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Adsorption Configuration-Determined Selective Hydrogenative Ring Opening and Ring Rearrangement of Furfural over Metal **Phosphate**

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80.2% yield of 1,2,5-pentanetriol was reported for the first time via a hydrogenative ring-opening route over CoP, whereas Ni₂P shows a high catalytic efficiency for cyclopentanol with a 62.8% yield via a hydrogenative ring-rearrangement route. Based on the catalytic performance of Pd/C and the result of attenuated total



reflectance-infrared spectroscopy, the route difference is derived from the adsorption configuration of furfural on the catalyst. After loading on the insert support, the metal phosphate/support catalysts show high activity and stability during the recycling experiments. This work provides an effective strategy to regulate the reaction path through an adsorption mechanism and shows the precise synergistic effect of hydrogenation and acid catalysis.

KEYWORDS: metal phosphate, furfural, adsorption configuration, hydrogenative ring rearrangement, hydrogenative ring opening

INTRODUCTION

Biorefining of biomass into high value-added chemicals is a promising route for the future sustainability of the economy. Biomass-derived furfural, which is easily obtained from the dehydration of pentoses, has been commercially available at a low price.¹ It has been considered the most important biobased platform compound for the subsequent transformation to a wide range of high-value chemicals such as furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), furoic acid, 2-methyl furan, 2-methyl tetrahydrofuran, cyclopentanone (CPO), cyclopentanol (CPL), and C₅ linear polyols.² Among these fine chemicals, alcohols (e.g., linear alcohol and CPL) are important commodity chemicals for various upgrades because of the reactivity of the hydroxyl group.

Linear polyols are widely used as building blocks to manufacture polyesters, polyurethanes, and polyethers. The synthesis of biobased pentanediols (such as 1,2-pentanediol and 1,5-pentanediol) has been widely studied using furfural or furfural-derived chemicals (such as FA and THFA) as a reactant via a hydrogenolysis ring-opening reaction at 120-180 °C.³ However, the synthesis of 1,2,5-pentanetriol (PTL), which has special potential as a plasticizer, wetting agent, and solvent, has rarely been reported.^{4,5} Some efforts have been devoted to their synthesis by promoting the hydrolysis of the furan ring over a reduced metal/acidic support (i.e., Ni/ HZSM-5 and Rh-Ir-ReO_x/SiO₂) in water (6.0-8.0 MPa H_2 pressure, 250 °C temperature).⁶ The hydrogenative ring opening of furfural to PTL proceeded with hydrogenation, hydrolysis, and subsequent hydrogenation steps. Unfortunately, the yield of PTL is unsatisfactory (approximately 20%) because the hydrogenolysis reaction tends to be faster than the hydrolysis reaction. The complex reaction route and side reactions make efficient PTL synthesis very challenging.

Meanwhile, CPL is widely applied in the fungicide, fragrance, and pesticide industries. Their biomass-based synthesis aims to replace the petroleum-based cyclization of 1,6-hexanediol or oxidation of cyclopentene. As widely accepted, the conversion of furfural to C-C cyclic compounds (i.e., CPO and CPL) must undergo a series of C=O

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Figure 1. (A) XRD patterns of metal phosphides; (B) TEM micrographs of CoP, (C) Co₂P, and (D) Ni₂P; (E) XPS spectra of metal phosphides.

hydrogenation, ring-rearrangement, hydrogenation, and dehydration steps over reduced metals/solid acids in water (2.0-8.0 MPa H₂ pressure, 140–180 °C temperature). Many research groups and our group reported various reduced metals (such as Pd, Pt, Ru, Au, Ni, and Co) supported on all types of acidic supports (such as metal oxides, zeolites, double-metal cyanides, metal-organic frameworks, and carbon materials) as bifunctional catalysts for the reaction.⁸ Noble metal-based catalysts commonly show a higher activity because of their efficiency in activating H₂, whereas CPO is the main product because the in situ-produced intermediates and humins can be strongly attached to the metal surface and hinder the C=O hydrogenation of CPO. By contrast, non-noble metal-based catalysts can show the synthesis of CPL, but the catalytic activity is not desirable. Recent studies have suggested that the ring rearrangement proceeds through a two-step hydrolysis and

intramolecular aldol reaction over the Lewis acid catalysis whereas through a one-step Piancatteli reaction over the Brønsted acid catalysis. Both Lewis and Brønsted acids catalyze the ring-rearrangement step, while Brønsted acids easily incur the polymerization of intermediates to macromolecular humins.⁹ The development of highly efficient catalysts for CPL is very important for fine chemicals.

