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Unique Catalysis of Nickel Phosphide Nanoparticles to Promote the Selective Transformation of Biofuranic Aldehydes into Diketones in Water

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KEYWORDS: nickel phosphide, heterogeneous catalyst, hydrogenation, biofuranic aldehydes, diketones.

ABSTRACT: Although the development of metal nanoparticle catalysts for organic synthesis has been widely studied, the catalytic potential of 'metal phosphide nanoparticles' has little been studied. Herein, we describe that nickel phosphide nanoparticles (Ni₂P NPs) act as a highly efficient heterogeneous catalyst for the selective transformation of biofuranic aldehydes into diketones, which is a useful biorefinery technology. The biofuranic aldehydes are hydrogenated in water without any additives, giving the corresponding diketones in high yields. The catalytic performance of Ni₂P NPs demonstrated here is significantly different from conventional Ni(0) and NiO NPs, and other metal phosphide NPs, which show no activity, indicating the unique catalysis of Ni₂P NPs. Spectroscopic analyses showed that bifunctional Ni₂P NP catalysis combining their hydrogen-activating ability and surface acidity plays a crucial role, leading to the selective biofuranic aldehydes transformations.

The integration of additional metals into metal nanoparticles (NPs) to obtain nanoallovs represents a promising method for producing novel catalysis or achieving significant improvements that are not possible using single metal NPs.¹⁻³ Nanoalloy catalysts have been broadly employed in diverse areas, such as oil refineries, automobile exhaust gas cleaning, petrochemical manufacturing, fine chemical synthesis, and electrocatalytic and photocatalytic hydrogen evolution reactions.⁴⁻⁶ Many studies on metal-metal nanoalloy catalysts have been reported. However, the catalytic functions of metal-nonmetal or metalmetalloid nanoalloys have not been widely explored.⁷ In this context, metal phosphide NPs, such as Ni₂P and Co₂P NPs, are less common metal-nonmetal nanoalloys that have recently attracted attention as a new family of electrocatalysts for the hydrogen evolution reaction.⁸⁻¹⁰ These nanoalloys have also been applied in hydrotreating reactions in the petroleum industry.^{11–} ¹⁴ However, the study of metal phosphide catalysts in fine and bulk chemical synthesis is extremely rare, despite their high catalytic potential.^{15–20} Therefore, exploring the unique catalytic functions of metal phosphide nanoparticles is of great interest in the field of organic synthesis.21

The transformation of 5-(hydroxymethyl)furfural (HMF) derivatives to give 2,5-diketones has attracted much attention as an important biorefinery technology, because HMF derivatives can be produced from the dehydration of glucose and fructose, and 2,5-diketone products are valuable intermediates for surfactants, polymers, and solvents.^{22–28} Several homogeneous^{29–35} and heterogeneous³⁶⁻⁴² catalysts have been reported for this transformation. However, these catalyst systems inevitably require expensive and rare metals, such as Ir, Pd, Ru, and Au, and the addition of toxic acids, such as hydrochloric acid and phosphoric acid.^{29,32,35,39} The difficulty of catalyst reuse is also problematic.^{32,40} Therefore, the development of a cost-effective and efficient catalytic system for diketone production from the HMF derivatives using highly active nonprecious metals in the absence of organic solvents and additives, which will be a promising and powerful tool for future biorefinery processes, remains highly challenging.

In this study, we report that well-ordered nickel phosphide nanoparticles (Ni₂P NPs) showed high catalytic activity and selectivity for the transformation of HMF derivatives to 2,5diketones in water without any additives. This is the first example of nonprecious metal catalysts for the production of 2,5diketones from HMF derivatives. The outstanding catalytic performance of Ni₂P NPs was very different to those of other metal phosphide NPs and conventional Ni NPs, such as Raney Ni, Ni(0) and NiO, which showed almost no activity. Furthermore, Ni₂P NPs were easily recoverable after the reaction and could be reused without a significant loss in activity and selectivity.

