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Selective glucose transformation by titania as a heterogeneous Lewis acid catalyst

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ABSTRACT

The Lewis acidity of phosphate-immobilized anatase TiO_2 (phosphate/TiO_2) 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_2 surface function even in water. phosphate/TiO_2 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_2 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.

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 $CrCl_2$, 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 $AlCl_3$, BF_3, 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^{4+}-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_4 tetrahedra present in insoluble niobic acid ($Nb_2O_5{\cdot}nH_2O$) act as Lewis acids even in water [10]. Many metal oxides of groups 4 and 5, including niobic acid, are composed of octahedral MO_6 (M: metal) units with saturated coordination spheres, and polyhedral MO_x with unsaturated coordination spheres, such as tetrahedral MO_4, are also present on

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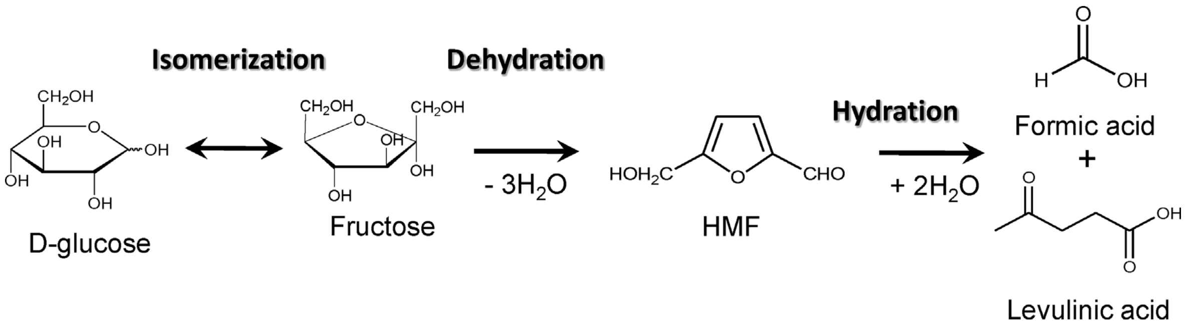

Scheme 1. Reaction pathway for acid-catalysed conversion of glucose into HMF in water.

the surface. Unsaturated coordination MO_4 tetrahedra act as Lewis acids; however, MO_4 species are considered to not function as well in water as other Lewis acids. Niobic acid with NbO_4 species as water-tolerant Lewis acid sites suggests that anatase TiO_2, a ubiquitous material, with 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 TiO_2 as a heterogeneous water-tolerant Lewis acid was investigated in this study.

2. Experimental

2.1. Preparation of anatase TiO_2 and phosphate/TiO_2

Anatase TiO_2 was synthesized by the addition of 20 mL Ti(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 Ti-$OCH(CH_3)_2$ 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 TiO_2 catalyst.

Phosphate/TiO_2 was prepared by immobilizing H_3PO_4 on anatase TiO_2. 5 g of TiO_2 was stirred in 200 mL of 1 M H_3PO_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/TiO_2 catalyst.

2.2. FT-IR measurement and estimation of the amounts of Lewis acid sites for anatase TiO_2 and phosphate/TiO_2

Lewis acid densities on anatase TiO_2 and phosphate/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 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 cm^{-1} (pyridine coordinatively bonded to Lewis acid sites, molecular absorption coefficient: 4.86 $\mu mol\,cm^{-1}$) 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 H_2O vapor (20–25 Torr) at room temperature for 60 min. 4.2 layers of H_2O molecules were adsorbed on the TiO_2 and phosphate/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 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® HPH-87H column (300 mm × 7.8 mm, Bio-Rad Laboratories) with diluted H_2SO_4 solution (5 mM) of eluent, 0.5 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 TiO_2 and phosphate/TiO_2

Structural information for the anatase TiO_2 and phosphate/TiO_2 catalysts was obtained by XRD and N_2 adsorption analyses. Fig. 1 shows XRD patterns and (B) N_2 adsorption–desorption isotherms for (a) anatase TiO_2 and (b) phosphate/TiO_2. Diffraction peaks due to anatase TiO_2 are evident in the XRD patterns for anatase TiO_2 and phosphate/TiO_2, which indicates that both samples are mainly composed of anatase TiO_2. There was no significant difference in the XRD patterns of anatase TiO_2 and phosphate/TiO_2; therefore, phosphoric acid modification of anatase TiO_2 does not change the original anatase TiO_2 structure. 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 TiO_2 and phosphate/TiO_2 were estimated to be 252 $m^2\,g^{-1}$ and 0.31 $mL\,g^{-1}$, and 266 $m^2\,g^{-1}$ and 0.25 $mL\,g^{-1}$, respectively. SEM images revealed that the prepared TiO_2 sample is composed of 10–20 nm TiO_2 particles. There was no significant difference in the morphology of TiO_2 and phosphate/TiO_2. The amount of immobilized phosphate on anatase 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 TiO_2 by ester formation between phosphoric acid and neutral OH groups.