By comparing the synthesis paths for CPL and linear alcohols, both Lewis acid support and reduced metal are important for the hydrogenative ring rearrangement and ringopening reactions. An obvious difference is that the CPL synthesis requires selective C=O hydrogenation, but PTL requires both C=O and furan ring hydrogenation. Recently, transition-metal phosphide nanoparticles have been considered promising candidates to replace noble-metal catalysts in electrochemistry due to their high activities and acid

Table 1. Physicochemical Properties of Catalysts^a

samples	$\binom{S_{\rm BET}}{(m^2/g)}$	pore volume (cm ³ /g)	metal (wt %)	P (wt %)	molar ratio of metal/P	total Lewis acid amount (μmol/g)	strong Lewis acid amount (µmol/g)	Brønsted acid amount (µmol/g)	acid amount (µmol/g)
CoP	15.2	0.139	41.2	40.8	0.53	78.4	56.3	2.3	80.7
Ni ₂ P	10.9	0.055	60.3	24.3	1.30	104.3	43.2	3.5	107.8
Co ₂ P	3.4	0.017	55.3	36.2	0.80	80.2	50.7	15.5	95.7

^{*a*}Correspondingly, framework P has a lower binding energy than monoplasmatic P⁰ (P $2p_{3/2}$, 130.2 eV; P $2p_{1/2}$, 134.6 eV).²⁰ These results indicate the generation of Co^{δ +} and P^{δ -} via the electron transformation from the P atom to Co atoms.



Figure 2. (A) Pyridine-adsorbed FTIR spectra of metal phosphides at 150 °C; (B) MS signals of HD generation over metal phosphides during H_2-D_2 exchange reaction.

compatibility.¹⁰ In thermochemistry, metal phosphides is mainly used in hydrotreating reactions, such as hydrogenation reactions,¹¹ Fischer–Tropsch synthesis,¹² hydrodeoxygenation,¹³ hydrodesulfurization,¹⁴ hydrodenitrogenation,¹⁵ and hydrodechlorination.¹⁶ Practically, they demonstrated their ability to selectively hydrogenate C=O and C=C for cinnamaldehyde by adjusting the adsorption configuration of the reactants on the surface.^{11c} Meanwhile, coordinative unsaturated metal ions on the catalyst surface provide a Lewis acidic nature.^{13–16} Therefore, transition-metal phosphides may achieve both goals: they boost both hydrogenation and acid-catalyzed reaction steps. It provides the possibility to promote the synthesis of CPL or PTL by regulating the adsorption configuration.

Here, a series of metal-phosphide nanoparticles (i.e., CoP, Co_2P , and Ni_2P) was synthesized with different crystal structures and metal compositions, which show a tailorable Lewis acidity and H₂ activation ability. In the hydrogenative conversion of FFA, CoP shows a PTL yield of above 80%, whereas Ni_2P shows a 62.8% yield of CPL. Attenuated total reflectance—infrared (ATR—IR) spectroscopy clearly illustrates the influence mechanism of adsorption configuration. After loading the nanoparticle on the insert support (i.e., active carbon and silicon dioxide), composite catalysts maintain high activity and selectivity and have excellent stability and recycling performance.

