Biomass Conversion

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Porous Zirconium–Phytic Acid Hybrid: a Highly Efficient Catalyst for Meerwein–Ponndorf–Verley Reductions**

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Abstract: *The utilization of compounds from natural sources to prepare functional materials is of great importance. Herein, we describe for the first time the preparation of organic–inorganic hybrid catalysts by using natural phytic acid as building block. Zirconium phosphonate (Zr-PhyA) was synthesized by reaction of phytic acid and* $ZrCl_4$ *and was obtained as a mesoporous material with pore sizes centered around 8.5 nm. Zr-PhyA was used to catalyze the mild and selective Meerwein–Ponndorf–Verley (MPV) reduction of various carbonyl compounds, e.g., of levulinic acid and its esters into* γ*-valerolactone. Further studies indicated that both Zr and phosphate groups contribute significantly to the excellent performance of Zr-PhyA.*

The assembly of compounds from natural sources to form functional materials has been recognized as an important area in synthetic chemistry.[1] The diversity of natural compounds provides many opportunities for designing functional materials. In particular, some naturally occurring compounds (e.g. porphyrin, polyphenol and polyacids) can chelate with various metal ions to form useful materials with a range of functions, such as Cu^{2+}-heme for oxygen transport,[2] amino acids-based materials for catalysts,[3] Fe^{3+}-phenolic complexes for adhesion,[4] and metal-phenolic networks for coatings and capsules.[5] Inspired by these useful examples, attention was paid to the preparation of functional materials by the coordination of natural building blocks with metal ions. Especially, the diversity of natural compounds provides a range of possibilities for designing efficient catalysts.

The Meerwein–Ponndorf–Verley (MPV) reaction is a highly chemoselective reduction method for carbonyl compounds, which provides an attractive alternative to H_2 by using secondary alcohols as the hydrogen resource.[6] It has been reported that MPV reaction can be efficiently catalyzed by diverse catalysts, such as metal alkoxides,[7] metal complexes,[8] hydrotalcites,[9] metal oxides or hydroxides,[10] and various zeolites,[11] etc. Among the catalysts, Zr-containing catalysts including ZrO_2,[10b] zirconium alkoxides,[7b] Zr-containing zeolites[11a] and $Zr(OH)_4$[10c] are the commonly used ones. However, there are still some drawbacks for Zr-based catalysts, such as deactivation and need of harsh reaction conditions. Therefore, exploration of efficient and stable heterogeneous Zr-based catalysts for MPV reductions is highly desirable.

Phytic acid (PhyA, Scheme S1 in the Supporting Information) obtained from seeds and grains is a major phosphorus resource in plants.[12] It is widely used as food additive and antioxidant. Due to the existence of six phosphate groups in its structure, it can coordinate with metal ions, and this characteristics has been used in water treatment and metal material protection.[13] As far as we know, preparation of organic–inorganic hybrid catalysts using PhyA as a building block has not been reported. Herein, we designed a new porous zirconium phosphonate simply by the reaction of $ZrCl_4$ and PhyA, denoted as Zr-PhyA. The Zr-PhyA could be used as highly efficient heterogeneous catalyst for MPV reactions of carbonyl compounds.

The prepared Zr-PhyA was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and N_2 adsorption–desorption methods. The Zr-PhyA material was formed from small particles with the diameter of about 80 nm (Figure 1B,C). The catalyst was porous with mesopores centered around 8.5 nm (Figure 1E), and the surface area and pore volume were $215\,m^2\,g^{-1}$ and $0.42\,cm^3\,g^{-1}$, respectively (Table S1). In addition, the material had low crystallinity (Figure 1F). All these parameters indicate that Zr-PhyA may serve as a good catalyst. For comparison, other metal (Sn, Nb, Cr, Cu)–phytic acid hybrids were also synthesized with similar textural and structural properties (Figures S1–S3 and Table S2).

