Enhanced catalytic performance in dehydration of sorbitol to isosorbide over a superhydrophobic mesoporous acid catalyst

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ABSTRACT

A superhydrophobic mesoporous polymer-based acid catalyst (P-SO$_3$H) was synthesized from solvothermal co-polymerization. The N$_2$ sorption isotherms indicate the rich porosity of P-SO$_3$H, confirmed by the TEM image. The IR spectra indicate the presence of sulfonic acid groups. Interestingly, P-SO$_3$H gives contact angle of water droplet on the sample surface at 154°, suggesting its superhydrophobicity. More importantly, P-SO$_3$H is highly efficient catalyst for dehydration of sorbitol to isosorbide, giving sorbitol conversion higher than 99.0% and isosorbide yield at 87.9%. In addition, P-SO$_3$H exhibits excellent recyclability. After recycles for 5 times, the isosorbide yield is still 77.7%. In contrast, conventional acid catalyst of Amberlyst-15 shows the yield at only 15.4% after recycles for 3 times. The unique catalytic properties are reasonably related to the superhydrophobicity and porosity of P-SO$_3$H. The sample large porosity offers a high degree of the exposed acidic sites to the reactants, and the sample superhydrophobicity would keep the water formed in the dehydration away from the catalyst, promoting the reaction equilibrium. As a result, the catalytic performance in dehydration of sorbitol to isosorbide over the superhydrophobic P-SO$_3$H catalyst is significantly enhanced, compared with conventional acid catalyst of Amberlyst-15.

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The production of fine chemicals and alternative fuels from renewable biomass has been paid much attention recently [1–10]. Particularly, the conversion of biomass-derived materials from cellulose into valuable fine chemicals is greatly important because cellulose is easily obtained [2–10]. Notably, the cellulose-derived chemicals are generally oxygen-rich, having low energy density. Therefore, deoxygenation of these oxygen-rich chemicals is a hot topic currently [6,9].

An efficient methodology to reduce the oxygen content of cellulose-derived chemicals is dehydration over acid catalysts [1,5,10]. Generally, liquid acids of H$_2$SO$_4$ and HCl as homogeneous acid catalysts have been used. However, these liquid acids have an obvious drawback in separation and regeneration from the reaction system [1,2,10]. Therefore, it is strongly desirable to use solid acids to heterogeneously catalyze the dehydration of cellulose-derived chemicals. Up to now, there are many successful examples for using acidic solid catalysts such as Amberlyst-15 resin, zeolites, sulfated carbons, metal phosphates [2,7–21]. However, their

activities and selectivities for the target products are still not good enough [6,13–15]. Therefore, it is a challenge to develop highly efficient solid acid catalysts for the dehydration of cellulose-derived chemicals [22–41].

Considering the fact that dehydration always forms by-product of water, we propose that the dehydration equilibrium would be effectively promoted to move product side by keeping the water formed in the dehydration away from the catalysts, giving relatively high catalytic activities and selectivities [29]. According to this design, we have used a superhydrophobic mesoporous acid (P-SO$_3$H) to catalyze the dehydration of oxygen-rich sorbitol to isosorbide as a model reaction of biomass dehydration. As we expected, the P-SO$_3$H has very high activity, good isosorbide selectivity, and excellent recyclability, compared with conventional acid catalyst of Amberlyst-15.
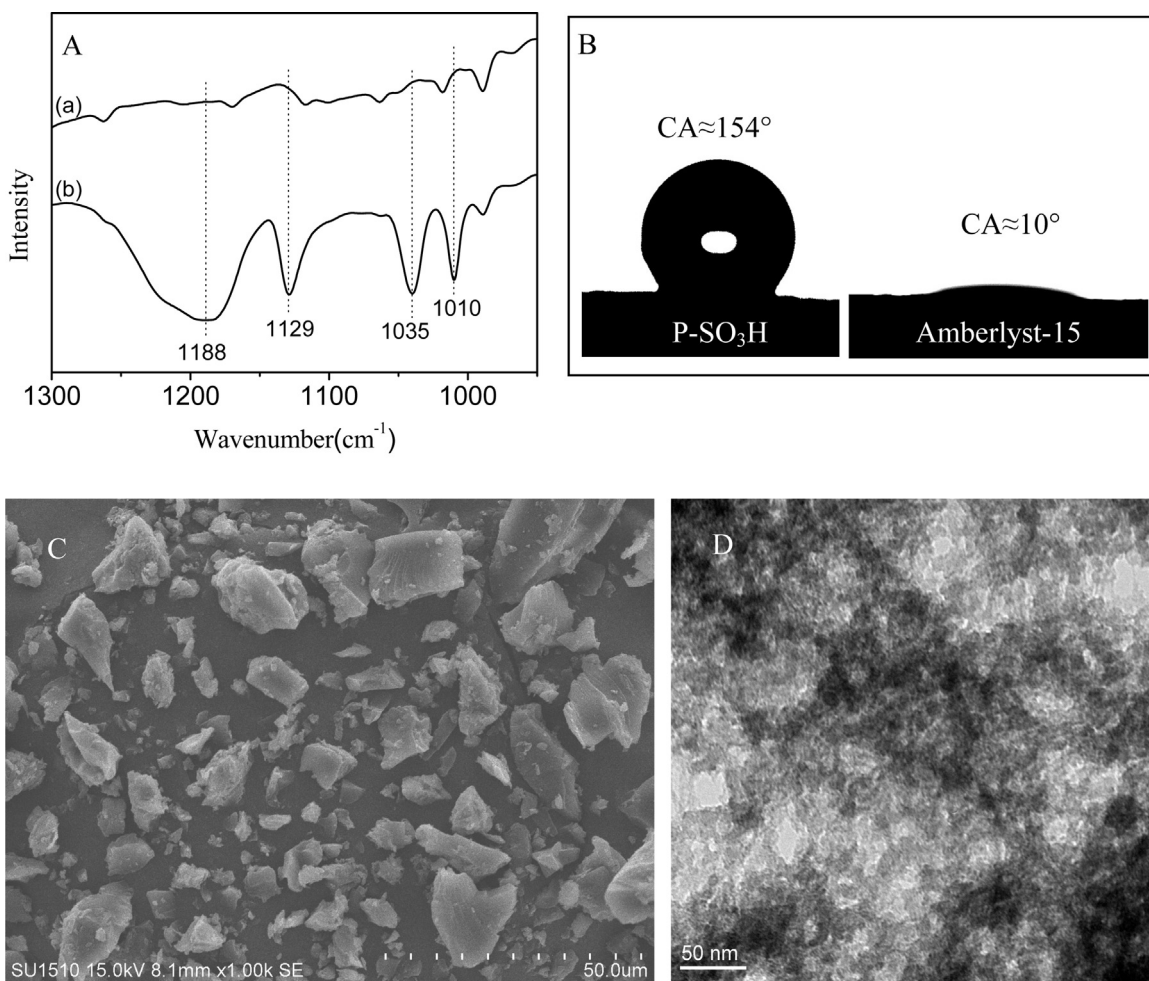
1. Experiment

