High Yield Production of 5-Hydroxymethylfurfural from Carbohydrates Over Phosphated TiO_2-SiO_2 Heterogeneous Catalyst

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An efficient and selective process for the conversion of carbohydrates to 5-hydroxymethylfurfural (HMF) was applied over a novel phosphated TiO_2-SiO_2 (P-TiO_2-SiO_2) catalyst. The catalyst, synthesized by a facile sol-gel technique, was characterized by X-ray diffraction (XRD), N_2 sorption, NH_3 temperature-programmed-desorption, and Fourier transform infrared spectroscopy (FT-IR) study of the pyridine adsorbed. The highest HMF yield of 63.0 mol% was achieved at 170 °C for 90 min over P-TiO_2-SiO_2 catalyst in a tetrahydrofuran (THF)/H_2O-NaCl system. The P-TiO_2-SiO_2 catalyst showed a predominant catalytic performance in the synthesis of HMF, a result of its moderate acid density and suitable Brønsted/Lewis (B/L) acid ratio. Additionally, the catalyst was shown to be efficient in the conversion of more complex cellulose with the high HMF yield of 56.0 mol%. More importantly, this mesoporous catalyst exhibited high stability and recyclability, making it a promising choice for the future production of HMF.

Keywords: Solid acid; P-TiO_2-SiO_2; 5-Hydroxymethylfurfural; Biphasic system; Carbohydrate

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INTRODUCTION

Converting renewable lignocellulose into high value-added chemicals is a promising alternative for the petrochemical industry (Zhang *et al.* 2016; Mika *et al.* 2017). 5-Hydromethylfurfural (HMF), obtained from lignocellulosic C6 sugars, is a versatile platform chemical due to its wide application in producing bulk chemicals and renewable materials (Van Putten *et al.* 2013). Achieving a remarkable yield and a feasible, commercial-scale synthesis method of HMF has drawn considerable attention. Numerous important works have focused on the efficient conversion of fructose to HMF (Antonetti *et al.* 2017; Raveendra *et al.* 2017). However, on the commercial-scale, fructose is always obtained from glucose catalyzed by isomerase; the high costs and strict conditions of such processing have markedly limited HMF's industrial production. Compared to using fructose as the feed, glucose is a possible alternative due to its cost-effectiveness and high availability (Yang *et al.* 2015). The conversion of glucose to HMF has only been achieved with low yields under Brønsted acids. However, the HMF yield can be improved *via* an additional, tandem step: the isomerization of glucose to fructose by isomerase (Huang *et al.* 2014) or a Lewis acid (Yang *et al.* 2015) or a base catalyst (Watanabe *et al.* 2005), following the fructose transformation to HMF, as well as some undesired side reactions (for example, the HMF conversion to levulinic acid (LA)) (Scheme 1). Consequently, designing a catalytic process for the efficient transformation of glucose to HMF is both desirable and economically important for industrial production.

Many types of homogeneous catalytic systems have been explored with high HMF yields, such as Lewis acid metal halides and a few inorganic acids (Wang *et al.* 2017) or Lewis acid metal halides and acidic ionic liquids (Zhao *et al.* 2007). Safe catalyst handling, complete separation, and simple catalyst recycling still remain as important concerns in the development of these methods into large-scale, final industrial processes. Moreover, the high cost of ionic liquids limits the economic feasibility of the large-scale synthesis of HMF. Therefore, heterogeneous catalytic systems have recently received much attention due to their operational safety, ease of separation, and reusability. Many excellent heterogeneous catalysts, such as acidic resins, zeolites, and super-acid catalysts, have been reported (Otomo *et al.* 2014; Liu *et al.* 2015; Shen *et al.* 2016). Yang *et al*. reported that an optimized HMF yield of 47.6% was obtained over $SO_4^{2-}/ZrO_2\text{-}Al_2O_3$ catalysts (Yan *et al.* 2009), wherein the catalysts suffered from easy deactivation during the recycling process. Xu *et al*. (2014) explored HMF production from glucose with a 70.0% yield, using a solid acid catalyst (Sn-MCM-41) in [EMIM]Br ionic liquids at 110 °C for 4 h. However, the solid acid catalysts required a complex preparation process, and expensive ionic liquids are not appropriate for commercial-scale syntheses of HMF.

