

A bifunctional cerium phosphate solid catalyst for chemoselective acetalization of carbonyl compounds

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Abstract: A CePO₄ catalyst was synthesized by the hydrothermal method and found to exhibit high catalytic performance for the chemoselective acetalization of 5-hydroxymethylfurfural (HMF) 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 CePO₄ 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.

Keywords: acetalization, cerium phosphate, bifunctional catalyst.

1. Introduction

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 reported unique base catalysis with oxoanions including [WO₄]²⁻ and [PO₄]³⁻.^{1,2} 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. 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. Herein, we report the highly chemoselective acetalization of 5-hydroxymethylfurfural, which has alcohol and aldehyde functionalities, with alcohols using a monoclinic CePO₄ catalyst synthesized by the hydrothermal method.³

2. Experimental

CePO₄ was synthesized by the hydrothermal reaction and characterized by elemental analysis, XRD, SEM, IR, XPS, and N₂ adsorption-desorption measurements. The catalytic acetalization of various carbonyl compounds was conducted in a 30 mL glass vessel containing a magnetic stirring bar. The reaction solution was periodically analyzed by GC, GC-MS, and NMR. After the reaction was completed, the analytically pure product was isolated using a flash chromatography separation system.

3. Results and discussion

The powder XRD pattern measured for CePO₄ was in good agreement with that reported for the monoclinic CePO₄ structure, in which a Ce³⁺ ion connects seven tetrahedral PO₄³⁻ groups [space group P2₁/n] (Figure 1). Impurity phases of other cerium and phosphorus oxides were not observed. The Ce 3d XPS spectrum of CePO₄ exhibited four peaks with binding energies of 904.9, 901.0, 806.5, and 883.0 eV and are in good agreement with the reported Ce 3d spectra for Ce(III) oxides. The specific surface area of CePO₄ was up to 37 m² g⁻¹. The SEM image of CePO₄ showed the formation of rod-like shaped particles 100–500 nm long and 20–50 nm wide. The acid-base properties of CePO₄ were evaluated by IR spectroscopy for a sample with adsorbed pyridine and CHCl₃. Differential IR spectra of CePO₄ indicate the

presence of Lewis acid sites ($0.096 \text{ mmol g}^{-1}$) and the base sites located in close proximity to the Lewis acid sites, in agreement with the structure of CePO_4 .

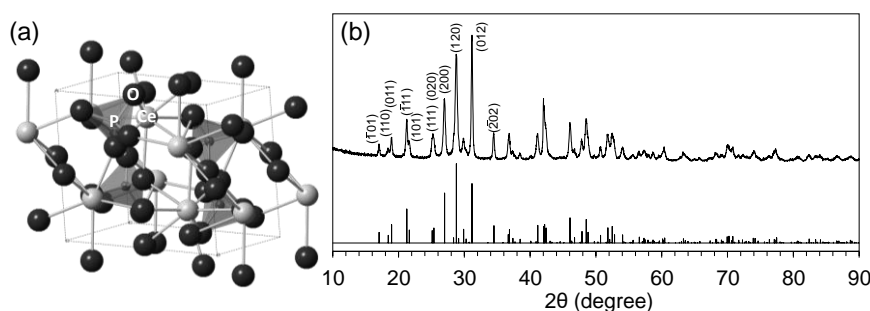


Figure 1. (a) Structure of CePO_4 . (b) XRD patterns for CePO_4 (upper) and monoclinic CePO_4 (lower, ICSD79748).

The reaction of HMF with methanol was examined in the presence of various catalysts that have been reported as effective for acetalization. The reaction did not proceed in the absence of a catalyst. Among the catalysts tested, CePO_4 exhibited the highest activity for the acetalization of HMF to give the corresponding acetal in 78% yield. In this case, the selectivity toward the acetal reached 96% without the formation of ethers. Homogeneous Brønsted and Lewis acid, homogeneous base, metal oxide, and typical solid acid catalysts were not effective for acetalization, which indicates that CePO_4 plays an important role in the acetalization reaction. 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. In addition, the present catalytic system was applicable to a gram-scale reactions. For example, CePO_4 efficiently catalyzed the gram-scale regioselective acetalization of acetone with glycerol into an industrially important chemical, 2,2-dimethyl-1,3-dioxolan-5-ol (solketal), which has been used as a highly soluble additive to increase the octane number of fuel, and 1.29 g of analytically pure solketal was successfully isolated (Figure 2).

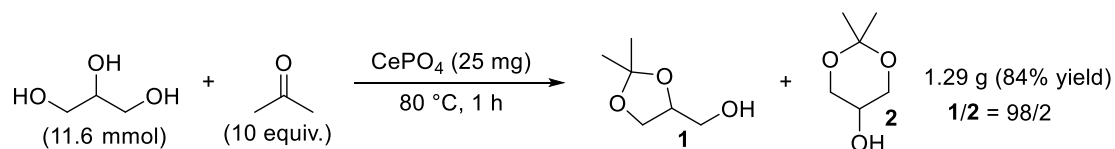


Figure 2. Gram-scale regioselective acetalization of acetone with glycerol catalyzed by CePO_4 .

The activation mode of substrates with CePO_4 was confirmed by IR measurements for samples with adsorbed acetone and methanol. One strong $\text{C}=\text{O}$ stretching band of acetone adsorbed on CePO_4 was observed at lower wavenumber (1699 cm^{-1}) than that of acetone in the gas phase (1731 cm^{-1}), indicating the interaction between the carbonyl oxygen of the ketone and the uniform Lewis acid sites on CePO_4 without the promotion of aldol condensation. For the IR spectrum of methanol adsorbed on CePO_4 , the appearance of broad bands between 3000 and 3500 cm^{-1} and the band positions (2952 and 2849 cm^{-1}) of $\nu(\text{CH}_3)$ indicate that methanol is adsorbed molecularly on CePO_4 via hydrogen bonds. Thus, CePO_4 most likely acts as a bifunctional catalyst through interaction of the uniform Lewis acid sites and weak base sites with HMF and alcohol molecules, respectively, which results in highly efficient and chemoselective acetalization.

4. Conclusions

In conclusion, CePO_4 efficiently catalyzes the acetalization of various aryl and aliphatic carbonyl compounds containing hydroxyl groups, $\text{C}=\text{C}$ bonds, and heteroatoms with alcohols.

References

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