Chemoselective acetalization by a bifuncional cerium phosphate catalyst

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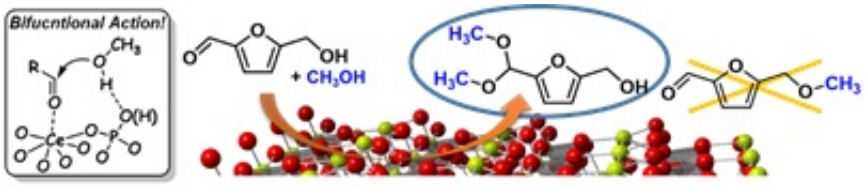

CePO4-Catalyzed acetalization of HMF with alcohols through bifunctional activation. Credit: Tokyo Institute of Technology

Scientists at Tokyo Institute of Technology have developed a bifunctional cerium phosphate catalyst for the chemoselective acetalization of biomass-derived 5-hydroxymethylfurfural with alcohols. This research demonstrates potential as the heterogeneous catalyst system is reusable, widely applicable to various substrates (16 examples), and affords high chemoselectivity.

Acid-base bifunctional catalysts exhibit wide applicability for atom-efficient functional group transformation, tandem reactions, and asymmetric synthesis. In heterogeneous catalysis, the acid-base properties of metal-oxide-based materials have been extensively studied. Nevertheless, it is difficult to construct uniform acid-base sites with controlled electrical and structural properties, which in turn restrains the fine-tuning and reactivity of catalysts. Although oxide surfaces can be readily modified with organic acids or bases, organic functional groups

are susceptible to oxidation or thermal degradation, limiting the utility of such catalysts. Thus, it is imperative to design novel high-performance inorganic heterogeneous acid-base catalysts, especially for the manufacture of high value-added products from renewable biomass as a sustainable feedstock.

In this regard, a team of scientists led by Michikazu Hara (Tokyo Institute of Technology) has reported the highly chemoselective acetalization of biomass-derived 5-hydroxymethylfurfural (HMF) with alcohols using a monoclinic $CePO_4$. $CePO_4$, corresponding to rare earth (RE) orthophosphates, are expected to be suitable bifunctional acid-base catalysts, where the synergistic promotion of electrophilicity and nucleophilicity in reactive partners could be achieved.

Mechanistic studies indicated that $CePO_4$ most probably serves as a bifunctional catalyst via the interaction of uniform Lewis acid and weak base sites with HMF and alcohol molecules, respectively, leading to high catalytic performance. Activation of HMF and methanol by $CePO_4$ facilitates the nucleophilic attack of OH in methanol on the carbon atom of C=O, affording the hemiacetal derivative. Next, the reaction between the derivative and methanol by the assistance of $CePO_4$ leads to the acetal. The effectiveness of the bifunctional properties of $CePO_4$ was evidenced by the wide applicability to various acetals including industrially important solketal.

This study discusses a promising strategy employing highly efficient heterogeneous catalysts via the non-dissociative activation of electrophiles and nucleophiles under extremely mild conditions.

More information: Shunsuke Kanai et al, A bifunctional cerium phosphate catalyst for chemoselective acetalization, *Chem. Sci.* (2017). DOI: 10.1039/C6SC05642C

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