3.2. Lewis acid sites on anatase TiO_2

Difference Fourier transform infrared (FT-IR) spectra for pyridine adsorption on dehydrated anatase TiO_2 and phosphate/TiO_2 are shown in Fig. 2, where pyridine is employed as a basic probe molecule for characterization of the acid sites [11]. Dehydrated TiO_2 exhibits several bands (Fig. 2(A)), but there is no signal for pyridinium ions formed on Brønsted acid sites (1540 cm^{-1}), because TiO_2 has no Brønsted acid sites. The intensities of the two bands at 1445 and 1440 cm^{-1}, which are assigned to adsorbed pyridine on Lewis acid sites (TiO_4) and physisorbed pyridine [12], respectively, increase with the amount of introduced

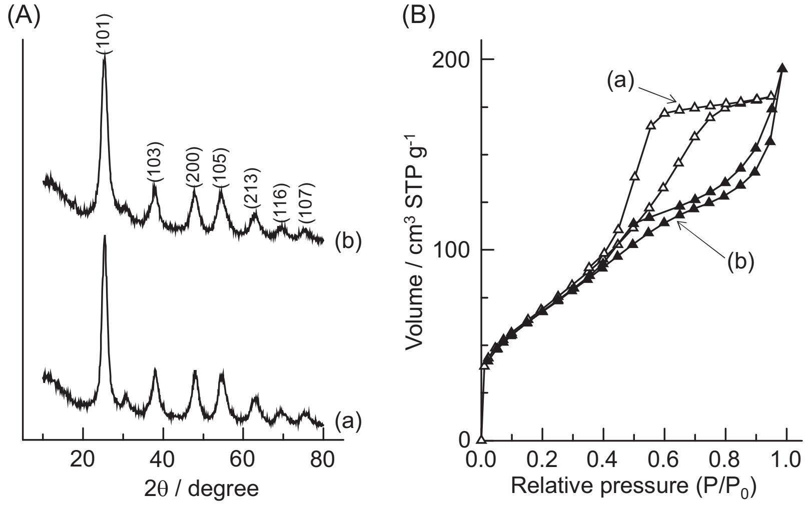

Fig. 1. (A) XRD patterns and (B) N_2 adsorption–desorption isotherms for (a) anatase TiO_2 and (b) phosphate/TiO_2.

pyridine, and the band intensities due to acid sites reach plateaus at $P_{\text{pyridine}} > 2.8 \times 10^{-2}$ kPa. Fig. 2B shows difference FT-IR spectra for pyridine-adsorbed anatase TiO_2 and phosphate/TiO_2. The samples were treated with saturated pyridine vapor and subsequently evacuated at room temperature for 60 min to remove physisorbed pyridine. Evacuation of the samples results in no change of the band for pyridine adsorbed on Lewis acid sites, whereas the signal for physisorbed pyridine is eliminated. Thus, the maximum intensity of the band at 1445 cm^{-1} corresponds to the total amount of Lewis acid sites with adsorbed pyridine. The amounts of Lewis acid sites on the dehydrated TiO_2 and phosphate/TiO_2 samples were estimated to be 0.25and 0.23 mmol g^{-1}, respectively, from the maximum band intensities and molecular absorption coefficients at 1445 cm^{-1}. Fig. 3(A) and (B) shows FT-IR spectra for pyridine-adsorbed TiO_2 and phosphate/TiO_2, respectively, in the presence of saturated water vapor. Large amounts of physisorbed H_2O molecules are presented on the TiO_2 and phosphate/TiO_2 surface prior to pyridine introduction under the experimental conditions; therefore, two large and diffuse bands due to water are observed at 2500–3700 and 1500–1700 cm^{-1} in Fig. 3(A)(a) and (B)(d). Even in the case of such water-saturated samples, the band due to pyridine adsorbed on Lewis acid sites (1445 cm^{-1}) appears in Fig. 3(A)(b) and 3(B)(e), in addition to pysisorbed pyridine (1440 cm^{-1}). Although the band for pysisorbed pyridine disappears after evacuation of the samples at room temperature, the signal for Lewis acid sites remains unchanged. The effective Lewis acid densities of TiO_2 and phosphate/TiO_2 in the presence of saturated water vapor (water-tolerant Lewis acid density) were 0.24 and 0.22 mmol g^{-1}, respectively. This implies that most unsaturated coordination TiO_4 tetrahedra still act as Lewis acid sites, even in water, because water does not deactivate these Lewis acid sites, and all unsaturated coordination TiO_4 tetrahedra still act as Lewis acid sites even in water and the Lewis acid sites are not covered with phosphate ions on phosphate/TiO_2.

