## Catalytic Conversion of Glucose to 5-Hydroxymethyl-furfural with a Phosphated TiO<sub>2</sub> Catalyst

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Nanosized phosphated  $TiO_2$  catalysts with different phosphate contents were synthesized and tested for the conversion of glucose to 5-hydroxymethylfurfural. The resulting materials were characterized by using N<sub>2</sub>-adsorption, XRD, inductively coupled plasma atomic emission spectroscopy, X-ray spectroscopy, TEM, temperature-programmed desorption of ammonia, and FTIR spectroscopy of pyridine adsorption techniques to determine their structural, bulk, surface, and acid properties. We found that  $TiO_2$  nanoparticles catalyzed this reaction under mild conditions in a water–butanol biphasic system. The incor-

Introduction

Conversion of sugars to platform chemicals is a promising process for sustainable production of value-added chemicals. The sugars obtained from nonedible biomass resources have attracted considerable attention owing to their potential to offset the dependence on fossil fuels.<sup>[1]</sup> Cellulose is an inexpensive and readily available raw material that can undergo hydrolysis to produce C<sub>6</sub> sugars (hexoses). The subsequent dehydration of these sugars produces 5-hydroxymethylfurfural (HMF), which has been identified as a key biorefining intermediate for chemicals and fuels.<sup>[2]</sup>

Hexose conversion to HMF is primarily an acid-catalyzed reaction. Mineral acids such as H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and HCl<sup>[3]</sup> were conventionally used as catalysts for this reaction, which can cause significant corrosion and environmental problems. In recent times, various solid acids such as zeolites,<sup>[4]</sup> acidic ion-exchange resins,<sup>[4c, 5]</sup> oxides, sulfates, and phosphates,<sup>[6]</sup> and heteropoly acid salts<sup>[4c, 7]</sup> have been investigated in search of a suitable and efficient catalyst for the synthesis of HMF. The production of HMF from fructose is widely studied, and significant progress has been made. However, glucose is cost-effective and readily available in comparison to fructose.<sup>[8]</sup> Therefore, an efficient process for the direct conversion of glucose and its poly-

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poration of phosphorus into the TiO<sub>2</sub> framework remarkably enhances the target product selectivity, which is ascribed to increased surface area, enhanced acidity, as well as thermal stability resulting from the Ti–O–P bond formation. Under optimal reaction conditions, phosphated TiO<sub>2</sub> was found to exhibit excellent catalytic performance, which resulted in 97% glucose conversion and 81% HMF yield after 3 h of reaction at 175 °C. More importantly, the catalyst showed good stability and could be reused for several reaction cycles.

mers to HMF is desirable for industrial production. Although the use of homogeneous metal halides with ionic liquids results in high selectivities and yields of HMF from glucose, catalyst handling, separation, and reuse remain a concern in scaling up for industrial application.<sup>[9]</sup> Therefore, it is essential to develop a heterogeneously catalyzed process that enables high HMF selectivity along with high glucose conversion.

Titania (TiO<sub>2</sub>) serves as a cheap, sustainable, and ecofriendly metal oxide with various applications such as photocatalysis,<sup>[10]</sup> sensors,<sup>[11]</sup> and electrodes.<sup>[12]</sup> Owing to its chemical stability and rich surface chemistry, the acid-base property of TiO<sub>2</sub> can be modified and used in heterogeneous catalysis.<sup>[13]</sup> Several authors have reportedly used TiO<sub>2</sub> to catalyze the transformation of carbohydrates to HMF. Watanabe et al.<sup>[14]</sup> studied the dehydration of glucose to HMF in hot compressed water catalyzed with anatase TiO<sub>2</sub>. They suggested that the presence of high-density acid and basic sites influenced the catalytic activity of TiO<sub>2</sub>. Basic sites were responsible for glucose isomerization to fructose, whereas acid sites facilitated the successive dehydration to HMF. De et al.<sup>[15]</sup> described the catalytic dehydration of glucose with use of self-assembled mesoporous TiO<sub>2</sub> nanospheres. They also identified that the surface acidity of mesoporous TiO<sub>2</sub> was responsible for catalyzing the dehydration reaction. Likewise, mesoporous TiO<sub>2</sub> nanospheres templated with sodium salicylate were tested for the dehydration of various carbohydrate substrates.<sup>[16]</sup> The high surface area and Lewis acidity of the nanoparticles (NPs) played a significant role in the microwave-assisted conversion of carbohydrates to HMF. A later study by the same group also achieved efficient conversion of biomass and carbohydrates to HMF with titanium phosphate NPs under microwave-assisted heating conditions.<sup>[17]</sup> Kuo et al.<sup>[18]</sup> recently explored the synthesis of acidic TiO<sub>2</sub> NPs and their application for the catalytic conversion of



biomass-derived carbohydrates. They observed that the NPs could promote the dehydration of carbohydrates to HMF as well as other value-added products such as levulinic acid and HMF-derived esters. Nakajima et al.<sup>[19]</sup> significantly improved the performance of TiO<sub>2</sub> to catalyze the conversion of glucose to HMF by immobilizing TiO<sub>2</sub> with H<sub>3</sub>PO<sub>4</sub>. As such, TiO<sub>2</sub> NPs have shown great potential in the catalytic transformation of carbohydrates to HMF. A limitation of the TiO<sub>2</sub> catalyst reported so far is that it exhibits only Lewis acid sites. Convincing evidence has shown that bifunctional catalytic systems with both Lewis and Brønsted acid functionalities exhibit an improved performance for HMF formation than catalysts with either Lewis or Brønsted acid functionalities only.<sup>[7,20]</sup> Therefore, we believe that the TiO<sub>2</sub> catalyst with Lewis and Brønsted acid functionalities would be more effective in HMF production from glucose.

