

Acid–Base Bifunctional Zirconium *N*-Alkyltriphosphate Nanohybrid for Hydrogen Transfer of Biomass-Derived Carboxides

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Supporting Information

ABSTRACT: Catalytic transfer hydrogenation (CTH) reactions are efficient transformation routes to upgrade biobased chemicals. Herein, we report a facile and template-free route to synthesize a series of heterogeneous nitrogen-containing alkyltriphosphonatemetal hybrids with enhancive Lewis acid and base sites, and their catalytic activity in converting biomass-derived carbonyl compounds to corresponding alcohols in 2-propanol. Particularly, a quantitative yield of furfuryl alcohol (FFA) was obtained from furfural (FUR) over organotriphosphate-zirconium hybrid (ZrPN) under mild conditions. The presence of Lewis basic sites adjacent to acid sites with an appropriate base/acid site ratio (1:0.7) in ZrPN significantly improved the yield of FFA. Mechanistic studies for the transformation



of FUR to FFA with ZrPN in 2-propanol- d_8 evidently indicate CTH reaction proceeding via a direct intermolecular hydrogen transfer route. It was also found that ZrPN could catalyze isomerization of C_3-C_6 aldoses to ketoses involving intramolecular hydrogen transfer in water.

KEYWORDS: biofuels, hydrogen transfer, heterogeneous catalysis, acid-base catalyst, mesoporous materials

L ignocellulose-based feedsocks are promising renewable carbon sources to produce downstream biochemicals and fuels, and they are potential alternatives to fossil-based ones because of their reactive functional groups.¹ The catalytic transformations of oxygenated biochemicals via hydrodeoxygenation or hydrogenolysis with noble or transition metals have been widely explored.² However, some major drawbacks such as overhydrogenation, unselective C–C cleavage, and use of flammable H₂ with high pressure and temperature are entailed, which may result in the decrease of selectivity toward targeted products.³ The development of more efficient and selective routes operated by robust and low-cost catalysts can be expected to increase the feasibility of upgrading biomass.⁴

Lewis acid-containing solid catalysts for inter- and intramolecular hydrogen transfer have been recently employed as one of the efficient catalytic routes for biomass upgradation.⁵ The use of organic H-donors, such as alcohols and formic acid, instead of natural-gas-based H₂ can significantly alleviate the carbon footprint of valuable chemicals derived from biomass. In connection to this, Lewis acidic zeolites, such as Sn- and Zrbeta, have been recently reported for hydrogenation of biomass-derived carboxides to corresponding alcohols via Meerwein–Ponndorf–Verley (MPV) reduction.⁶ Moreover, Zr-containing catalysts such as ZrO₂ and ZrOCl₂·8H₂O have also been illustrated to be active for transforming levulinic acid and its esters to γ -valerolactone (GVL) through the catalytic transfer hydrogenation (CTH) pathway.⁷ However, the role of HCl produced from ZrOCl₂·8H₂O on the product yield has not been disclosed.^{7b} Furthermore, it has been reported that ZrO(OH)_x containing acidic and basic sites could give an excellent yield of 2,5-bis(hydroxymethyl)furan (94%) from 5hydroxymethyl furfural (HMF) via the CTH reaction.⁸ These previous reports prompted us to explore Zr-based acid—basecouple-site-containing hybrids for CTH reactions, which could not only overcome the drawbacks like catalyst deactivation and rigorous conditions encountered in the catalytic systems mediated by, for example, ZrOCl₂,^{7b} ZrO₂,^{7c} and ZrO(OH)_x,⁸

Inorganic—organic metal phosphonates, which exhibit superior hydrolytic stability to silica and polymers,⁹ have been recently explored for adsorption and separation of toxic and pollutant species, storage of energy, and drug delivery,¹⁰ but to a lesser extent studies as catalysts.¹¹ In order to facilitate

