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ARTICLE

Photoassist-phosphorylated TiO_2 as a catalyst for direct formation of 5-(hydroxymethyl)furfural from glucose

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Photo-assisted phosphorylation of anatase TiO_2 catalyst was examined to improve its catalytic performance for the direct production of 5-(hydroxymethyl)furfural (HMF), a versatile chemical platform, from glucose. In phosphorylation based on simple esterification between phosphoric acid and surface OH groups on anatase TiO_2 with water-tolerant Lewis acid sites, the density of phosphates immobilized on TiO_2 is limited to 2 phosphates nm^{-2}, which limits selective HMF production. Phosphorylation of the TiO_2 surface under fluorescent light irradiation increases the surface phosphate density to 50%, which is higher than the conventional limit, thus preventing the adsorption of hydrophilic glucose molecules on TiO_2 and resulting in more selective HMF production over photoassist-phosphorylated TiO_2.

1. Introduction

Biomass conversion has been extensively investigated to provide a renewable feedstock for the production of useful chemicals and fuels. 5-(hydroxymethyl)furfural (HMF) is an attractive intermediate for such a biomass-derived chemical platform because it can be further converted into various polymers, such as polyesters, polyamides and polyurethanes.[1–3] HMF is currently produced by the acid-catalyzed dehydration of fructose obtained by the enzymatic isomerization of glucose,[4] whereas the direct production of HMF from glucose would provide larger amounts of this versatile intermediate with much lower energy consumption. However, direct HMF production from glucose has not yet been commercialized, because there is no practical process to selectively produce HMF from concentrated glucose solutions with low energy consumption.

Zhao et al. first demonstrated an HMF yield of 70% in an ionic liquid system using a $CrCl_2$ catalyst, homogeneous Lewis acid catalyst, where isomerization of glucose into fructose and subsequent dehydration of fructose into HMF proceed in the system.[5] Davis et al. also succeeded in direct HMF production from glucose in a biphasic reaction system composed of a water-insoluble organic extraction phase and an aqueous phase with Sn-incorporated beta zeolite and HCl, a homogeneous Brønsted acid.[6,7] Sn-incorporated beta zeolite as a Lewis acid catalyst isomerizes glucose, and the resulting fructose is dehydrated into HMF by HCl.[7] We have reported that MO_x unsaturated coordination spheres, Lewis acid sites, on group 4 and 5 oxides such as Nb_2O_5 and TiO_2 are workable even in water, and the immobilization of phosphate species on Nb_2O_5 and TiO_2 largely improves selective HMF production from glucose.[8,9] In particular, phosphate-immobilized TiO_2 (P-TiO_2) acts as a highly efficient heterogeneous catalyst for HMF formation in biphasic reaction systems.[10,11] Dutta et al. reported that porous titanium and tin phosphates exhibit high catalytic performance for HMF production from glucose and fructose, due to the enhancement of surface acidity by surface phosphorylation.[12,13] On the other hand, there is no significant difference in acidity and acid site density between bare TiO_2 and P-TiO_2: the catalysis of P-TiO_2 cannot be simply explained by acidity and acid site density.[9,11] Through a detailed experiment using deuterated glucose molecules, we have determined that glucose is not converted into HMF on the catalyst by isomerization and subsequent dehydration but only by dehydration through 3-deoxyglucosone, a highly reactive intermediate.[11] While an increase in surface immobilized phosphate species (Ti-O-PO$(OH)_2$) that are formed by esterification between phosphoric acid and surface terminal OH groups on TiO_2 improves the HMF selectivity, the role of the phosphate species has not been clarified. In addition, the density of surface OH groups on TiO_2 is limited, so that the amount of phosphate species immobilized on TiO_2 through esterification is also restricted, which limits further improvement of the HMF selectivity for the catalyst. Here, we report the photo-assisted phosphorylation of anatase TiO_2 to prepare a catalyst for efficient HMF production. TiO_2 is known to exhibit super-hydrophilicity during and after UV light irradiation due to excess formation of surface OH groups under light irradiation.[14,15] The esterification of phosphoric acid and OH groups on such TiO_2 would increase the density of surface phosphate species, thereby enhancing the catalytic performance.