The design of an optimum catalyst is one of the most crucial roadblocks in HMF synthesis. However, the solvent environment can also significantly influence reaction pathways. Therefore, the role of an appropriate reaction medium cannot be overlooked.<sup>[21]</sup> The synthesis of HMF from hexoses can generally involve isomerization, dehydration, fragmentation, reversion, and condensation steps either in an aqueous or a nonaqueous reaction medium.<sup>[22]</sup> The reaction in an aqueous medium suffers a low HMF yield owing to its concomitant rehydration to levulinic acid and its degradation to polymeric humins. Ionic liquids<sup>[23]</sup> and polar organic solvents, such as DMSO,<sup>[6b]</sup>  $\mathsf{DMF}^{[5a,24]}_{,}$  and dimethylacetamide,  $^{[25]}_{,}$  are found to be efficient for high-yield HMF production owing to their capacity to inhibit undesirable reactions. Nevertheless, poor solubility of hexoses/cellulosic biomass and the associated high separation cost of the target product are the major disadvantages of these solvents. Various biphasic systems of the water-organic reaction medium have been developed to facilitate selective production of HMF, and these have proved to be effective in overcoming the limitations of either aqueous or nonaqueous reaction media.<sup>[3]</sup>

Herein, we report the synthesis of a series of bifunctional phosphated  $TiO_2$  NPs with both Lewis and Brønsted acid functionalities. The catalysts were extensively characterized by using N<sub>2</sub>-adsorption, XRD, inductively coupled plasma atomic emission spectroscopy (ICP-AES), TEM, FTIR spectroscopy of pyridine adsorption, temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD), and X-ray spectroscopy (XPS) techniques. The catalytic activity of phosphated  $TiO_2$  for glucose conversion was evaluated in a water–butanol biphasic system. *n*-Butanol is a cheap, biorenewable, and environmentally friendly solvent. In addition, it is a promising medium for upgrading HMF to useful fuels and chemicals, which helps reduce overall process costs. The effects of reaction time and temperature, catalyst loading, and substrate concentration were also investigated to optimize the process.

## **Results and Discussion**

The phosphated  $TiO_2$  catalyst was prepared through the impregnation of freshly prepared hydrated  $TiO_2$  with ammonium

phosphate monobasic. After impregnation, the sample was dried and then calcined at 600 °C for 4 h to obtain the phosphated TiO<sub>2</sub> NP. The phosphated TiO<sub>2</sub> catalysts with different phosphate contents were obtained by varying the amount of the precursor loaded during the impregnation step. The samples obtained after calcination were denoted as xP-TiO<sub>2</sub>, in which x represents the theoretical weight percentage of phosphorus in the catalyst based on the amount of the phosphate precursor added.

#### Powder XRD

The XRD patterns of  $TiO_2$  NPs with 0–25 wt% phosphate content are shown in Figure 1. The diffraction patterns of all the samples can be indexed as an anatase phase of  $TiO_2$  (JCPDS No. 21-1272). The diffraction pattern of pure  $TiO_2$  appeared



**Figure 1.** XRD patterns of a)  $TiO_2$ , b)  $5P-TiO_2$ , c)  $10P-TiO_2$ , d)  $15P-TiO_2$ , e)  $20P-TiO_2$ , and f)  $25P-TiO_2$  NPs.

sharp and intense, which indicated high crystallinity of the NPs. In contrast, the crystallinity of TiO<sub>2</sub> particles reduced after phosphate treatment, indicated by peak broadening and reduction in peak intensity. This result suggests the incorporation of phosphorus into the TiO<sub>2</sub> framework.<sup>[26]</sup> All the samples were composed of nanosized crystals, and their mean sizes obtained by using the Debye–Scherrer equation ranged from 5.3 to 27.3 nm (Table 1). An increase in phosphate content resulted in a decrease in the crystal size of the NP.

