Chemical Science

EDGE ARTICLE



Cite this: Chem. Sci., 2017, 8, 3146

A bifunctional cerium phosphate catalyst for chemoselective acetalization*

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Acid-base solid catalysts synthesized with structurally controlled uniform active sites can lead to unique catalysis. In this study, a CePO₄ catalyst was synthesized using a hydrothermal method and found to exhibit high catalytic performance for the chemoselective acetalization of 5-hydroxymethylfurfural with alcohols, in sharp contrast to other homogeneous and heterogeneous acid and/or base catalysts. In the presence of CePO₄, various combinations of carbonyl compounds and alcohols are efficiently converted into the corresponding acetal derivatives in good to excellent yields. Mechanistic studies show that $CePO_4$ most likely acts as a bifunctional catalyst through the interaction of uniform Lewis acid and weak base sites with 5-hydroxymethylfurfural and alcohol molecules, respectively, which results in high catalytic performance.

Received 23rd December 2016 Accepted 6th February 2017

DOI: 10.1039/c6sc05642c

rsc li/chemical-science

Introduction

Synergistic and cooperative activation by two or more catalytically active sites with acidic, basic or redox properties can allow high catalytic activity and specific selectivity.1 In particular, acid-base bifunctionality has received much attention because such concepts are widely applied to catalyses related to hydrocarbon conversion, atom-efficient functional group transformation, tandem reactions, and asymmetric syntheses.² In the fields of heterogeneous catalysis, the acid-base properties of metal oxide-based materials have been extensively studied, and various effective simple and mixed oxide catalysts have been reported.3 However, difficulty in the construction of uniform electrically and structurally controlled acid-base sites often leads to a problem where the fine-tuning of the catalyst structure and the reactivity are restrained. While the modification of oxide surfaces with organic acids and/or bases is a powerful method,⁴ the susceptibility of the organic parts to oxidative/thermal degradation has limited the usefulness of such catalysts. Therefore, the design and development of new high-performance all-inorganic heterogeneous acid-base catalysts remains a strongly desired and challenging subject of research.

We have recently reported unique base catalysis using oxoanions including $[WO_4]^{2-}$ and $[PO_4]^{3-5}$. Despite their

basicities being weaker than those of inorganic and organic strong bases, their specific activation of nucleophiles such as alcohols and amines results in atom-efficient reactions such as the chemical fixation of CO2, regioselective N-alkylation of indoles, and chemoselective acylation of alcohols. On the other hand, rare earth (RE) metal species act as Lewis acid catalysts for various carbon-carbon bond forming reactions through the activation of carbonyl compounds.6 Against this background, we anticipated that RE orthophosphates, REPO₄, would be good candidates as bifunctional acid-base catalysts that can work in concert to promote electrophilicity and nucleophilicity in reactive partners. In this communication, we report the highly chemoselective acetalization of 5-hydroxymethylfurfural (1a), which has alcohol and aldehyde functionalities,⁷ with alcohols using a monoclinic CePO₄ catalyst synthesized by a hydrothermal method (Fig. 1(a)). Compound 1a is a versatile carbonyl compound with sensitive functional groups. For reactions of 1a with alcohols in the presence of acid catalysts,^{8,9} ethers or a complex mixture of products are typically obtained due to the presence of the Brønsted acid-sensitive hydroxyl groups in 1a.8 The present system has the following significant advantages: (i) high yields and chemoselectivity toward acetals, even for substrates with hydroxyl groups, (ii) applicability to various combinations of substrates and larger-scale syntheses, and (iii) reusability as a heterogeneous catalyst system. While metal phosphates and related materials have been extensively investigated for the conversion of carbohydrates into 1a,10 acid-base catalysis over CePO₄ has not been reported to date¹¹ and the present bifunctionality can lead to the chemoselective acetalization of carbonyl compounds containing sensitive functional groups, such as 1a.





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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c6sc05642c



Fig. 1 (a) Structure of CePO₄. Green, gray, and red spheres represent Ce, P, and O atoms, respectively. (b) XRD patterns for CePO₄ (upper) and monoclinic CePO₄ (lower, ICSD 79748). (c) XPS Ce 3d spectrum and (d) SEM image of CePO₄.

