Synthesis of 5-Hydroxymethylfurfural from Glucose over Titania-based Water-tolerant Bifunctional Solid Acid Catalysts in a Biphasic System

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5-Hydroxymethylfurfural (HMF) represents one of the key biobased platform chemicals for the production of diverse value-added chemicals, materials and fuels. The development of efficient heterogeneous catalytic processes for the synthesis of HMF from biomass-derived carbohydrates represents an important research topic for a more sustainable future in the chemical industry. In this work, an experimental study has been performed on the preparation and characterization of a series of titania-based bifunctional water-tolerant solid acid catalysts for the synthesis of HMF from glucose in a biphasic system.

Phosphated titania was prepared by different methods such as in-situ sol-gel, impregnation and post-treatment. The phosphate loading was varied to adjust the ratio of Bronsted acid to Lewis acid and thus to optimize the catalyst performance. Reaction conditions such as time, temperature, solvent and catalyst loading for the selected catalyst were optimized. A HMF yield over 50% from glucose can be achieved in 75 min at 160 °C in a water-MIBK system. In order to further improve the textural property, anatase titania layers were supported on SBA-15 silica by a layer-wise grafting method, followed by simply treating the prepared anatase layers with phosphoric acid. The crystalline phase formed on SBA-15 surface was identified by thermogravimetric analysis (TGA) and the wide-angle (X-ray diffraction) XRD as a layered titanium phosphate TiO(HPO)·2H2O according to the literature. High resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray spectroscopy (EDS) confirmed the uniform distribution of titanium phosphate on the SBA-15 surface. The reaction test showed that a HMF yield over 60% could be achieved from glucose in 90 min at 170 °C in a water-mTHF system over the prepared catalyst. IR spectroscopy, N2 sorption, ammonia-temperature programmed desorption (NH3-TPD) and XRD were conducted to determine the functional groups, surface area, total acidity and crystallinity of the synthesized catalyst. Reaction mechanisms were investigated with additional experiments starting with fructose, HMF with or without catalyst. The reusability test indicates that the prepared catalyst show no distinct performance loss after three sequential runs.


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