The Ni₂P NPs were synthesized by adding NiCl₂ to 1-octadecene in the presence of hexadecylamine and triphenylphosphite. This mixture was stirred at 120 °C for 1 h in vacuo before increasing the temperature to 300 °C, which was held for 2 h with

stirring under an argon atmosphere to give a black colloidal solution. After cooling to room temperature, the precipitate was recovered by centrifugation. The obtained precipitate was then washed with chloroform-acetone (1:1, v/v), to afford the Ni₂P NPs.⁴³ Other metal phosphide NPs, namely, Fe₂P NPs and Co₂P NPs, and nickel phosphide NPs with different compositions, such as Ni₅P₄ NPs and NiP₂ NPs, were also synthesized using a similar method (see Supporting Information (SI) for details). In the X-ray diffraction (XRD) pattern of the prepared Ni₂P NP, the peak positions are consistent with those of bulk Ni₂P, and weak and broad diffraction peaks that suggested the formation of nanosize Ni₂P (Figure 1a). A high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image of Ni₂P showed that NPs with a mean diameter of 5.4 nm with narrow size distribution (±1.4 nm) were regularly formed (Figure 1b). Energy-dispersive X-ray (EDX) line scan analysis and elemental mapping of Ni₂P NPs confirmed the presence of nickel and phosphorus elemental components distributed homogeneously within each Ni₂P NP (Figure 1c-1f). The corresponding EDX spectrum also revealed the atomic ratio between Ni and P was close to 2:1. These results clearly demonstrated the successful synthesis of uniform Ni₂P NPs.

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Figure 1. (a) XRD pattern of Ni₂P NPs. The reference JCPDS pattern of Ni₂P (03-0953) is also included in the XRD graph. (b) HAADF-STEM image of Ni₂P NPs with (c) EDX line scan analysis and elemental mapping images of (d) Ni and (e) P. (f) Composite overlay image formed from (d) and (e).

Initially, the catalytic potential of metal phosphide NPs was investigated in the hydrogenation of 5-methylfurfural (1) under 20 atm of H₂ at 130 °C in water without any additives. The results are shown in Figure 2a. Interestingly, Ni₂P NPs gave 2,5hexanedione (2) in 38% yield with high selectivity. Nickel phosphide NPs with different compositions, such as Ni₅P₄ and NiP₂, also afforded 2. Although Ni₅P₄ NPs exhibited slightly lower activity than Ni₂P NPs, NiP₂ NPs gave poor yield of 2. Other metal phosphide NPs, Fe₂P and Co₂P NPs, hardly showed any activity, indicating the unique catalysis of nickel phosphide NPs. To our knowledge, this is the first example of the direct conversion of 1 into 2 using a nonprecious metal catalyst.

Next, to improve the catalytic activity of Ni_2P NPs and allow easy handling of the catalyst, Ni_2P NPs were dispersed on several supports, including SiO₂, mordenite, and ZSM-5 (Figure 2b). The support effect provided improved yields of **2**, with Ni_2P /mordenite showing the highest activity, affording **2** in 86% yield under the optimized conditions, which is the highest yield among those previously reported (see SI for details, Table S3). In a control experiment, conventional non-phosphide Ni catalysts, such as Raney Ni, mordenite-supported Ni(0) NPs and NiO NPs (see SI for details), and commercially available bulk Ni₂P were tested in the hydrogenation of **1**. In sharp contrast to the high activity of Ni₂P/mordenite, Raney Ni, Ni(0)/mordenite and NiO/mordenite did not produce **2**, and bulk Ni₂P was almost inactive in the reaction. These results clearly confirmed that the Ni₂P NPs showed high catalytic activity distinguishable from bulk Ni₂P and conventional Ni catalysts. These above results strongly suggested that both phosphidation and nanosizing of the Ni play vital roles in generating the unique catalytic activity of Ni for the transformation of **1** into **2**.



Figure 2. (a) Catalytic performance of various metal phosphide NPs in the hydrogenation of **1**. (b) Catalytic performance of Ni₂P NPs supported on different supports, Raney Ni, mordenite-supported Ni(0) NPs, mordenite-supported NiO NPs, and bulk Ni₂P. Reaction conditions: Catalyst (metal: 6 mol%), **1** (0.25 mmol), H₂O (10 mL), H₂ (20 atm), 130 °C, 2 h.