Titania (TiO_2) functions as an inexpensive metal oxide with wide applications (O'Regan and Grätzel 1991; Sang *et al.* 2014; Dhawale *et al.* 2017). Attributable to its acid-base property and chemical stability, TiO_2 has been reportedly applied in the transformation of sugar to HMF (Qi *et al.* 2008; De *et al.* 2011; Dutta *et al.* 2011). De *et al*. (2011) investigated the glucose transformation to HMF with mesoporous TiO_2 spheres. The HMF yield was only 21.5%. To improve the HMF yields, modified and mixed TiO_2 is essential. Dutta *et al*. (2012) found that the hierarchically porous titanium phosphate nanoparticles efficiently converted glucose to HMF. Wang *et al*. (2015) reported that SO_4^{2-}/TiO_2 solid acids, formed by the precipitation/impregnation method, were evaluated for the transformation of fructose corn syrup to HMF. However, the catalyst structure was not stable in the reaction system, so catalytic reactivity was noticeably decreased after recycling. Compared to TiO_2, the mixed-oxide $TiO_2\text{-}SiO_2$ has a high thermal stability and a benign structural stability (Notari *et al.* 2006). Furthermore, having appropriate acidic properties of catalysts after sulfonation and phosphorylation makes the glucose conversion to HMF much more efficient. Therefore, the development of a low-cost and stable, modified solid acid $TiO_2\text{-}SiO_2$ with high catalytic activity is expected for glucose conversion to HMF.

Herein, the authors synthesized a novel, mesoporous phosphated $TiO_2\text{-}SiO_2$ catalyst ($P\text{-}TiO_2\text{-}SiO_2$) *via* a sol-gel approach. The application of the solid acid has not been investigated to date. The mesoporous $P\text{-}TiO_2\text{-}SiO_2$ catalyst was well characterized and evaluated for the transformation of carbohydrates to HMF in the $THF/H_2O\text{-}NaCl$ system. The optimization of temperature, time, and catalyst dosages, as well as the effects of the number of recycles, were systematically investigated.

EXPERIMENTAL

Materials

Glucose (99.0%), fructose (99.0%), NaCl (99.5%), ammonium dihydrogen phosphate ($NH_4H_2PO_4$) (99.0%), titanium butoxide (99.0%), tetraethoxysilane (TEOS), ethanol, ammonium hydroxide solution (NH_4OH, 25.0 wt%), and THF (99.0%) were all supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Micro-crystalline cellulose (MCC) was obtained from Sigma-Aldrich (Beijing, China). Acetic acid (99.5%) was purchased from Guangfu Technology Development Co. Ltd. (Tianjin, China). The HMF (98.0%) and levulinic acid (98.0%) were supplied by Aladdin Industrial Corporation (Shanghai, China). All of the reagents were used without any purification.

Preparation of solid acid catalysts

The mesoporous TiO_2-SiO_2 and P-TiO_2-SiO_2 catalysts were prepared by a neutral amine sol-gel approach. The titanium butoxide and TEOS were used as the TiO_2 and SiO_2 precursors. The precursors were added to the aqueous solution of $NH_4H_2PO_4$, acetic acid, and ethanol in a dropwise manner. The mixture was constantly stirred, and the sol was formed. The mole ratio of ethanol/titanium butoxide/TEOS/acetic acid/$NH_4H_2PO_4$/H_2O was 1.0/0.0625/0.0625/0.04/0.0124/2.0. The pH of the sol was adjusted to approximately 7.0 by adding NH_4OH. The sol was retained under reflux conditions (80 °C, 24 h). Leftover solvents were evaporated, and the gel was oven-dried at 80 °C for 12 h. Finally, the resulting samples were calcined at 500 °C for 3 h. The TiO_2-SiO_2 was prepared without the addition of ammonium phosphate.

Methods

Characterization of the catalysts

X-ray diffraction (XRD) plots were recorded on a Bruker D8 ADVANCE X-ray diffractometer (Bruker AXS Karlsruhe, Germany). Imaging of the different morphology of two catalysts was performed by S-3400 N scanning electron microscope (HITACHI, Japan). The N_2-sorption test was performed on a Builder SSA-7000 instrument (Beijing, China), and the specific surface areas were determined by the Brunauer-Emmett-Teller (BET) method. The pore size distribution plots were computed *via* the Barrett-Joyner-Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) spectra were collected in a VG CLAM 4 MCD (PSP Vacuum Technology, Macclesfield, UK). Ammonia temperature-programmed-desorption (NH_3-TPD) was carried out on the Micromeritics AutoChem Ⅱ chemisorption instrument (Atlanta, GA, USA). The pyridine-IR of two catalysts were scanned on a TENSOR27 FT-IR spectrometer (Bruker, Karlsruhe, Germany). Quantification of acid sites was achieved according to the method reported by Emeis (1993).