2. Methods

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2.1. Preparation of Catalyst

Anatase TiO_2 was prepared by a simple sol-gel reaction of titanium tetraisopropoxide ($Ti(O\text{-}i\text{-}Pr)_4$). A mixture of $Ti(O\text{-}i\text{-}Pr)_4$ (40 g; Kanto Chemicals) and distilled water (160 mL) was stirred at 313 K for 6 h. The filtrated precursor was repeatedly washed with distilled water and then was dispersed in distilled water (500 mL). After the dispersion was heated at 373 K for 6 h, the resulting solid material was filtrated and dried at 353 K for use of anatase TiO_2 catalyst. Phosphate species were immobilized on TiO_2 simply by immersing 2 g of TiO_2 in 100 mL of 1 M H_3PO_4 solution for 2–7 days at 303 K. The collected white powders were washed with distilled water and were dried at 353 K overnight. The resulting material, denoted as P-TiO_2 was used for HMF production from glucose. Phosphate-immobilization on TiO_2 was also performed by immersing TiO_2 in H_3PO_4 solution in a similar manner as above, except under 100 W fluorescent light irradiation. The phosphate-immobilized TiO_2 prepared under fluorescent light irradiation was used as P-TiO_2-L.

2.2. Characterization

X-ray photoelectron spectroscopy (XPS; Shimadzu ESCA-3400) analysis was performed using Mg K*α* radiation (10 kV, 25 mA). The binding energy was corrected with Au $4f_{7/2}$ of Au-deposited samples. Powder X-ray diffraction (XRD; Rigaku Ultima IV) pattern was obtained using Cu K*a* radiation (40 kV, 40 mA). Nitrogen adsorption–desorption isotherms were measured at 77 K with a surface-area analyzer (Quantachrome Nova-4200e). The samples were heated at 423 K for 1 h under vacuum to remove physisorbed water before measurement. The Brunauer-Emmett-Teller (BET) surface areas were estimated over the relative pressure (P/P_0) range of 0.05–0.30. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses were performed with a Shimadzu ICPS-8100 spectrometer. The morphology of the samples was examined by using scanning electron microscopy (SEM; S-5500, Hitachi). Lewis acid densities of catalysts were estimated from the Fourier transform-infrared (FT-IR) spectroscopy measurement of pyridine-adsorbed samples. The sample was pressed into a self-supporting disk (20 mm diameter, ca. 20 mg) and was placed in an IR cell attached to a closed glass-circulation system. The sample was heated at 423 K for 1h under vacuum for removing physically adsorbed water and then was exposed to pyridine vapor at room temperature. After the pyridine-adsorbed sample was evacuated under vacuum to remove physisorbed pyridine, the intensity of the IR band at 1445 cm^{-1} (absorption coefficient =4.86 μmol cm^{-1}), due to pyridine bonded to TiO_2 Lewis acid sites, was measured. The band intensity increased with increasing the amount of introduced pyridine, reaching a plateau. The density of Lewis acid sites was obtained from the band intensity at the plateau. NH_3 temperature-programmed-desorption (NH_3-TPD) was examined for TiO_2 samples before and after phosphorylation by using a flow system equipped with a mass spectrometer (BEL Japan, BELCAT-A). The TiO_2 samples were heated at 423 K for 1 h under He flow to remove adsorbed H_2O, and then NH_3 gas (5% NH_3/He, 30 mL min^{-1}) was flowed through the dehydrated samples (150 mg) at 373 K. After 0.5 h, the samples were heated at 10 K min^{-1} from 373 to 1273 K under a He flow (30 mL min^{-1}). Desorbed species were detected by the mass spectrometer.

2.3. Catalytic Reaction

0.125 or 0.25 g of each prepared catalyst was examined through HMF production from glucose in a biphasic reaction system consisting of 3 mL of 2-*sec*-Butylphenol (SBP; Kanto Chemicals) and an aqueous glucose solution (distilled water; 1 mL, ᴅ-glucose (Sigma-Aldrich); 0.01–0.2 g). The biphasic mixture was heated in a sealed Pyrex tube. After reaction, the solution was analyzed using high performance liquid chromatography (HPLC; Jasco LC-2000 plus) with an Aminex HPH-87H column and gas chromatography (GC; Shimadzu GC-17 A) with an InertCap 17 capillary column.

