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Promotion Effect of PrPO₄ for Hydrogenation Transformation
of Biomass-derived Compounds over Pr-Ni-P Composites

Ya-Fang Zhang#, Ben Dai#, Dan Zhao*, Di-Hui Zhang, Meng-Xing Xu, Xiang-Hua He, Chao Chen*

Key Laboratory of Jiangxi Province for Environment and Energy Catalysis, College of Chemistry, Nanchang University, Nanchang, Jiangxi, 330031, China

# These authors contribute equally
* Corresponding authors: Associate Professor Dan Zhao
Professor Chao Chen
E-mail: zhaodan@ncu.edu.cn (Dan Zhao)
chaochen@ncu.edu.cn (Chao Chen)
Phone: +86-15879176996 (Dan Zhao)
+86-15179167359 (Chao Chen)
Abstract

To span the inherent application limitation of state-of-the-art catalysts for chemical transformation of biomass derivatives, here, we formulate a series of Pr-Ni-P catalysts for hydrogenation transformation of biomass-derived levulinic-acid, furfural and maleic-anhydride. With comprehensive characterizations, the Pr-Ni-P samples are verified as \((\text{PrPO}_4)_m/\text{Ni}_2\text{P}\) nanocomposites with molar ratio \((m)\) in range of 0.24-11.0; in comparison with the poor catalytic performance of \(\text{Ni}_2\text{P}\), ten-folds enhancement in TOF up to 0.45 s\(^{-1}\) and at least five-times promotion on the yield of objective product up to 91-98% are achieved by introducing proper amount of PrPO\(_4\) to form the reusable \((\text{PrPO}_4)_m/\text{Ni}_2\text{P}\) nanocomposites; surface chemistry and kinetic mechanism studies further disclose that the cooperative catalytic function of two components, particular the exclusive capability of PrPO\(_4\) to activate hydrogen, is responsible for the promoted hydrogenation transformation of biomass-derivatives through a quick Langmuir-Hinshelwood process over \((\text{PrPO}_4)_m/\text{Ni}_2\text{P}\). These findings imply that the easily-obtainable, cost-affordable and robust rare earth phosphate like present PrPO\(_4\) could be a potential replacement catalytic component for traditional metal catalyst in hydrogenation transformation reactions of biomass-derivatives, which was also worth noting as a new kind of basic material for other green mass-transformation techniques involving hydrogen activation process such as corresponding optical and electrical transformations.

Key words: Biomass derivatives; hydrogenation transformation; Pr-Ni-P composite; PrPO\(_4\)
1. Introduction

As one of the most promising resources to replace fossil reserves for sustainable producing fuels and chemicals, biomass particular plant-base materials and corresponding chemical transformations have drew a persistent interest from both academic research and industrial application.\textsuperscript{1, 2} The raw materials from plant biomass including cellulose, hemi-cellulose and lignin cannot be directly used, an pretreatment involving acid-catalyzed hydration process is always necessary for acquiring a great deal of platform compounds, which are most in form of C\textsubscript{3}-C\textsubscript{6} oxygen-containing hydrocarbon molecules such as levulinic-acid, furfural and maleic-anhydride. Due to the fact, the meaningful biomass application has been focused on producing value-added chemicals from these platform compounds, in the field, an efficient and reliable catalytic system is essential for implementing the chemical transformations\textsuperscript{3-6} however, there has been still a big gap between the application requirement and the developed catalytic systems.

In the chemical reaction network raised from the biomass platform molecules, hydrogenation transformation could be the most popular or primary pathway since a large proportion of biomass-derivatives contain unsaturated C=O or C=C bond, such as hydrogenation of levulinic-acid (LA) to gamma-valerolactone (GVL), hydrogenation of furfural (FAL) to furfuryl alcohol (FOH) and hydrogenation esterification of maleic anhydride (MA) to diethyl succinate (DES). Based on the reality, metal catalysts have stayed at the center of the reaction network till now, in virtue of the exclusive ability of metal site to activate reactants in particular to activate hydrogen.\textsuperscript{5-7} A wide scope of metals has been applied to the chemical transformation of some typical biomass platform compounds. Nobel metals like Pt, Pd, Ru have been testified to be efficient and stable catalyst for hydrogenation transformations of levulinic-acid and furfural under relatively mild conditions.\textsuperscript{6-9} Considering the cost limitation of precious metal for scaled-up application, some researchers paid attentions to cheap transition metal catalysts such as Cu, Co and Ni,\textsuperscript{10-16} and attractive catalytic performance over the deliberately fabricated metallic catalysts mostly in fashion of diverse nanostructures
were shown in literature. For example, Liu et al prepared a Ni-embedded hierarchically-porous carbon catalyst for hydrogenation of LA to GVL,\textsuperscript{17} the exquisite design of protecting highly-dispersed Ni nanoparticle in carbon coverage prevented the Ni-leakage in reaction mixture and maintained catalytic performance in reuse processes. These reports exhibit that the state-of-the-art catalysts mainly composed by metallic component are promising for chemical transformation of biomass derivatives, however, some inherent defects from metal nature for catalytic transformation of biomass should be also carefully considered when extending the discovery into application. At first, for transition metal catalysts, their surfaces are easily corrupted in liquid reaction mixture particularly when acidic substrate such as levulinic acid present, which could lead to the severe leakage of metal and quick deterioration in performance,\textsuperscript{11-15, 18, 19} thus greatly limit the application of such catalysts. In addition, there are more than one unsaturated bond in some biomass platform molecules, which means that the selective hydrogenation of definite bond is crucial for the application of these molecules, with furfural hydrogenation as example, ensuring the ideal selectivity to the objective product of furfuryl alcohol is highly desired in industry,\textsuperscript{20, 21} but it could still be a challengeable task even if using precious metal catalysts, since the metallic surface is prone to be equally functional for the hydrogenation of C=C on the ring and C=O on the branch.\textsuperscript{8, 9}

In view of defects of metal catalysts, we have attempted to employ intermetallic compound such as metal phosphide (M$_2$P, M= Ni or Co) as hydrogenation catalysts,\textsuperscript{22, 23} in consideration of the following interesting features of the compound. Firstly, although metal phosphide is a kind of covalent compound with metal component in oxidized state, the compound could present properties analogous to metal alloy in both structure and catalytic performance;\textsuperscript{24, 25} secondly, the cost-affordable compound could be more robust to bear the corruption in liquid reaction system than its metallic counterpart.\textsuperscript{22, 23} Unfortunately, it were testified that the isolated M$_2$P catalysts were not efficient for liquid hydrogenation reactions, for instance, when using Co$_2$P for hydrogenation of levulinic acid, the desired gamma-valerolactone was just produced in the low yield due to the poor capability of phosphide to activate hydrogen.\textsuperscript{23} However,
when introducing Ce to fabricate Ce-Co-P composites, the ability of CePO₄ to chemically activate hydrogen that is comparable to metal surface was discovered, which made the decisive contribution in improving catalytic efficiency on the composites.²², ²³ Recently, Wang et al also found that CePO₄/Ni₃P could act as efficient and durable heterogeneous catalyst for hydrodeoxygenation of phenol and hydrogen-transferring transformation of biomass derivatives in liquid environment.²⁶, ²⁷ These findings prompt us to suppose that the composites consisting of rare earth, metal and phosphorus could be a kind of potential catalyst to span the defects of metallic structures for chemical transformation of biomass-derived compounds. Along the expectation, in this work, we formulated a series of Pr-Ni-P composites to investigate their catalytic performance and corresponding origin for hydrogenation transformations of typical biomass derivatives such as levulinic-acid, furfural and maleic-anhydride.

