

Direct formation of 5-(hydroxymethyl)furfural from glucose with photoassisted-phosphorylated TiO₂ catalyst

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Abstract: For improving catalytic performance for the direct production of 5-(hydroxymethyl)furfural (HMF) from glucose, Photo-assisted phosphorylation of anatase TiO₂ catalyst was examined. Phosphorylation based on simple esterification between phosphoric acid and surface OH groups on anatase TiO₂ with water-tolerant Lewis acid sites has limited the density of phosphates immobilized on TiO₂, limiting HMF selectivity. Phosphorylation of the TiO₂ surface under light irradiation increases the surface phosphate species to prevent the adsorption of hydrophilic glucose molecules on TiO₂, resulting in a higher HMF selectivity.

Keywords: HMF formation from glucose, phosphorylated TiO₂

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. HMF is currently produced by the acid-catalyzed dehydration of fructose obtained by the enzymatic isomerization of glucose. However, direct HMF production from glucose has not yet been commercialized because there is no practical process selectively to produce HMF from concentrated glucose solutions.

We have reported that TiO₂ have Lewis acid sites workable even in water, and phosphate-immobilized TiO₂ (P-TiO₂) acts as a highly efficient heterogeneous catalyst for HMF formation in biphasic reaction systems.¹⁻³ 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 TiO₂ improves the HMF selectivity, the role of the phosphate species has not been clarified. In addition, the density of surface OH groups on TiO₂ is limited, so that the amount of phosphate species immobilized on TiO₂ 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 TiO₂ to prepare a catalyst for efficient HMF production. TiO₂ is known to exhibit super-hydrophilicity during and after UV light irradiation due to excess formation of surface OH groups under light irradiation.⁴ The esterification of phosphoric acid and OH groups on such TiO₂ would increase the density of surface phosphate species, thereby enhancing the catalytic performance.

2. Experimental

Anatase TiO₂ was prepared by a simple sol-gel reaction of titanium tetraisopropoxide (Ti(O-*i*-Pr)₄). A mixture of Ti(O-*i*-Pr)₄ (40 g) 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 TiO₂ catalyst. Phosphate species were immobilized on TiO₂ simply by immersing 2 g of TiO₂ in 100 mL of 1 M H₃PO₄ 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-TiO₂ was used for HMF production from glucose. Phosphate-immobilization on TiO₂ was prepared by immersing TiO₂ in H₃PO₄ solution under 100 W fluorescent light irradiation. The phosphate-immobilized TiO₂ prepared under fluorescent light irradiation was used as P-TiO₂-L.

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) and an aqueous glucose solution (distilled water; 1 mL, D-glucose (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) and gas chromatography (GC).

3. Results and discussion

Fig. 1A shows the catalytic activities (408 K, 4 h) of phosphate-immobilized TiO₂ prepared with (P-TiO₂-L) and without (P-TiO₂) fluorescent light irradiation for HMF production. In the case of P-TiO₂ (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 surface atomic ratios of P to Ti (P/Ti) on P-TiO₂ are shown in Figs. 1B. The P/Ti ratios were estimated from the P 2p_{3/2} and Ti 2p_{3/2} peaks in the X-ray photoelectron spectroscopy spectrum for each sample. The immersion time-HMF selectivity curve in Fig. 1A is similar to the immersion time-P/Ti curve in Fig. 1B. These results indicate that HMF selectivity of the catalyst depends on the density of phosphate species bonded to TiO₂.

The results for P-TiO₂-L are also demonstrated in Fig. 1 (open circles). P-TiO₂-L has both higher HMF selectivity and a higher density of surface phosphate species than P-TiO₂ 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-TiO₂. These results indicate that phosphate-immobilization under light irradiation provides a higher density of surface phosphate species than conventional methods, which increases the HMF selectivity of P-TiO₂-L up to 80% under optimal conditions. Glucose adsorption experiments on TiO₂ suggest that phosphates immobilized TiO₂ prevent glucose adsorption, resulting in higher HMF selectivity.⁴

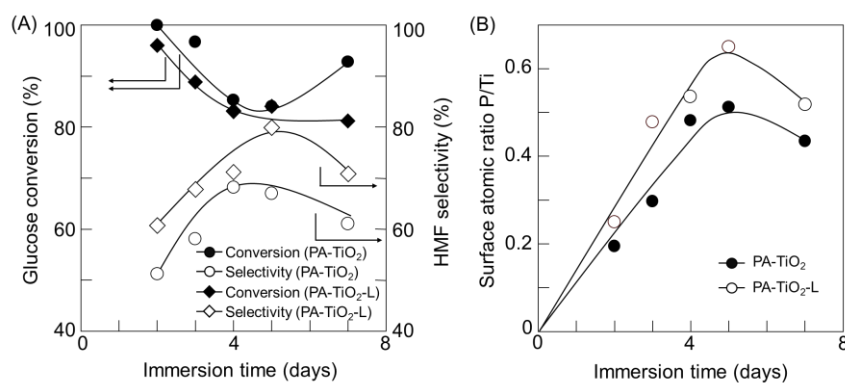


Figure 1. (A) Glucose conversion and HMF selectivity in P-TiO₂ and P-TiO₂-L, (B) Correlation of the surface atomic ratio of P to Ti (P/Ti) on P-TiO₂ and P-TiO₂-L.

4. Conclusions

Phosphorylation based on simple esterification between phosphoric acid and surface OH groups on anatase TiO₂ limits the density of phosphates immobilized on the TiO₂ surface. In contrast, esterification under light irradiation increases the phosphate density beyond this limit because photo-induced surface OH groups enhance phosphorylation.

References

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