#### N<sub>2</sub> adsorption-desorption

As shown in Figure 2, the N<sub>2</sub> adsorption–desorption isotherms of all the samples are of type IV, with a capillary condensation step characteristic of mesoporous materials having narrow pore size distribution. The onset of the mesoporous filling step for phosphated TiO<sub>2</sub> shifts to a lower pressure in comparison with pure TiO<sub>2</sub>. Likewise, a shift in pore diameter to lower values indicates a distortion in the mesoporous structure of TiO<sub>2</sub> by the incorporation of phosphorus. The specific surface area ( $S_{\text{BET}}$ ) of the NPs is given in Table 1. The surface area of



Table 1. Physical, compositional, and acid properties of TiO <sub>2</sub> NPs.								
Entry	Sample	Ti/P molar ratio	Ti/P molar ratio ICP <sup>[a]</sup>	$S_{BET}$ $[m^2g^{-1}]^{[b]}$	Pore volume [cm <sup>3</sup> g <sup>-1</sup> ]	Crystal size [nm] <sup>[c]</sup>	Total acidity $[mmol g^{-1}]^{[d]}$	
1	TiO <sub>2</sub>	-	-	54.7	0.22	27.3	0.76	
2	5P-TiO <sub>2</sub>	31.1	33.5	124.8	0.31	7.34	1.92	
3	10P-TiO <sub>2</sub>	14.7	15.8	146.8	0.36	6.36	1.96	
4	15P-TiO₂	9.3	10.1	151.0	0.43	6.12	2.36	
5	20P-TiO <sub>2</sub>	6.5	7.1	145.7	0.34	5.55	1.99	
6	$25P-TiO_2$	4.9	5.1	79.4	0.25	5.30	1.40	

[a] Determined from ICP-AES analysis; [b] BET surface area; [c] Measured by XRD using the Debye–Scherrer equation for the (101) plane; [d] Determined from  $NH_3$ -TPD analysis.



Figure 2. A) BET isotherms and B) pore size distributions of a)  $TiO_2$ , b) 5P- $TiO_2$ , c) 10P- $TiO_2$ , d) 15P- $TiO_2$ , e) 20P- $TiO_2$ , and f) 25P- $TiO_2$  NPs.

the samples increased from 54.7 to 151.8 m<sup>2</sup>g<sup>-1</sup> with an increase in phosphate content up to 15 wt%. A further increase in phosphate content led to a reduction in the surface area to 79.4 m<sup>2</sup>g<sup>-1</sup>, which can be attributed to partial pore blockage by excess phosphate.<sup>[27]</sup> All phosphated TiO<sub>2</sub> samples have higher surface area in comparison with pure TiO<sub>2</sub>, which can be related to the stabilization effect of phosphate anions against sintering. This stabilization effect is assumed to be due to phosphate anions replacing some of the hydroxyl bridges originally present in the dried uncalcined TiO<sub>2</sub> during impregnation. After calcination, these impregnated anions result in the formation of Ti–O–P bond linkages. Dalai et al.<sup>[28]</sup> also reported a similar beneficial role of incorporated sulfate ions in TiO<sub>2</sub> in retarding sintering through bond strengthening.

#### Compositional and surface analysis

The elemental composition of the catalyst samples was determined from ICP-AES analysis. The results summarized in Table 1 indicate that the theoretical values of the Ti/P molar ratio estimated from the loaded phosphate precursor are in good agreement with the values determined from ICP analysis. XPS measurements were used to identify the oxidation states and bonding characteristics of the elements. The deconvoluted XPS spectrum of the O1s region of TiO<sub>2</sub> (Figure 3 a) revealed two peaks indicating the presence of two oxygen species. The oxygen peak observed at 530.1 eV is ascribed to the lattice oxygen of TiO<sub>2</sub>, and the peak centered at 531.7 eV corresponds to the oxygen from the hydroxyl group.<sup>[29]</sup> After phosphate treatment, an additional peak was observed at 531.5 eV, which can be assigned to oxygen species of P–O bond linkages.<sup>[30]</sup>

The oxygen peaks representing Ti–O and hydroxyl group shifted to higher binding energies of 530.6 and 533.6 eV, respectively. As shown in Figure 3 b, the Ti $2p_{3/2}$  peaks of pure and phosphated TiO<sub>2</sub> centered

at 458.8 and 459.4 eV, respectively, can be fitted as a single peak, which confirms the presence of Ti ions in an octahedral environment. Notably, there is a shift of lattice oxygen in the O1s region and Ti2p<sub>3/2</sub> of the phosphated sample to higher binding energies. This shift is due to partial electron transfer from Ti to P owing to the incorporation of phosphorus into the TiO<sub>2</sub> lattice, which thus decreases the electron density on Ti. This result is consistent with the report of Guo et al.<sup>[31]</sup> The high-resolution spectra of P2p shown in Figure 3 c reveals a single peak at 134.1 eV, which indicates the existence of phosphorus in the pentavalent oxidation state.<sup>[31]</sup> This peak was not observed in the pure TiO<sub>2</sub> sample (Figure 3 d). Hence, the XPS results confirmed the incorporation of phosphorus into the TiO<sub>2</sub> framework and the XRD and BET results suggested the existence of a Ti–O–P linkage.



Figure 3. High-resolution XPS spectra of a) O1s, b) Ti2p, c) P2p, and d) widescan survey.