2. Experimental

2.1 Materials

Nickel (II) nitrate, diammonium hydrogen phosphate and γ-valerolactone (GVL) were purchased from Sinopharm Chemical Reagent Co., Ltd; Praseodymium (III) nitrate and levulinic acid (LA) were procured from Aladdin Reagent Co., Ltd; Furfural (FAL), furfuryl alcohol (FOH), maleic anhydride (MA) and diethyl succinate (DES) were obtained from Innochem Reagent Co., Ltd. All chemical reagents in chemical analysis purity commercially obtained are used directly without further purification.

2.2 Preparation of catalysts

Samples with different Pr/Ni molar ratios were prepared from a one-pot solvothermal synthesis system. Briefly, nickel (Ni) nitrate and praseodymium (Pr) nitrate at different molar ratios were dissolved in deionized water, then the aqueous solution of diammonium hydrogen phosphate (0.2 mol/L) were added dropwise into the above mixture; after the solution was well mixed for 30 min under stirring speed of 800 rpm, the solution was transferred into the hydrothermal kettle treatment system to react at 180 °C for 24 h; then the system is naturally cooled down to room temperature, the precipitation in reaction system was separated by centrifugation, washed and dried at
60 °C for 12 h to obtain the precursor; the obtained precursor was calcined at 600 °C in air for 4 h and successively reduced for 2 h in a hydrogen flow with rate of 50 mL/min to acquire catalyst sample; for characterizations and catalytic measurements, the precursor was treated according to the thermal reduction procedure to get fresh catalyst for investigation. As reference catalysts, Pr-P and Ni-P samples were also prepared from the same preparation procedure.

2.3 Characterizations

The actual compositions of metal components (Pr and Ni) in catalyst samples were determined by the ICP-OES analysis of the aqua regia solution which completely dissolves all parts of catalyst, on an Agilent Technologies 5100 ICP-OES (inductively coupled plasma-optical emission spectrometer) apparatus.

Micromeritics ASAP 2020 analyzer was used to carry the Brunauer–Emmett–Teller (BET) method for determining the specific surface area of the samples.

Powder diffraction (XRD) patterns of samples were performed on a Persee XD-3 X-ray diffractometer with Cu Kα(1.5406 Å) as radiation source. The samples were scanned at a rate of 2°/min in the angle (2θ) range of 5-90°.

X-ray photoelectron spectroscopy measurements (XPS) of the samples were analyzed on an Axis Ultra DLD Electron-Spectrometer equipped with a monochromatic Al Kα source (hv =1486.6 eV). The C 1s peak of adventitious carbon at 284.5 eV was referred to rectify the binding energy in XPS spectra.

Transmission electron microscopy (TEM) of samples were taken on a JEOL JEM-2100 microscope configurated with an energy dispersive X-ray spectroscopic analyzer conducted at acceleration voltage of 200 kV. The samples were prepared by sonicating in hydrous ethanol and then the suspended sample was dropped and dried on a carbon film coated 400 mesh copper grids.

Temperature programmed desorption of H₂ and LA [H₂-TPD and LA-TPD] experiments were carried out on a Micrometeric-Auto-Chem II 2920 chemisorption analyzer combined with a thermal conductivity detector and a computer-controlled furnace. Prior to measurement, approximately 50 mg of fresh catalyst was placed in a U-shaped quartz tube for pretreatment at 400 °C for 60 min in pure argon (30 mL/min)
to exclude the possibly adsorbed air components on the fresh sample during transferring process. For H\textsubscript{2}-TPD measurements, the system was cooled to room temperature under the protection of argon and saturated with flowing H\textsubscript{2} (30 mL/min) for 60 min, then pure argon was switched into the system again to exclude free adsorbate for 30 min; subsequently, the sample was heated to 300 °C at a heating rate of 10 °C/min and desorption signals were monitored by TCD. For LA-TPD measurements, the LA steam at 100 °C balanced by pure argon (30 mL/min) was bubbled into system for 60 min; then the system was blowing by pure argon (30 mL/min) until the system was cooled to 50 °C, the temperature was raised with a heating rate of 10 °C/min and TCD signals were recorded simultaneously.

2.4 Catalytic measurements

The catalytic hydrogenation transformation reactions such as hydrogenation of levulinic acid (LA) to gamma-valerolactone (GVL), hydrogenation of furfural (FAL) to furfuryl alcohol (FOH) and hydrogenation esterification of maleic anhydride (MA) to diethyl succinate (DES) were all performed at 353-393 K under 3.0-5.0 MPa H\textsubscript{2} in a 50 mL Teflon reactor with a stainless-steel autoclave heater equipped with liquid-sampling device. According to the typical compositions of reaction mixture employed in literature works\textsuperscript{28-34} the initial compositions of three reaction systems were set as followings, for LA reaction system, the mixture contained 2 mmol LA, 100 mg catalyst and 10 mL deionized water; for FAL reaction, the mixture was composed by 1 mmol FAL, 100 mg catalyst and 20 mL isopropanol; for MA reaction, the solution contained 5 mmol MA, 50 mg catalyst and 10 mL ethyl alcohol. Prior to the reaction, the system was purged 3-5 times with H\textsubscript{2} to exclude air and kept stirring at speed of 800 rpm, and then reaction condition was carefully manipulated to the desired pressure (3.0, 4.0 or 5.0 MPa) and temperature (353, 373 or 393K). After the reaction condition was raised to the set value, the composition change of reaction solution with time was recorded and analyzed by a gas chromatograph [GC 7820A, equipping a flame ionization detector and a Agilent 19091J-413 capillary column (DB-WAX, 30 m × 320 μm × 0.25 μm)] and a gas chromatograph mass spectrometry [GC-MS 7890B-5977A, equipping a Agilent 19091S-433 capillary column (HP-5MS, 30 m × 250 μm × 0.25 μm)].
conversion of reactant and the yield of objective product were simultaneously analyzed according to the standard composition curves, and the average result from more than three repeat measurements was recorded in plots.

3. Results and discussion

3.1 Composition and structure of catalysts

The metal compositions of prepared Pr-Ni-P samples were measured by ICP-OES measurements, and the Pr/Ni molar ratio range of 0.12-5.5 for five samples were clarified. With Ni-P and Pr-P as reference, three Pr-Ni-P samples with Pr/Ni molar ratio at 0.12, 0.95 and 5.5 were selected as representative samples, and analyzed by XRD and XPS measurements, as shown in Figure 1. In Figure 1A, feature diffractions of Ni$_2$P (PDF cards No. #03–0953) and PrPO$_4$ (PDF cards No.#32-0885) crystalline were resolved on Ni-P and Pr-P samples, respectively; by increasing Pr/Ni ratio, both Ni$_2$P and PrPO$_4$ phases were observed with a gradual intensity increase in PrPO$_4$ diffractions among Pr-Ni-P samples, suggesting that Pr-Ni-P samples were mainly composed of combined crystalline of PrPO$_4$-Ni$_2$P. In following XPS spectra of samples given in Figure 1B-D, the main peak around 853.2 eV marked as Ni$^{6+}$ in Ni 2p spectra (Figure 1B) and the peak at 130.0 eV marked as P$^{5-}$ in P 2p spectra (Figure 1C) appeared simultaneously on Ni contained samples, the co-existence of Ni$^{6+}$ and P$^{5-}$ photo emissions was always attributed to the surface properties of Ni phosphide;$^{35, 36}$ meanwhile, all of Pr contained samples showed two peaks located around 934.0 eV and 954.0 eV in Figure 1D, which are belonged to Pr(III) 3d photoemissions.$^{37, 38}$ It was not surprised to see that the signals for Pr(III) peaks evolved in intensity with increasing Pr composition among Pr-Ni-P samples, interestingly, the P(V) peak around 133.6 eV pertinent to PO$_4^{3-}$ group$^{39, 40}$ (Figure 1C) also showed the same change trend, which indicated that Pr(III) species could combine with PO$_4^{3-}$ to form PrPO$_4$ on the surface layers of Pr-Ni-P samples. These XPS analysis results are in accordance with the findings on PrPO$_4$-Ni$_2$P crystalline feature for Pr-Ni-P samples recognized by XRD measurements; moreover, linking all of XPS spectra, the relative composition of Pr to Ni on surface is much higher than that in body, suggesting that the Ni$_2$P surface was
gradually covered by PrPO$_4$ to from PrPO$_4$/Ni$_2$P composite structure among Pr-Ni-P samples. In addition, besides of Ni$^{5+}$ species for phosphide, Ni(II) species in minor proportion were also found on the surface of Ni-P and Pr-Ni-P samples, although the samples were previously reduced in H$_2$ atmosphere, they would be inevitably exposed in air during the delivery process to measurements, so Ni$_2$P component could be suffered from the oxidation and leave Ni(II) species on surface.$^{24,41}$