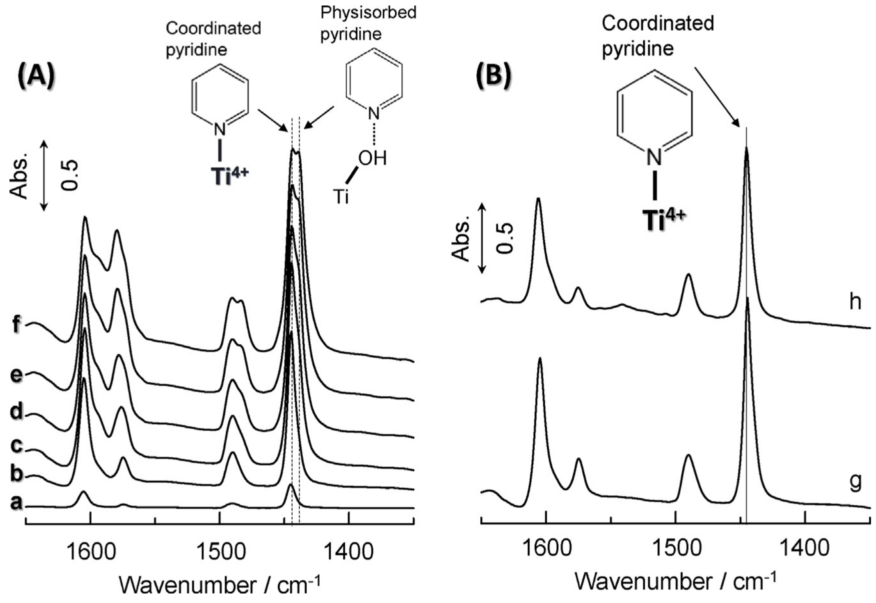

Fig. 2. FT-IR spectra for pyridine-adsorbed dehydrated TiO_2 and phosphate/TiO_2 at 298 K. (A) Difference FT-IR spectra for dehydrated TiO_2. Prior to pyridine adsorption, the TiO_2 sample was heated at 473 K for 1 h under vacuum to remove physisorbed H_2O. Gas phase pyridine pressure: (a) 1.4×10^{-2}; (b) 6.7×10^{-2}; (c) 1.3×10^{-1}; (d) 2.8×10^{-2}; (e) 6.7×10^{-1}; (f) 1.4 kPa. (B) Difference FT-IR spectra for pyridine-adsorbed (g) TiO_2 and (h) phosphate/TiO_2. Prior to pyridine adsorption, the samples were heated at 473 K for 1 h under vacuum to remove physisorbed H_2O. After pyridine adsorption, the samples were evacuated at 298 K for 60 min.