#### TEM

The TEM image of  $TiO_2$  (Figure 4a) shows a plate-like morphology. The crystal size estimated from the particle size distribution curve shown in Figure S1 ranges from 23 to 38 nm, which is similar to the particle size estimated from XRD analysis. The high-resolution TEM (HRTEM) image of  $TiO_2$  is shown in Figure 4b, which shows clear crystalline lattice fringes with a mea-



**Figure 4.** TEM images of a and b)  $TiO_2$  and c and d) 15P- $TiO_2$ . Images (b) and (d) represent HRTEM images of  $TiO_2$  and 15P- $TiO_2$ , showing lattice fringes of the (101) plane.

sured spacing of 0.351 nm, assigned to the (101) plane.<sup>[32]</sup> In contrast to pure TiO<sub>2</sub>, phosphated TiO<sub>2</sub> shows a significant decrease in the particle size, forming clusters of small nanosized crystals (Figure 4c). The HRTEM image of phosphated TiO<sub>2</sub> (Figure 4d) also shows lattice fringes, which suggests that the TiO<sub>2</sub> structure is retained after phosphate treatment.

#### **Acidity measurement**

The acidity measurement of  $TiO_2$  NPs was performed by using  $NH_3$ -TPD. The total acid amount evaluated by the quantity of desorbed ammonia is summarized in Table 1. All phosphated samples exhibited high acidity than pure  $TiO_2$ . A progressive increase in total acidity was observed with an increase in phosphate loading up to 15 wt%; thereafter, acidity decreased in a trend similar to that of surface area. Surface area could be relatively responsible for influencing the total acidity in terms of accessibility of the probe gas to available acid sites. On the basis of the temperature of the desorption peak, acid sites can be categorized into low (< 200 °C), medium (200–400 °C), and high (>400 °C) strength.<sup>[33]</sup> The desorption spectra of ammonia shown in Figure S2 indicate that the bulk of acid sites present is of low to medium strength even after phosphate treatment. The nature of acid sites was examined by using FTIR spectros-



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Figure 5. IR spectra of pyridine adsorbed on a) TiO<sub>2</sub> and b) 15P-TiO<sub>2</sub> after evacuation at 150  $^\circ\text{C}.$ 

copy of pyridine adsorption. The characteristic absorption bands at 1443 and 1600 cm<sup>-1</sup> observed in pure TiO<sub>2</sub> are typical of surface coordinated pyridine molecules with Lewis acid sites<sup>[6b,34]</sup> (Figure 5 a). As shown in Figure 5 b, phosphate treatment results in the appearance of a peak at 1540 cm<sup>-1</sup> assigned to the pyridinium ion coordinated with Brønsted acid sites, as well as in the disappearance of the peaks at 1565 and 1600 cm<sup>-1</sup>. However, the peak at 1443 cm<sup>-1</sup> was retained but has a weak intensity. In addition, an intense peak at 1490 cm<sup>-1</sup> is assigned to the superimposed signals of pyridine adsorbed on both Lewis and Brønsted acid sites.<sup>[35]</sup> Therefore, in contrast to pure TiO<sub>2</sub>, phosphated TiO<sub>2</sub> is characterized with two types of acid functionalities, that is, Lewis and Brønsted acidity.

#### **Catalytic activity**

The dehydration of glucose to HMF was investigated with pure and phosphated TiO<sub>2</sub> catalysts. The initial tests were performed with 2 wt% glucose concentration in the water–butanol biphasic system. The conversion of glucose was only 53.8% with 27.6% HMF yield if the reaction was performed with pure TiO<sub>2</sub>. Under similar reaction conditions, phosphated TiO<sub>2</sub> was substantially more active than pure TiO<sub>2</sub>, with HMF yield ranging from 60 to 70% depending on the phosphate content as shown in Figure 6.

The enhanced catalytic activity of phosphated TiO<sub>2</sub> can be ascribed to the presence of Brønsted acid sites. This view is clarified by the activity results summarized in Table S1, which indicate the beneficial role of a catalytic system consisting of both Brønsted and Lewis acidity in HMF formation. With a pure solid Brønsted acid catalyst (Amberlyst 70), a low HMF yield of 8.3% at 70% glucose conversion could be achieved, whereas a pure Lewis acid catalyst in the form of TiO<sub>2</sub> gave a 27.6% HMF yield at 53.8% conversion. Conversion and HMF yield reached 76.6 and 31.2%, respectively, for a physical mixture of Amberlyst 70 and pure TiO<sub>2</sub>, which thus demonstrated the beneficial role of the two acid functionalities in promoting higher glucose conversion and HMF yield.





**Figure 6.** Effect of phosphate content on the catalytic activity of  $TiO_2$  NPs. Reaction conditions: glucose (2 g), catalyst weight (0.4 g), water (30 mL), *n*-butanol (70 mL), *T*=160 °C, *t*=5 h. •, Glucose conversion;  $\bigcirc$ , HMF yield.

Notably, both conversion and yield on phosphated  $TiO_2$  increased as the phosphate loading increased to 15 wt%. A further increase in phosphorus content led to a reduction in catalytic activity. The optimal catalytic performance of  $TiO_2$  was achieved at 15 wt% phosphate loading corresponding to the NP with highest surface area and acidity, which indicated that catalytic activity can be correlated with surface acidity. Moreover, the formation of small nanosized particles contributed to the overall higher catalytic performance of  $TiO_2$  after phosphate treatment.