The morphological feature of Pr-Ni-P samples refer to that of Pr-P and Ni-P was disclosed by TEM measurements, as shown in Figure 2 and Figure 3. In Figure 2, Ni-P sample showed as dark particles in size of 200-400 nm with smooth projection edge, in contrast, Pr-P sample arranged as packed nanorods, and two representative Pr-Ni-P samples all exhibited as particle aggregations, in which the big particles with size around 120 nm were surrounded by nanoparticles in size of ca. 20 nm. In high resolution TEM images, the big dark particles observed in Ni-P and Pr-Ni-P samples were clarified as Ni$_2$P[111] crystalline with characteristic diffraction d-space around 0.222 nm ([Ni$_2$P]-PDF#03–0953), in contrast, the nanoparticles in Pr-Ni-P samples showed feature d-spaces around 0.296 nm, 0.406 nm and 0.467 nm, which were close to the typical [210], [101] and [011] diffractions of PrPO$_4$ crystalline ([PrPO$_4$]-PDF#32-0885) observed on Pr-P sample. With the elemental distribution map shown in Figure 3, it was also observed that Ni was concentrated within the range of big particles, and Pr was well dispersed on the areas surrounding these big particles for Pr-Ni-P samples. These images further confirmed the results from the previous XRD and XPS measurements, that the prepared Pr-Ni-P catalysts were verified as PrPO$_4$/Ni$_2$P nanocomposites. According to the resolved Pr:Ni ratio of 0.12-5.5, Pr-Ni-P catalysts can be readily denoted as (PrPO$_4$)$_m$/Ni$_2$P, in which $m$ present molar ratio between two components in the range of 0.24-11.0.

3.2 Catalytic performance of catalysts

Considering that the corruption effect from acid reactant would greatly depress the application potential of Ni involved catalysts,$^{11-15}$ we employed levulinic acid (LA) as the primary reactant to investigate the catalytic hydrogenation performance of prepared
catalysts in this work. Figure 4 showed the dependences of LA conversion and gamma-valerolactone (GVL) yield on reaction time over (PrPO₄)ₘ/Ni₂P, PrPO₄, and Ni₂P catalysts. During reaction time of 120 mins, PrPO₄ showed insignificant activity in view of almost unchanged LA concentration and absence of GVL in reaction mixture; over Ni₂P, not more than 25% LA were converted to the objective product of GVL; in contrast, the obvious increase in both LA conversion and GVL yield from 40% to 97% was exhibited on (PrPO₄)ₘ/Ni₂P catalysts. By modulating the molar ratio m of two components among five (PrPO₄)ₘ/Ni₂P catalysts, the highest LA conversion and GVL yield beyond 95% were achieved on (PrPO₄)ₙ/Ni₂P; for other (PrPO₄)ₘ/Ni₂P samples, GVL yield also increased proportionally with LA conversion by prolonging reaction time, and the almost-quantitative yield of GVL with a superior selectivity above 95% for all (PrPO₄)ₘ/Ni₂P samples can be resolved. These results indicated that the hydrogenation reactivity on (PrPO₄)ₘ/Ni₂P catalyst was obviously enhanced by the introduction of PrPO₄ in view of the poor performance of isolated Ni₂P.

Considering that the hydrogenation reactivity of catalyst was directly dependent on its ability to activate hydrogen, we employed H₂-TPD measurements to clarify the feature of current catalysts, and the profiles were given in Figure 5. In comparison with the nearly-flat line observed on Ni₂P, all of three typical (PrPO₄)ₘ/Ni₂P catalysts showed an obvious H-desorption peak around 70 °C as similar as the peak appeared on PrPO₄ sample, the contrast result clearly exhibited that PrPO₄ was the key component responsible for activating hydrogen in (PrPO₄)ₘ/Ni₂P catalysts. As known, the area of H-desorption peak from H₂-TPD profile is always employed to calculate the number of active sites for hydrogenation reactions by using a known Pt-based catalyst as calibrating reference.²², ²³, ⁴², ⁴³ The widely-accepted method is based on the assumption that actively-adsorbed H-atom on active site for a given catalyst would follow the quantitative ratio of 1:1 between H-atom and site analogous to Pt catalyst, so the essence of the method is to calibrate out the active site comparable with Pt site for the given catalyst. In our case, although the real H₂ activation process on (PrPO₄)ₘ/Ni₂P and PrPO₄, particularly its similarity or difference from the process on metal catalysts (as pointed out by a reviewer), still need be clarified from more experiment...
measurements or theory simulations in future, it could not hamper us to calibrate the 
H₂ activation site comparable with Pt site on (PrPO₄)₅/Ni₂P and PrPO₄ as similar as the 
literature works, so the amount of desorbed H-atom or the numbers of active site on our 
typical catalysts were also estimated by the method. In addition, it should be pointed 
out that the metal active site in an oxidized state (being not functional to raise H-
adsorption-desorption signal) should be previously reduced and then measured with 
above H₂-TPD method, for Ni based compound, the method is the widely accepted and 
the most reliable one to determine Ni site on surface; but for Ni₂P, the method is not 
practical due to that Ni₂P is difficult to be reduced even with pure H₂ to treat 4 h under 
873 K, so we had to measure the site number of Ni₂P by calibrating its specific area to 
the surface molecular density of Ni₂P crystalline. The resolved numbers of active site, 
taken together with other feature parameters such as crystalline size (from XRD), the 
specific surface area (from BET tests), metal element surface distributions (Pr/Ni molar 
ratio determined by XPS measurements) and GVL yield for samples, were collected in 
Table 1.