Inductively coupled plasma (ICP) analysis showed that the Zr/P molar ratio in Zr-PhyA was about 1:2 (Supporting Information), which indicates one Zr^{4+} can coordinate with two phosphate groups. Due to the coordination ability of all the six phosphate groups in a PhyA molecule and the steric hindrance of PhyA, the most possible connectivity pattern is shown in Scheme 1 and the network of Zr-PhyA was mainly generated through this connectivity pattern. However, the XRD pattern (Figure 1F) indicates that the material has low crystallinity or is poorly ordered. Thus, it can be deduced that there are many defects or irregular connectivity in Zr-PhyA, which is consistent with the fact that the pore size distribution was relatively wide (Figure 1E).

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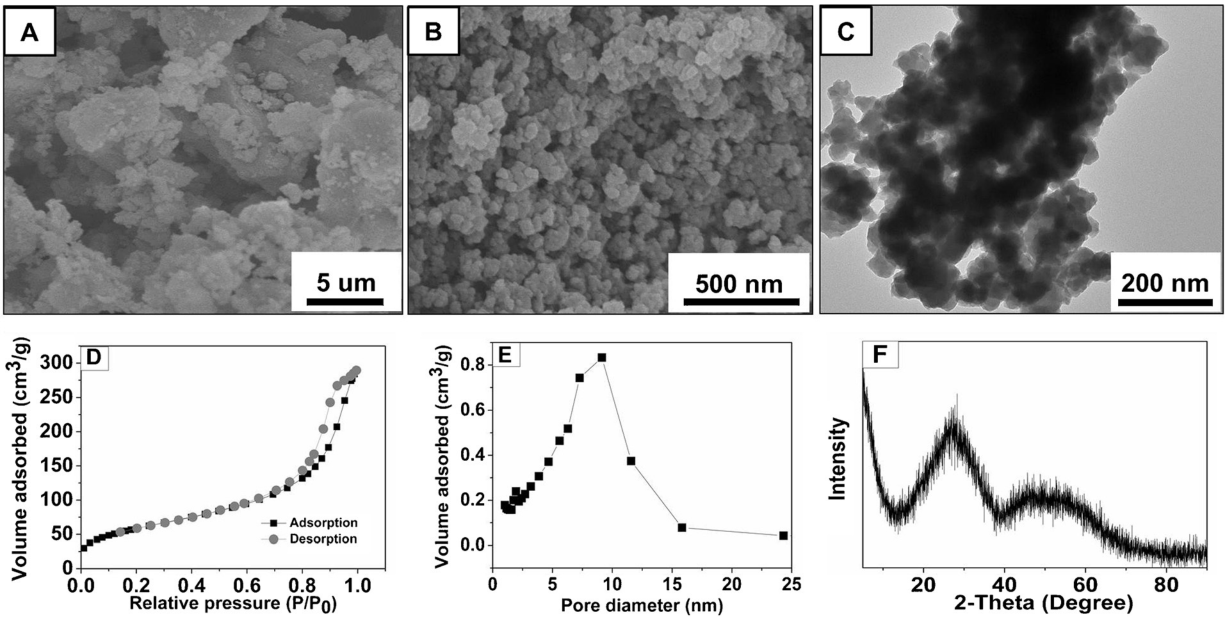
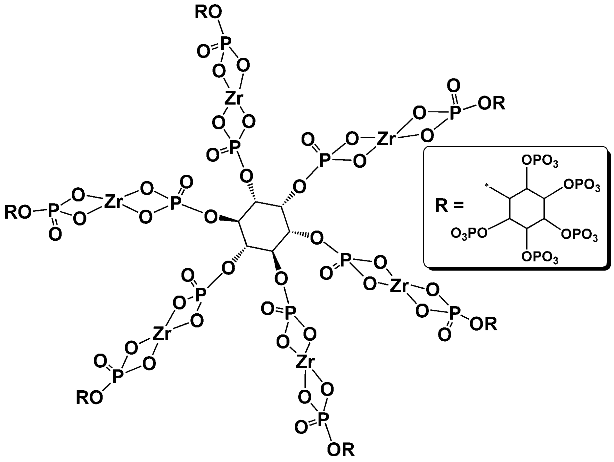


Figure 1. Characterization of the prepared Zr-PhyA. A,B) SEM images, C) TEM image, D) N_2 adsorption–desorption isotherm, E) pore size distribution, and F) powder XRD pattern.