In an attempt to investigate the effect of crystal size and acidity on the catalytic activity of the NPs, TiO<sub>2</sub> was calcined at varying temperatures (400-700 °C) before and after phosphate treatment. Calcination temperature is believed to influence the crystal growth of TiO<sub>2</sub> NPs,<sup>[36]</sup> and this is evidenced by the XRD results presented in Figure S3a. The variations reflected in the peak intensities represent a range of crystal sizes. The estimated crystal size of the NPs increased considerably from 6.8 to 34.1 nm with increasing temperature. Crystallinity also increased with increasing temperature. The transformation of the anatase phase to the rutile phase was observed for TiO<sub>2</sub> calcined at 700 °C. The catalytic activity of TiO<sub>2</sub> NPs calcined at different temperatures is presented in Figure 7a. We observed that an increase in temperature corresponds to an increase in crystal size, which led to a significant decrease in activity. For instance, at 400 °C, 81.8% glucose conversion and 41.4% HMF yield were attained but decreased to 31.8 and 19.0%, respectively, after calcination at 700 °C. Small nanosized crystals have been reported to contribute to a large surface area, which facilitate the adsorption of reactants.<sup>[37]</sup> Dutta et al.<sup>[17]</sup> also reported that smaller nanosized particles facilitated the mass transport of substrate within the catalytic material. This affords better access to the internal mesoscopic void spaces and ultimately exposes more active sites for surface interaction with reactants for enhanced reactivity. Meanwhile, if TiO<sub>2</sub> was treated with phosphate (15 wt%) before calcination at various temperatures, no distinct structural changes were observed from





**Figure 7.** Effect of calcination temperature on the crystal size and catalytic activity of TiO<sub>2</sub> NPs: a) pure TiO<sub>2</sub> and b) phosphated TiO<sub>2</sub> (15 wt %). Reaction conditions: glucose (2 g), catalyst weight (0.4 g), water (30 mL), *n*-butanol (70 mL), T = 160 °C, t = 5 h.  $\bigcirc$ , Glucose conversion;  $\triangle$ , HMF yield;  $\blacksquare$ , crystal size.

the XRD patterns (Figure S3 b) and the calculated crystal size ranges from 5.61 nm at 400 °C to 7.82 nm at 700 °C. Moreover, the anatase to rutile transformation was inhibited at 700 °C, which was present in pure TiO<sub>2</sub> calcined at the same temperature. Hence, we may conclude that phosphate treatment significantly inhibited the crystal growth of anatase TiO<sub>2</sub> and its transformation to rutile TiO<sub>2</sub> at temperatures up to 700 °C. This result was supported by the report of Körösi et al.,<sup>[38]</sup> who showed that phosphate treatment enhanced the thermal stability of TiO<sub>2</sub> NPs.

All the phosphated NPs calcined at various temperatures exhibited identical performance for glucose conversion. In all cases, approximately 80% glucose conversion with 70% HMF yield was recorded (Figure 7b). This result indicates that a slight change in crystal size has a negligible effect on the catalytic performance. Hence, we may conclude that similar activity can be achieved with nanosized  $TiO_2$  crystals of similar dimensions and acid contents.

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To explore the effect of acid content on glucose dehydration to HMF, we examined TiO<sub>2</sub> NPs of similar crystal sizes but different acid contents, that is, pure  $TiO_2$  at 400 °C (crystal size: 6.82 nm,  $S_{BET}$ : 136.9 m<sup>2</sup>g<sup>-1</sup>, and acidity: 1.28 mmolg<sup>-1</sup>) and 15P-TiO<sub>2</sub> at 600 °C (crystal size: 6.12 nm,  $S_{BET}$ : 151 m<sup>2</sup>g<sup>-1</sup>, and acidity: 2.36 mmol  $g^{-1}$ ). As shown in Figure 7, approximately 80% glucose conversion was achieved on both samples. However, a remarkable increase in HMF yield was attained on 15P-TiO<sub>2</sub>, which may be associated with increased acid sites. This result suggests that both TiO<sub>2</sub> and 15P-TiO<sub>2</sub> of similar crystal sizes had comparable activity for glucose conversion. However, modification of the catalyst surface through phosphate treatment was essential to enhance the selectivity toward HMF. Hence, we conclude that the crystal size reduction achieved by only thermal treatment is insufficient in enhancing the activity of the TiO<sub>2</sub> catalyst for HMF synthesis.

#### Effect of reaction parameters

As shown in the previous section,  $15P-TiO_2$  was most active for glucose to HMF conversion. This catalyst was used to evaluate the effect of critical reaction parameters. The effect of catalyst loading on conversion and yield is presented in Figure 8. We observed a progressive increase in both conversion and yield with an increase in catalyst loading up to 0.6 g. The yield of HMF appeared to plateau after 0.6 g with a slight increase in the conversion. Hence, the optimum catalyst loading was 0.6 g, which corresponds to a glucose/catalyst weight ratio of 10:3.