Catalytic evolution for glucose transformation to HMF

Glucose transformations to HMF were evaluated in 15-mL glass reactors. Typically, glucose (0.1 g), NaCl (0.2 g), and certain amounts of catalysts were added into a 5 mL THF-H_2O mixture (THF/H_2O volume ratio of 4/1). Then, the reactor was placed on heating equipment (Wuzhoudingchuang Technology Co., Ltd., Beijing, China) at a desired temperature under magnetic stirring (300 rpm) for a desired time. After the reaction, aqueous and organic phases were separated by extraction. Prior to analyses, samples were collected by filtering through a 0.22-µm syringe filter.

Mechanocatalytic pretreatment of MCC

The mechanocatalytic pretreatment of MCC was conducted using a modified procedure based on the ball-milling of acidic biomass feeds. Typically, MCC was added in a 0.075 M H_2SO_4 solution in batches, and the mixed solution was stirred for 10 min. The solid/liquid was filtered under reduced pressure, followed by vacuum drying overnight at 50 °C. The acidic MCC was ball-milled for 8 h.

Products analysis

The aqueous layer was analyzed with an Agilent 1260 system (Agilent, Santa Clara, USA) equipped with an organic acid column (Bio-Rad Aminex HPX-87H, Richmond, USA) and a refractive index detector. 5 mM H_2SO_4 solution was used as the mobile phase with a flow rate of 0.6 mL/min. The organic layer was determined using a Symmetryshield RP C18 column (Waters, Milford, MA, USA), a diode array detector, and an acetonitrile-water gradient with a flow rate of 1.0 mL/min. The yield and selectivity of liquid products were defined as shown in the subsequent set of equations:

$$\text{Glucose conversion (\%)} = \frac{\text{Glucose converted (g)}}{\text{Glucose (g)}} \times 100 \tag{1}$$

$$\text{Cellulose conversion (\%)} = \frac{\text{Cellulose converted (g)}}{\text{Cellulose (g)}} \times 100 \tag{2}$$

$$\text{Glucose yield } (mol\%) = \frac{\text{Glucose amount (mol)}}{\text{Calculated glucose in cellulose (mol)}} \times 100 \tag{3}$$

$$\text{HMF yield } (mol\%) = \frac{\text{HMF amount (mol)}}{\text{Glucose amount (mol)}} \times 100 \tag{4}$$

$$\text{LA yield } (mol\%) = \frac{\text{LA amount (mol)}}{\text{Glucose (mol)}} \times 100 \tag{5}$$

$$\text{HMF selectivity (\%)} = \frac{\text{HMF amount (mol)}}{\text{Converted glucose (mol)}} \times 100 \tag{6}$$

RESULTS AND DISCUSSION

Characterizations of Catalysts

Figure 1 depicts the XRD patterns of the two catalysts. It presents that only one wide band was observed from 2θ = 15° to 40° for each catalyst. No evidence of the crystalline phases of the anatase TiO_2 polymorphs were detected in Fig. 1. This suggested that TiO_2 could be present in an amorphous phase or as crystals with tiny sizes that are not detectable by XRD (Atanda *et al.* 2015). It also can indicate that the addition of phosphate did not change the TiO_2-SiO_2 structures. The SEM micrograph (Fig. 2) shows that the two samples consisted of plate-like clusters of size 1 to 4 μm.

The experimental data related to N_2 sorption are presented in Table 1. The two catalysts had high specific surface areas. The surface area of the P-TiO_2-SiO_2 decreased from 431.1 m^2g^{-1} to 337.2 m^2g^{-1} with the addition of phosphate to pristine TiO_2-SiO_2. The decrease of the pore diameter from 3.6 nm to 2.7 nm after phosphorylation may be explained by the possible existence of a stratified structure inside the pore.