As disclosed, the amount of desorbed H-atom showed a positive dependence on the 
increase in the molar surface distribution of PrPO₄ among (PrPO₄)₅/Ni₂P catalysts, 
further confirming that PrPO₄ was the decisive component to activate hydrogen. With 
the analysis, the intrinsic activity present as the turnover frequency (TOF) number can 
be estimated by calibrating the initial reaction rate to the active site number determined 
from H-desorption signals. In our case, because of the operation complexity of 
high-pressure reactor, as the closest moment to the zero moment of reaction, we had to 
have a delay about 3 min after reaction temperature reached to the setting point to 
measure the first data. Notably, the observed values of LA conversion at the moment 
were not more than 3% for all samples, such small value suggested that the conversion 
of LA during temperature raising process can be ignored in our reaction systems. With 
the observation as baseline, considering that the values of initial reaction rate were 
widely accepted as the instant or average rate for reactant with low conversion around 
10% in reports, we followed the way to resolve TOF numbers over present catalysts, 
and the numbers were also listed in Table 1. Interestingly, (PrPO₄)₅/Ni₂P catalyst with
manipulated m at 1.9 would achieve a ten-fold enhancement in activity (TOF: 0.45 s⁻¹) versus isolated Ni₂P (TOF: 0.04 s⁻¹), which further confirmed the outstanding promotion effect of PrPO₄. The contrast result was analogous to the finding in our previous work,²³ in which a higher TOF of 0.61 s⁻¹ over (CePO₄)m/Ni₂P versus 0.15 s⁻¹ over Co₂P was resolved for hydrogenation of LA, in view of the TOF enhancement factor to isolated metal phosphide [11(0.45/0.04) versus 4 (0.61/0.15)], it implied that PrPO₄ could be more efficient than CePO₄ as the promotion component for liquid hydrogenation reactions. Linking with other parameters in Table 1, one may question that the difference in crystalline size or specific area among (PrPO₄)m/Ni₂P and reference samples could be a factor to be responsible for their different performance observed. Indeed, both PrPO₄ and Ni₂P phases in (PrPO₄)m/Ni₂P samples showed a slight decrease tendency in the values of crystalline size compared with the numbers for isolated PrPO₄ and Ni₂P reference catalysts, which could be the reason for the observed increase in specific area among (PrPO₄)m/Ni₂P samples by increasing PrPO₄ composition. As known, the decrease in crystalline size or the increase in specific area of catalysts could greatly enhance catalytic performance, however, in our case, the expectation was not true for (PrPO₄)m/Ni₂P samples, for instance, (PrPO₄)₁₁/Ni₂P was not the best sample in view of GVL yield in spite of the sample had the largest specific area among samples. In addition, the differences in crystalline size for both phases between (PrPO₄)m/Ni₂P and single component samples are in the low level not more than 10 nm, therefore, it is reasonable to believe that the difference in crystalline size or specific area was not the responsible factor to lead to the performance gap among present catalysts.

A further comparison of the catalytic performance of (PrPO₄)m/Ni₂P catalyst relative to the performance of the state-of-the-art catalysts was given in Table 2. In view of that the Ni contained catalysts in this work were employed in a high-pressure liquid hydrogenation system, and that the reaction conditions particularly H₂ pressure played important roles in not only governing the performance of reaction, but also determining the feasibility of application, so we mainly collected reported Ni-based catalysts for the reaction under H₂ pressure in 1.5-5.0 MPa as comparison references;¹⁰,¹³,¹⁵,¹⁷,⁴⁷-⁵²
further understanding the performance difference between Ni-based catalysts and precious metal catalysts, we also listed the parameters of some precious metal catalysts in the table.\textsuperscript{53-57} As shown, Ni\textsubscript{2}P itself exhibited the poor catalytic performance in view of the low level of GVL yield among Ni-based catalysts, however, with the combination of PrPO\textsubscript{4} to form (PrPO\textsubscript{4})\textsubscript{0.24-11}/Ni\textsubscript{2}P, the obvious enhancement in GVL yield up to the close level of reported Ni-based catalysts (93-100%) was achieved under moderate H\textsubscript{2} pressure and relatively lower temperature or shorter period, such performance was even comparable with that of precious metal catalysts, indicating that the present cost-affordable (PrPO\textsubscript{4})\textsubscript{m}/Ni\textsubscript{2}P catalysts could act as a kind of competitive candidate catalyst for hydrogenation of LA to GVL in virtue of the distinct promotion effect of PrPO\textsubscript{4}.

Because the reaction mixture for hydrogenation of LA is an acid aqueous solution, the leakage of metal from acid-corruption should be carefully considered when estimating the application potential of catalytic system for the reaction.\textsuperscript{11-15, 58, 59} Here, (PrPO\textsubscript{4})\textsubscript{1.9}/Ni\textsubscript{2}P was subjected to successive catalytic reuse test, while the metal leakage particularly the Ni ion concentration in liquid was monitored by ICP-OES analysis during reuse process. As shown in Figure 6A, both LA conversion and GVL yield were kept at almost constant level from the low-conversion stage (t = 30 min) to the high-conversion stage (t = 120 min) during four catalytic cycles; simultaneously, a small Ni leakage around 2 % was resolved from the reaction solutions of cycle runs. The possible influence of Ni leakage on reaction performance was further investigated by filtration comparison experiments, as shown in Figure 6B. In contrast to the continuous increase in LA conversion for reaction solution containing catalyst during whole reaction period, the reaction immediately suspended once the catalyst was filtered out of reaction solution, indicating that even Ni could leak and stay in reaction solution, the contribution of the resolved Ni species to reaction performance was not evident. These results clarified that the leakage of Ni on (PrPO\textsubscript{4})\textsubscript{1.9}/Ni\textsubscript{2}P catalyst was not significant and the corresponding influence on catalytic performance could be ignored. In addition, the XRD patterns and Ni 2p XPS spectra of fresh and reused (PrPO\textsubscript{4})\textsubscript{1.9}/Ni\textsubscript{2}P samples were compared in Figure 6C and 6D, the almost unchanged signals on two samples further confirmed that both the body and the surface of (PrPO\textsubscript{4})\textsubscript{m}/Ni\textsubscript{2}P catalysts were
robust to undergo the catalytic reuse processes even the catalysts were used in a harsh acid-corruption environment. As far as the small leakage of Ni found in reaction solution, the leakage could be attributed the dissolved Ni(II) species from Ni$_2$P surface that was evidenced by previous XPS measurements (Figure 1).

The potentials of $(\text{PrPO}_4)_m$/Ni$_2$P catalysts for hydrogenation transformation of other biomass-derived platform molecules were further investigated by employ furfural (FAL) and maleic anhydride (MA) as reactants. The typical catalytic performances were shown in Figure 7. In Figure 7A1-A3, for hydrogenation of FAL to furfuryl alcohol (FOH), both of two single component catalysts PrPO$_4$ and Ni$_2$P showed insignificant FAL conversion during reaction period of 240 min; distinctly, the considerable FAL conversion of 61-92% and FOH yield of 59-91% were achieved on $(\text{PrPO}_4)_m$/Ni$_2$P catalysts; on $(\text{PrPO}_4)_{0.66}$/Ni$_2$P with the best catalytic performance among $(\text{PrPO}_4)_m$/Ni$_2$P catalysts, both FAL conversion and FOH yield exhibited slight fluctuations from low-conversion stage ($t=30$ min) to high-conversion stage ($t=240$ min) during four successive cycle runs, meanwhile, there were not evident metal leakage found from the reaction solutions of cycle runs. These results indicated that $(\text{PrPO}_4)_m$/Ni$_2$P composites could also act as efficient and robust catalysts for hydrogenation of FAL to FOH. Figure 7B1-B3 showed the catalytic performance for hydrogenation esterification of MA to diethyl succinate (DES). As shown, the similar final MA conversion during reaction period of 120 min up to 80% was observed on PrPO$_4$ and Ni$_2$P catalysts, however, there was not significant yield of objective hydrogenation esterification product DES appeared on two reference catalysts, instead of DES, only unsaturated esterification product (Diethyl fumarate, DEF) present in two reaction systems; in contrast, the quick conversion of MA up to approach 100% within 60 min and the final DES yield as high as 98% (when reaction performed for 120 min) were achieved on $(\text{PrPO}_4)_m$/Ni$_2$P catalysts by manipulating $m$ at 0.66. Furthermore, the superior catalytic performance of $(\text{PrPO}_4)_{0.66}$/Ni$_2$P would reappear during four catalytic runs (Figure 7B3), and the metal leakages were almost absent in all of reaction solutions from cycle runs, these results indicated that the $(\text{PrPO}_4)_m$/Ni$_2$P composite with properly manipulated component composition was also advanced for hydrogenation esterification of MA in view of the
superior catalytic performance and good reusability.