3. Results and discussion

3.1. Catalytic activities of P-TiO_2 and P-TiO_2-L

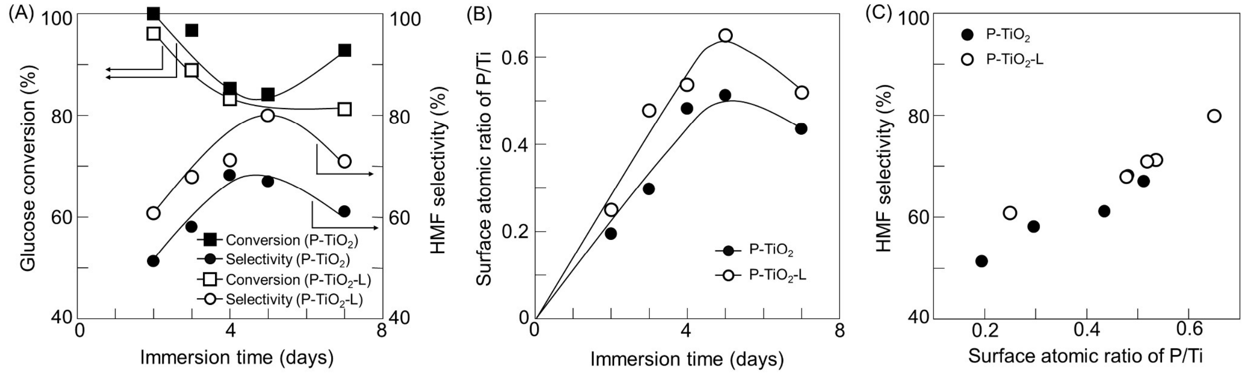

Fig. 1 (A) Glucose conversion and HMF selectivity in P-TiO_2 and P-TiO_2-L, (B) Correlation of the surface atomic ratio of P to Ti (P/Ti) on P-TiO_2 and P-TiO_2-L, (C) HMF selectivity and P/Ti ratio. Reaction conditions: catalyst, 0.25 g; distilled water, 1 mL; 2-*sec*-butylphenol, 3 mL; glucose, 0.1 g; 408 K, 4 h.

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Table 1 Catalytic activities of P-TiO_2 and P-TiO_2-L for HMF production from glucose

Immersion time (days)	P/Ti	Conversion (%)	HMF selectivity (%)
0	-	> 99	16
2 (dark)	0.19	> 99	51
3 (dark)	0.30	97	58
4 (dark)	0.48	85	68
5 (dark)	0.51	84	67
7 (dark)	0.43	93	61
2 (light irradiation)	0.25	96	61
3 (light irradiation)	0.48	89	68
4 (light irradiation)	0.54	83	71
5 (light irradiation)	0.65	84	80
7 (light irradiation)	0.52	81	71

Reaction conditions: catalyst, 0.25 g; distilled water, 1 mL; 2-*sec*-Butylphenol, 3 mL; glucose, 0.1 g; 408 K; 4 h.

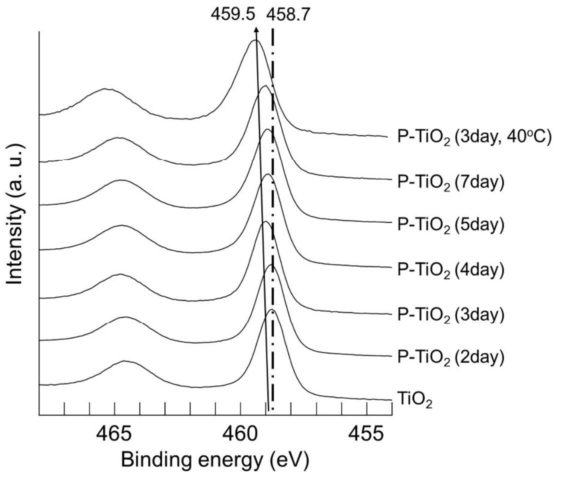

Fig. 2 The XPS spectra of the Ti 2p from the surface of P-TiO_2 catalysts prepared by various conditions.

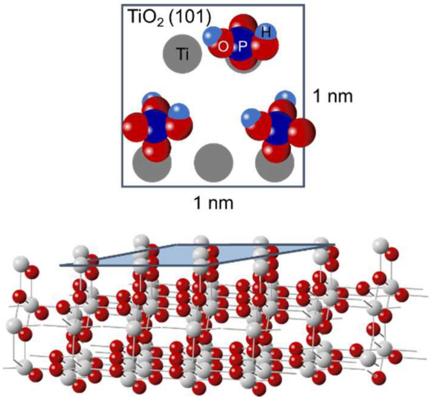

Fig. 3 Schematic view of immobilized phosphate on P-TiO_2-L (P/Ti = 0.65).