RESULTS AND DISCUSSION

Structural Characteristics of the Metal Phosphide. Metal phosphides were synthesized using a phosphating reduction method.¹⁷ The X-ray diffraction (XRD) patterns of metal phosphides are shown in Figure 1A. The diffraction peaks of all samples are consistent with their crystallographic standard data, which proves that the metal phosphide was successfully synthesized with high crystallinity by the phosphating reduction method. Among them, CoP has an orthorhombic distortion of the hexagonal structure with the Pnma space group, where the Co atom connected to four neighboring Co atoms is coordinated by six phosphorus atoms in a distorted octahedral configuration.¹⁸ Meanwhile, the phosphorus atoms are surrounded by six Co atoms at the corners of a distorted triangular prism. Co₂P and Ni₂P have similar diffraction peaks and a hexagonal structure with a P62m space group, where the phosphorus atoms are ninecoordinated by six metal atoms at the corners of a triangular prism and three additional metal atoms on the outside of the three rectangular faces of the triangular prism.^{19a,b} Meanwhile, there are two types of metal atoms (i.e., M_1 and M_2) in the M_2P structure. The M_1 atom is connected to eight neighboring metal atoms and tetracoordinated by four phosphorus atoms, and the M₂ atom is connected to six neighboring metal atoms and surrounded by five phosphorus atoms in a square pyramid. Compared with Co₂P, the diffraction peak position of Ni₂P has shifted to a larger angle because Ni₂P, which contains a smaller atomic radius (Ni: 0.124 vs Co: 0.125 nm),^{19c} decreases the lattice parameter. As shown by transmission electron microscopy (TEM) (Figure 1B-D), all phosphide particles are nanosized and range from 50 to 100 nm. The type-IV N₂ adsorption-desorption isotherms and pore distribution of all samples in Figure S1 show that there are mesoporous structures generated by particle accumulation. Compared with Co₂P, Ni₂P has a larger Brunauer-Emmett-Teller (BET) surface area and pore volume (10.9 vs 3.4 m^2/g ; 0.055 vs 0.017 cm³/g, respectively). Among these metal phosphides, CoP possesses the largest BET surface area of 15.2 m^2/g and the highest pore volume of 0.139 cm³/g (Table 1).

The surface composition of metal phosphides was studied by X-ray photoelectron spectroscopy (XPS) (Figure 1E). For all samples, the XPS peaks of P_{2p} appear at 129.4 and 130.3 eV (ascribed to $P_{2p3/2}$ and $P_{2p1/2}$ peaks in framework P) and 133.3 and 134.5 eV (ascribed to $P_{2p3/2}$ and $P_{2p3/2}$ and $P_{2p1/2}$ in P^{5+} of surface

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Figure 3. (A) Reaction pathway of the FFA reaction; (B) time-dependent product concentration over CoP; (C) Co₂P; (D) Pd/C. (E) Catalytic performance of the FFA reaction over various catalysts. Reaction conditions: H_2O (10 mL), metal phosphate (0.05 g) or Pd/C (0.1 g), FFA (2.0 mmol), temperature 150 °C, time 6 h, 4.0 MPa H_2 pressure.

 PO_4^{3-}).¹¹ The binding energies of 778.1 and 792.9 eV in the Co_{2p} peaks of Co_2P are characteristic of the $2p_{3/2}$ and $2p_{1/2}$ peaks of framework Co.¹² CoP also shows additional binding energies of 778.6 and 796.6 eV (related to the $2p_{3/2}$ and $2p_{1/2}$ peaks of framework Co, respectively) and 798.5 and 782.1 eV (related to the $2p_{3/2}$ and $2p_{1/2}$ peaks of Co^{2+} of $Co_3(PO_4)_2$, respectively). The Ni 2p spectra of Ni₂P show contributions at 852.6 and 870.1 eV (framework Ni) and 856.1 and 876.5 eV (Ni²⁺ of Ni₃(PO₄)₂).¹⁵ The binding energies of frameworks Co and Ni in metal phosphides are slightly higher than those of metallic Co (Co $2p_{3/2}$, 778.5 eV; Co $2p_{1/2}$, 793.0 eV) and Ni (Ni $2p_{3/2}$, 852.4 eV; Ni $2p_{1/2}$ 869.5 eV). It is worth to be noted that besides the Co²⁺ and Ni²⁺, frameworks Co^{+} and Ni^{+} can also provide Lewis acidity.^{15b}

The elemental analysis results show the metal and P amounts (Table 1). These metal phosphides show similar metal amounts of approximately 50 wt %. However, the molar ratio of metal/P is strikingly lower than the stoichiometric ratio