In general, the superior catalytic performance of \((\text{PrPO}_4)_m/\text{Ni}_2\text{P}\) composite catalysts compared with \(\text{Ni}_2\text{P}\) were clearly demonstrated through three typical hydrogenation transformation reactions, the dramatic promotion effect of \(\text{PrPO}_4\) was evident not only on enhancing the yields of objective products, but also on speeding the transformation process. To further clarify the catalytic origin of \((\text{PrPO}_4)_m/\text{Ni}_2\text{P}\) composites, we performed the kinetic and corresponding mechanism measurements in following section.

### 3.3 Kinetic measurements and mechanism screen

Considering that hydrogenation and chain-ring transformation were the typical processes or steps during chemical transformation of biomass-derived platform molecules, and it happened that these processes were simultaneously involved in hydrogen of LA to GVL, therefore, the reaction was chosen as a typical system for investigation of kinetic and mechanism feature of \((\text{PrPO}_4)_m/\text{Ni}_2\text{P}\) catalysts. Firstly, temperature effect (by altering reaction temperature to 353, 373 and 393 K) and corresponding kinetic data were measured, as shown in Figure 8. It was resolved that \(\ln C_t\) (\(C_t\): LA concentration) correlated well with reaction time (\(t\)) in linear relations at every employed reaction temperature on \((\text{PrPO}_4)_{1.9}/\text{Ni}_2\text{P}\) and \(\text{Ni}_2\text{P}\) samples (Figure 8A1 and 8B1), indicating that the dependences of reaction rate on LA concentration over two catalysts all could follow a pseudo first order kinetic process.\(^{60,61}\) From the kinetic lines in Figure 8A1, the reaction rate constant \(k\) on \((\text{PrPO}_4)_{1.9}/\text{Ni}_2\text{P}\) can be directly recognized as the slope of the linear \(\ln C_t\)-\(t\) correlation, then \(\ln k\) was fitted with reciprocal of reaction temperature (\(T^{-1}\)) according to Arrhenius equation in Figure 8A2, and the well-fitted linear dependence was acquired to resolve 53.6 kJ/mol as the apparent reaction activation energy (Ea) for \((\text{PrPO}_4)_{1.9}/\text{Ni}_2\text{P}\). Following the same procedure, the Arrhenius correlation on \(\text{Ni}_2\text{P}\) was also resolved and given in Figure 8B2, in which, the Ea for \(\text{Ni}_2\text{P}\) was estimated as 66.3 kJ/mol. In view of the obvious quenched Ea value on \((\text{PrPO}_4)_{1.9}/\text{Ni}_2\text{P}\) compared with \(\text{Ni}_2\text{P}\), it was not surprised that the much higher TOF was obtained on \((\text{PrPO}_4)_{1.9}/\text{Ni}_2\text{P}\). In addition, with the resolved rate
constant k on (PrPO₄)₁₀/Ni₂P and Ni₂P, the TOF values on two samples were re-estimated and given in Table 1, with (PrPO₄)₁₀/Ni₂P as example, the calculated value of 0.42 s⁻¹ is very close to the experimental value of 0.45 s⁻¹, suggesting that the precision of above curve fitting measurements was in an acceptable level.

Besides of temperature, the influence of H₂ pressure on reaction properties was also investigated on (PrPO₄)₁₀/Ni₂P. By manipulating H₂ pressure [P(H₂)] at 3.0, 4.0 and 5.0 MPa, the dependences of LA concentration on reaction time were collected in Figure 9A, from these curves, the correlation between ln r (r: reaction rate) and ln P(H₂) was fitted in Figure 9B, it can be found that a linear dependence was resolved, upon the line, the reaction order n for H₂ pressure was estimated as 0.54. According to above kinetic measurements, the experimental reaction rate equation was determined as
\[ r = k \cdot [LA] \cdot [H₂]^{0.54}. \]

From the reaction rate equation, it suggested that the reaction behaviors for hydrogenation of LA on (PrPO₄)ₘ/Ni₂P surface could be conjunctively governed by the interactions between catalyst surface and both of reactants, LA and H₂. As disclosed by previous H₂-TPD files (Figure 5), PrPO₄ was the essential component to activate H₂, to clarify the interaction between catalyst and LA, LA-TPD measurements were carried on Ni₂P, (PrPO₄)₁₀/Ni₂P and PrPO₄ catalysts, as shown in Figure 10. In comparison with the slightly-varied baseline-like signal on PrPO₄, the obvious desorption peaks calibrated with the similar baseline appeared on Ni₂P and (PrPO₄)₁₀/Ni₂P catalyst, the result clearly indicated that LA was mainly activated by Ni₂P surface rather than PrPO₄, in other words, the function of Ni₂P surface is to activate LA.

In view of the different role of PrPO₄ and Ni₂P component for catalytic hydrogenation of LA, a Langmuir-Hinshelwood mechanism composed by the following elemental steps was speculated for the reaction process on (PrPO₄)ₘ/Ni₂P composite catalyst, in which M presents active site of PrPO₄ component to activate H₂ and N denotes Ni₂P site to activate LA.

\[
\begin{align*}
H₂ + 2M & \leftrightarrow 2H-M \quad (1) \\
LA + N & \leftrightarrow LA-N \quad (2) \\
H-M + LA-N & \Rightarrow HLA-N + M \quad (3)
\end{align*}
\]
By assuming the elemental reaction (3) as the rate-determining step, the general reaction rate equation could be expressed as \( r = k_3 \cdot [\text{LA-N}] \cdot [\text{H-M}] \) (\( k_3 \) is the rate constant of step (3)). According to the equilibrium states of reaction (1) and (2), [H-M] and [LA-N] would be directly resolved with following equations.

\[
\begin{align*}
[H-M] & = K_1^{0.5} \cdot [H_2]^{0.5} \cdot [M] \\
[LA-N] & = K_2 \cdot [\text{LA}] \cdot [\text{N}]
\end{align*}
\]

(K1: the equilibrium constant of step (1))

(K2: the equilibrium constant of step (2))

Thus, the general reaction rate equation can be transformed to \( r = k \cdot [\text{LA}] \cdot [H_2]^{0.5} \) (\( k = k_3 \cdot K_1^{0.5} \cdot K_2 \cdot [M] \cdot [N] \)). The deduced rate equation was close to that resolved from experimental measurements, so the Langmuir-Hinshelwood mechanism could be a reasonable pathway for hydrogenation of LA to GVL on \((\text{PrPO}_4)_m/\text{Ni}_2\text{P}\) composite structure, in which, \( H_2 \) and LA were respectively adsorbed-activated on \( \text{PrPO}_4 \) and \( \text{Ni}_2\text{P} \) to facilitate a quick hydrogen transformation of LA to GVL. The analysis also implied that the low reaction speed and poor conversion of LA observed on isolated \( \text{Ni}_2\text{P} \) could be attributed to its poor ability to activate hydrogen although \( \text{Ni}_2\text{P} \) is alive to activate LA; once it was combined with \( \text{PrPO}_4 \), an efficient transformation of LA to GVL in virtue of the unique capacity of \( \text{PrPO}_4 \) to activate hydrogen become sound on \((\text{PrPO}_4)_m/\text{Ni}_2\text{P}\) since a quick Langmuir-Hinshelwood process would present and greatly facilitate the transformation. As a consequence of such kinetic-mechanism behavior on \((\text{PrPO}_4)_m/\text{Ni}_2\text{P}\), the exposed surface for two components in a proper ratio allocated by the component composition (\( m \)) was another factor to optimize reaction performance, this could be the reason for the difference in catalytic performance observed on \((\text{PrPO}_4)_m/\text{Ni}_2\text{P}\) by manipulating \( m \).