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Table 1. Catalytic Transfer Hydrogenation of FUR to FFA with Different Catalysts⁴

entry	catalyst	$[m^2/g]^b$	$V_{\text{pore}} \ [\text{cm}^3/\text{g}]^c$	${D_{{ m meso}}\atop{\left[{ m nm} ight]}}^d$	base/acid ratio ^e	conv. [%] ^f	yield [%] ^f	selec. [%] ^f	initial rate $[\mu mol m^{-2} h^{-1}]^g$	$(h^{-1})^{h}$
1	none					<1	0	0		
2	Et ₃ N					9	<1			
3	$ZrCl_4$					58	6	10		
4	ZrPN	154	0.46	12.4	1:0.7	98/41 ⁱ	98/40 ⁱ	>99/98 ⁱ	314	22.5
5	SnPN	28	0.12	13.7	1:1.7	29	13	45	58	0.6
6	TaPN	15	0.04	10.0	1:17.6	24	2	8	20	0.2
7	NbPN	17	0.05	11.3	1:22.5	27	<1		7	< 0.1
8	AlPN	39	0.13	12.3	1:0.9	30	15	50	48	1.1
9	NiPN	25	0.16	21.3	1:3.4	14	9	64	33	0.4
10 ¹	ZrO_2	22	0.06	9.3	1:0.6	36	27	75	129	9.3
11 ^k	ZrO_2	138	0.04	3.5	1:1.1	68	46	68	83	11.2
12 ¹	ZrO_2	215	0.03	2.4	1:1.0	89	60	67	97	12.7
13 ^m	ZrPN					72	58	81		
14 ⁿ	ZrPN					47	33	70		
15	ZrPPh	119	0.07	3.0	1:0.9	94	78	83	210	15.6
16°	ZrPN	154	0.46	12.4	1:0.7	>99	97	97	302	22.1
17°	ZrO_2	22	0.06	9.3	1:0.6	37	19	51	89	4.8
18 ^p	ZrPN	154	0.46	12.4	1:0.7	93	90	97	45	3.1
19 ^p	ZrO_2	22	0.06	9.3	1:0.6	17	12	71	8	0.3

^{*a*}Reaction conditions: 2.5 mmol furfural (FUR); 0.1 g catalyst; 10 mL 2-propanol; 140 °C and 2 h. ^{*b*}BET surface area was obtained from N₂ adsorption isotherm. ^{*c*}Pore volume was estimated from BJH adsorption cumulative volume of pores. ^{*d*}Mesopore size was estimated from the BJH adsorption average pore diameter. ^{*e*}The contents of acid/base sites were determined by CO₂/NH₃-TPD, respectively. ^{*f*}FUR conversion (Conv.) and furfuryl alcohol (FFA) yield were determined by gas chromatography (GC); Selec.: Selectivity. ^{*g*}Initial rate is defined as (FFA mol)/(BET surface area × catalyst weight × time) at a fixed conversion of ~30%. ^{*h*}Y_{rate} is defined as (FFA mol)/(acid–base site content × catalyst weight × time) at a fixed conversion of ~15%. ^{*i*}Reaction time: 10 min. ^{*j*}Calcined at 500 °C for 6 h. ^{*k*}Calcined at 300 °C for 6 h. ^{*k*}Calcined at 150 °C for 6 h. ^{*m*}Lewis acid sites of ZrPN were covered by pretreatment with 50 mg pyridine. ¹⁶ ^{*n*}Lewis base sites of ZrPN were poisoned by titration with 50 mg benzoic acid. ¹⁶ °S wt % water relative to FUR was introduced. ^{*p*}Reaction temperature: 100 °C, time: 15 h.

the access of substrates to the active sites in the catalytic process, controllable mesopores and macropores are highly required. However, a complex sol-gel approach assisted with different surfactants is commonly used to augment the microporous structure of metal-organic framework topology.¹² Herein, we report a facile, template-free approach to synthesize various heterogeneous nitrogen-containing alkyltriphosphonate-metal hybrids (MPN) functionalized with enhancive acid and base sites (see Supporting Information for catalyst synthesis and charaterization), and their catalytic applications toward CTH reactions of biomass-derived carbonyl compounds to alcohols and aldoses to ketoses. Moreover, this study focuses on the role of synergic effect of acid-base couple sites on the product yield as it has been scarcely reported.

