



## Selective glucose transformation by titania as a heterogeneous Lewis acid catalyst



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### ABSTRACT

The Lewis acidity of phosphate-immobilized anatase TiO<sub>2</sub> (phosphate/TiO<sub>2</sub>) has been studied to develop novel environmentally benign reaction systems. Fourier transform infrared (FT-IR) measurements suggested that most Lewis acid sites on bare and phosphate/TiO<sub>2</sub> surface function even in water. phosphate/TiO<sub>2</sub> exhibits high catalytic performance for selective 5-(hydroxymethyl)furfural (HMF) production from glucose in THF/water (90/10 vol.%) solution. This is attributed to water-tolerant Lewis acid sites on phosphate/TiO<sub>2</sub> that promote step-wise conversion of glucose into HMF. The catalyst was easily recovered from reaction solution by simple decantation or filtration, and can be used repeatedly without significant loss of original activity for subsequent reactions.

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### 1. Introduction

The effective conversion of glucose, a key component of cellulosic biomass, into HMF is an attractive route to sustainable chemical production [1]. HMF is a versatile and key platform chemical because it can be further converted into various polymers such as polyesters and polyamides, and pharmaceuticals [1,2]. However, the lack of a simple and highly efficient process for HMF production from glucose has been an obstacle to the utilization of HMF, a so-called “sleeping giant” [2]. A proposed reaction mechanism for HMF formation from glucose is shown in Scheme 1, where glucose derived from cellulosic biomass or starch is converted into HMF through isomerization, followed by dehydration in the presence of appropriate catalysts [2]. Zhao and co-workers demonstrated that CrCl<sub>2</sub>, a soluble homogeneous Lewis acid catalyst, dissolved in an ionic liquid functions as the most efficient catalytic system for the reaction, although the maximum HMF yield in the reaction system is still only in the order of 60% [3]. While serious problems, such as HMF selectivity, separation of the catalyst and HMF from the ionic liquid, reuse of the catalyst, and handling in practical processes

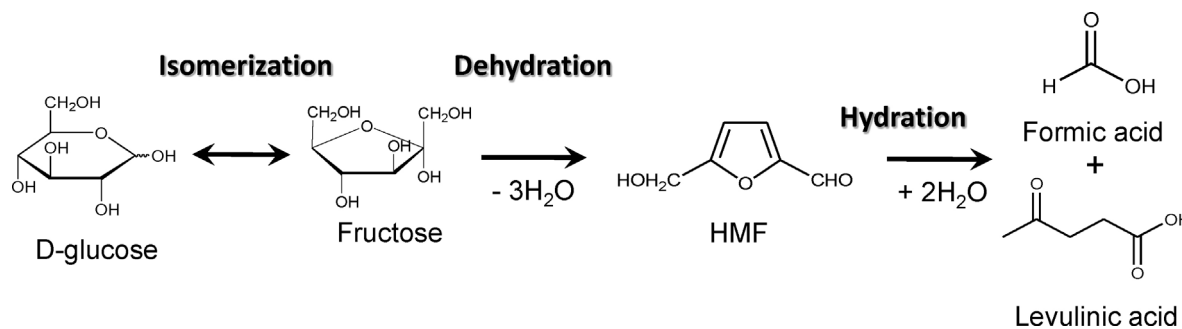
remain for this catalytic system with respect to the effective use of glucose and energy costs, the results of this reaction system suggest that Lewis acids function as effective catalysts for the efficient production of HMF from glucose.

Lewis acid catalysts such as AlCl<sub>3</sub>, BF<sub>3</sub>, and transition metal halides are essential for the production of industrially important chemicals, including polymers and pharmaceuticals [4]. However, most Lewis acids decompose or are ineffective in the presence of water, and thereby require dehydrated environment, which results in significant energy consumption. In addition, they have serious drawbacks, such as the production of waste and corrosion of equipment, in addition to requiring separation from the product [5]. Although a few exceptions (rare earth metal triflate complexes [6,7] and Sn<sup>4+</sup>-incorporated zeolites [8,9]) are known to exhibit Lewis acid catalysis in water, the scarcity of rare earth metals in the former and the narrow reaction space available in the latter limit their utility. Thus, heterogeneous Lewis acid catalysts that are ubiquitous, insoluble, easily separable from products, and highly active for various reactions in water would be applicable to environmentally benign chemical production.