(i.e., CoP 1:1, Co₂P 1:0.5, and Ni₂P 1:0.5) due to the abundant generation of phosphate from the superficial oxidation of metal phosphides.²¹

As shown in Table 1, the acid content of metal phosphides was determined by the NH₃ pulse purge, which was calculated by the consumed amount of NH₃ (Figure S2). These samples have an acid density of $80-120 \ \mu \text{mol/g}$. Subsequently, the acid type and acid strength were characterized by the pyridineabsorbed Fourier transform infrared (FTIR) spectra. The peaks at 1540 and 1450 cm⁻¹ are attributed to the chemisorbed pyridine on the Brønsted and Lewis acidic sites (Figure 2A). Co₂P possesses both Lewis and Brønsted acidity; the Brønsted and Lewis acid sites result from surface phosphoric acid and framework Co^{δ_+}, respectively.²² Because PO₄³⁻ anions are completely associated with Co²⁺ and Ni²⁺, CoP and Ni₂P show a pure Lewis acidity. The concentration ratio of Brønsted and Lewis acidity was obtained according to the Emeis equation.²³ Combined with the NH₃-TPD results,



Figure 4. (A) Hydrogenation and acid-catalyzed rate of various metal phosphides, (B) catalytic performance of various supported catalysts, (C) catalytic performance of CoP/SiO₂ under different H₂ pressures, (D) recycling performance of CoP/SiO₂. Reaction conditions: H₂O (10 mL), FFA (2.0 mmol), temperature 150 °C, time 6 h, metal phosphide (0.05 g), CoP/C (0.1 g), CoP/SiO₂ (0.1 g), Pd/C (0.1 g). (A,B) 4.0 MPa H₂ pressure, (D) 5.0 MPa H₂ pressure.

the quantified concentrations of Brønsted and Lewis-acid sites were calculated. The Lewis acid amount follows the order Ni₂P $(104.3 \ \mu mol/g) > CoP (78.4 \ \mu mol/g) > Co_2P (80.2 \ \mu mol/g)$ because Ni₂P and CoP have many metal ions on the surface. The Brønsted acid amount follows the order CoP (2.3 μ mol/ g) < Ni₂P ($3.5 \mu mol/g$) < Co₂P ($15.5 \mu mol/g$) due to the lack of metal ions on the catalyst surface and presence of phosphate anions on the Co₂P surface. Meanwhile, the concentration of strong acidic sites was obtained based on the signal at 250 °C (Figure S3). CoP shows more strong Lewis acid (56.3 μ mol/g) than Ni₂P (43.2 μ mol/g) due to the stronger Lewis acidity of Co²⁺. The hydrogen activation ability of metal phosphides was obtained by the H₂-D₂ exchange test. Under 70 °C, the H₂ and D₂ were exchanged, and HD was generated. As shown in Figure 2B, the HD generation rate follows the order CoP > $Ni_2P > Co_2P$. Therefore, the CoP and Ni_2P catalysts could accelerate activated dissociation of hydrogen and subsequently promote the hydrogenation reaction of furfural.

As shown in Figure S4, the thermal stability results for metal phosphides indicate a weight loss at 30-300 °C due to the loss of crystal and noncrystal water. The structure remained intact above 300 °C, which indicates its stability under severe reaction conditions.

Hydrogenative Reaction of Furfural. As previously mentioned, the hydrogenative ring rearrangement of furfural (FFA) to C–C cyclic compounds (i.e., CPL and CPO) involves C=O hydrogenation to generate FA, ring rearrangement to 4-hydroxy-2-cyclopentenone (HCPEO), and subsequent dehydration and hydrogenation reactions (Figure 3A, route 1). A hydrogenative ring opening of FFA to PTL was first reported to involve C=O hydrogenation to form FA,