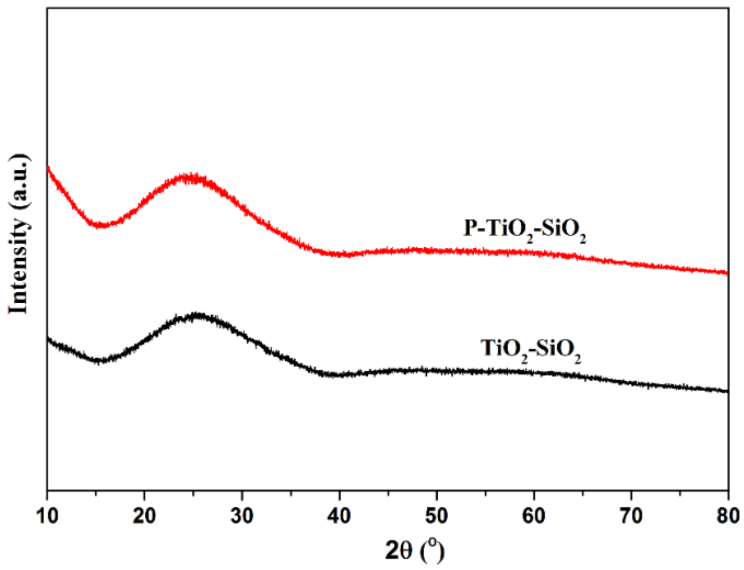

Fig. 1. The XRD patterns of TiO_2-SiO_2 and P-TiO_2-SiO_2

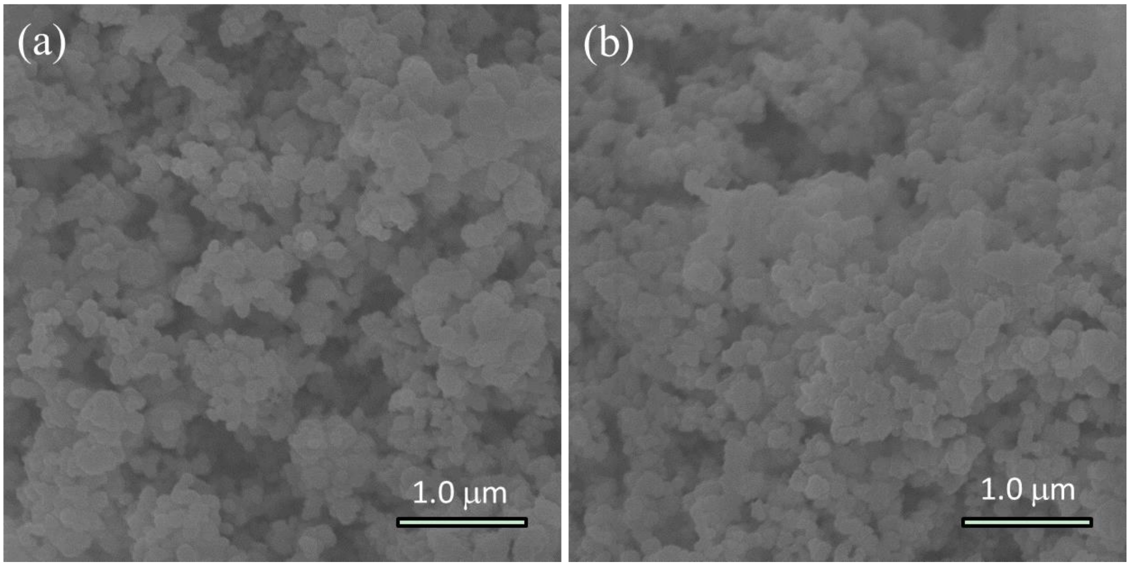

Fig. 2. The SEM of TiO_2-SiO_2 and P-TiO_2-SiO_2. (a) TiO_2-SiO_2, (b) P-TiO_2-SiO_2

It is well known that suitable pore sizes enhance the diffusion of glucose and HMF and inhibits the undesired rearrangement of HMF (Karinen *et al*. 2011). It can be seen that most pore sizes of the P-TiO_2-SiO_2 catalyst were closer to the molecular sizes of glucose (0.9 nm) than that of TiO_2-SiO_2, which indicated the P-TiO_2-SiO_2 catalyst will give the advantages of shape selectivity in the conversion of glucose to HMF.

Table 1. Physicochemical Properties of the Two Catalysts

Sample	Surface Area (m^2g^{-1})^a	Pore Size (nm)	Pore Volume (cm^3g^{-1})	B/L^b	Total Acid (mmol g^{-1})^c
TiO_2-SiO_2	431.1	3.6	0.68	0.41	3.11
P-TiO_2-SiO_2	337.2	2.7	0.45	0.21	2.64

^{a} Surface area: BET surface area; ^{b} B/L: Brønsted/Lewis acid ratio; ^{c} Total acid: Determined from NH_3-TPD analysis

Figure 3 shows the XPS curves for TiO_2-SiO_2 and P-TiO_2-SiO_2. The Ti 2*p* and Si 2*p* spectra show typical peaks (Figs. 3a and 3b), which exhibit the characteristic Ti^{4+} and Si^{4+}peaks. The P-TiO_2-SiO_2 exhibited signals from the P 2*p*, implying the successful grafting of P onto the TiO_2-SiO_2 particles (Samantaray and Parida 2001; Guo *et al.* 2013).