Furfufral (FUR) derived from carbohydrates is one of crucial components in bio-oil, while its reactive aldehyde group is susceptible to formation of humins by condensation reactions.¹³ Hydrogenation of C=O to C-OH was thus developed to stabilize the compounds containing reactive carbonyl groups.¹⁴ The catalytic activity of characterized MPN was initially studied toward hydrogenation of FUR to furfuryl alcohol (FFA) in 2-propanol, and the catalytic results with physicochemical parameters are presented in Table 1. No significant conversion of FUR was observed without a catalyst (entry 1). The precursors Et₃N and ZrCl₄ used for ZrPN synthesis yielded less than 6% of FFA (entries 2-3), wherein some side reactions such as FUR condensation and FFA etherification/alcoholysis took place, resulting in a low selectivity toward the product (Scheme S1). Intriguingly, ZrPN afforded a near quantitative yield of FFA (98%) with a high Y_{rate} of 22.5 h⁻¹ at 140 °C (entry 4), showing the highest activity compared to other metal-incorporated organotriphosphonate hybrids (entries 5-9). It seems that relatively higher content of acid-base sites (5 mmol/g), more appropriate molar ratio of base/acid sites (1:0.7; Tables 1 and S1, Figures S1 and S2), stronger Lewis acidity (Figures S3 and S4), and larger surface area $(154 \text{ m}^2/\text{g} \text{ with an initial rate of})$ 314 μ mol m⁻² h⁻¹, Tables 1 and S2) primarily contribute to the superior catalytic activity of ZrPN. In addition, the obtained results revealed that the moderate mesopore diameter (12 nm) and particle size (20-50 nm), and amorphous structure might have also played a certain role in part on enhancing the performance of the ZrPN catalyst (Tables 1 and S2; Figures S5-S8). It is worthwhile to note that theose organotriphosphonate hybrids contain only Lewis acid sites (1450 cm⁻¹) but no Brønsted acid sites with absence of peak at 1540 $\rm cm^{-1}$, as manifested by pyridine-adsorbed FT-IR (Figures S3 and S4).

To compare with ZrPN, ZrO₂ samples treated at different calcination temperatures were subjected to catalytic transfer hydrogenation of FUR to FFA (Table 1, entries 10-12). The notable changes in the content and distribution of base-acid sites were found to have significant influence on the yield of FFA (Tables 1 and S1). ZrO₂ calcined at 150 °C with more acid-base sites (0.55 mmol/g, base/acid site ratio: 1:1) and high surface area (215 m²/g) could effectively catalyze FUR being converted to FFA in a moderate yield of 63%, whereas the corresponding FFA selectivity (71%) and initial rate (97 μ mol m⁻² h⁻¹) were a little lower than those (75%, 129 μ mol $m^{-2} h^{-1}$) obtained over ZrO₂ calcined at 500 °C, which has a relatively higher base/acid site ratio (1:0.6) and stronger Lewis acidity (Figure S9) but a lower acid-base site content (0.14 mmol/g) and surface area (22 m^2/g), as well as absence of Bronsted acid sites (Figure S10). These results corroborate that

an appropriate base/acid site ratio and strong Lewis acidity of ZrPN are important and responsible for improving FFA selectivity and reaction rate, whereas the increase of FUR conversion is dependent on a high total content of acid—base sites and large surface area. Above preliminary studies clearly demonstrate the promotional role of Zr present in the network of the ZrPN hybrid, where strong Lewis acid sites are created in the vicinity of base sites according to the proposed structure of ZrPN in Scheme 1 (~1:2 Zr/P molar ratio; Table S3).

Scheme 1. Plausible Structure of Acid–Base Bifunctional *N*-Alkyltriphosphonate–Zirconium Hybrid (ZrPN)



Moreover, the incorporation of Zr into the network of ZrPN was corroborated with FT-IR analysis by assigning the appearance of sharp band at 1035 cm⁻¹ to Zr–O–P stretching vibration (Figure S11).¹⁵ For subsequent catalytic studies and comparison, ZrO_2 -500 was chosen to be a more suitable candidate because it has similar properties to ZrPN: close base/ acid molar ratio, strong Lewis acidity, and absence of Bronsted acid sites.