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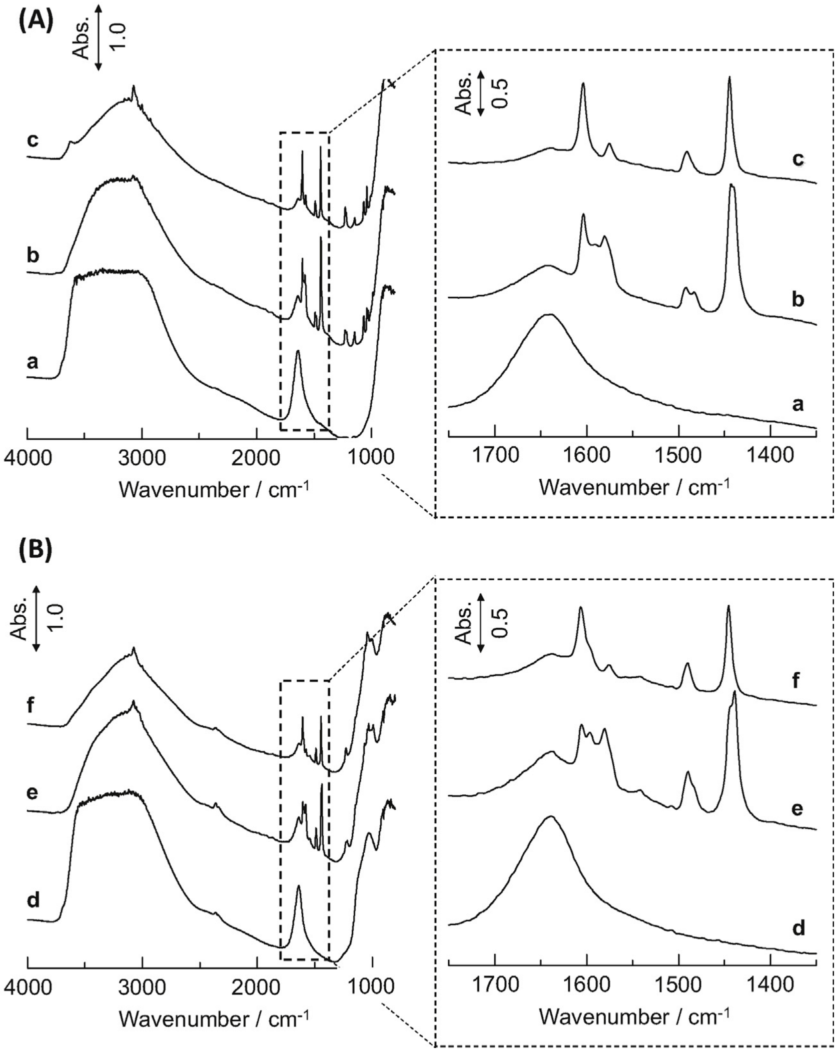

Fig. 3. Difference FT-IR spectra for (A) TiO_2 (B) phosphate/TiO_2 in the presence of saturated H_2O vapor. (a) Hydrated TiO_2 in saturated H_2O vapor, (b) TiO_2 obtained by the introduction of pyridine (2.7 kPa) after H_2O adsorption under H_2O vapor, (c) TiO_2 sample obtained by evacuation (room temperature) for 60 min after (b), (d) a hydrated phosphate/TiO_2 in saturated H_2O vapor, (e) phosphate/TiO_2 obtained by the introduction of pyridine (2.5 kPa) after H_2O adsorption under H_2O vapor, (f) phosphate/TiO_2 obtained by evacuation (room temperature) for 60 min after (e).

3.3. *Catalytic studies*

The catalysis of anatase TiO_2 was evaluated through the conversion of glucose into HMF in water. Table 1 summarizes results for the conversion of glucose into HMF in an aqueous solution of tetrahydrofuran (THF) at 393 K. The efficiency for HMF production from glucose has been reported to be improved by using THF aqueous solution as a solvent [9]. Homogeneous (HCl and H_3PO_4) and heterogeneous Brønsted acids (SO_3H-bearing resins: Nafion®NR50 and Amberlyst-15) that were also tested exhibit moderate glucose conversion and HMF yield. Brønsted acids are not effective for the conversion of glucose into HMF at such low reaction temperatures [13], and the HMF produced is decomposed by hydration in water without extraction by appropriate organic solvents [13–15]. Although rare earth metal triflate complexes ($Sc(OTf)_3$ and $Yb(OTf)_3$) exhibit high glucose conversion, most of the reacted glucose is converted into unknown species. This can be attributed to the formation of polymerized species [10,15,16]. Complex intermolecular side reactions, such as aldol condensation, among reducing saccharides with formyl groups (—CHO) in the presence of acid catalysts result in the formation of complex polymers as unknown species that cannot be detected by HPLC and gas chromatography–mass spectrometry (GC–MS) [10]. Anatase TiO_2 also converts most of the glucose into complex by-products, including polymerized species, as with rare earth metal triflate complex catalysts. In contrast to bare TiO_2, TiO_2 modified with H_3PO_4 (phosphate/TiO_2), where —OH groups on TiO_2 are esterified into —O-PO$(OH)_2$ by phosphoric acid, exhibits significant catalytic performance for HMF production; the HMF yield exceeded 80% within 2 h. There is large difference between levulinic acid and formic acid yield on phosphate/TiO_2. One possible explanation is adsorption of the evolved levulinic acid on phosphate/TiO_2 [17]. After reaction for 2 h at 393 K, the phosphate/TiO_2 particles could be readily separated from the solution by decantation and the recovery of the catalyst exceeded 99%. The results for reuse experiments of this catalyst are presented in Fig. 4. The recovered catalyst was repeatedly evaluated for HMF production from glucose for 2 h at 393 K. No decrease in activity was observed, even after 4 reuses of the catalyst sample and the total turnover number reached ca. 40. It was also confirmed that the phosphate ions are not desorbed from the sample during reaction. Therefore, phosphate/TiO_2 functions as a stable and highly selective heterogeneous catalyst for simple HMF production from glucose. Fig. 5 shows the time courses for the conversion of glucose into HMF on phosphate/TiO_2.