Results from NH_3-TPD were used to determine the acidity and the total acid amounts of catalysts. The total acid amounts were calculated and are shown in Table 1. A decrease in total acidity from 3.11 $mmolg^{-1}$ to 2.64 $mmolg^{-1}$ was observed. After phosphorylation, the one Ti-OH group was replaced by two P-OH groups. The acidity of the P-OH was weaker than that of Ti-OH, resulting into the decrease of the strong Brønsted (B) acid sites and the slightly increase of the weak B acid sits. Another reason was that the P covered some acid sites on the surface of solid acid catalyst, which may have been related to the specific surface area. It may also be attributable to the accessibility of the NH_3 sites to the acid sites on the surface of the catalysts (Atanda *et al.* 2015).

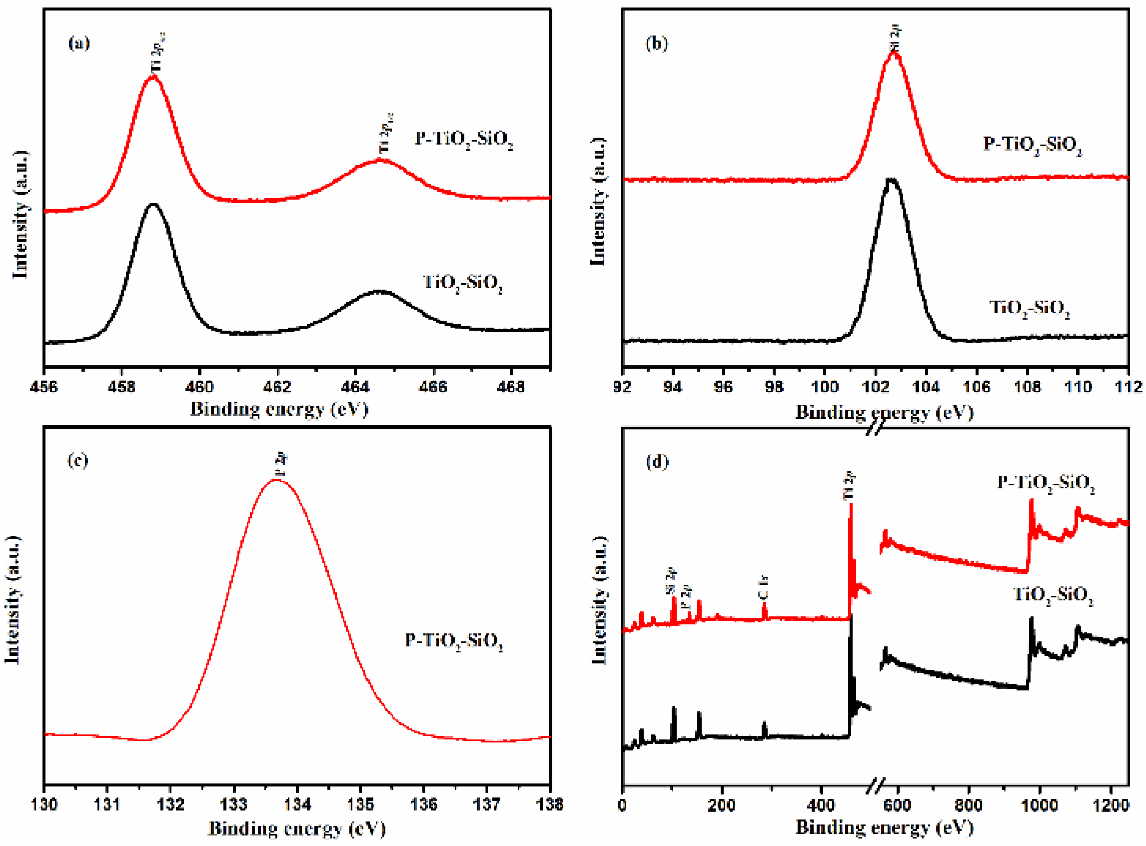

Fig. 3. Shown above are the XPS analyses of P-TiO_2-SiO_2 and TiO_2-SiO_2, where (a) shows Ti 2*p*, (b) shows Si 2*p*, (c) shows P 2*p*, and (d) shows the wide survey scan

The feature of Brønsted and Lewis acidity on the two catalysts was determined by Pyridine-IR. The intense bands at 1445 cm^{-1} and 1540 cm^{-1} confirmed the absorption of pyridine on the Lewis (L) and Brønsted (B) acid sites (Emeis 1993). The L sites originated from unsaturated, six-coordinated Ti, and the hydroxyls on the oxides' surfaces contributed to the formation of B sites. The results shown in Table 1 demonstrate that the B/L ratios of P-TiO_2-SiO_2 and TiO_2-SiO_2 were 0.21 and 0.41, respectively. Hence, the two catalysts were characterized as containing two types of acids (B and L).