The present simple catalyst system using Ni₂P/mordenite in water without additives was also applicable to a gram-scale reaction, with 2 g of 1 converted into 2 in 74% isolated yield (Scheme 1a). Furthermore, Ni₂P/mordenite promoted the transformation of platform biomass derivative molecule HMF, affording 1-hydroxy-2,5-hexanedione in 84% yield (Scheme 1b). The reusability of Ni₂P/mordenite was also investigated, because facile catalyst recovery and reuse are the major advantages of heterogeneous catalysts over homogeneous catalysts. After the reaction, the spent Ni2P/mordenite catalyst was easily recovered by simple centrifugation and reused. Ni₂P/mordenite was found to maintain its high activity and selectivity over several recycling experiments without requiring any catalyst pretreatment (Figure 3a). The transmission electron microscopy (TEM) images of the spent Ni₂P/mordenite (Figure S3) showed that the average diameter of the Ni₂P NPs was 5.7 nm, similar to that of the fresh catalyst, which thus confirmed the high durability of the Ni₂P/mordenite. To determine whether the leached Ni species from Ni₂P NPs participated in the reaction, Ni₂P/mordenite was filtered from the reaction mixture at 30% conversion of 1 and the filtrate was treated again under the same reaction conditions. No additional products were formed, as shown in Figure 3b, proving that the reaction occurred on the surface of Ni₂P/mordenite. This result was also consistent with the high reusability of Ni₂P/mordenite, demonstrating its high

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Scheme 1. (a) Gram-scale experiment using Ni₂P/mordenite. (b) Transformation of HMF to 1-hydroxy-2,5-hexanedione using Ni₂P/mordenite.



Figure 3. (a) Ni₂P/mordenite reuse experiments in the transformation of 1 to 2. (b) Hot filtration experiment of Ni₂P/mordenite in the transformation of 1 to 2. Reaction conditions: Ni₂P/mordenite (50 mg), 1 (0.25 mmol), H₂O (10 mL), H₂ (20 atm), 130 °C, 6 h.

durability. These results show that the Ni₂P NP catalyst system is a cost-effective, efficient, and reusable catalytic system for diketone production from HMF derivatives.

To investigate the origin of the specific activity of Ni₂P NPs, X-ray absorption fine structure (XAFS) analysis was performed under ambient temperature and atmosphere. The X-ray absorption near-edge structure (XANES) spectra of Ni foil, NiO references, Ni₂P, Ni₅P₄, and NiP₂ NPs are shown in Figure 4a. The absorption edge energies of Ni_xP_y NPs (Ni₂P, Ni₅P₄, and NiP₂ NPs) were located between Ni foil and NiO standards, indicating that the average oxidation state of Ni species in Ni_xP_y NPs ranged from 0 to 2.¹⁸ In particular, the absorption edge energies of Ni₂P and Ni₅P₄ NPs were close to that of Ni foil, which suggested that the Ni species in Ni₂P and Ni₅P₄ NPs represented metal-like states in air. Fourier transform Ni K-edge extended X-ray absorption fine structure (EXAFS) spectra were also shown in Figure 4b. Ni₂P and Ni₅P₄ NPs showed two peaks at distances of 1.7 Å and 2.3 Å, corresponding to Ni-P and Ni-Ni bond distances, respectively.^{44,45} In contrast, no Ni–Ni bond was detected in the NiP₂ NPs. The catalytic activities of Ni₂P and Ni₅P₄ NPs were superior to that of NiP₂ NPs, as shown in Figure 2a, indicating that the Ni–Ni bond in Ni_xP_y NPs played an important role in promoting the transformation of 1 to 2.

The electronic states of surface Ni and P in the Ni₂P NPs were also investigated by X-ray photoelectron spectroscopy (XPS). The Ni 2p spectrum of Ni₂P NPs showed Ni $2p_{3/2}$ and Ni $2p_{1/2}$ binding energy peaks, located predominantly at 853.1 eV and



Figure 4. (a) Ni K-edge XANES spectra of Ni foil, NiO, Ni₂P NPs, Ni₅P₄ NPs, and NiP₂ NPs. (b) Fourier transform k^3 -weighted EXAFS of Ni foil, NiO, Ni₂P NPs, Ni₅P₄ NPs, and NiP₂ NPs, and fitting results for Ni₂P, Ni₅P₄, and NiP₂ NPs.



Figure 5. XPS spectra of (a) Ni 2p and (b) P 2p for Ni₂P NPs.