With above characterizations and analyses, it was demonstrated that the robust and cost-affordable \((\text{PrPO}_4)_m/\text{Ni}_2\text{P}\) nanocomposite was worth noting as an efficient and universal catalyst for sustainable chemical transformation of biomass derivatives, in which, the capability of \( \text{PrPO}_4 \) to activate \( H_2 \) and corresponding promotion effect for hydrogenation reactions could be an notable reference for designing novel non-metallic materials in hydrogen-involved applications.
Conclusions

A series of Pr-Ni-P catalysts in PrPO₄/Ni₃P nanocomposite structure was testified to be efficient, reusable and general catalyst for hydrogenation transformations of representative biomass-derivatives. The catalysis advance of the composite is mainly dependent on the unique capability of PrPO₄ to activate hydrogen, with introduction of PrPO₄ in a proper amount, dramatic promotions in both yield of objective product and speed of transformation compared with Ni₃P were achieved on PrPO₄/Ni₃P nanocomposite. The findings verified that rare-earth phosphates like PrPO₄ could be a potential replacement component to conventional metal component for hydrogenation reactions, in view of such salt could have special optical and electronical properties, the corresponding applications, particularly other mass-transformation green techniques such as optical or electronical transformations involving hydrogen, on the mimic rare-earth compounds were also worthy of expectation.

Conflicts of interest
There are no conflicts of interest to declare.

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References

1 C. Somerville, H. Youngs, C. Taylor, S. C. Davis and S. P. Long, *Science*, 2010, **329**, 790-792.
2 Y. Roman-Leshkov, C. J. Barrett, Z. Y. Liu and J. A. Dumesic, *Nature*, 2007, **447**, 982-985.
3 L. T. Mika, E. Csefalvay and A. Nemeth, *Chem. Rev.*, 2018, **118**, 505-613.
4 E. Mahmoud, D. A. Watson and R. F. Lobo, *Green Chem.*, 2014, **16**, 167-175.
5 K. Yan, C. Jarvis, J. Gu and Y. Yan, *Renewable Sustainable Energy Rev.*, 2015, **51**, 986-997.
6  X. Zhang, K. Wilson and A. F. Lee, Chem. Rev., 2016, 116, 12328-12368.
7  K. Dhanalaxmi, R. Singuru, S. Mondal, L. Bai, B. M. Reddy, A. Bhaumik and J. Mondal, ACS Sustainable Chem. Eng., 2016, 5, 1033-1045.
8  L. Liu, H. Lou and M. Chen, Appl. Catal. A., 2018, 550, 1-10.
9  P. de Souza, L. Silvester, A. da Silva, C. Fernandes, T. Rodrigues, S. Paul, P. Camargo and R. Wojcieczak, Catalysts, 2019, 9,132.
10  K.-i. Shimizu, S. Kanno and K. Kon, Green Chem., 2014, 16, 3899-3903.
11  A. M. Hengne and C. V. Rode, Green Chem., 2012, 14,1064-1072.
12  L. Zhang, J. Mao, S. Li, J. Yin, X. Sun, X. Guo, C. Song and J. Zhou, Appl.Catal. B., 2018, 232, 1-10.
13  S. Gundekari and K. Srinivasan, Catal. Commun., 2017, 102, 40-43.
14  G. B. Kasar, N. S. Date, P. N. Bhosale and C. V. Rode, Energy Fuels, 2018, 32, 6887-6900.
15  R. Rodiansono, M. D. Astuti, T. Haru, N. Ichikuni and S. Shimazu, Catal. Sci. Technol., 2016, 6, 2955-2961.
16  K. Yan and A. Chen, Energy, 2013, 58, 357-363.
17  D. Liu, L. Zhang, W. Han, M. Tang, L. Zhou, Y. Zhang, X. Li, Z. Qin and H. Yang, Chem. Eng. J., 2019, 369, 386-393.
18  Z. Yu, X. Lu, J. Xiong and N. Ji, ChemSusChem, 2019, 12, 3915-3930.
19  R. Weng, Z. Yu, J. Xiong and X. Lu, Green Chem., 2020, 22, 3013-3027.
20  Y. Nakagawa, M. Tamura and K. Tomishige, ACS Catal., 2013, 3, 2655-2668.
21  S. Chen, R. Wojcieszk, F. Dumeignil, E. Marceau and S. Royer, Chem. Rev., 2018, 118, 11023-11117.
22  J.-J. Shi, H.-J. Feng, C.-L. Qv, D. Zhao, S.-G. Hong and N. Zhang, Appl. Catal. A., 2018, 561, 127-136.
23  H.-J. Feng, X.-C. Li, H. Qian, Y.-F. Zhang, D.-H. Zhang, D. Zhao, S.-G. Hong and N. Zhang, Green Chem., 2019, 21, 1743-1756.
24  S. Tian, X. Li, A. Wang, R. Prins, Y. Chen and Y. Hu, Angew. Chem., Int. Ed., 2016, 55, 4030-4034.
25  S. T. Oyama, J. Catal., 2003, 216, 343-352.
26  Z. Yu, F. Meng, Y. Wang, Z. Sun, Y. Liu, C. Shi, W. Wang and A. Wang, Ind. Eng. Chem. Res., 2020, 59, 7416-7425.
27  Z. Yu, Y. Wang, S. Liu, Y. Yao, Z. Sun, X. Li, Y. Liu, W. Wang, A. Wang, D. M. Camaioni and J. A. Lercher, Ind. Eng. Chem. Res., 2018, 57, 10216-10225.
28  S. Song, S. Yao, J. Cao, L. Di, G. Wu, N. Guan and L. Li, Appl. Catal. B., 2017, 217, 115-124.
29  Q. Xu, X. Li, T. Pan, C. Yu, J. Deng, Q. Guo and Y. Fu, Green Chem., 2016, 18, 1287-1294.
30  X. Huang, K. Liu, W. L. Vrijburg, X. Ouyang, A. I. Dugulan, Y. Liu, M. W. G. M. T. Verhoeven, N. A. Kosinov, E. A. Pidko and E. J. M. Hensen, Appl. Catal. B., 2020, 278,119314.
31  Z.-X. Li, X.-Y. Wei, Z. Yang, J. Li, W.-W. Yan, L.-L. Bie, Y.-Y. Zhang, S. Li and Z.-M. Zong, Mol. Catal., 2020, 492,111007.
32  X. Meng, Y. Yang, L. Chen, M. Xu, X. Zhang and M. Wei, ACS Catal., 2019, 9,
33 S. Nandi, A. Saha, P. Patel, N. H. Khan, R. I. Kureshy and A. B. Panda, ACS Appl. Mater. Interfaces, 2018, 10, 24480-24490.
34 D. Gao, H. Yin, A. Wang, L. Shen and S. Liu, J. Ind. Eng. Chem., 2015, 26, 322-332.
35 C. An, Y. Wang, Y. Wang, G. Liu, L. Li, F. Qiu, Y. Xu, L. Jiao and H. Yuan, RSC Adv., 2013, 3, 4628-4633.
36 J. Li, Y. Chai, B. Liu, Y. Wu, X. Li, Z. Tang, Y. Liu and C. Liu, Appl. Catal. A., 2014, 469, 434-441.
37 J. Gurgul, M. T. Rinke, I. Schellenberg and R. Pöttgen, Solid State Sci., 2013, 17, 122-127.
38 R. Krishnan, H. C. Swart, J. Thirumalai and P. Kumar, Appl. Surf. Sci., 2019, 488, 783-790.
39 X. Lan, E. J. M. Hensen and T. Weber, Catal. Today, 2017, 292, 121-132.
40 Y. Li, Z. Jin, H. Wang, Y. Zhang and H. Liu, J. Colloid Interface Sci., 2019, 537, 629-639.
41 J. A. Cecilia, A. Infantes-Molina, J. Sanmartín-Donoso, E. Rodríguez-Aguado, D. Ballesteros-Plata and E. Rodríguez-Castellón, Catal. Sci. Technol., 2016, 6, 7323-7333.
42 X. Han, R. Zhou, B. Yue and X. Zheng, Catal. Lett., 2006, 109, 157-161.
43 O. A. Yakovina and A. S. Lisitsyn, Langmuir, 2016, 32, 12013-12021.
44 T. J. Schwartz, S. D. Lyman, A. H. Motagamwala, M. A. Mellmer and J. A. Dumesic, ACS Catal., 2016, 6, 2047-2054.
45 W. Qian, L. Lin, Y. Qiao, X. Zhao, Z. Xu, H. Gong, D. Li, M. Chen, R. Huang and Z. Hou, Appl. Catal. A., 2019, 585, 117183.
46 S. Wei, Y. Zhao, G. Fan, L. Yang and F. Li, Chem. Eng. J., 2017, 322, 234-245.
47 K. Hengst, M. Schubert, H. W. P. Carvalho, C. Lu, W. Kleist and J.-D. Grunwaldt, Appl. Catal. A., 2015, 502, 18-26.
48 Z. Yi, D. Hu, H. Xu, Z. Wu, M. Zhang and K. Yan, Fuel, 2020, 259, 116208.
49 M. N. Gebresillasse, R. Q. Raguindin, H. Kim and J. G. Seo, Catalysts, 2020, 10, 1354.
50 K. Jiang, D. Sheng, Z. Zhang, J. Fu, Z. Hou and X. Lu, Catal. Today, 2016, 274, 55-59.
51 J. Lv, Z. Rong, Y. Wang, J. Xiu, Y. Wang and J. Qu, RSC Adv., 2015, 5, 72037-72045.
52 S. Gundekari and K. Srinivasan, Catal. Lett., 2018, 149, 215-227.
53 J. Molleti, M. S. Tiwari and G. D. Yadav, Chem. Eng. J., 2018, 334, 2488-2499.
54 M. Nemanashi, J.-H. Noh and R. Meijboom, Appl. Catal. A., 2018, 550, 77-89.
55 K. Yan, T. Lafleur, G. Wu, J. Liao, C. Ceng and X. Xie, Appl. Catal. A., 2013, 468, 52-58.
56 Y. Yang, G. Gao, X. Zhang and F. Li, ACS Catal., 2014, 4, 1419-1425.
57 X. Zhang, P. Zhang, C. Chen, J. Zhang, G. Yang, L. Zheng, J. Zhang and B. Han, Green Chem., 2019, 21, 54-58.
58 H. Wang, C. Chen, H. Zhang, G. Wang and H. Zhao, Chin. J. Catal., 2018, 39,
1599-1607.
59 R. Wang, L. Chen, X. Zhang, Q. Zhang, Y. Li, C. Wang and L. Ma, RSC Adv., 2018, 8, 40989-40995.
60 M. Chalid, A. A. Broekhuis and H. J. Heeres, J. Mol. Catal. A: Chem., 2011, 341, 14-21.
61 J. Tan, J. Cui, X. Cui, T. Deng, X. Li, Y. Zhu and Y. Li, ACS Catal., 2015, 5, 7379-7384.
62 A. B. Jain and P. D. Vaidya, Can. J. Chem. Eng., 2016, 94, 2364-2372.
63 O. A. Abdelrahman, A. Heyden and J. Q. Bond, ACS Catal., 2014, 4, 1171-1181.
Table 1. Parameters of surface properties and catalytic performance on representative samples.