Catalytic Performance

To demonstrate the catalytic performance, direct glucose transformation to HMF was conducted at 170 °C for 60 min over P-TiO_2-SiO_2 and TiO_2-SiO_2 catalysts. A relatively low HMF yield of 18.5 mol% was obtained when water was used as the reaction media (Table 2, entry 1). When a biphasic system was used, the HMF yield increased to 33.0 mol%. A high HMF yield of 53.0 mol% was obtained in the THF/H_2O-NaCl system because of the salt-out effect. Compared with the TiO_2-SiO_2 catalyst, the P-TiO_2-SiO_2 catalysts had better reaction activities, demonstrating that introducing P to TiO_2-SiO_2 enhanced performance. Processing the P-TiO_2-SiO_2 catalyst to a lower acid density (2.61 $mmolg^{-1}$) than the TiO_2-SiO_2 (3.11 $mmolg^{-1}$) proved to be more efficient, achieving a 59.0% HMF selectivity and a 53.0 mol% overall yield. The higher catalyst activity of solid catalysts with lower acid densities has also been demonstrated in previous studies (Yang *et al.* 2011; Zhao *et al.* 2011). Furthermore, the introduction of P to TiO_2-SiO_2 provided a lower B/L ratio and more strong and medium acid sites than non-phosphated TiO_2-SiO_2. The obtained results demonstrated that a higher ratio of B/L acid sites decreased HMF selectivity (from 59.0% to 43.5%) (Corma 1995; Li *et al.* 2016). Therefore, a suitable B/L ratio was the primary effect on the synthesis of HMF. Thus, the phosphated TiO_2-SiO_2 catalyst was used as the desired catalyst in the following sections.

Table 2. Catalytic Behaviors of Glucose Conversion to HMF

Entry	Catalyst	Solvent	Conversion (%)	HMF Yield (mol%)	LA Yield (mol%)	HMF Selectivity (%)
1	P-TiO_2-SiO_2	H_2O	67.0	18.5	2.5	27.8
2	P-TiO_2-SiO_2	THF/H_2O (4/1)	95.0	33.0	1.0	35.0
3	TiO_2-SiO_2	THF/H_2O-NaCl (4/1)	92.0	40.0	5.0	43.5
4	P-TiO_2-SiO_2	THF/H_2O-NaCl (4/1)	90.0	53.0	0.5	59.0

Reaction conditions: glucose (0.1 g), P-TiO_2-SiO_2 (10 mg, 10 wt%), NaCl (0.2 g), solvent (5 mL), 170 °C, 60 min

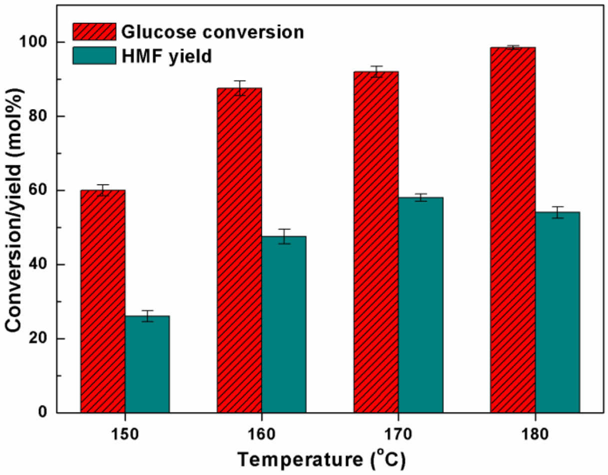

Fig. 4. Effect of temperature on glucose conversion and HMF yield; reaction conditions: glucose 0.1 g, NaCl 0.2 g, THF/H_2O = 4/1; catalyst 10 mg (10 wt%), 90 min

Effect of Process Parameters on Glucose Transformation

Effects of various process parameters on glucose transformation to HMF were systematically investigated (Fig. 4, 5, and 6) to obtain the optimum conditions. At relatively low reaction temperatures (150 °C), the HMF yield was 24.5 mol% and the glucose conversion was 60.0% (Fig. 4).

As the reaction temperature increased from 150 °C to 170 °C, the catalytic activity of the P-TiO_2-SiO_2 catalyst improved rapidly. Namely, both the HMF yield and the glucose conversion increased with the temperature increase from 150 °C to 170 °C. A high HMF yield of 59.5 mol% was achieved at 170 °C.