Furthermore, we examined the effect of both reaction temperature and time at this optimum catalyst loading. The effect of both reaction temperature and time on HMF yield is presented in Figure 9.

The time analysis shows that the reaction proceeded rapidly in the first 3 h to produce HMF and thereafter the product



**Figure 8.** Glucose dehydration to HMF as a function of catalyst loading in a water–butanol biphasic solvent on the 15P-TiO<sub>2</sub> catalyst. Reaction conditions: glucose (2 g), water (30 mL), *n*-butanol (70 mL),  $T = 160 \degree C$ , t = 5 h.  $\bullet$ , Glucose conversion;  $\bigcirc$ , HMF yield.

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**Figure 9.** Effect of reaction time and temperature on glucose dehydration on the 15P-TiO<sub>2</sub> catalyst. Reaction conditions: glucose (2 g), catalyst weight (0.6 g), water (30 mL), *n*-butanol (70 mL). ■, 160 °C; ●, 170 °C; ▲, 175 °C; ▼, 180 °C.

yield increases gradually with time. Temperature had a significant effect on both glucose conversion and HMF yield. At 180°C glucose conversion was 97% after 4 h of reaction, whereas at 160°C glucose conversion was 93% after 8 h of reaction. This result indicates that longer time is needed at lower temperature to reach similar glucose conversion at higher temperature. However, because HMF is more reactive at high temperature, <sup>[3c]</sup> a longer reaction time resulted in the decrease in HMF yield at 180°C after 6 h. According to these results, the optimal condition for this reaction was 3 h of reaction time at 175°C. Under these optimal conditions, we investigated the effect of initial glucose concentration. The effect of glucose concentration on HMF yield is presented in Figure 10. Glucose



**Figure 10.** Effect of initial glucose concentration on HMF yield on the 15P-TiO<sub>2</sub> catalyst. Reaction conditions: glucose/catalyst weight ratio = 10:3, water (30 mL), *n*-butanol (70 mL),  $T = 175 \degree$ C, t = 3 h. , Glucose conversion; , HMF yield.

conversion was similar but HMF yield decreased with an increase in the initial glucose concentration. The decrease in HMF yield with increasing glucose concentration may be due to the propensity to form humins via condensation polymerization of HMF with glucose and other reactive intermediates in the aqueous phase.<sup>[39]</sup>

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#### Plausible reaction pathway

The scope of this study does not entail an in-depth elucidation of the reaction mechanism. This comprises our future work, and the results will be the focus of a subsequent publication. However, on the basis of the composition of the products, we proposed a plausible reaction pathway shown in Scheme 1. Major intermediates and byproducts formed during the reacruns (Figure 11). However, HMF yield decreased continuously over the first three runs from 81 to 70%. We observed a change in color of the catalyst from white to dark brown, which is likely due to the deposition of humin compounds on the catalyst surface, causing deactivation of the active sites. The Lewis acid-catalyzed isomerization of glucose to fructose is unaffected because of the minor change in glucose conversion. We hypothesized that the humins deposited on the cata-



**Scheme 1.** Glucose conversion to HMF in a water–butanol (30:70 v/v) biphasic system on 15P-TiO<sub>2</sub> NPs. FA = formic acid; LA = levulinic acid.

tion were identified by using HPLC and GC-MS (Figure S4). Small amounts of levoglucosan, furfural, formaldehyde, formic acid, and levulinic acid were detected along with HMF. The time course of the products is shown in Figure S5. The presence of levoglucosan is indicative of the loss of one molecule of water from glucose.<sup>[24]</sup> In addition to the anticipated products of HMF rehydration (levulinic acid and formic acid), the formation of furfural indicates that HMF decomposed via loss of formaldehyde.<sup>[40]</sup> In addition, formic acid may be produced as a result of hydrolytic fission of furfural.<sup>[40b]</sup> On the basis of these results, we propose that the isomerization of glucose to fructose is accompanied by the concurrent dehydration reaction of glucose to form levoglucosan. After the formation of HMF via dehydration of fructose, HMF undergoes rehydration to produce levulinic acid and formic acid. Furthermore, the decomposition of HMF can occur via loss of formaldehyde to produce furfural.

#### **Catalyst reusability**

One of the most important factors contributing to catalytic performance is the catalyst stability and reusability during the reaction. The reusability of the 15P-TiO<sub>2</sub> catalyst was investigated by performing the glucose dehydration reaction up to six cycles. After the completion of each reaction cycle, the catalyst was recovered through filtration, washed with acetone, dried, and then used for the next reaction run. There was no significant change in the conversion of glucose for all the reaction

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lyst surface most likely affect the dehydration step catalyzed by Brønsted acid. HMF is reported to have stronger adsorption affinity for the Brønsted acid site.[35,41] HMF adsorbed on the surface of the recycled catalyst undergoes a condensation reaction to form humins; this finding is consistent with the catalyst color change. The strongly adsorbed HMF on the Brønsted acid sites can also cause blockage of active sites as well as undergo further rehydration to form organic acids.

