Efficient formation of 5-(hydroxymethyl)furfural from glucose with photoassist-phosphorylated TiO₂ catalyst

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Biomass conversion has been extensively investigated to provide a renewable feedstock for the production of useful chemicals. 5-(hydroxymethyl)furfural (HMF) is an attractive intermediate for such a biomass-derived chemical platform because it can be further converted into various polymers. We have reported that phosphate-immobilized TiO₂ (P-TiO₂) acts as a highly efficient heterogeneous catalyst for HMF formation in biphasic reaction systems [1,2]. 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 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. The esterification of phosphoric acid and OH groups on such TiO₂ would increase the density of surface phosphate species, thereby enhancing the catalytic performance.

Phosphate species were immobilized on TiO₂ prepared by a sol-gel reaction simply by immersing TiO₂ in 1 M H₃PO₄ solution for 2–7 days at 303 K with and without 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 (0.1 g).

Fig. 1 shows the catalytic activities (408 K, 4 h) and the surface atomic ratios of P to Ti (P/Ti) of P-TiO₂-L and P-TiO₂. The P/Ti ratios were estimated from the X-ray photoelectron spectroscopy spectrum for each sample. Both HMF selectivity and P/Ti ratio shows higher value in the case of P-TiO₂-L than that of 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 [3].

![Fig. 1](image-url)  
(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.

REFERENCES