Recently, we reported that a part of NbO<sub>4</sub> tetrahedra present in insoluble niobic acid (Nb<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O) act as Lewis acids even in water [10]. Many metal oxides of groups 4 and 5, including niobic acid, are composed of octahedral MO<sub>6</sub> (M: metal) units with saturated coordination spheres, and polyhedral MO<sub>x</sub> with unsaturated coordination spheres, such as tetrahedral MO<sub>4</sub>, are also present on

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**Scheme 1.** Reaction pathway for acid-catalysed conversion of glucose into HMF in water.

the surface. Unsaturated coordination  $\text{MO}_4$  tetrahedra act as Lewis acids; however,  $\text{MO}_4$  species are considered to not function as well in water as other Lewis acids. Niobic acid with  $\text{NbO}_4$  species as water-tolerant Lewis acid sites suggests that anatase  $\text{TiO}_2$ , a ubiquitous material, with  $\text{TiO}_4$  species on the surface would also function as an insoluble, easily separable, and water-tolerant Lewis acid catalyst. Therefore, the potential of anatase  $\text{TiO}_2$  as a heterogeneous water-tolerant Lewis acid was investigated in this study.

## 2. Experimental

### 2.1. Preparation of anatase $\text{TiO}_2$ and phosphate/ $\text{TiO}_2$

Anatase  $\text{TiO}_2$  was synthesized by the addition of 20 mL  $\text{Ti}(\text{i-pro})_4$  to 100 mL distilled water, followed by stirring at room temperature. After 6 h, the filtrated white precipitate was stirred in 200 mL of 1 M HCl solution for 2 h to complete the hydrolysis of residual  $\text{Ti-OCH}(\text{CH}_3)_2$  species. The obtained powder was repeatedly washed with distilled water (ca. 1000 mL) until the pH of the filtrate became neutral. The resulting material was dried overnight at 353 K and then used as the anatase  $\text{TiO}_2$  catalyst.

Phosphate/ $\text{TiO}_2$  was prepared by immobilizing  $\text{H}_3\text{PO}_4$  on anatase  $\text{TiO}_2$ . 5 g of  $\text{TiO}_2$  was stirred in 200 mL of 1 M  $\text{H}_3\text{PO}_4$  solution. After stirring for 48 h, the collected sample was washed repeatedly with distilled water until phosphate ions were no longer detected. The resulting material was dried overnight at 353 K and then used as the phosphate/ $\text{TiO}_2$  catalyst.

### 2.2. FT-IR measurement and estimation of the amounts of Lewis acid sites for anatase $\text{TiO}_2$ and phosphate/ $\text{TiO}_2$

Lewis acid densities on anatase  $\text{TiO}_2$  and phosphate/ $\text{TiO}_2$  were estimated for pyridine-adsorbed samples at 298 K by FT-IR measurements. The samples were pressed into self-supporting disks (20 mm diameter, ca. 20 mg) and placed in an IR cell attached to a closed glass-circulation system ( $0.38 \text{ dm}^{-3}$ ). The disk was dehydrated by heating at 423 K for 1 h under vacuum to remove physisorbed water and was exposed to pyridine vapor at 423 K. The intensities of the bands at  $1445 \text{ cm}^{-1}$  (pyridine coordinatively bonded to Lewis acid sites, molecular absorption coefficient:  $4.86 \mu\text{mol cm}^{-1}$ ) were plotted against the amounts of pyridine adsorbed on the Lewis acid sites of the samples.

In the case of the sample in the presence of saturated water vapor, the disk placed in the IR cell was exposed to saturated  $\text{H}_2\text{O}$  vapor (20–25 Torr) at room temperature for 60 min. 4.2 layers of  $\text{H}_2\text{O}$  molecules were adsorbed on the  $\text{TiO}_2$  and phosphate/ $\text{TiO}_2$  surfaces, as estimated from water vapor-adsorption-desorption isotherms. Pyridine vapor was then added to the reaction system, and the intensity of the  $1445 \text{ cm}^{-1}$  band (pyridine coordinatively bonded to Lewis acid sites) increased with increasing amount of introduced pyridine, reaching a plateau.