Fig. 1A shows the catalytic activities (408 K, 4 h) of phosphate-immobilized TiO_2 prepared with (P-TiO_2-L) and without (P-TiO_2) fluorescent light irradiation for HMF production. TiO_2 (anatase) was prepared by a simple sol-gel reaction of titanium tetraisopropoxide (Ti(O-*i*-Pr)$_4$),[9,11] with subsequent phosphorylation in an aqueous phosphoric acid solution with and without fluorescent light irradiation (Supporting Information). The HMF selectivity of this catalytic system is independent of the reaction time and conversion rate (see below). In the case of P-TiO_2 (filled circles), HMF selectivity increases with the immersion time in the phosphoric acid solution and reaches a maximum (67–68%) at 4–5 days. The HMF selectivity decreases with further immersion beyond 4–5 days. The correlation of the immersion time and the HMF selectivity with the surface atomic ratios of P to Ti (P/Ti) on P-TiO_2 are shown in Figs. 1B and C, respectively. The P/Ti ratios were estimated from the P $2p_{3/2}$ and Ti $2p_{3/2}$ peaks in the XPS spectrum for each P-TiO_2 sample. In our previous work, most surface phosphorus can be attributed to terminal monophosphate (Ti-O-PO(OH)$_2$).[9] The immersion time-HMF selectivity curve in Fig. 1A is similar to the immersion time-P/Ti curve in Fig. 1B. While the HMF selectivity was only 16% with P/Ti = 0 on bare anatase TiO_2, it jumps to 50% for a P/Ti ratio of ca. 0.2 and increases in proportion to the amount of immobilized phosphate species. These results are summarized in Table 1. The surface areas and amounts of Lewis acid sites for all the tested samples given in Table 1 were estimated to be 220–240 $m^2\ g^{-1}$ and 0.1–0.2 mmol g^{-1}, respectively. The acidities of prepared samples were also examined by NH_3-TPD. The NH_3-TPD results for TiO_2 and P-TiO_2 prepared by immersing 5 days in 1 M phosphate acid solution are shown in Fig. S1. The amounts of Lewis acid sites on TiO_2 and P-TiO_2 were estimated to be 2.4 and 2.5 mmol g^{-1}, respectively, from NH_3-TPD experiments. While the NH_3 desorption peak for P-TiO_2 slightly differs in shape from that of bare TiO_2 in Fig. S1, the formation of stronger Lewis acid sites was not observed on P-TiO_2. Fig. S2 shows the SEM images of P-TiO_2 and TiO_2. Both samples are composed of TiO_2 particles of ca. 10 nm in diameter, meaning that phosphorylation does not result in large morphological change of TiO_2. These results indicate that the catalyses of bare TiO_2 and P-TiO_2 cannot be simply explained by morphology and acid strength and density.

It should be noted that the immersion of TiO_2 in phosphoric acid solution beyond 4–5 days decreases both the P/Ti ratio and the selectivity toward HMF (Fig. 1). Fig. 2 shows XPS Ti 2p spectra for bare TiO_2 and P-TiO_2. The top of the Ti $2p_{3/2}$ peak gradually shifts toward larger binding energy with an increase in the immersion time. When TiO_2 was treated in phosphoric acid solution for 3 days at a higher temperature (313 K) than that (303 K) for the typical preparation of P-TiO_2, the Ti $2p_{3/2}$ peak was observed at 459.5 eV, as shown in Fig. 2. This peak appears at ca. 1 eV higher than that of anatase TiO_2 and is assignable to Ti $2p_{3/2}$ of titanium(IV) hydrogen phosphate (Ti(HPO$_4$)$_2$·nH$_2$O).[16,17] These results suggest that both terminal monophosphates and titanium hydrogen phosphate are formed on the TiO_2 surface in phosphoric acid solution; therefore, long exposure to phosphoric acid solution or higher treatment temperatures are favorable for the formation of titanium hydrogen phosphate, which decreases the surface monophosphate density and HMF selectivity. In fact, conventional immobilization of phosphate species on TiO_2 limits the maximum value of P/Ti to 0.5, and the density of phosphate species cannot be further increased beyond this