1.1. Materials

All chemicals were analytical grade and used without further treatments. Sorbitol was purchased from Aladin Co. 1,

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Fig. 1. (A) IR spectra of (a) polydivinylbenzene and (b) P-SO$_3$H; (B) water droplet contact angle on P-SO$_3$H, and Amberlyst-15; (C) SEM and (D) TEM images of P-SO$_3$H.

4-anhydro-d-sorbitol was purchased from J&k Chem. Co. Divinylbenzene (DVB) was obtained from Tianjin Chem. Co. Nonionic block copolymer surfactant (Pluronic 123, molecular weight of about 5800), 3-mercaptopropyltrimethoxysilane (3-MPTMS) and sodium p-styrene sulfonate were bought from Alfa Aesar Co. Tetrahydrofuran, azobisisobutyronitrile (AIBN), H$_2$O$_2$ (30 wt%), and TEOS were obtained from Shanghai Chem Co.

1.2. Synthesis of P-SO$_3$H

As a typical run, 2 g of DVB was introduced into a solution containing 20 ml of THF and 0.05 g of AIBN, followed by addition of 2 ml H$_2$O and 0.64 g sodium p-styrene sulfonate. After stirring for 3 h, the solution was transferred into an autoclave, solvothermally treating at 100 °C for 24 h. After evaporating the solvent at room temperature for 2 days, ion-exchanged with 1 M sulfuric acid and ethanol, and washed thoroughly with water and alcohol, the final product designated as P-SO$_3$H was obtained.

1.3. Synthesis of Nonporous-P-SO$_3$H

Nonporous-P-SO$_3$H was prepared according to almost the same procedures to those of P-SO$_3$H, except for the absence of THF and water in the synthesis.

1.4. Synthesis of SBA-15-SO$_3$H

As a typical run, 4.0 g of P123 was dissolved in 125 g of 1.9 M HCl aqueous solution. After heating to 40 °C, 7.2 ml of TEOS was added into the solution, stirring for 40 min. After adding 0.77 ml of 3-MPTMS and 1.25 g of H$_2$O$_2$, the mixture was stirred for 20 h at 40 °C. Then, the mixture was transferred into an autoclave and heated at 100 °C for 24 h. After washing with a mixture of ethanol and sulfuric acid and drying at 60 °C, the final product designated as SBA-15-SO$_3$H was obtained.

1.5. Characterization

Transmission electron microscopy (TEM) was performed on a HT-7700 electron microscope (Hitachi, Japan) with an acceleration voltage of 100 kV. Scanning electron microscope (SEM) experiments were performed on a SU-1510 microscope (Hitachi, Japan). Nitrogen sorption isotherms at the temperature of liquid nitrogen were measured using a Micromeritics ASAP 2020 M system. The samples were outgassed for 10 h at 100 °C before the measurements. The pore-size distribution for mesopores was calculated using the Barrett–Joyner–Halenda (BJH) model. FTIR spectra were performed on a Nicolet FTIR spectrometer (ThermoFisher, USA). The acid content in the acidic catalysts was measured by acid-base titration.