Scheme 1. The most plausible connectivity pattern between PhyA and Zr^{4+}.

Table 1: MPV reaction of EL with isopropyl alcohol over various catalysts under different conditions.[a]

Entry	Catalyst	T [°C][b]	Time [h]	Conv. [%][c]	GVL yield [%][c]	Sel. [%][d]
1	None	150	6	0	0	–
2	Zr-PhyA	150	6	100	96.7	96.7
3	Zr-BTC	150	6	78.7	30.5	38.7
4	ZrO_2	150	6	24.1	21.1	87.6
5	Sn-PhyA	150	6	5.2	2.1	40.4
6	Nb-PhyA	150	6	1.9	0	0
7	Cu-PhyA	150	6	<1	0	0
8	Cr-PhyA	150	6	<1	0	0
9	Zr-PhyA	130	8	98.9	95.4	96.5
10	Zr-PhyA	100	24	86.6	74.6	86.1
11	Zr-BTC	130	8	46.6	9.6	20.6
12	ZrO_2	130	8	10.5	7.8	74.3
13[e]	Zr-PhyA	130	8	100	95.8	95.8
14[f]	Zr-PhyA	130	8	83.4	72.9	87.4
15[g]	Zr-PhyA	130	2	100	98.7	98.7
16[h]	Zr-PhyA	150	6	100	97.8	97.8
17[h,i]	ZrO_2	150	16	100	84.7	84.7
18	Zr-PhyA	200	1	100	98.5	98.5
19[j]	$Zr(OH)_4$	200	1	93.6	88.5	94.5
20[g, h]	Zr-PhyA	150	1	100	96.7	96.7
21[g, h, k]	Zr-Beta	150	6	100	92	92

[a] Reaction conditions: catalyst 0.2 g; reactant 1 mmol; isopropyl alcohol 4 mL. [b] T = Temperature. [c] Conversion (Conv.) and GVL yield were determined by GC. [d] Sel. = Selectivity. [e] The reactant was ML. [f] The reactant was BL. [g] The reactant was LA. [h] The hydrogen donor was 2-butanol. [i] Data obtained from Ref. [15]. [j] Data obtained from Ref. [10c]. [k] Data obtained from Ref. [16].

Conversion of levulinic acid (LA) and its esters into γ-valerolactone (GVL) is an important reaction in biomass conversion.[14] The process involves the reduction of carbonyl groups. Therefore, we selected MPV reduction of LA and its esters to study the activity of Zr-PhyA. Ethyl levulinate (EL) was used as the model reactant to study the influence of various parameters (Table 1). The reaction did not proceed without catalyst (entry 1). Among the examined catalysts, Zr-PhyA showed the highest activity with a GVL yield of 96.7 % at 150 °C (entry 2). In contrast, Zr-BTC, a common metal–organic framework based on $ZrCl_4$ and 1,3,5-benzenetricarboxylate (BTC), only gave a moderate GVL yield of 30.5 % (entry 3). Commercial ZrO_2 also showed lower activity with a GVL yield of 21.1 % (entry 4). Other metal–phytic acid hybrids were not active under the reaction conditions (entries 5–8). Furthermore, it was also demonstrated that Zr-PhyA had better performance than other Zr-based catalysts reported in the literature under comparable reaction conditions (entries 16–21). These results indicated that Zr-

PhyA is a superior catalyst for MPV reaction of EL due to its higher acidity and basicity, as we discuss below.

As expected, the activity of Zr-PhyA increased with rising temperature (Table 1, entries 2, 9, 10, and Figure S4). To our delight, Zr-PhyA maintained its high activity in the MPV reaction of EL under lower temperatures. The reaction could be completed with a GVL yield of 95.4% at 130°C in 8 h (entry 9), which is a much higher yield as obtained over Zr-BTC or ZrO_2 (entries 11 and 12). Importantly, a GVL yield of 74.6% could be obtained from EL even at 100°C when the reaction time was prolonged to 24 h (entry 10). In contrast, there was no GVL produced at 100°C over Zr-BTC or ZrO_2. Moreover, methyl levulinate (ML) also gave a high GVL yield (entry 13). Butyl levulinate (BL) had lower activity than ML and EL, with a GVL yield of 72.9%, due to the steric hindrance of the butyl group (entry 14). Compared with esters, LA had a higher reactivity and was fully converted with a GVL yield of 98.7% within 2 h at 130°C (entry 15). This may result from LA being itself acidic, which could improve the lactonization of 4-hydroxypentanoate (Scheme 2) and thus increase the reaction rate.