furan ring semihydrogenation to form dihydrofurfuryl alcohol (DHFA), hydrolysis to form 1,5-dihydroxy-2-pentanone (DHPO), and C=O hydrogenation (route 2). Figures 3B-D and S5 show the temporal evolution of solution composition over CoP, Co₂P, and Ni₂P with Pd/C as a comparison. The amount of PTL and CPL is synchronously increased, which indicates that the hydrogenative ring rearrangement and hydrogenative ring opening are parallel reactions. For the hydrogenative ring rearrangement, the concentration of the intermediate HCPEO is a trace, indicating the C=O hydrogenation of FFA, acid-catalyzed ring rearrangement of FA and C=O hydrogenation of CPO are rate-limiting steps. During the reaction, the concentrations of FA and CPO first increase and then decrease, indicating they are the intermediates for CPL. Meanwhile, the intermediates of hydrogenative ring opening (DHFA and DHPO) have a very low concentration (approximately 2%) in the reaction system, indicating the C=O hydrogenation of FFA and semihydrogenation of FA are rate-limiting steps. These intermediates were verified by gas chromatography (GC)-mass spectrometry (MS) (Figure S6), which is agreed with previous reports.^{6b,24} In addition to the generation of CPL and PTL, some humins are inevitably generated via the polymerization of reactive intermediates, which results in carbon loss. The H₂¹⁸O isotopic labeled experiment shows that the position of the PTL ion peak (m/z = 91), belonging to the fragment of HOCH₂CH₂CH₂CH(¹⁸OH)-) is higher than its counterpart under the $H_2^{16}O$ solvent (m/z = 89, belonging to the fragment of HOCH₂CH₂CH₂CH(¹⁶OH)-), which indicates that ¹⁸O of water was located at the C(2) site of PTL (Figure S7).

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Figure 5. (A) ATR-IR spectra of FFA adsorbed over various metal phosphides. (B) Adsorption kinetics of FFA under CoP and Co₂P.

For comparison, Pd/C shows a complete conversion of FFA, and only 12.0% selectivity CPO is synthesized after 6 h (Figure 3D). Meanwhile, a 65.0% selectivity of THFA is obtained because Pd/C with a rapid hydrogenation ability causes the excessive hydrogenation of FA. The CPL cannot be generated because in situ-produced intermediates and humins can be strong to the noble-metal surface and hinder further C=O hydrogenation of CPO.^{8a} All metal phosphates exhibit powerful bifunctional catalytic properties, including hydrogenation ability and acid-catalyzed ring-rearrangement or ringopening ability. Although metal phosphates have a relatively slow conversion rate, they show an efficient synthesis of final alcohols (i.e., CPL and PTL), and the THFA byproduct cannot be generated. Among these metal phosphates, there are three significant differences in their catalytic performance. First, after 6 h, CoP had the fastest FFA conversion rate, followed by CoP (99.5%) > Ni_2P (98.9%) > Co_2P (83.9%). Second, CoP shows a 60.6% selectivity for PTL and 37.8% selectivity for CPL, while Ni₂P shows high selectivity for cyclic products (CPO and CPL). The reaction mixtures can be further converted with a 99.8% conversion of FFA and 62.9% selectivity of CPL by extending the reaction time to 12 h. Third, the CoP and Ni₂P show a very low amount of humins (less than 4%) due to their pure Lewis acidity, whereas Co₂P suffers a 23.4% carbon loss because of the presence of Brønsted acidity (Figure S8). Finally, PTL and CPL can be selectively synthesized over different metal phosphates with a PTL yield of 60.3% over CoP, and a CPL yield of 62.8% over Ni2P (Figure 3E). The kinetic study of FFA hydrogenation reveals that C=O of furfural hydrogenation is a pseudo-first-order kinetic reaction (Figure S9A). Combined with the result of H_2-D_2 exchange, the catalytic hydrogenation kinetics constant of metal phosphates depends on their H₂ activation ability: $Pd/C (1.23 h^{-1}) > CoP (0.80 h^{-1}) > Ni_2P (0.75 h^{-1}) > Co_2P$ $(0.33 h^{-1})$ (Figure 4A). The adsorption and activation of H₂ is the first step in hydrogenation.