| Catalysts | PrPO₄ Crystallite Size* (nm) | Ni₃P Crystallite Size* (nm) | Surface Area (m²/g) | Surface composition (Pr:Ni) | H desorption amount (µmol g⁻¹) | GVL yield (%) | TOFb (s⁻¹) |
|-----------|-------------------------------|-----------------------------|---------------------|----------------------------|-------------------------------|----------------|----------|
| Ni₃P      | -                             | 41.8                        | 10                  | -                          | 0                             | 22             | 0.04(0.02) |
| (PrPO₄)₃ₓ/₂ₙ/Ni₃P | 10.8                          | 38.2                        | 36                  | 0.6                        | 31                            | 41             | 0.26     |
| (PrPO₄)₃ₓ/₅ₙ/Ni₃P | 12.1                          | 34.6                        | 66                  | 3.3                        | 106                           | 95             | 0.45(0.42) |
| (PrPO₄)₃ₓ/₇ₙ/Ni₃P | 13.9                          | 31.1                        | 92                  | 14.1                       | 238                           | 52             | 0.10     |
| PrPO₄     | 18.5                          | -                           | 58                  | -                          | 113                           | 0              | 0        |

* PrPO₄ and Ni₃P crystallite size were calculated from XRD spectra using Scherrer equation. b Turnover frequency (TOF) values over (PrPO₄)ₙ/Ni₃P were resolved as the initial reaction rate (LA conversion within 10%) calibrated by active site number (determined by H desorption amount) on every sample [42-46]; for Ni₃P, the TOF was calculated as the initial reaction rate calibrated by the surface molecule number of Ni₃P crystalline[22]; the values in blanket are calculated with the rate constant k obtained from kinetic fitting measurements.
Table 2. The comparison of key conditions [pressure of H$_2$, temperature and reaction period] and corresponding GVL yield for hydrogenation of LA to GVL among Ni-based catalysts and some precious metal catalysts from literature and this work.