In addition, the heterogeneous nature of Zr-PhyA in the catalytic process was evaluated by removing the catalyst from the mixture after reaction for 2 h at 130°C, and stirring the reaction mixture for 24 h without solid catalysts. No further reaction occurred (Figure S5), verifying that Zr-PhyA was heterogeneous. Meanwhile, the concentration of Zr was extremely low (<0.5 ppm) in the reaction solutions as detected by ICP, suggesting that leaching of active species was negligible. Moreover, it was shown that Zr-PhyA could be reused at least five times without decline of activity (Figure 2). Zr-PhyA recovered after five times reuse was characterized by FT-IR, XRD, SEM, and TEM (Figure S6), and the results indicated that the properties of Zr-HBA remained unchanged. The surface characteristics, chemical composition, textural properties and acidic properties of fresh and used Zr-PhyA were also examined by XPS (Table S3), ICP and elemental analysis (Table S3), N_2 adsorption–desorption (Figure S6E and Table S1), and NH_3-TPD (Figure S6F). The results showed that these properties of fresh and used Zr-PhyA also remained almost unchanged after 5 catalytic recycles.

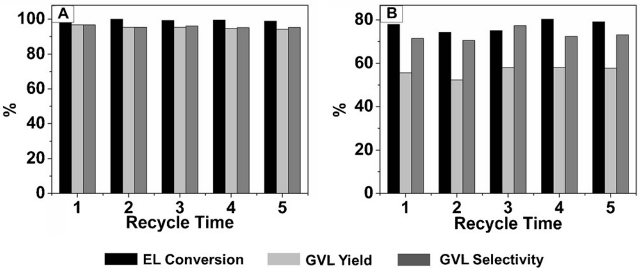


Figure 2. Reusability of Zr-PhyA at 130°C with reaction times of A) 8 h and B) 3 h. Reaction conditions: Zr-PhyA 0.2 g; EL 1 mmol; isopropyl alcohol 4 mL.

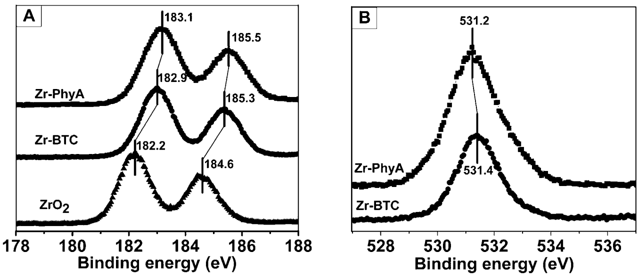


Figure 3. XPS spectra of A) Zr 3d in Zr-PhyA, Zr-BTC and ZrO_2 and B) O 1s in Zr-PhyA and Zr-BTC.

As discussed above, Zr element was crucial for the MPV reaction. We examined the local environment of Zr species in Zr-PhyA, Zr-BTC and ZrO_2 by XPS. As shown in Figure 3 A, the binding energies of Zr in Zr-PhyA were higher than in Zr-BTC and ZrO_2. The higher binding energy of Zr 3d in Zr-PhyA indicates a higher positive charge on the Zr atoms, which results in a stronger Lewis acidity of Zr.[17] The higher Lewis acidity of Zr-PhyA was also confirmed by NH_3-TPD (Figure S7). The higher Lewis acidity of Zr in Zr-PhyA is beneficial to activating the carbonyl groups and thus increased the total reaction rate. Further, we have conducted two Lewis acid-catalyzed reactions, that is, alcoholysis of epoxides[18] (Table S4) and cyanosilylation of cyclohexanone[19] (Table S5). As shown in the two tables, Zr-PhyA is more active than Zr-BTC and ZrO_2 in both reactions. These results confirmed the higher Lewis acidity of Zr-PhyA compared to Zr-BTC and ZrO_2.

