A Bifunctional Cerium Phosphate Catalyst for Chemoselective Acetalization of 5-Hydroxymethylfurfural

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The acid-base properties of metal oxide-based materials have been extensively studied, and various effective simple and mixed oxide catalysts have been reported. However, difficulty in the construction of uniform electrically and structurally controlled acid-base site often leads to a problem where the fine-tuning of the catalyst structure and the reactivity are restrained. We anticipated that rare earth (RE) orthophosphates, $REPO_4$, 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-hydroxymethlfurfural (HMF),[1] which has alcohol and aldehyde functionalities, with alcohols using a monoclinic $CePO_4$ catalyst synthesized by the hydrothermal method.

$CePO_4$ was synthesized through the hydrothermal reaction of $Ce(NO_3)_3$ and $(NH_4)_2HPO_4$ at 180 °C, followed by calcination at 900 °C. Figure 1 shows a scanning electron microscopy (SEM) image of $CePO_4$ with rod-like shaped particles 100–500 nm long and 20–50 nm wide.

The reaction of HMF with alcohols was examined in the presence of various catalysts that have been reported as effective for acetalization and the results are summarized in Table 1. Three products of 5-(dimethoxymethyl)-2-furanmethanol (**A**), 5-methoxymethylfurfural (**B**), and 2-(dimethoxymethyl)-5-(methoxymethyl)furan (**C**) were mainly formed. Among the catalysts tested, $CePO_4$ exhibited the highest activity for the acetalization of HMF in 78% yield. Brønsted acid catalysts (*p*-toluenesulfonic acid (TsOH) and Nafion® NR50) and a Lewis acid catalyst (cerium trifluoromethanesulfonate ($Ce(OTf)_3$)), gave complex mixture of **A**, **B** and **C**. In addition, no product was obtained with a homogeneous base catalyst of K_3PO_4 and a metal oxide catalyst of CeO_2. Thus, $CePO_4$ catalyst plays an important role in the chemoselective acetalization of HMF.

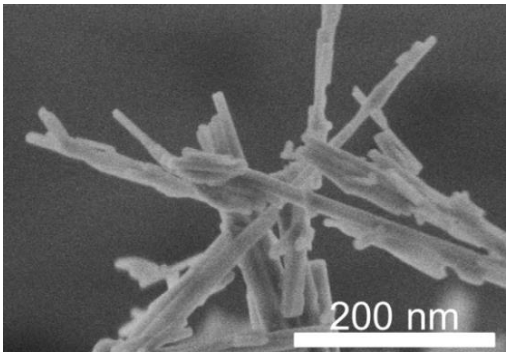
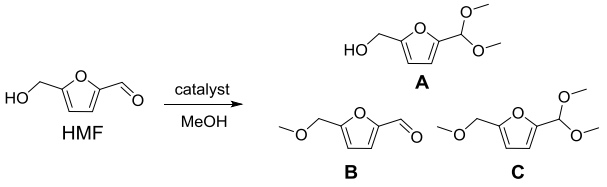


Figure 1. SEM image of $CePO_4$.

Table 1. Effect of catalysts on the reaction of HMF with methanol.[a]



catalyst	conv. / %	yield /%		
		A	**B**	**C**
$CePO_4$	81	78	<1	<1
TsOH[b]	>99	<1	54	2
Nafion® NR50	95	1	42	21
$Ce(OTf)_3$[b]	74	<1	27	<1
K_3PO_4	81	<1	<1	<1
CeO_2	5	<1	<1	<1

[a] Reaction conditions: Catalyst (0.1 g), HMF (1.0 mmol), methanol (5 mL), reflux, 1 h. Conversion and yield were determined by GC analysis. Conversion (%) = converted HMF (mol)/initial HMF (mol) × 100. Yield (%) = product (mol)/initial HMF (mol) × 100.
[b] Catalyst (0.43 mmol; i.e., equivalent to the Ce content in $CePO_4$ (0.1 g)).

REFERENCES

[1] A. Corma, K. S.Arias, S. I. Al-Resayes, M. J. Climent, S. Iborra, *ChemSusChem*, 6 (2013) 123.