To verify the acid-catalyzed ability of different metal phosphates, a kinetic study of FA conversion was conducted in an N₂ atmosphere. Analogous to the hydrogenation step, the acid-catalyzed step follows the pseudo-first-order kinetics (Figure S9B). According to the NH₃-TPD and Py-FTIR results, the ring-rearrangement kinetics constant is related to the concentration of strong Lewis-acid sites in the order CoP $(0.76 \text{ h}^{-1}, 56.3 \ \mu \text{mol/g}) > \text{Ni}_2\text{P} (0.63 \text{ h}^{-1}, 43.2 \ \mu \text{mol/g}) \approx \text{Co}_2\text{P} (0.47 \text{ h}^{-1}, 50.7 \ \mu \text{mol/g}) > \text{Pd/C} (0.10 \text{ h}^{-1}) (Figure 4A).$ The Pd/C and blank experiment shows a slow catalytic ability

due to the lack of acid sites. Only HCP can be generated under the reaction with no linear products. When THFA was used as a reactant, it cannot be converted under the reaction conditions due to its inertness (Figure S10). These results confirm that the PTL was synthesized via the first semihydrogenation of FA and subsequent hydration over the excellent synergistic effect of hydrogenation catalysis and acid catalysis. To the best of our knowledge, this is the first report on the hydrotreating reaction of FA to PTL.

To facilitate the separation of nanoparticles, CoP was loaded on the inert support (i.e., activated carbon and SiO₂). The TEM, inductively coupled plasma–MS, XPS, and NH₃-TPD results indicate that the supported catalysts have a particle size range of 1–2 μ m and chemical composition (Figure S11), surface properties, and acid properties similar to the parent nanoparticles (Table S1). As shown in Figure 4B, their catalytic activity and selectivity follow the order CoP/SiO₂ (99.9, 76.0%) > CoP (99.5, 60.6%) > CoP/C (99.0, 48.2%). The contact angle test of water indicates that CoP/SiO₂ is the most easily dispersed in the aqueous phase, which is conducive to the accessibility of organic substrates and reactant water (Figure S12).

Subsequently, the H₂ pressure and reaction temperature are optimized over CoP/SiO₂ (Figures 4C and S13). When the H₂ pressure decreased to 1.0 MPa, only 85.5% FFA is converted, and 65.9% selectivity of CPO is obtained. Further increasing the H₂ pressure to 5.0 MPa can promote the generation of PTL with an 80.2% yield because a higher H₂ pressure benefits the semihydrogenation step of FA. Similarly, the main product has changed from cyclic products (i.e., CPO and CPL) to a linear PTL with increase of the reaction temperature. Under the optimal conditions (150 °C, 5.0 MPa), FFA is completely converted with 80.3% PTL selectivity and 80.2% PTL yield over CoP/SiO₂. The supported catalyst is easily separated by filtration and reused after washing with water. After four cycles, the catalyst shows a stable catalytic performance with no apparent degradation of activity and selectivity (Figure 4D). Moreover, the TEM, XPS, and XRD data of the recycled catalysts exhibit a stable crystal structure and chemical properties (Figure S14). Similarly, Co₂P is also stable during the recycled experiment, and the active sites cannot be leached or transformed (Figure S15).

Reaction Path and Catalytic Mechanism. To investigate different reaction paths of metal phosphates, ATR-IR spectroscopy of the adsorbed FFA was carried out to obtain molecular insights into the interaction of the reactant and