870.1 eV, respectively, which were close to those of metallic Ni $2p_{3/2}$ (852.8 eV) and Ni $2p_{1/2}$ (870.0 eV) (Figure 5a). These data were consistent with the XANES results (Figure 4a). The P 2p spectrum showed two peaks, indicating the coexistence of phosphorus atoms with different electronic states on the surface of the Ni₂P NPs (Figure 5b). The first peak at 129.5 eV was close to that of P⁰ (130.0 eV) and assigned as P^{5–} (0 < δ < 1),^{46,47} while the other peak at 134.4 eV was assigned to unreduced phosphate species PO₄^{3–} arising from the superficial oxidation of Ni₂P NPs.⁴⁸

To elucidate the reaction pathway from 1 to 2, several control experiments were conducted (Scheme 2). First, the reaction was conducted using 5-methylfurfuryl alcohol as the starting material in the presence of Ni₂P NPs in water under pressurized H₂, similar to the conditions shown in Figure 2. This resulted in 96% conversion of 5-methylfurfuryl alcohol into 2 (Scheme 2a). Furthermore, 5-methylfurfuryl alcohol was transformed into 3hexene-2,5-dione under a N₂ atmosphere instead of under H₂ (Scheme 2b). This ring-opening reaction is known to occur using acid catalysts.³² We also confirmed that 3-hexene-2,5-dione was hydrogenated to 2 by Ni₂P NPs (Scheme 2c). These results suggested that 1 transformed into 2 through the formation of 5methylfurfuryl alcohol and 3-hexene-2,5-dione as intermediates. It is reported that the Ni-Ni site of Ni₂P NPs is important for in the activation of H₂.⁴⁹ which is well consistent with our experimental and XAFS results where Ni₂P and Ni₅P₄ NPs having the Ni–Ni site showed high activity for the hydrogenation of 1. We

also confirmed that Ni₂P NPs have acidic properties by temperature-programmed desorption of ammonia (Figure S4 and Table S2). The presence of Brønsted acid in the surface of N₂P NPs is reported, which is formed with the reaction of phosphate species with water and H_2 .⁵⁰⁻⁵²

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Based on the results of these control experiments, we proposed a possible reaction pathway for the transformation of **1** to **2** using Ni₂P NPs, as shown in Scheme 3. First, **1** is hydrogenated into 5-methylfurfuryl alcohol at the Ni–Ni site of Ni₂P NPs. Subsequently, 5-methylfurfuryl alcohol intermediate is transformed into 3-hexene-2,5-dione through hydrolysis, followed by a ring-opening reaction promoted by surface acid sites of PO–H.⁵³ Finally, successive hydrogenation of the C=C bond of 3-hexene-2,5-dione proceeds to give desired product **2**. In the above catalytic cycle, bifunctional catalysis of Ni₂P NPs, involving the H₂-activating ability of Ni–Ni sites and surface

Scheme 2. Control experiments under various conditions over Ni₂P NPs.



Scheme 3. Plausible reaction pathway for the conversion of 1 into 2 over Ni_2P NPs.



acidity derived from P–OH, played a key role, leading to the highly efficient transformation of 1 into 2 without any additives.

In conclusion, we found that less common Ni₂P NPs showed high catalytic activity for the selective transformation of biofuranic aldehydes to 2,5-diketones. This study represents the first example of a nonprecious metal catalyst promoting this reaction. Although conventional Ni catalysts and other metal phosphides showed poor activity, the Ni₂P catalyst efficiently promoted the transformation in water as solvent under additive-free conditions. Furthermore, the Ni₂P/mordenite catalyst was easily recoverable and reusable without losing activity and selectivity. Spectroscopic analyses showed that the Ni₂P NPs had an intrinsic metal-like nature, with Ni-Ni species as H₂ activation sites and P-OH as surface acid sites. Bifunctional catalysis of Ni₂P NPs, combining its hydrogenation ability and acidity, was key to the successful transformation of 1 into 2, providing a new cost-effective and efficient method for diketone synthesis from biofuranic aldehydes.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the xxx.

Experimental details, characterization of catalysts and NMR data. (PDF)

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The authors declare no competing financial interest.

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(53) **1** was treated with ¹⁸O-labeled water ($H_2^{18}O$) under similar conditions as Figure 2. In the initial phase of the reaction in the presence of $H_2^{18}O$, ¹⁸O-labeled **2** was produced (Scheme S1a). This result suggested that hydration occurred in the transformation of 1 to 2. Next, the products in Scheme S1a were isolated and treated with $H_2^{16}O$, affording 2 without ¹⁸O atoms (Scheme S1b). This result showed that an oxygen atom was scrambled between 2 and H₂O. In Scheme S1a, two types of product, namely, **2** with one ¹⁸O atom introduced by hydration and 2 with another ¹⁸O atom derived from H₂¹⁸O, were speculated to be generated.