In order to gain more insight toward the role of active sites in ZrPN on FFA yield, Lewis acid/base sites were separately passivated with pyridine (Py) and benzoic acid (BA), respectively. Py-treated ZrPN yielded 58% FFA, which is 40% lower than pristine ZrPN but 25% higher than BA-poisoned ZrPN, implying the more pronounced effect of base than acid sites and evidnetly displaying the concerted effect of acid-base couple sites for this reaction (Table 1, entries 13 and 14).¹⁶ ZrPPh with no nitrogen center (see Scheme S2) also applied as catalyst and gave 78% yield of FFA (Table 1, entry 15), substantiating the key role of base sites generated from the nitrogen centers on improving the performance. The relatively high molar ratio of Lewis base/acid sites (1:0.7) is consistent with the result where acid-poisoned ZrPN led to a high FFA yield (58%), that is, a pronounced influence of basic sites. ZrO_2 has a similar ratio of base/acid sites, but only 32% FFA yield was obtained, further corroborating the essential role of nitrogen centers that largely contributed to the active basic sites. Furthermore, the high hydrophobicity of ZrPN (Figure S12) was likely to facilitate the adsorption of FUR (logP: 0.712) and desorption of FFA (logP: 0.213), thereby partially enhancing the catalytic activity. To substantiate this hypothesis, an additional experiment was conducted with ZrPN by adding 5 wt % water, wherein the activity of ZrPN remained the same (Table 1, entry 16) while the FFA yield descended from 27 to 19% over ZrO₂ (Table 1, entry 17).

The influence of reaction time and temperature on synthesis of FFA from FUR was also investigated (Figure S13). A high FFA yield of 90% was achieved over ZrPN at a relatively low temperature of 100 $^{\circ}$ C (Table 1, entry 18), but ZrO₂ only gave

12% yield of FFA (Table 1, entry 19). The activation energy and rate constant were calculated, as summarized in Table S4. The rate constant for ZrPN at 100 °C was found to be 3.6 × 10^{-3} s⁻¹ which is 12-fold higher than ZrO₂. Moreover, activation energy for ZrPN and ZrO₂ was 70.5 and 79.1 kJ/ mol, respectively. To get more insight toward understanding the activity discrepancy between these two materials, XPS analysis was conducted and the resulting spectra of ZrPN and ZrO₂ are shown in Figure 1. The binding energy of Zr 3d in



Figure 1. XPS spectra of Zr 3d (A) and P 2p (B) in ZrPN, ZrO_2 , and ZrPPh.

ZrPN at 182.9 and 185.2 eV is slightly higher than that of ZrO₂ (Figure 1A), manifesting the generation of zirconium species with stronger Lewis acidity.¹⁷ Moreover, a peak at 133.5 eV belonging to P 2p species in ZrPN, evidently indicated that alkylphosphate group in ZrPN might facilitate the formation of stronger basic sites due to the enhanced electronic interaction between Zr-O-P bond (Figure 1B). These results are consistent with the NH₃ and CO₂ desorption profiles of ZrPN, where the gas desorption occurred at relatively higher temperature due to the existence of strong Lewis acid/base sites (Table S1; Figures S1-S2). The presence of strong Lewis acid sites was further confirmed by Py-adsorbed FT-IR (Figure S3), where it can be seen that Py can strongly bound with Lewis acid sites, with the appearance of the peak at 1450 cm⁻¹, even after desorption at 250 °C. Notably, a close Lewis acidity between ZrPN and ZrPPh can be observed (Figure 1A), which demonstrates that the organic moiety in the hybrids (MPN) is beneficial and assisting to stabilize the Lewis acid sites derived from Zr, thus increasing the strength of Lewis acid centers in both ZrPN and ZrPPh. On the other hand, additional base sites generated by the organic moiety itself (i.e., nitrogen center) in ZrPN indicate that it plays a promotional role in enhancing the selectivity toward furfuryl alcohol (FFA), thus resulting in the superior catalytic performance of ZrPN to that of ZrPPh. As the reaction temperature increased to 160 °C with prolonged duration, a certain amount of byproducts such as 2-isopropoxymethyl furan (5-16% yield), isopropyl levulinate (2-8% yield), GVL (3-5% yield), and 2,2'-difurfuryl ether (1-4% yield) were formed at the expense of FFA, identified by GC-MS (Figure S14), which are generally promoted by acid-base sites with high strength.¹⁸