Results and discussion

Synthesis and characterization of CePO₄

Monoclinic CePO₄ was synthesized through the hydrothermal reaction of Ce(NO₃)₃ and (NH₄)₂HPO₄ at 180 °C, followed by calcination at 900 °C (see details in the ESI[†]). Fig. 1(b) shows the powder X-ray diffraction (XRD) pattern measured for CePO₄, which is in good agreement with that reported for the monoclinic CePO₄ structure, in which a Ce³⁺ ion connects to seven tetrahedral PO_4^{3-} groups [space group $P2_1/n$].¹² The impurity phases of other cerium and phosphorus oxides were not observed. The infrared (IR) spectrum of CePO₄ is shown in Fig. S1.[†] Asymmetric stretching vibrations of the PO₄^{3–} groups were split into bands at 1091, 1062, 1028, 994, and 956 cm⁻¹ due to a decrease in the symmetry of PO_4^{3-} from T_d to C_1 .¹³ The bands in the range of 500–700 cm^{-1} are assigned to the bending of the P-O links in the distorted PO₄³⁻ tetrahedra, and these band positions are similar to those previously reported for monoclinic CePO₄.¹³ The elemental analysis of bulk CePO₄ using energy dispersive X-ray spectroscopy (EDX) revealed that the molar ratio of Ce : P is 1 : 1. The valence state of the surface Ce was investigated using X-ray photoelectron spectroscopy (XPS) (Fig. 1(c)). The Ce $3d_{3/2,5/2}$ spectra are composed of two multiplets (v and u), which correspond to the spin-orbit split 3d_{5/2} and 3d_{3/2} core holes.¹⁴ The Ce 3d spectrum of CePO₄ exhibits four peaks with binding energies of 904.9, 901.0, 806.5, and 883.0 eV, which correspond to the u', u⁰, v', and v⁰ peaks, respectively, and are in good agreement with the reported Ce 3d spectra for Ce(m) oxides.¹⁵ The specific surface area of CePO₄ calculated from a Brunauer-Emmett-Teller (BET) plot of the N2 adsorption isotherm (77 K) was up to 37 m² g⁻¹. Fig. 1(d) shows a scanning electron microscopy (SEM) image of CePO₄ with rodlike shaped particles 100-500 nm long and 20-50 nm wide.

The acidic properties of CePO₄ were evaluated using IR spectroscopy for a sample with adsorbed pyridine as a probe base (see details in the ESI[†]).^{3,10,16} Differential IR spectra of CePO₄ with adsorbed pyridine are shown in Fig. 2(a) and S2.[†] The band at 1445 cm⁻¹ is assigned to the pyridine species coordinated to the Lewis acid sites, while no band due to pyridinium ions bonded to the Brønsted acid sites was observed at *ca.* 1540 cm⁻¹. The amount of Lewis acid sites on CePO₄ was estimated from the intensity of the band at 1445 cm⁻¹ to be 0.096 mmol g^{-1} . The difference IR spectrum for CePO₄ with adsorbed CHCl₃ is shown in Fig. 2(b). The red-shift of the original C-H stretching mode of the CHCl3 molecule (from 3034 cm^{-1} to 3008 cm^{-1}) indicates the presence of basic sites on the surface.¹⁶ In addition, a new broad shoulder band appeared at 1250 cm⁻¹, which was assigned as δ (ClC-H) for the CHCl₃ molecules due to the interaction of the acidic hydrogen and chlorine atoms with the basic oxygen and Lewis acid sites, respectively.16 Thus, the base sites on CePO4 could be located in close proximity to the Lewis acid sites, in agreement with the structure of CePO₄.

Catalytic acetalization of 1a with methanol

The reaction of **1a** with methanol was examined first in the presence of various catalysts that have been reported to be effective for acetalization,¹⁷ and the results are summarized in Table 1. The three products 5-(dimethoxymethyl)-2-fur-anmethanol (**2a**), 5-methoxymethylfurfural (**3a**), and 2-(dimethoxymethyl)-5-(methoxymethyl)furan (**4a**) were mainly formed. The reaction did not proceed in the absence of a catalyst (entry 27). Among the catalysts tested, CePO₄ exhibited the highest activity for the acetalization of **1a** to give **2a** in 78% yield (entry 1). In this case, the selectivity toward **2a** reached 96% without the formation of **3a** or **4a**. In the presence of homogeneous



Fig. 2 Difference IR spectra for (a) pyridine-, (b) chloroform-, (c) acetone-, and (d) methanol-adsorbed CePO₄ at 25 °C