To prove the importance of phosphate groups, we synthesized several Zr-containing catalysts with different mole ratios of PhyA and BTC and compared their activities at 150°C and 130°C (Figure 4). N_2 adsorption–desorption examinations indicated similar textural properties of these materials (Figure S8 and Table S1). However, the activity of the catalysts increased with increasing PhyA content. This finding shows that phosphate groups are essential for the high activity of Zr-PhyA. The main reason is that phosphate groups are more basic than carboxyl groups, which could be verified by the higher activity of Na_3PO_4 compared to CH_3COONa in the transesterification of EL with isopropyl alcohol (Table S6). We further examined the local environment of the O element in Zr-PhyA and Zr-BTC (Figure 3B).

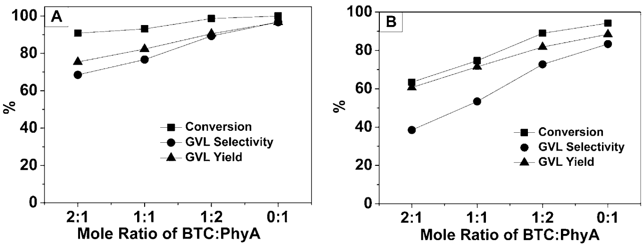
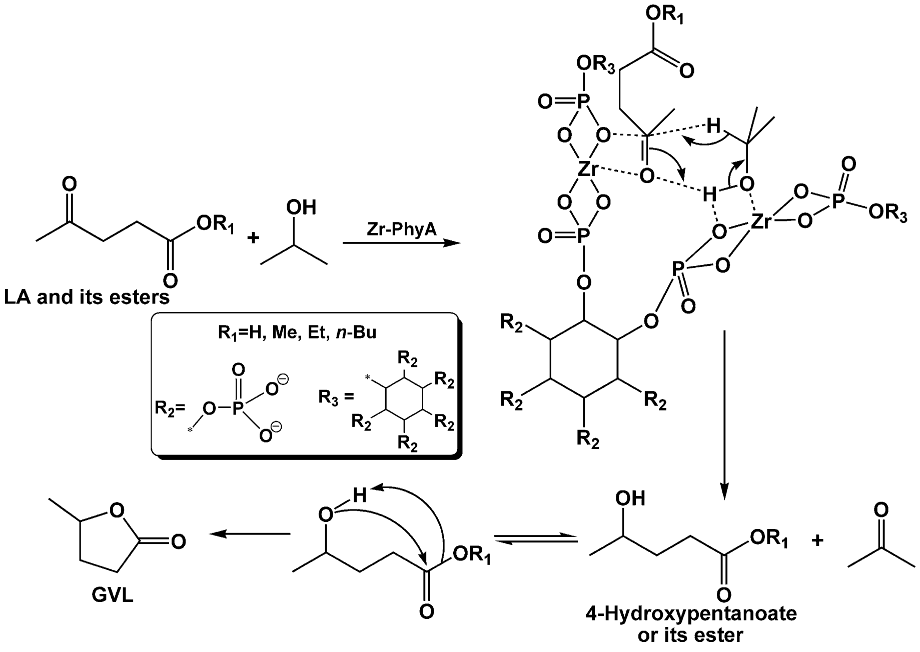


Figure 4. Influence of mole ratio of BTC and PhyA at A) 150°C and B) 130°C. Reaction conditions: catalyst 0.2 g; EL 1 mmol; isopropyl alcohol 4 mL, reaction time 6 h.



Scheme 2. Possible mechanism for Zr-PhyA-catalyzed MPV reaction of LA and its esters to produce GVL.

