 32 scans and a resolution of 4 cm⁻¹ was obtained to analyze the feature. Sample (10 mg) was activated at 200 °C for 0.5 h under vacuum (10⁻⁴ mmHg). The background spectrum was recorded after cooling the sample to 50 °C. Afterward, the sample was exposed to pyridine (Aldrich, GC, ≥99%) vapors for 15 min. The FTIR spectrum for each sample was obtained after pyridine desorption by evacuation for another 0.5 h at 40, 150, and 240 °C, respectively. All the spectra were recorded at room temperature after pyridine desorption at each temperature. The spectra were finally obtained by subtracting the background spectrum previously recorded.

Samples involved in our research were characterized by an FTIR spectrometer ( Nicolet Nexus 10, Thermo Fisher Scientific, Waltham, MA) via the KBr pellet method (samples were analyzed at an average of 32 scans from 400 to 4000 cm⁻¹ at 2 cm⁻¹ resolution).

4.4. Catalytic Performance. Freshly reduced Ni/ZrP (0.1 g) was mixed with 0.25 g (1.98 × 10⁻³ mol) of HMF in 40 mL of THF solvent, and the reactions with specific reaction time were performed in a 100 mL autoclave (MS-100-C276, Anhui Kemi Machinery Technology Co., Ltd, Hefei, China) under the stirring rate of 500 rpm. Before each run, the autoclave was purged three times with H₂ to exclude the air residual in the reactor. The reaction was conducted at a certain temperature, H₂ pressure (inflated at room temperature), and time. After the reaction, the reactor was quickly quenched in an ice-water bath. Subsequently, filtration steps (through a 0.22 μm Millipore filter) were conducted, and the reaction solution was collected to analyze the products. The products were quantitatively analyzed by a gas chromatograph ( GC-2014C, Shimadzu, Kyoto, Japan) equipped with a flame-ionized detector and a HP-Innowax capillary column (30 m × 0.25 mm, 0.25 μm film thickness, Hewlett Packard, Palo Alto, CA). The products were qualitatively analyzed by a gas chromatograph—mass spectrometer (Trace 1300-ISQ, Thermo Fisher Scientific Inc., Waltham, MA) with a HP-Innowax column, and their yields were calculated based on the internal standard by using cyclohexanone as the internal standard. The conversion (C mol, %) of HMF and the yield (C mol, %) of product were calculated as follows:

\[
\text{Conversion (C mol, %)} = \frac{\text{Mole of HMF converted}}{\text{Mole of HMF fed}} \times 100
\]

\[
\text{Yield (C mol, %)} = \frac{\text{Mole of product produced}}{\text{Mole of HMF fed}} \times 100
\]

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