Brønsted acid catalysts (H₂SO₄, *p*-toluenesulfonic acid (TsOH), and H₃PW₁₂O₄₀) and Lewis acid catalysts (scandium trifluoromethanesulfonate (Sc(OTf)₃) and Ce(OTf)₃), only 3a and/or 4a were obtained in low to moderate yields (entries 2-6). The reaction of 1a with methanol in the presence of these homogeneous acid catalysts was carried out by reducing the amounts of the catalysts to match the surface Ce content (i.e. 9.6 µmol) with the Lewis acid sites measured using pyridine-IR (Table S1[†]). While the conversions using these homogeneous acid catalysts were higher than that using CePO₄, 2a was not formed under the reaction conditions. In addition, no product was obtained using the homogeneous base catalysts of K₃PO₄, K₂HPO₄, and KH₂PO₄ (entries 7-9). Thus, homogeneous acid or base catalysts themselves are not deemed as effective for the chemoselective acetalization of 1a. Acetalization over Nb2O5 was less effective than over CePO₄, and other metal oxide catalysts including SiO₂, ZrO₂, CeO₂, Al₂O₃, MgO, TiO₂, and SnO₂ were almost inactive (entries 13-20). Typical solid acid catalysts such as sulfated zirconia, sulfonated carbon, Nafion, mordenite, and montmorillonite gave complex mixtures of 2a, 3a, and 4a (entries 21–26). The catalyst precursors of $Ce(NO_3)_3$, (NH₄)₂HPO₄, and a mixture of Ce(NO₃)₃ and (NH₄)₂HPO₄ were not effective for acetalization (entries 10-12), which indicates that CePO₄ plays an important role in the acetalization reaction.18

To verify whether the observed catalysis is derived from solid CePO₄ or from leached cerium or phosphorus species, the reaction of **1a** with methanol was conducted under the conditions described in entry 1 of Table 1, and CePO₄ was removed from the reaction mixture by hot filtration at *ca.* 30% conversion of **1a** (at t = 15 min). The filtrate was then heated again under the same reaction conditions. In this case, no further production of **2a** was observed, as shown in Fig. 3. No leaching of

cerium or phosphorus species into the filtrate was observed using inductively coupled plasma atomic emission spectroscopy (ICP-AES, with detection limits for Ce and P atoms of *ca.* 1 and 3 ppb, respectively). Therefore, there was no contribution to the observed catalysis from cerium or phosphorus species leached into the reaction solution, and the nature of the observed catalysis is confirmed as truly heterogeneous.¹⁹ The used CePO₄ catalyst could be readily recovered from the reaction mixture by simple filtration (96% recovery). The recovered CePO₄ catalyst could then be reused without a significant decrease in the yield of **2a** or the selectivity: 78% yield of **2a** at 81% conversion (fresh) and 78% yield of **2a** at 80% conversion (reused). There was no significant difference in the XRD patterns of the fresh and reused CePO₄ catalysts, which indicates the high durability of CePO₄ (Fig. S3[†]).

Reaction mechanism for the CePO₄-catalyzed acetalization

While it has been reported that other metal oxides (*e.g.* CeO₂) can function as effective acid–base catalysts,^{3,17d} only CePO₄ exhibited high catalytic activity and chemoselectivity for acetalization. Thus, the activation mode of substrates with CePO₄ and CeO₂ was confirmed using IR measurements of samples with adsorbed acetone and methanol. As shown in Fig. 2(c), one strong C=O stretching band of acetone adsorbed on CePO₄ was observed at a lower wavenumber (1699 cm⁻¹) than that of acetone in the gas phase (1731 cm⁻¹).²⁰ In addition, the IR spectrum of acetone adsorbed on CeO₂ exhibited a shoulder at 1700 cm⁻¹ and a strong band at 1673 cm⁻¹ due to acetone molecules coordinated to different types of Lewis acid sites, and absorptions at 1627 cm⁻¹ and 1570–1550 cm⁻¹ are assignable to condensed species (Fig. S4†).²⁰ These results indicate the interaction between the carbonyl oxygen of the ketone and the