The thermal stability of ZrPN was studied by TG analysis and found to be stable up to ~250 °C (Figure S15). To understand the reactive stability, ZrPN was treated in 2propanol at 140 °C for 72 h in the absence of the substrate FUR. Upon completion, the resulting solid catalyst was filtered, washed with ethanol and ethyl ether for 3 times, dried at 80 °C overnight, and found to be still active for this reaction, yielding 94% FFA that is close to the parent ZrPN after reacting at 140 °C for 2 h. No significant difference in TG thermograms of the solvent-treated and fresh ZrPN catalysts can be seen (Figure S16). Moreover, the catalytic behavior of ZrPN was also studied by filtering the catalyst off from the hot reaction mixture after reacting for 1 h at 120 $^{\circ}$ C (Figure 2A), and no



Figure 2. Catalytic behavior study of ZrPN; reaction conditions: FUR 2.5 mmol, ZrPN 0.1 g, 2-propanol 10 mL, 120 $^{\circ}$ C (A). Catalyst recycling study of ZrPN; reaction conditions: FUR 2.5 mmol, ZrPN 0.01 g, 2-propanol 10 mL, 140 $^{\circ}$ C and 2 h (B).

reaction took place even after another 9 h. The filtrate was then subjected to ICP analysis, and the low leaching content of zirconium (<1 ppm) revealed the intactness of ZrPN during reactions. Furthermore, the recyclability of ZrPN was examined by keeping approximately 25% FUR conversion and less catalyst dosage (0.01 g) at 140 °C for 2 h (Figure 2B), and the performance of ZrPN was found to be almost constant (>98% selectivity) in six consecutive runs. FT-IR, XRD, and N₂ adsorption-desorption analyses show a slight change in the structure between fresh and reused ZrPN catalysts (Figure S17), which can be ascribed to the adsorption of organic species (e.g., isopropoxide) primarily into micropores (with micropore surface area decreasing from 37 to 8 m^2/g) of the ZrPN catalyst during the recycles (Figures S17 and S18). FT-IR spectrum of six-time-used ZrPN revealed that the peak appeared at 1035 cm⁻¹ assigned to Zr-O-P stretching vibration was not perturbed, implying the intactness of the network. Notably, no significant decrease in mesopores of ZrPN is observed after six recycles (with mesopore surface area marginally reducing from 117 to 102 m^2/g and average pore size increasing from 6.1 to 7.3 nm), inferring that acid and base sites in mesopores available to the substrate are dominantly responsible for the catalytic process of hydrogen transfer.

Mechanistic insight into the catalytic hydrogenation of FUR to FFA was performed by ex situ NMR studies in 2-propanol- d_8 with ZrPN at various times, and the corresponding ¹H NMR spectra of the reaction mixture are provided in Figure 3. The aldehydic proton of FUR (1a) gradually disappeared with increasing addition of deuterium (D) from isotopic 2-propanol to C=O, consequently leading to the formation of $-CH_2$ moiety in FFA (1b). However, it is ambiguous whether the reaction takes place via direct hydrogen transfer or metal hydride route owing to the unselective addition of D (Scheme S3). In order to clearly distinguish these two pathways, tertbutanol was added as cosolvent with isotopic 2-propanol in a molar ratio of 3:1. As a result, tert-butanol is not able to act as H-donor due to the absence of β -H, but it can exchange most D species of -OD group in isotopic 2-propanol to -OH and replace D on the metal surface with H (Scheme S4).¹⁹ Through GC-MS analysis, the molecular ion peak of FFA was detected with an additional 1 amu (m/z = 99), whereas D will not be available for the metal hydride route, thus substantiating the occurrence of direct hydrogen transfer with ZrPN (Scheme S4, Figure S19). On the basis of the results obtained from the mechanistic study, it can be postulated that base sites could



Figure 3. Reaction kinetics study of FUR-to-FFA hydrogenation in isotopic 2-propanol (d_8) using ¹H NMR; other unmarked major bonds in ¹H NMR spectra belonged to the solvent, water, and in situ-formed acetone with constant chemical shifts.