This finding is evidenced by the slightly increased yields of fructose and levulinic acid (Figure S6). To test the aforementioned hypothesis, we decided

to regenerate the catalyst before subsequent reaction runs. A post-treatment of the catalyst was performed through calcination at 600 °C for 4 h. The recovered catalyst after post-treatment was approximately 0.51 g. The catalyst loss was during the decantation and filtration process. The fresh catalyst (15%



**Figure 11.** Reusability test of the 15P-TiO<sub>2</sub> catalyst for the conversion of glucose to HMF. Reaction conditions: glucose (2 g), catalyst weight (0.6 g), water (30 mL), *n*-butanol (70 mL),  $T = 175 \degree$ C,  $t = 3 h. \bigcirc$ , Glucose conversion; , HMF yield.



of the total catalyst weight) was supplemented to achieve an initial catalyst weight of 0.6 g for the next reaction. The reaction was then repeated under similar conditions as described previously for the first three reaction runs. A comparable activity was achieved both before and after catalyst regeneration, which suggests that the catalytic activity can be restored. XRD and HRTEM were used to analyze the structural stability of the spent catalyst. The results of these analyses (Figures S7 and S8) compared with those for the fresh sample indicate that no significant changes occurred in the structural framework of the NPs after the reaction. Overall, these findings from the reusability test suggest the stability and recyclability of the catalyst. Moreover, catalyst deactivation due to humin deposition is reversible by regeneration.

## Conclusions

We demonstrated the conversion of glucose to 5-hydroxymethylfurfural (HMF) in the water-butanol biphasic system catalyzed by TiO<sub>2</sub> nanoparticles, which were synthesized by using the sol-gel method. TiO<sub>2</sub> was modified via phosphate treatment by impregnation. Phosphorus was incorporated into the structural framework of TiO<sub>2</sub>, as confirmed by XPS analysis. Phosphate treatment enhanced the thermal stability of TiO<sub>2</sub> and prevented the phase transformation from anatase to rutile at high temperature. The N<sub>2</sub> adsorption-desorption analysis revealed that phosphated TiO<sub>2</sub> has a larger surface area than unmodified TiO<sub>2</sub>. Furthermore, the presence of Lewis and Brønsted acid functionalities was confirmed by using FTIR spectroscopy of pyridine adsorption. Phosphated TiO<sub>2</sub> was effective for the catalytic conversion of glucose to HMF owing to the formation of small nanosized crystals with enhanced surface acidity. We studied the effects of reaction temperature and time, catalyst weight, and substrate concentration. In general, all these parameters influence the catalytic performance and yield of HMF. Under optimal reaction conditions, a remarkably high HMF yield of approximately 81 and 97% glucose conversion was achieved at a glucose concentration of 2 wt %. Under similar reaction conditions, an HMF yield of 60 and 45% was attained at a glucose concentration of 5 and 10 wt%, respectively. Finally, catalyst stability under the given reaction conditions afforded its recycling for multiple reaction runs.

## **Experimental Section**

#### Materials and catalyst synthesis

Titanium(IV) butoxide, *n*-butanol, ammonium phosphate monobasic, ammonium hydroxide solution (28%), glucose, fructose, HMF, cellobiose, levoglucosan, and furfural were all purchased from Sigma–Aldrich. Levulinic acid was purchased from Merck Schuchardt, and formic acid was supplied by Ajax Finechem. All solutions were prepared using water with a conductivity of 18 M $\Omega$  cm<sup>-1</sup> obtained with an ELGA ultrapure water distillation apparatus.

 $TiO_2$  NPs were prepared following the neutral amine sol-gel synthesis technique, using titanium(IV) butoxide as the precursor. The sol was prepared by the dropwise addition of the alkoxide precursor to an aqueous solution containing *n*-butanol under stirring.

The pH of the solution was adjusted to 7 by adding ammonium hydroxide solution, and the resulting solution was maintained under reflux for 24 h. After gelation, excess solvent was removed with a rotary evaporator followed by vacuum drying at 80 °C to obtain titanium hydroxide hydrate. Phosphated TiO<sub>2</sub> was prepared through the impregnation of titanium hydroxide hydrate with an aqueous solution of the required amount of ammonium phosphate monobasic to give TiO<sub>2</sub> NPs with 5–25 wt% phosphate content. A typical synthesis of 5 wt% phosphate loading on TiO<sub>2</sub> (5P-TiO<sub>2</sub>) was as follows: The phosphate precursor (0.085 g) was dissolved in water. Then, dried hydrated TiO<sub>2</sub> (2 g) was added, followed by stirring at RT for 4 h. Excess water was evaporated, and the resulting solid was dried at 80 °C for 12 h. Finally, pure and phosphated TiO<sub>2</sub> NPs were obtained after calcination at 600 °C for 4 h.