When the temperature was increased to 180 °C, the HMF yield decreased, which indicated that that high reaction temperature caused further conversion of HMF to undesired substrates (Atanda *et al*. 2015).

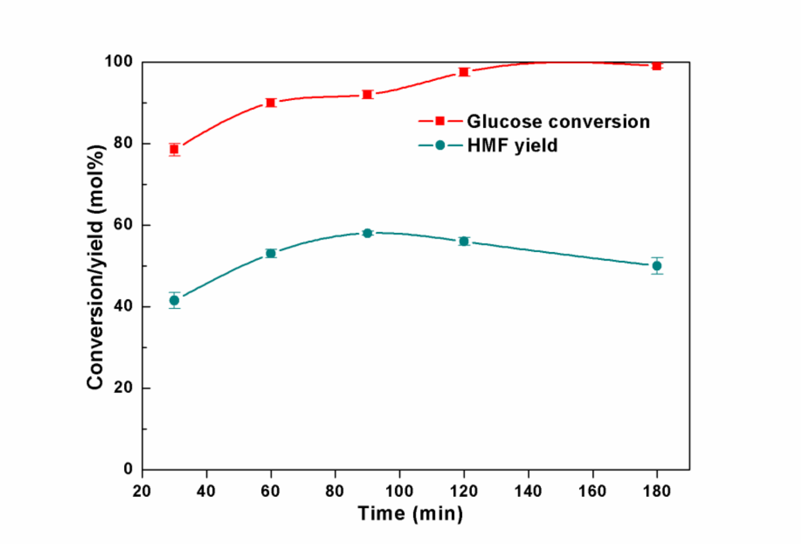

Fig. 5. The effect of time on glucose conversion and HMF yield; reaction conditions: glucose 0.1 g, NaCl 0.2 g, THF/H_2O = 4/1; catalyst 10 mg (10 wt%), 170 °C

The effect of reaction time on glucose transformation to HMF is shown in Fig. 5. The conversion reaction occurred rapidly in the 90 min to synthesize HMF; the HMF yield increased with the reaction time as it approached 90 min. The highest HMF yield was achieved at 90 min. After a reaction time of 90 min, the obtained HMF yield slightly decreased, which was possibly attributed to the HMF of THF organic phase trending to saturation (Pande *et al.* 2018). The newly formed HMF may be transformed to undesired products.

The effect of catalyst amount on the HMF yield was investigated and the results are shown in Fig. 6. The loading of the catalyst was changed from 5 wt% to 40 wt% based on the glucose mass. It can be seen that the HMF yield increased with the increase in catalyst amount from 5 wt% to 20 wt%. The HMF yield appeared to slightly decrease after a catalyst loading of 20 wt%. Hence, the maximum HMF yield of 63.0 mol% was achieved at 20 wt% of P-TiO_2-SiO_2.

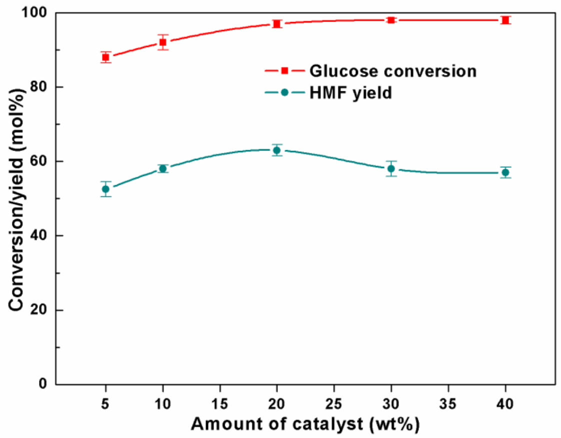

Fig. 6. Effect of amount of catalyst on glucose conversion and HMF yield; reaction conditions: glucose 0.1 g, NaCl 0.2 g, THF/H_2O = 4/1; 170 °C 90 min

Table 3. Effect of Cellulose Depolymerization on HMF Production

Feeds	Conversion %	Glucose Yield (mol%)	HMF Yield (mol%)
MCC	40.5	3.5	28.5
Ball-Milling MCC	54.0	1.5	36.5
Mechanocatalytic Pretreated MCC	93.5	2.5	56.0

Reaction conditions: cellulose (100 mg), P-TiO_2-SiO_2 (20 mg), THF/H_2O-NaCl (4 mL/1 mL, 0.2 g NaCl), 180 °C, 2 h