Table 1
Catalytic activity for HMF production from glucose over acid catalysts.[a]

Catalyst	Acid density (mmol g^{-1})[b]		Conv. (%)[d]	Product yield (%)[e]				
	BAS	LAS		Fru	HMF	FA	LA	Unknown
HCl	9.9	0.0	56.2	0.0	29.4	0.0	0.0	26.9
H_3PO_4	10.2	–	9.2	0.0	1.2	0.0	0.0	8.0
Amberlyst-15	4.8	–	69.9	2.0	12.0	0.0	24.9	31.0
Nafion NR50	0.9	–	28.7	0.0	3.1	0.0	0.0	25.6
$Sc(OTf)_3$	–	2.0	>99.9	1.5	13.9	0.0	0.0	84.6
$Yb(OTf)_3$	–	1.9	89.4	0.0	10.6	0.0	0.0	78.8
TiO_2	–	0.24[c]	>99.9	0.0	8.5	0.0	0.0	91.5
phosphate/TiO_2	–	0.22[c]	98	0.0	81.2	10.5	0.0	8.3

[a] Reagents and conditions: distilled water, 0.2 mL; THF, 1.8 mL; D-glucose, 0.02 g (0.11 mmol); catalyst weight, 0.05 g; temperature, 393 K; time, 2 h.
[b] BAS, Brønsted acid sites; LAS, Lewis acid sites.
[c] Water tolerant acid sites.
[d] Glucose conversion for 2 h.
[e] Fru, fructose; FA, formic acid; LA, levulinic acid; unknown, undetectable species.

Although a small amount of fructose is observed at the initial stage of the reaction (15–30 min), beyond 30 min, fructose cannot be detected. This suggests that produced fructose is immediately consumed for the subsequent reaction and glucose is converted into HMF through isomerization, followed by dehydration even on phosphate/TiO_2 as the proposed reaction mechanism shown in Scheme 1. Phosphoric acid itself cannot work as an effective catalyst for the conversion of glucose as shown in Scheme 1: phosphoric acid has much smaller glucose conversion and HMF yield than that bare TiO_2 and phosphate/TiO_2. Therefore, highly efficient HMF production on phosphate/TiO_2 may be due to catalysis of TiO_2 Lewis acid sites that interact with reactants even in water. In order to compare the rate of HMF formation from glucose and fructose over phosphate/TiO_2, HMF production from fructose was carried out under same reaction condition. THF/aqueous solution (2.0 mL (THF, 1.8 mL; distilled water, 0.2 mL)) containing D-fructose (0.02 g) and catalyst (0.05 g) was heated in a sealed Pyrex tube at 393 K for 30 min. Rate of HMF formation from fructose was estimated to be 0.026 mmol g^{-1} min^{-1} which is slightly larger than that from glucose (0.017 mmol g^{-1} min^{-1}). This result also supports that glucose is converted into HMF via fructose. Large-scale experiment was also performed to clarify the recovery of the catalyst. THF/aqueous solution (2.0 mL (THF, 1.8 mL; distilled water, 0.2 mL)) containing D-glucose (0.2 g) and catalyst (0.5 g) was heated in a sealed Pyrex tube at 393 K for 30 min. There was no difference in glucose conversion and HMF yield between small and large-scale experiment, and more than 99% of catalyst was successfully recovered by simple decantation and filtration.