catalyst under the reaction conditions. The parent furfural spectra exhibit peaks at 767, 948, and 1016 cm^{-1} (ascribed to the signal of the furan ring group) and 1683 cm⁻¹ (ascribed to the signal of the C=O group).²⁵ Over the surface of Ni₂P and Co_2P , the C=O group peak red-shifted to 1717 cm⁻¹, but the positions of the furan ring peaks remain unchanged.²⁶ Thus, Ni_2P and Co_2P only absorb the C=O group of furfural by a vertical configuration. In contrast, over CoP and Pd/C, both C=O and furan ring group peaks have been red-shifted by approximately 10 and 30 cm⁻¹ (Figure 5A), which suggests that both furan and C=O groups can be adsorbed by a flat configuration. This adsorption configuration ensures highly selective C=O hydrogenation of Ni₂P and Co₂P, whereas both C=O and furan ring hydrogenation of CoP and Pd/C. Compared with Pd/C, the relatively weak hydrogenation ability and abundant acid sites of CoP make a semihydrogenation of the furan ring and subsequent ring opening, instead of the excessive hydrogenation of FA to THFA. To investigate previously reported solvent effects on selective hydrogenation of furfural, where H₂O-mediated protonation favors the selective hydrogenation of asymmetric C=O, methanol was used as the solvent for the hydrogenation reaction.²⁷ After 6 h, FA and THFA were the main products over Ni₂P and CoP (Figure S16). This suggests that selective hydrogenation is determined by the adsorption configuration of the reactant rather than by the H₂O-mediated effect.²⁸ To verify the interaction of the furan ring with the catalyst, an adsorption test of FA from H₂O over various metal phosphides was explored (Figures 5B and S17). The adsorption capacity and rate of CoP is larger than that of Ni₂P and Co₂P. Meanwhile, during the in situ reaction process, the concentration of FA in the reaction liquid mixture cannot be largely detected over CoP, whereas a maximum FA concentration of 10.0-20.0% appeared over Ni₂P and Co₂P. These results indicate the strong interaction of the furan ring over CoP and Ni₂P, which is conducive to the hydrogenation of the furan ring and subsequent ring opening for PTL. The PTL catalytic performance results from the precise synergistic effect of hydrogenation and acid catalysis over metal phosphates.

The blank experiment shows the slow generation of HCP from FA catalyzed by the water-dissociated H⁺, so FA that is not adsorbed by the catalyst tends to form cyclic compounds (Figure S9B).²⁹ To suppress the ring-rearrangement route, the pH of the reaction mixture was adjusted to decrease the concentration of H⁺. When the pH of the reaction solution was increased from 7.0 to 10.5 by adjusting the basic Na₂CO₃, the PTL selectivity increased from 60.6 to 65.7%. In contrast, the acidic reaction solution with a pH of 5 (adjusted by CH₃COOH) caused a large decrease in PTL selectivity (34.1%) and an increase in cyclic compound selectivities (CPL 40.7% and CPO 18.8%), which was accompanied by the 6.3% selectivity of humins by Brønsted acid catalysis (Figure S18). To better verify the relationship between acidity and catalytic performance, a series of in situ titrations was carried out using pyridine and 2,6-di-tert-butylpyridine as titrants. Pyridine can bind both Lewis- and Brønsted-acid sites, whereas 2,6-di-tert-butylpyridine is selective to Brønsted-acid sites.³⁰ For Co₂P, pyridine deactivates acid sites and the main product is changed from CPO to FA, whereas 2,6-di-tert-butylpyridine does not significantly reduce the yield of cyclic compounds, and the amount of carbon loss is greatly reduced (Figure S19). For CoP, 2,6-di-tert-butylpyridine does not change the catalytic

performance. These results indicate that Lewis acidity is responsible for ring rearrangement and hydrolysis steps, while Brønsted acidity tends to induce carbon loss.

CONCLUSIONS

A series of highly tunable metal phosphate nanoparticles was used as a bifunctional catalyst for the hydrogenative ring opening and ring rearrangement of furfural. The hydrogen activation ability, furfural adsorption configuration, and acidity of metal phosphate greatly affect their catalytic ability and selectivity. Compared with the result of Pd/C with THFA as the main product, the CoP shows a PTL yield above 80% due to the flat adsorption of furfural, suitable hydrogenation ability, and acid-catalyzed properties. Ni₂P shows a CPL yield of 62.8% due to the vertical adsorption. Furthermore, these nanoparticles maintain their catalytic activity after loading on the inert support and are easy to separate and be reused at least four times. This work provides an efficient synthetic path for PTL and CPL and shows an interesting strategy of the regulation reaction route by the adsorption configuration reactant.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c05497.

Some catalyst physicochemical properties and catalytic reaction results, namely, N_2 adsorption–desorption isotherms, NH_3 -TPD, pyridine-adsorbed FTIR spectra, thermogravimetric analysis, GC–MS patterns, XRD, TEM micrographs, XPS spectra, the catalytic effect of the Brønsted acid amount, temperature, and pH, catalytic kinetics, contact angle test, and UV–vis absorption spectrum (PDF)

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Notes

The authors declare no competing financial interest.

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