### 2.3. HMF production from glucose

THF/aqueous solution (2.0 mL (THF, 1.8 mL; distilled water, 0.2 mL)) containing D-glucose (0.02 g) and catalyst (0.05 g) was heated in a sealed Pyrex tube for 2 h at 393 K. After filtration, the solutions were analyzed using high performance liquid chromatography (HPLC; LC-2000 plus, Jasco) equipped with refractive index (RI) and photodiode array (PDA) detectors. Aminex<sup>®</sup> HPH-87H column (300 mm  $\times$  7.8 mm, Bio-Rad Laboratories) with diluted  $\text{H}_2\text{SO}_4$  solution (5 mM) of eluent,  $0.5 \text{ mL min}^{-1}$  of flow rate, and 308 K of column temperature was adopted in HPLC analysis.

## 3. Results and discussion

### 3.1. Structure of anatase $\text{TiO}_2$ and phosphate/ $\text{TiO}_2$

Structural information for the anatase  $\text{TiO}_2$  and phosphate/ $\text{TiO}_2$  catalysts was obtained by XRD and  $\text{N}_2$  adsorption analyses. Fig. 1 shows XRD patterns and (B)  $\text{N}_2$  adsorption-desorption isotherms for (a) anatase  $\text{TiO}_2$  and (b) phosphate/ $\text{TiO}_2$ . Diffraction peaks due to anatase  $\text{TiO}_2$  are evident in the XRD patterns for anatase  $\text{TiO}_2$  and phosphate/ $\text{TiO}_2$ , which indicates that both samples are mainly composed of anatase  $\text{TiO}_2$ . There was no significant difference in the XRD patterns of anatase  $\text{TiO}_2$  and phosphate/ $\text{TiO}_2$ ; therefore, phosphoric acid modification of anatase  $\text{TiO}_2$  does not change the original anatase  $\text{TiO}_2$  structure.  $\text{N}_2$  adsorption-desorption isotherms of the samples are similar to the type-IV pattern, which is typical of mesoporous solids. The Brunauer-Emmett-Teller (BET) surface areas and pore volumes of anatase  $\text{TiO}_2$  and phosphate/ $\text{TiO}_2$  were estimated to be  $252 \text{ m}^2 \text{ g}^{-1}$  and  $0.31 \text{ mL g}^{-1}$ , and  $266 \text{ m}^2 \text{ g}^{-1}$  and  $0.25 \text{ mL g}^{-1}$ , respectively. SEM images revealed that the prepared  $\text{TiO}_2$  sample is composed of 10–20 nm  $\text{TiO}_2$  particles. There was no significant difference in the morphology of  $\text{TiO}_2$  and phosphate/ $\text{TiO}_2$ . The amount of immobilized phosphate on anatase  $\text{TiO}_2$  was estimated by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), which revealed that 0.77 mmol of phosphate ions were tightly fixed on 1 g of  $\text{TiO}_2$  by ester formation between phosphoric acid and neutral OH groups.

### 3.2. Lewis acid sites on anatase $\text{TiO}_2$

Difference Fourier transform infrared (FT-IR) spectra for pyridine adsorption on dehydrated anatase  $\text{TiO}_2$  and phosphate/ $\text{TiO}_2$  are shown in Fig. 2, where pyridine is employed as a basic probe molecule for characterization of the acid sites [11]. Dehydrated  $\text{TiO}_2$  exhibits several bands (Fig. 2(A)), but there is no signal for pyridinium ions formed on Brønsted acid sites ( $1540 \text{ cm}^{-1}$ ), because  $\text{TiO}_2$  has no Brønsted acid sites. The intensities of the two bands at 1445 and  $1440 \text{ cm}^{-1}$ , which are assigned to adsorbed pyridine on Lewis acid sites ( $\text{TiO}_4$ ) and physisorbed pyridine [12], respectively, increase with the amount of introduced

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