assist the formation of isopropoxide moieties on the Lewis acid sites by abstraction of a proton from 2-propanol, thus facilitating the formation of a six-membered intermediate between alcohol, aldehyde, and Lewis acid sites, hereby transferring β -H as in line with the MPV-type mechanism.²⁰

As ZrPN exhibited remarkable activity toward intermolecular hydrogen transfer of FUR to FFA, the study has been extrapolated to understand the reactivity of various carbonyl compounds, including biomass-derived substrates (Table 2). All chosen aldehydes and ketones can be efficiently catalyzed by ZrPN to produce their corresponding alcohols in high yields. Biomass-derived HMF and its derivative (Table 2, entries 1 and 2) gave near quantitative yields. Another HMF-derivative ethyl

Table 2. CTH of Various Carbonyl Molecules with ZrPN^a

Entry	Substrate	Product	Temp. [°C]	Time [h]	Conv. [%] ^[b]	Yield [%] ^[b]
1	-10	- Он	140	2	>99	99
2	HO	НОСОН	140	2	>99	98
3		Он	140	2	99	98
4		ОН	140	2	97	96
5	HO	НОДОН	140	2	95	93
6	ŬO	ОН	140	1	98	97
7	\langle	ОН	140	5	91	90
8		О	140	5	90	89
9		C)	160	6	96	96
10	<u> </u>	OH	160	10	96	95
11			160	10	93	92

^{*a*}Reaction conditions: 2.5 mmol substrate; 0.1 g of catalyst and 10 mL of 2-propanol. ^{*b*}Conversion (Conv.) and yield were quantified using GC.

levulinate yielded 93% GVL, although a relatively higher reaction temperature and prolonged duration are needed (entry 11). It is well-known that aldehydes are generally more reactive than ketones due to the steric hindrance and electron-donating nature of the alkyl group in ketone.

The study has also been extended to explore the intramolecular hydrogen transfer of C_3-C_6 aldoses to the corresponding ketoses with ZrPN in water (Table S5). The product distribution of glucose isomerization reaction was found to be 52% glucose, 36% fructose, and 5% mannose at 90 °C for 50 min (Table S5, entry 1), which is comparable to that of Sn-Beta zeolite-mediated catalytic systems.²¹ Only 6-10% and 21% of fructose was formed when using ZrO₂ and ZrPPh as catalysts, respectively, inferring the positive role of Zr (Lewis acid sites) in the framework of ZrPN combined with the adjacent basic sites on accelerating fructose yield (Table S6). The poisoning experiments proved the synergic effect of acidbase sites in ZrPN on glucose-to-fructose isomerization (Table S5, entries 2 and 3). These results clearly indicate that Lewis acid sites present in ZrPN cannot be hampered by water, thereby enhancing the catalytic activity. In constrast, Al-zeolites cannot catalyze glucose isomerization due to weakening of Lewis acid sites in water.²² The other aldoses including xylose, erythrose, and glyceraldehyde can also give good yields of corresponding ketoses with ZrPN (Table S5, entries 4-6). Besides isomerization, epimerization also takes place in low degree over ZrPN for C_4 - C_6 sugars, and the in situ-formed C_3 ketose dihydroxyacetone from glyceraldehyde tends to be further converted to lactic acid via pyruvic aldehyde.²³

In summary, we have demonstrated that the mesoporous ZrPN nanohybrid with high surface area and enhancive Lewis acid (zirconium) and base (alkylphosphate and amino groups) centers can be synthesized by a facile and template-free approach. The bifunctional nanohybrid exhibited remarkable catalytic activity toward formation of near quantitative yields of valuable alcohols from biomass-derived carboxides via direct hydrogen transfer, and it was also effective for aldose-to-ketose isomerization in water. The obtained results from these studies clearly indicate that ZrPN can efficiently catalyze the inter- and intramolecular hydrogen transfer reactions and can be extrapolated to other similar lignocellulose-derived substrates for upgrading biomass.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b02431.

Experimental details of catalyst preparation and characterization; catalytic performance and mechanism (PDF)

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Notes

The authors declare no competing financial interest.

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