Conversion of Cellulose to HMF

The high-performance of the P-TiO_2-SiO_2 catalysts for glucose transformation to HMF was reason to utilize cellulose with high recalcitrance. The conversion of cellulose, an inexpensive and abundant component of lignocellulose, was examined, and the obtained results are shown in Table 3. Because cellulose has poor solubility in aqueous and commonly used organic solvents due to its inherent crystalline structure and high degree of polymerization (DP), cellulose conversion using solid acid catalysts has been a great challenge (Atanda *et al.* 2016). As is shown in Table 4, a low cellulose conversion of 40.5% and HMF yield of 28.5 mol% were achieved in conversion of MCC without pretreatment. To overcome the insolubility, pretreatment technologies were used that increased the accessibility and reactivity of cellulose to the solid acid catalysts (Zhang and Jerome 2013). When the MCC was ball-milled prior to conversion, the cellulose conversion increased from 40.5% to 54.0%. This result indicated that MCC was partially de-crystallized to its amorphous component and, thus, contained fewer hydrogen bonds (Shikinaka *et al.* 2016). As a result, the MCC became sparingly soluble in aqueous solutions after being ball-milled and, thereby, increased the contact area between the substrate and solid acid catalyst. Nonetheless, the solubility of milled, pretreated MCC in the aqueous solution was sparing, and single milling was unsatisfactory for achieving superb cellulose reactivity—the yield of HMF was less than 40 mol%. By acidulating cellulose before ball-milling (mechanocatalytic depolymerized MCC) and then reacting the resultant substrate, an HMF yield of 56.0 mol% was achieved when the cellulose conversion was 93.5%. This obtained result indicated that a nearly complete dissolution of MCC in the NaCl solutions was achieved due to effective de-crystallization and depolymerization to oligomers.

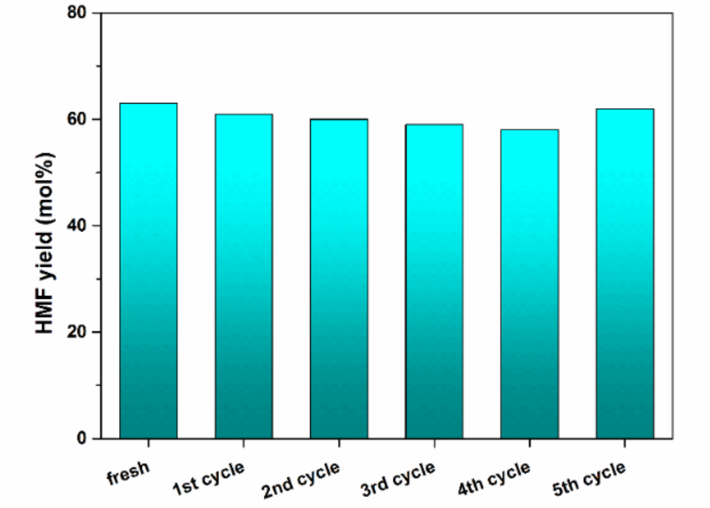

Fig. 7. Shown above is the reusability study of phosphated TiO_2-SiO_2 catalysts. Reaction conditions: glucose (0.1 g), catalyst (20 mg, 20 wt%), NaCl (0.2 g), solvent (5 mL), 170 °C, 90 min; the P-TiO_2-SiO_2 was treated under the calcination treatment (500 °C, 3 h) before the fifth cycle

Recycling Experiments of Catalyst

The catalytic activity of P-TiO_2-SiO_2 was further examined through the recycling experiment (Fig. 7). After the first reaction, the used P-TiO_2-SiO_2 was filtered, washed with anhydrous acetone, and then oven-dried. The yield of HMF declined from 63.0 mol% to 58.0 mol% by the fourth cycle. However, the catalyst was then treated under calcination (500 °C, 3 h) and reused. The catalytic activity of the catalyst was regained, resulting in a new HMF yield of 62.0 mol%.

CONCLUSIONS

1. A mesoporous P-TiO_2-SiO_2 catalyst was facilely prepared *via* a sol-gel method.
2. The mesoporous P-TiO_2-SiO_2 was an excellent solid acid catalyst for the transformation of glucose to HMF. A remarkable HMF yield of 63.0 mol% was achieved from glucose at 170 °C for 90 min in the THF/H_2O-NaCl system.
3. The P-TiO_2-SiO_2 catalyst showed the best catalytic reactivity of cellulose conversion, with a notable HMF yield of 56.0 mol%.
4. The phosphated TiO_2-SiO_2 catalyst is favorable for HMF production due to its moderate acid sites and suitable B/L ratio. Overall, the P-TiO_2-SiO_2 catalyst is a promising catalyst for the conversion of glucose and oligomers to HMF in industry applications.

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