| Catalysts          | P (H$_2$) | T (°C) | t (h) | Yield (%) | Ref. |
|--------------------|-----------|--------|-------|-----------|------|
| Pd/SiO$_2$         | H$_2$ (9.0 MPa) | 180 °C | 6 h   | 96.5      | 55   |
| Ru$_{85}$Ni$_{15}$-OMC | H$_2$ (4.5 MPa) | 150 °C | 2 h   | 94        | 56   |
| Ru/OMS             | H$_2$ (3.0 MPa) | 100 °C | 1 h   | 99.8      | 53   |
| Ru/Zr-BDC         | H$_2$ (3.0 MPa) | 90 °C | 1 h   | 100       | 57   |
| Pt$_{40}$/Meso-SiO$_2$ | H$_2$ (1.0 MPa) | 150 °C | 5 h   | 100       | 54   |
| Ni-MoOx/C         | H$_2$ (5.0 MPa) | 250 °C | 24 h  | 99        | 10   |
| Ni/Al$_2$O$_3$     | H$_2$ (5.0 MPa) | 200 °C | 4 h   | 92        | 47   |
| Ni/Al-LDH         | H$_2$ (4.0 MPa) | 200 °C | 6 h   | 100       | 13   |
| Ni-Sn(1.4)/AlOH   | H$_2$ (4.0 MPa) | 120 °C | 2 h   | 100       | 15   |
| Ni/HZSM-5         | H$_2$ (3.0 MPa) | 220 °C | 10 h  | 93.1      | 48   |
| Ni-Cu/Al$_2$O$_3$  | H$_2$ (3.0 MPa) | 220 °C | 0.5 h | >99       | 49   |
| Ni(0)/boehmite    | H$_2$ (3.0 MPa) | 200 °C | 6 h   | 100       | 13   |
| Ni@NCMs           | H$_2$ (3.0 MPa) | 200 °C | 4 h   | 99        | 17   |
| Ni/MgO–Al$_2$O$_3$ | H$_2$ (3.0 MPa) | 160 °C | 1 h   | 99.7      | 50   |
| Ni/MgO-N          | H$_2$ (2.0 MPa) | 150 °C | 2 h   | 93.3      | 51   |
| Ni/SiO$_2$–Al$_2$O$_3$ | H$_2$ (1.5 MPa) | 200 °C | 0.5 h | 100       | 52   |
| Ni$_2$P           | H$_2$ (4.0 MPa) | 100 °C | 2 h   | 23        |      |
| (PrPO$_4$)$_{0.24}$+Ni$_2$P | H$_2$ (4.0 MPa) | 100 °C | 2 h   | 41-95     |      |
Figure 1. XRD patterns (A) and XPS spectra (B: Ni2p; C: P2p; D: Pr3d) of representative samples. a. Ni$_2$P; b-d. Pr-Ni-P samples with different Pr:Ni molar ratio (b. Pr:Ni=0.12; c. Pr:Ni=0.95; d. Pr:Ni=5.5); e. PrPO$_4$;
Figure 2. Typical TEM (x-1) and HRTEM (x-2) images of samples (x=a,b,c,d). a. Ni$_2$P; b-c. Pr-Ni-P samples with different Pr: Ni molar ratio (b. Pr: Ni=0.12; c. Pr: Ni=0.95); d. PrPO$_4$;
Figure 3. The high-angle annular dark-field scanning TEM (HAADF-STEM) and Ni(x-2), P(x-3) and Pr (x-4) elementals mapping images of representative samples (x=a, b, c, d, e). a. Ni$_2$P; b-d. Pr-Ni-P samples with different Pr:Ni molar ratio (b. Pr:Ni=0.12; c. Pr:Ni=0.95; d. Pr:Ni=5.5); e. PrPO$_4$.
Figure 4. The dependences of levulinic acid (LA) conversion (A) and gamma-valerolactone (GVL) yield (B) on reaction time (t) over prepared Ni$_2$P, (PrPO$_4$)$_m$/Ni$_2$P ($m$ presents molar ratio of PrPO$_4$:Ni$_2$P) and PrPO$_4$ catalysts. Reaction conditions: 100 mg Catalyst, 2 mmol LA, 10 mL deionized water, 100 °C, 4 MPa H$_2$. a. Ni$_2$P; b. (PrPO$_4$)$_{0.24}$/Ni$_2$P; c. (PrPO$_4$)$_{0.66}$/Ni$_2$P; d. (PrPO$_4$)$_{1.9}$/Ni$_2$P; e. (PrPO$_4$)$_{3.6}$/Ni$_2$P; f. (PrPO$_4$)$_{11}$/Ni$_2$P; g. PrPO$_4$
Figure 5. H₂-TPD profiles of catalysts. a. Ni₂P; b. (PrPO₄)₀.₂₄/Ni₂P; c. (PrPO₄)₁.₉/Ni₂P; d. (PrPO₄)₁₁/Ni₂P; e. PrPO₄
Figure 6. Catalytic reuse test results of (PrPO$_4$)$_{1.9}$/Ni$_2$P for hydrogenation of LA to GVL. A. The catalytic performance (LA conversion and GVL yield) and Ni leakage variations during catalytic recycles from low conversion range (t=30 min) to high conversion range (t=120 min); B. LA conversion as a function of time derived from the reaction mixtures with (a) (PrPO$_4$)$_{1.9}$/Ni$_2$P-presence and (b) (PrPO$_4$)$_{1.9}$/Ni$_2$P-absence (Catalyst was separated out of reaction mixture after 60 min of reaction period). C. Comparison of XRD patterns between fresh sample and the sample after catalytic use; D. Comparison of Ni-2p XPS spectra between fresh sample and the sample after catalytic use. Reaction conditions: 100 mg Catalyst, 2mmol LA, 10 mL deionized water, 100 °C, 4 MPa H$_2$. 
Figure 7. Catalytic performance for hydrogenation of furfural (FAL) to furfuryl alcohol (FOH) and hydrogenation esterification of maleic anhydride (MA) to diethyl succinate (DES) over prepared Ni$_2$P, (PrPO$_4$)$_m$/Ni$_2$P and PrPO$_4$ catalysts. A1. The dependences of FAL conversion on reaction time; A2. The variations of FOH yield with reaction time; A3. Variations of FAL conversion, FOH yield and Ni leakage during different catalytic recycles from low conversion stage (t=30 min) to high conversion stage (t=240 min) over (PrPO$_4$)$_{0.66}$/Ni$_2$P catalyst; B1. MA conversion as a function of reaction time; B2. DES yield as a function of reaction time; B3. Variations of MA conversion, DES yield and Ni leakage during different catalytic recycles from low conversion stage (t=30 min) to high conversion stage (t=240 min) over (PrPO$_4$)$_{0.66}$/Ni$_2$P catalyst. a. Ni$_2$P; b. (PrPO$_4$)$_{0.24}$/Ni$_2$P; c. (PrPO$_4$)$_{0.66}$/Ni$_2$P; d. (PrPO$_4$)$_{1.0}$/Ni$_2$P; e. (PrPO$_4$)$_{3.6}$/Ni$_2$P; f. (PrPO$_4$)$_{1.1}$/Ni$_2$P; g. PrPO$_4$. Reaction conditions: 100 mg catalyst, 1 mmol FAL, 20 mL isopropanol, 100 °C, 4 MPa H$_2$ (for hydrogenation of FAL); 50 mg catalyst, 5 mmol MA, 10 mL ethyl alcohol, 100 °C, 4 MPa H$_2$ (for hydrogenation esterification of MA).
Figure 8. Kinetic relations for hydrogenation of LA over (PrPO$_4$)$_{1.9}$/Ni$_2$P (A) and Ni$_2$P (B) samples at diverse reaction temperature T=353 K, 373 K or 393 K. A1 and B1: The dependences of ln C$_t$ (C$_t$: the concentration of LA) versus reaction time (t); A2 and B2: Arrhenius correlations between ln k (k: reaction rate constant) and reciprocal of reaction temperature (T$^{-1}$). Other reaction conditions:100 mg catalyst; 2 mmol LA; 10 mL deionized water; 4 MPa H$_2$; 2 h.
**Figure 9.** Kinetic measurements by altering H\(_2\) pressure at p(H\(_2\)) = 3.0 MPa, 4.0 MPa or 5.0 MPa on (PrPO\(_4\))\(_{1.9}/\)Ni\(_2\)P. A. LA concentration (Ct) variations with reaction time under different H\(_2\) pressure. B. Plot of ln r (r: reaction rate) vs. ln p(H\(_2\)). Other reaction conditions: 100 mg catalyst, 2 mmol LA, 10 mL deionized water, 100 °C, 2 h.
Fig. 10. LA-TPD profiles of catalysts. a. Ni$_2$P; b. (PrPO$_4$)$_{1.9}$/Ni$_2$P; c. PrPO$_4$. 