It should be noted that only water-tolerant Lewis acids on phosphate/TiO_2 efficiently catalyze the conversion of glucose into HMF. $Sc(OTf)_3$ catalyzes various reactions as an excellent water-tolerant Lewis acid. However, only a small part of the reacted glucose is converted into HMF on the catalyst. Therefore, Lewis acid catalysis on this complex promotes intermolecular side reactions, including aldol condensation among reducing saccharides, in preference to the isomerization of glucose to fructose and the intramolecular dehydration of fructose. Bare anatase TiO_2 also results in significant glucose conversion and low HMF selectivity similar to $Sc(OTf)_3$. As a result, highly efficient HMF production on phosphate/TiO_2 cannot be solely explained by only Lewis acid sites workable in aqueous solution. Phosphoric acid modification on anatase TiO_2 causes a significant improvement in HMF production by decreasing side reactions, and the Lewis acid sites are not covered with phosphate ions, as the IR experimental results indicated. This suggests a synergistic effect between Lewis acid sites

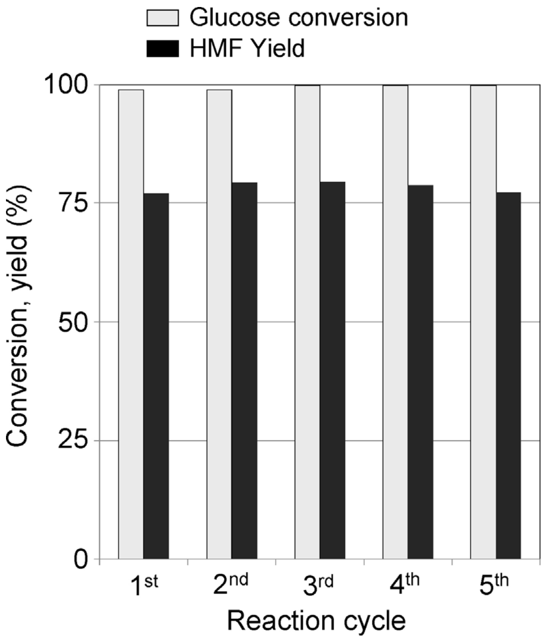

Fig. 4. Catalytic activity of reused phosphate/TiO_2 for HMF production from D-glucose. Reagents and conditions: catalyst, 0.05 g; water: 0.2 mL; THF, 1.8 mL; D-glucose: 0.02 g; temperature, 393 K.

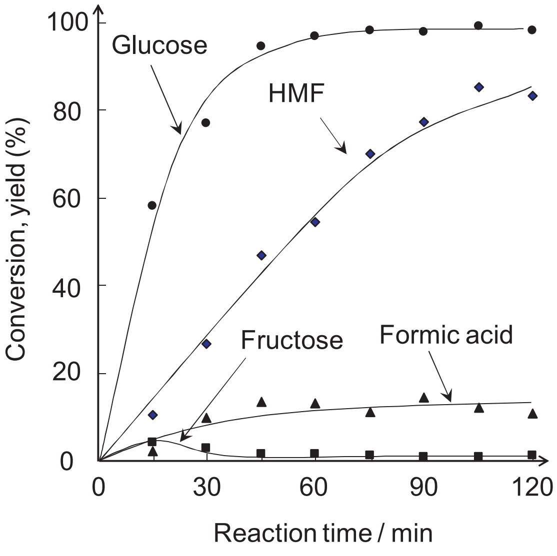

Fig. 5. Time courses for the conversion of glucose into HMF on phosphate/TiO_2. Reagents and conditions: catalyst, 0.05 g; water: 0.2 mL; THF, 1.8 mL; D-glucose: 0.02 g; temperature, 393 K.

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and phosphate ions essentially changes the acid catalysis on TiO_2. The details are currently under investigation.

4. Conclusion

In summary, anatase TiO_2, an abundant and inexpensive material, has water-tolerant Lewis acid sites. Bare anatase TiO_2 cannot function as an efficient heterogeneous catalyst for selective transformation of glucose into HMF, requiring selective isomerization of glucose into fructose and intramolecular dehydration of fructose, because of intermolecular side reactions. On the other hand, TiO_2 modified with H_3PO_4 (phosphate/TiO_2), where —OH groups on TiO_2 are esterified into —O-PO$(OH)_2$ by phosphoric acid, exhibits high HMF yield (ca. 80%) in THF–water mixture (THF/H_2O = 90/10). Such high HMF yield can be achieved under diluted glucose solution (ca. 1 wt%) and high catalyst/glucose ratio (50/20 wt%). No decrease in original activity for subsequent reactions demonstrated that phosphate/TiO_2 can function as a stable and reusable heterogeneous catalyst for HMF production.

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[17] We performed adsorption experiment of levulinic acid on phosphate/TiO_2. THF/aqueous solution (2.0 mL (THF, 1.8 mL; distilled water, 0.2 mL)) containing levulinic acid (0.11 mmol) and catalyst (0.05 g) was stirred at 393 K for 30 min. The amount of adsorbed levulinic acid was estimated to be ca. 0.10 mmol g^{-1} which corresponds to ca. 5% yield.

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