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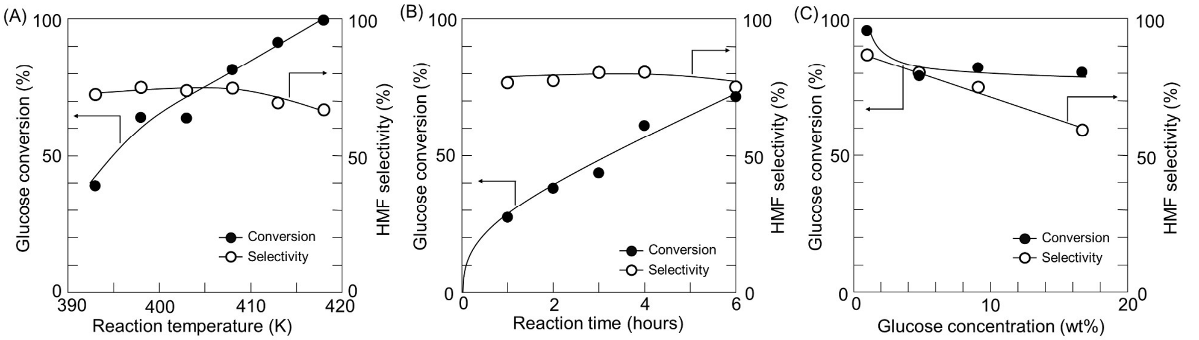

Fig. 4 Glucose conversion and HMF selectivity of glucose into HMF reaction of P-TiO_2-L (P/Ti = 0.65) as a function of (A) reaction temperature, (B) reaction time and (C) glucose concentration. Reaction conditions: catalyst, 0.25 g; distilled water, 1 mL; 2-*sec*-butylphenol, 3 mL; glucose, 0.1g (in (A), (B)), 0.01 g, 0.05 g, 0.1 g, 0.2 g (in (C)); 398 K (in (B)), 408 K (in (A), (B)); 4 h (in (A), (C)).

value. There was no significant difference in intensity among the Ti $2p_{3/2}$ peaks of P-TiO_2 samples prepared by immersion in phosphoric acid solution for 4, 5 and 7 days, suggesting that the formation of titanium(IV) hydrogen phosphate are limited only on TiO_2 surface under the present preparation conditions at the low temperature of 303 K and prevents further phosphorylation of surface OH groups.

The results for P-TiO_2-L prepared under fluorescent light irradiation are also demonstrated in Fig. 1 (open circles). P-TiO_2-L has both higher HMF selectivity and a higher density of surface phosphate species than P-TiO_2 over the whole region of immersion time examined. The P/Ti ratio exceeds 0.6 after immersion for 5 days, although immersion for 7 days decreased the phosphate density and HMF selectivity, as with that for P-TiO_2 prepared without light irradiation. Fig. 1C summarizes these results and indicates that phosphate-immobilization under light irradiation provides a higher density of surface phosphate species than conventional methods, which increases the HMF selectivity of P-TiO_2-L up to 80% under optimal conditions (P/Ti = 0.65). ICP-AES analysis revealed that ca. 3 phosphates are immobilized on P-TiO_2-L (P/Ti = 0.65) with 0.4 Lewis acid sites contained within 1 nm^2 of the TiO_2 surface (3 nm^{-2}), as expressed in Fig. 3. Assuming anatase TiO_2 (101) surface, where there are 8 Ti atoms (surface 1st layer: 5 atoms, 2nd layer: 3 atoms) within 1 nm^2, phosphates are expected to be bonded 3 Ti atoms of 5 Ti atoms on the 1st layer. In the case of P-TiO_2, the surface phosphate density is limited to 2 nm^{-2}. The higher density of phosphate species immobilized on P-TiO_2-L can be attributed to photo-induced superhydrophilization of TiO_2.[14,15] Excess surface OH groups are formed on TiO_2 under UV light irradiation, which leads to the superhydrophilization of TiO_2. During phosphate immobilization under light irradiation, excess surface OH groups are expected to occur on TiO_2, which suggests that esterification between such a high density of OH groups and phosphoric acid would result in a higher density of phosphate species and higher HMF selectivity.