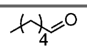
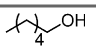
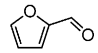
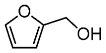
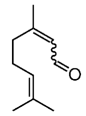
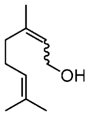
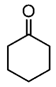
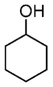
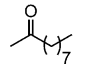
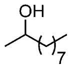
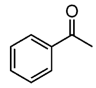
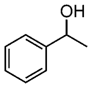
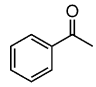
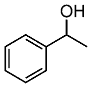
The binding energy of O 1s corresponding to P-O-Zr interactions (in coexistence with the P=O species) in Zr-PhyA was lower than for C-O-Zr interactions (in coexistence with the C=O species) in Zr-BTC.[20] P-O-Zr and C-O-Zr in the two catalysts are active species for MPV reaction of EL. The lower binding energy of O 1s in Zr-PhyA should result in a higher negative charge on the O atoms, which could increase the basicity of O. CO_2-TPD methods also indicated that Zr-PhyA has higher basicity (Figure S9). The results above revealed that Zr-PhyA has a higher basicity than Zr-BTC, which is favorable for the dissociation of the hydroxy groups in isopropyl alcohol occurring through activation by basic sites (O^{2-}) with the aid of Lewis acidic sites (Zr^{4+}) (Scheme 2), thus increasing the reaction rate of the MPV reaction of EL.[15] Therefore, Zr-PhyA with the most phosphate groups showed the highest activity for MPV reaction of EL.

As discussed above, acidic and basic sites are crucial for MPV reaction. NH_3-TPD (Figure S7) and CO_2-TPD (Figure S9) indicate that there are both acid sites (originating from Zr^{4+}) and basic sites (originating from O^{2-} in phosphate groups) on Zr-PhyA. On the basis of the experimental results and a previous report,[21] a possible mechanism for Zr-PhyA-catalyzed MPV reaction of LA and its ester was proposed (Scheme 2). In the catalytic cycle, isopropyl alcohol is adsorbed on Zr-PhyA, resulting in its dissociation to the corresponding alkoxide and hydrogen by the acid–basic sites (Zr^{4+}–O^{2-}).[6] Concurrently, the carbonyl group in LA and its esters is activated by Zr^{4+}. Next, 4-hydroxypentanoate or its ester is formed by hydrogen transfer between the dissociated alcohol and the activated LA or ester levulinate through a six-link intermediate. Finally, GVL is obtained from 4-hydroxypentanoate through intramolecular esterification or transesterification.

Delighted by the excellent performance of Zr-PhyA for MPV reaction of LA and its esters, we explored the possibility of MPV reactions of other carbonyl compounds over Zr-PhyA. Zr-PhyA also showed very good activity for the examined compounds (Table 2). It can be seen that aldehydes are converted better than ketones due to their lower steric hindrance. Importantly, compounds with a double bond or benzene group afford longer reaction times or harsh conditions because the double bond or benzene group could occupy the Lewis acid centers due to their higher electron density, thus lowering the probability of carbonyl groups to reach the active centers.

In summary, a new porous zirconium phosphonate, Zr-PhyA, has been developed by the reaction of $ZrCl_4$ and naturally occurring PhyA. Zr-PhyA showed very high activity and selectivity for MPV reactions of various carbonyl compounds, especially for the conversion of LA and its esters to produce GVL. Systematic studies indicated that both the Lewis-acidic Zr element and the Lewis-basic phosphate groups contribute significantly to the excellent catalytic performance. We believe that the highly efficient and easily prepared catalyst has great potential of application in MPV

Table 2: MPV reaction of carbonyl compounds over Zr-PhyA.[a]

Entry	Reactant	Product	*T* [°C]	*t* [h]	Conv. [%][b]	Yield [%][b]
1			100	1	97.7	97.7
2			100	2	99.3	99.3
3			100	6	87.6	87.6
4			100	10	94.5	94.5
5			150	10	93.5	93.5
6			100	20	95.4	95.4
7			150	6	98.4	98.4

[a] Reaction conditions: catalyst 0.2 g; reactant 1 mmol; isopropyl alcohol 4 mL. [b] Conversion and yield were determined by gas chromatography (GC).

reductions and some other Lewis acid and Lewis base-catalyzed reactions, and that PhyA can be used to design other effective organic–inorganic catalysts.

Keywords: Meerwein–Ponndorf–Verley reduction · natural resources · phytic acid · porous materials · zirconium phosphonate

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