# Efficient formation of 5-(hydroxymethyl)furfural from glucose with photoassist-phosphorylated $TiO_2$ catalyst

Masashi Hattori[1], Keigo Kamata[2], Michikazu Hara[1]*

[1] Materials and Structures Laboratory, Tokyo Institute of Technology 4259-R3-33 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

*E-mail: hara.m.ae@m.titech.ac.jp

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 $TiO_2$ (P-$TiO_2$) 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 $TiO_2$ improves the HMF selectivity, 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. 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.

Phosphate species were immobilized on $TiO_2$ prepared by a sol-gel reaction simply by immersing $TiO_2$ in 1 M $H_3PO_4$ solution for 2–7 days at 303 K with and without fluorescent light irradiation. The phosphate-immobilized $TiO_2$ prepared under fluorescent light irradiation was used as P-$TiO_2$-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-$TiO_2$-L and P-$TiO_2$. 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-$TiO_2$-L than that of P-$TiO_2$. 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-$TiO_2$-L up to 80% under optimal conditions [3].

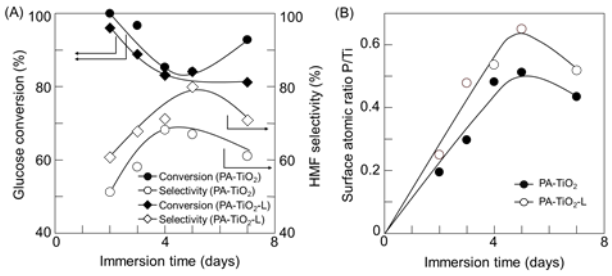


Fig. 1 (A) Glucose conversion and HMF selectivity in P-$TiO_2$ and P-$TiO_2$-L, (B) Correlation of the surface atomic ratio of P to Ti (P/Ti) on P-$TiO_2$ and P-$TiO_2$-L.

## REFERENCES

[1] K. Nakajima, R. Noma, M. Kitano, M. Hara, J. Mol. Catal. A: Chem., 388 (2014) 100.

[2] R. Noma, K. Nakajima, K. Kamata, M. Kitano, S. Hayashi, M. Hara, J. Phys. Chem. C, 119 (2015) 17117.

[3] M. Hattori, K. Kamata, M. Hara, Phys. Chem. Chem. Phys., DOI: 10.1039/C6CP06864B, (2016).