3.2. Catalytic properties and reaction mechanism of phosphate-immobilized TiO_2 in biphasic reaction system.

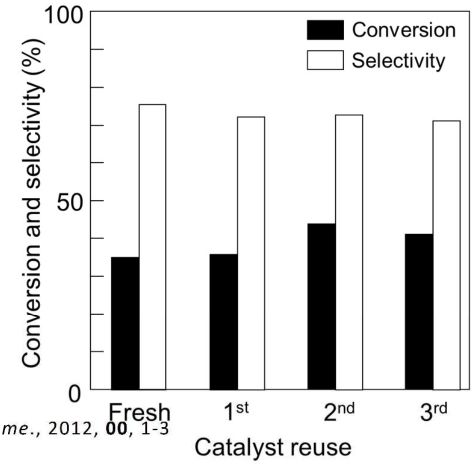

Fig. 5 Catalytic activity of reused P-TiO_2-L (P/Ti = 6.5) for glucose into HMF conversion. Reaction conditions: catalyst, 0.125 g; glucose, 0.1 g; distilled water, 1 mL; 2-*sec*-butylphenol, 3 mL; 398 K; 4 h.

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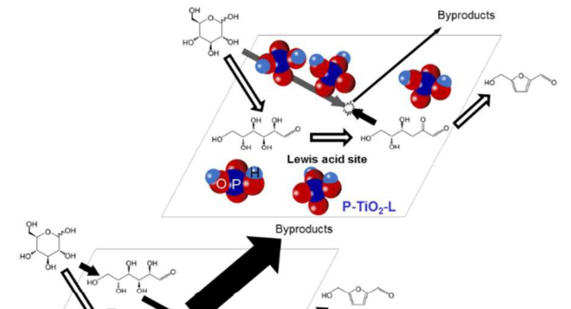

Fig. 7 Proposed reaction mechanism for HMF formation from glucose over TiO_2 with and without surface phosphates.

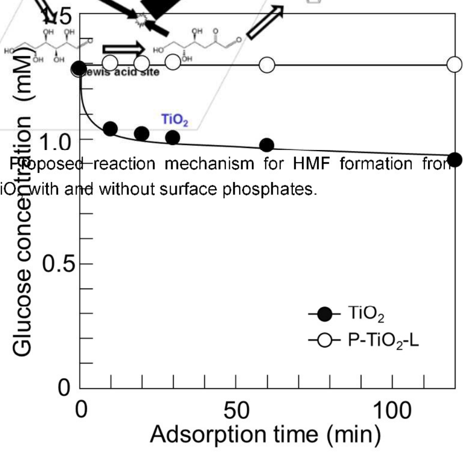

Fig. 6 The time course of glucose concentration in the mixture of catalyst and glucose solution. Reaction conditions: catalyst, 0.1 g; glucose, 1 mg; distilled water, 4 mL; room temperature.

The catalytic properties of phosphate-immobilized TiO_2 were examined through HMF production over P-TiO_2-L at P/Ti = 0.65 with respect to the reaction temperature, reaction time and glucose concentration. Although the glucose conversion at 4 h simply increases with the reaction temperature (Fig. 4A), an increase in the reaction temperature slightly decreases the HMF selectivity above 408 K because side reactions, including aldol condensation, are also accelerated at higher reaction temperatures.[18] Fig. 4B shows the glucose conversion and HMF selectivity with respect to the reaction time at 398 K. The glucose conversion increases proportionally to the reaction time, and the HMF selectivity is almost independent of the reaction time; the HMF selectivity was ca. 80% for the entire reaction period. The same observations were made for all tested P-TiO_2 and P-TiO_2-L.

The results for the P-TiO_2-L (P/Ti = 0.65) catalyst reuse experiment at 398 K are shown in Fig. 5. After reaction for 4 h at 398 K, the catalyst was collected by simple filtration and used for subsequent reactions. No decrease in HMF selectivity was observed after 2 reuses. A decrease in the surface phosphate species immediately decreases the HMF selectivity in the catalytic system; therefore, P-TiO_2-L works as a stable catalyst for the reaction without elution of the phosphate species. It was confirmed that the phosphates immobilized on TiO_2 were confirmed as stable and were not eluted during reaction.[9] Fig. 4C shows the dependence of glucose conversion and HMF selectivity on the glucose concentration at the initial stage of the reaction, where the HMF selectivity was largely dependent on the glucose concentration. For a 1 wt% aqueous glucose solution, the glucose conversion and HMF selectivity exceeded 95% and 85%, respectively, and the HMF yield reached 84%. However, the HMF selectivity was reduced with an increase in the initial glucose concentration, which indicates that side reactions that prevent selective HMF production may be correlated with the glucose concentration.