Table 1 Effect of catalysts on the reaction of 1a with methanol^a



^{*a*} Reaction conditions: catalyst (0.1 g), **1a** (1.0 mmol), methanol (5 mL), and reflux for 1 h. Conversion and yield were determined by GC analysis. Conversion (%) = converted **1a** (mol)/initial **1a** (mol) × 100. Yield (%) = product (mol)/initial **1a** (mol) × 100. ^{*b*} Catalyst (0.43 mmol; *i.e.* equivalent to the Ce content in CePO₄ (0.1 g)).

uniform Lewis acid sites on $CePO_4$ without the promotion of aldol condensation.^{21,22}

Fig. 2(d) shows the IR spectrum of methanol adsorbed on CePO₄. In the ν (O–H) region, negative OH bands were observed with the appearance of broad bands between 3000 and 3500 cm^{-1} . In addition, the IR spectrum shows bands at 2952 and 2849 cm⁻¹ that were assigned to asymmetric and symmetric CH₃ stretching modes, respectively. The appearance of such broad bands and the band positions of $v(CH_3)$ indicate that methanol is adsorbed molecularly on CePO₄ via hydrogen bonds, which is consistent with previous reports for the non-dissociative adsorption of methanol on metal oxides.²³ On the other hand, the IR spectrum for methanol adsorbed on CeO₂ has bands at 2911 and 2805 cm⁻¹ that were assigned to the $\nu_{as}(CH_3)$ and $v_{\rm s}({\rm CH}_3)$ modes of methoxide species, respectively (Fig. S4[†]). Therefore, CePO₄ most likely acts as a bifunctional catalyst through interaction of the uniform Lewis acid sites and weak base sites with 1a and alcohol molecules, respectively, which



Fig. 3 Effect of CePO₄ removal on the acetalization of **1a** with methanol. Without removal of CePO₄ (\bullet), and the arrow indicates the point of CePO₄ removal (\square). Reaction conditions: CePO₄ (0.1 g), **1a** (1.0 mmol), methanol (5 mL), and reflux.

results in highly efficient and chemoselective acetalization.²⁴ The present acetalization of **1a** with methanol possibly proceeds as follows (Fig. 4). First, the activation of both **1a** and methanol by CePO₄ facilitates nucleophilic attack of the OH group in methanol on the carbon atom of the carbonyl group in **1a** to give the corresponding hemiacetal derivative. Further reaction of the hemiacetal with methanol then occurs, most likely with the assistance of the CePO₄ catalyst, to give the corresponding acetal derivative.

Substrate scope for the CePO₄-catalyzed acetalization

To investigate the effectiveness of the bifunctional properties of $CePO_4$, $CePO_4$ -catalyzed acetalization was explored with various substrates. In the presence of $CePO_4$, various combinations of carbonyl compounds and alcohols were efficiently converted into the corresponding acetal derivatives in good to excellent yields (Table 2). The acetalization of **1a** with methanol and with diols such as ethylene glycol and **1**,3-propanediol proceeded selectively (entries 1–3). $CePO_4$ effectively catalyzed the acetalization of other aldehydes containing heteroatoms, such as furfural (**1b**) and 2-thiophenecarboxaldehyde (**1c**), into the corresponding dimethyl acetals, while the acetalization of



Fig. 4 Proposed reaction mechanism for the CePO₄-catalyzed acetalization of **1a** with methanol.

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Table 2	Acetalization of	carbonyl	compounds	with	alcohols	catalyzed	by CeP	0 ₄ ^{<i>a</i>}

Entry	Carbonyl compound	Alcohol	Time (h)	Product (yield (%))
1	о Тон	CH ₃ OH	1	O O O O H (78)
2^b	1a	ноон	1	O O O O H (80)
3 ^{<i>b</i>}	1a	он он	2	O O O O O O O O O O O O O O O O O O O
4	0 1b	CH ₃ OH	6	O 2b(79)
5	0 S 1c	CH ₃ OH	6	S 2c (70)
6	O Id	CH ₃ OH	6	Not detected
7	0 1e	CH ₃ OH	6	0 0 2e (91)
8	O Me 1f	CH ₃ OH	6	0 0 2f (75) 0Me
9	0 1g	CH ₃ OH	6	0 2g (89)
10	0 1h	CH ₃ OH	20	0 2h (91)
11	0 11	CH ₃ OH	6	0 0 (82)
12	0 11	CH ₃ OH	20	2j (95)
13	0 1k	CH ₃ OH	20	0 2k (76)
14 ^{<i>c</i>}	О Ц 11	ноон	6	2 I (99)
15	O 1m	ноон	6	2m (46)
16	O HO 1n	CH ₃ OH	6	0 0 H0 2n (85)

^{*a*} Reaction conditions: CePO₄ (0.1 g), **1** (1.0 mmol), alcohol (5 mL), and reflux. Yields were isolated yields. ^{*b*} Yield determined using nuclear magnetic resonance spectroscopy (NMR). ^{*c*} 120 °C.