#### **Catalyst characterization**

The wide-angle XRD patterns were recorded on a Rigaku Miniflex using monochromatic CoK $_{\alpha}$  radiation (30 kV, 15 mA). The data were collected at  $2\theta = 10-90^{\circ}$  (step size: 0.02; step time: 1 s). The N<sub>2</sub> adsorption-desorption isotherm measurement was done at  $-196\,^\circ\text{C}$ with a Micromeritics TriStar II 3020 surface area and porosity analyzer. Specific surface areas were calculated by using the BET method and pore size distributions using the BJH model on the desorption branch of the isotherm. Total pore volumes were estimated from the amount of N<sub>2</sub> adsorbed at  $P/P_0 = 0.99$ . Compositional analysis was performed by using ICP. The procedure involved sample digestion with a Milestone Ethos-1 microwave digester and then analysis by using a Varian Vista-PRO ICP-OES instrument. The XPS spectra were acquired with a Kratos AXIS Utlra X-ray photoelectron spectrometer equipped with a 165 mm hemispherical electron energy analyzer using a monochromatic AlK $_{\alpha}$  ( $h\nu =$ 1486.6 eV) X-ray source. A wide-scan survey spectrum was recorded at an analyzer pass energy of 160 eV and multiplex (narrow) high-resolution scans at 20 eV. The binding energies were referenced to the C1s peak of adventitious carbon at 284.8 eV to account for the charging effects. Data analysis was done by using the CasaXPS software, version 2.3.12, in which a Shirley background subtraction was used before fitting the spectra using Gaussian-Lorentzian curves. NH<sub>3</sub>-TPD was performed with a Micromeritics AutoChem II chemisorption analyzer to determine total acid sites on the catalyst samples. Each sample ( $\approx$  70 mg) was placed in a guartz U tube and pretreated at 500 °C in a flow of He (flow rate: 50 mLmin<sup>-1</sup>) for 1 h. Then, the sample was saturated with ammonia (15 vol% in He) at 100 °C for 30 min. Physisorbed ammonia on the sample surface was removed by purging the system with He stream at 100 °C for 2 h. The sample was then heated linearly from 100 to 800°C (heating rate: 10 Kmin<sup>-1</sup>) in a flow of He (flow rate: 25 mLmin<sup>-1</sup>) while monitoring the ammonia desorption profile with a thermal conductivity detector. Pyridine-IR spectroscopy was used to examine the nature of acid sites. Pyridine was chemisorbed on the catalyst surface (50 mg) at 150 °C. Excess gaseous and physisorbed pyridine were removed by holding the temperature for 30 min in  $N_2$  flow. The FTIR spectra were obtained at 128 scans and 4 cm<sup>-1</sup> resolution by using a Nicolet 6700 spectrometer (Smart Orbit Accessory). The TEM images were taken with a JEOL JSM-2100 microscope operating at an acceleration voltage of 200 kV.

#### **Catalytic evaluation**

Glucose dehydration to HMF was performed in a stainless steel Parr reactor. In a typical experimental run, the required amount of

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substrate, solvent, and catalyst was charged into a 300 mL reactor, purged, and then pressurized to 30 bar (1 bar = 100 kPa) with highpurity Ar. The water-n-butanol (30:70 v/v) biphasic mixture was used as the reaction medium. The reactor was heated to its set point temperature, which was measured by a thermocouple placed inside the reaction mixture. Time zero in the reaction was defined as the time when the reactor reached its set point temperature. Catalytic experiments were repeated to evaluate the reproducibility of data. Typical errors observed were in the range of  $\pm$ 2%. Product analysis was done with a Shimadzu Prominence HPLC system equipped with both refractive index (RID-10) and UV/ Vis (SPD-M20A) detectors and a Bio-Rad Aminex HPX-87H analytical column. The column was operated at 50  $^\circ$ C with H<sub>2</sub>SO<sub>4</sub> (5 mm) as the mobile phase at a flow rate of 0.6 mLmin<sup>-1</sup> for the analysis of both aqueous and organic phases. Product identification was performed with a Shimadzu GCMS-QP2010 Ultra equipped with an Rxi-5ms column. Glucose conversion and product yield were calculated by using Equations (1) and (2):

$$Conversion(\%) = \left(1 - \frac{n}{n_o}\right) \times 100\%$$
(1)

$$\mathsf{Yield}(\%) = \left(\frac{n_i}{n_o}\right) \times 100\% \tag{2}$$

in which  $n_o$  and n are the number of moles of glucose in the feed and product, respectively, and  $n_i$  is the number of moles of product *i* (e.g., HMF, fructose, levulinic acid, and levoglucosan).

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# **FULL PAPERS**

A moment of truth: The as-synthesized nanosized phosphated TiO<sub>2</sub> material serves as a bifunctional catalyst in the production of 5-hydroxymethylfurfural (HMF) from glucose. The relationship between catalyst synthesis, properties, and performance indicates a high potential of the TiO<sub>2</sub>-based catalyst for HMF production. This provides a step further toward a sustainable route to generate HMF from renewable carbohydrate feedstock.



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Catalytic Conversion of Glucose to 5-Hydroxymethyl-furfural with a Phosphated TiO<sub>2</sub> Catalyst