The selective HMF production by P-TiO_2 cannot be attributed to the chemical properties of phosphate species because phosphoric acid itself cannot work as an effective catalyst for HMF production[8,9] and it was confirmed that the addition of phosphates such as NaH_2PO_4, Na_2HPO_4 and Na_3PO_4 to the reaction system containing bare TiO_2 further lowers HMF yield and selectivity. To understand the reaction mechanism with this catalytic system, glucose adsorption on bare anatase TiO_2 and P-TiO_2-L in water was examined at room temperature. Time courses of the glucose concentration for an aqueous glucose solution (1 mg glucose, 4 mL distilled water) in the presence of bare anatase TiO_2 and P-TiO_2-L are shown in Fig. 6. While glucose conversion over TiO_2 without phosphate species exceeds 99% within 4 h, the HMF selectivity is only 16% (Table 1), i.e., most glucose is converted into undesired polymerized complex species.[9] Fig. 6 reveals that bare TiO_2 immediately adsorbs glucose during the early stage of the reaction (0–10 min) and the amount of adsorbed glucose gradually increases with time. In contrast to bare TiO_2, no glucose adsorption was observed on P-TiO_2-L, which indicates that the phosphate species on TiO_2 prevent glucose adsorption. The adsorption of hydrophobic benzaldehyde, in contrast to hydrophilic glucose, on TiO_2 and P-TiO_2-L was also examined using FT-IR to further clarify the role of the immobilized phosphate species. Fig. S3 shows FT-IR spectra for benzaldehyde adsorbed on TiO_2 and P-TiO_2-L (P/Ti = 0.65) at room temperature. After the benzaldehyde-adsorbed samples were evacuated under vacuum to remove physisorbed benzaldehyde, the FT-IR spectra were measured. The spectrum for TiO_2 has strong peaks at 1690, 1645, 1600 and 1580 cm^{-1}, which are derived from adsorbed benzaldehyde.[19,20] The same bands also appear in the spectrum for P-TiO_2-L; however, the band intensities are much smaller than those for bare TiO_2. Therefore, the phosphate species immobilized on TiO_2 prevent the adsorption of these hydrophilic and hydrophobic molecules. Consideration of this and the other results so far provides information regarding the decrease in HMF selectivity due to side reactions. The water-tolerant Lewis acid sites on TiO_2 with and without surface phosphate species convert glucose into HMF by stepwise dehydration through 3-deoxyglucosone on the Lewis acid sites.[11] Dense surface phosphate species decrease the glucose adsorption and increase the HMF selectivity; however, the HMF selectivity is largely dependent on the glucose concentration, even with TiO_2 fully covered in phosphate species. Thus, the main side reaction that decreases HMF formation is attributed to intermolecular reactions between adsorbed glucose molecules or between adsorbed glucose molecules and the highly reactive intermediate 3-deoxyglucosone.

To summarize, a proposed reaction mechanism for direct HMF production from glucose over phosphate-immobilized TiO_2 in a biphasic reaction system is shown in Fig. 7. Bare TiO_2 adsorbs a large amount of glucose, so that intermolecular reactions between adsorbed glucose molecules or between adsorbed glucose molecules and 3-deoxyglucosone are enhanced, and most glucose is not

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converted into HMF by the intramolecular dehydration of 3-deoxyglucosone. Phosphate-immobilization on TiO_2 decreases these intermolecular side reactions by decreasing the surface glucose concentration, which increases the HMF selectivity. Although phosphorylation based on simple esterification between phosphoric acid and OH groups on the TiO_2 surface limits the maximum amount of immobilized phosphates, photo-assisted phosphorylation to enhance surface OH groups on TiO_2 under light irradiation increases surface phosphate species beyond the conventional limit.

4. Conclusion

In phosphorylation based on simple esterification between phosphoric acid and surface OH groups on anatase TiO_2, titanium hydrogen phosphate and terminal monophosphate bonded to Ti are formed under the preparation conditions, which limits the density of phosphates immobilized on the TiO_2 surface to 2 nm^{-2}. In contrast, esterification under light irradiation increases the phosphate density beyond this limit because photo-induced surface OH groups enhance phosphorylation. The resultant surface prevents the adsorption of hydrophilic glucose molecules, which increases the selectivity toward HMF production.

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