2-pyridinecarboxaldehyde (1d) did not proceed (entries 4-6). The catalytic reactivity of CePO₄ in the presence of pyridine was investigated. It was confirmed that the presence of pyridine strongly inhibited the reaction of 1a with methanol (Fig. 5). The yield of 2a decreased with an increase in the small amount of pyridine added (3-12 µmol; ca. 0.3-1.3 equivalents with respect to the Lewis acid sites on CePO₄). The nitrogen atom of pyridine would strongly coordinate to the cerium metal center, which would inhibit the reaction. The reactions of benzaldehydes with electron-donating and electron-withdrawing para-substituents (1e-1g) proceeded to afford the corresponding dimethyl acetals in high yields (entries 7-9). Even the bulkier aldehyde 1-naphthaldehyde (1h) could be efficiently acetalized when the reaction time was prolonged to 20 h (entry 10). The acetalization of cinnamaldehyde (1i) with methanol proceeded smoothly without influence on the C=C double bond (entry 11). Not only were aromatic and α , β -unsaturated aldehydes converted but also 3-phenylpropionaldehyde (1j) and cyclohexanecarboxaldehyde (1k) were efficiently converted into the corresponding acetals in high yields (entries 12 and 13). Furthermore, the present system could effectively catalyze aliphatic and aromatic ketones with ethylene glycol. Cyclohexanone (11) was quantitatively converted into 2,2-pentamethylene-1,3-dioxolane (21), and acetophenone (1m) gave its corresponding ketal (2m) in moderate yield (entries 14 and 15). Even in the presence of hydroxyl groups in the substrate (5-hydroxy-2-adamantanone (1n)), the corresponding ketal (2n) was obtained in good yield (entry 16).

The present catalytic system was applicable to a gram-scale reaction of **1a** (10.5 mmol scale) with methanol and 1.46 g of analytically pure **2a** could be isolated (eqn (1)). In this case, the turnover number (TON) based on surface Lewis acid sites reached 177 and the corresponding turnover frequency (TOF) was 44 h⁻¹. In addition, CePO₄ efficiently catalyzed the gram-scale regioselective acetalization of acetone (**10**) with glycerol into the industrially important chemical 2,2-dimethyl-1,3-dioxolan-5-ol (solketal (**20**)).^{25,26} Solketal has been used as a highly



Fig. 5 Yields of 2a against the amount of pyridine added. Reaction conditions: CePO₄ (0.1 g), 1a (1.0 mmol), methanol (5 mL), and reflux for 30 min.

1.29 g (84% yield) **20/20'** = 98/2

soluble additive to increase the octane number of fuel, and as such many catalyst systems to aid its synthesis have been reported.^{25,26} CePO₄ exhibited high regioselectivity (2o/2o' = 98/2) and 1.29 g of analytically pure 20 was successfully isolated (eqn (2)), while the condensation of glycerol with 10 under acidic conditions sometimes affords a mixture of five- and sixmembered acetals (20 and 20', respectively).²⁵



Conclusions

In conclusion, CePO₄ efficiently catalyzes the acetalization of various aryl and aliphatic carbonyl compounds containing hydroxyl groups, C=C bonds, and heteroatoms with alcohols. This study suggests that the development of bifunctional solid catalysts with uniform active sites is of particular importance. This approach is a promising strategy for the development of highly efficient heterogeneously-catalyzed reactions through the non-dissociative activation of both electrophiles and nucleophiles under very mild conditions.

Acknowledgements

This work was supported in part by a Kakenhi Grant-in-Aid (No. 15K13802) from the Japan Society for the Promotion of Science (JSPS), the ALCA and CREST programs of the Japan Science and Technology Agency (JST), the Novel Cheap and Abundant Materials for Catalytic Biomass Conversion (NOVACAM) program of JST, and the European Commission Directorate-General for Research and Innovation.

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