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Conversion of fructose, glucose and sucrose to 5-hydroxymethyl-2-furfural over mesoporous zirconium phosphate catalyst

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ABSTRACT

5-Hydroxymethyl-2-furfural (HMF) is considered an important platform chemical among other intermediates derived from biomass. In this study, we have used mesoporous zirconium phosphate as a catalyst for the conversion of sugars into HMF. The catalyst was synthesized using a hydrothermal method and was characterized using powder XRD, FT-IR spectroscopy and FESEM. The as-prepared catalyst showed porous structure and a very high surface area. Mesoporous zirconium phosphate exhibited excellent catalytic activity for the formation of HMF, from fructose, glucose and sucrose. The effect of various factors such as reaction time, temperature and reaction systems on formation of HMF has been investigated.

1. Introduction

Diminishing natural recourses and their growing prices have led to extensive efforts focused on the waste biomass for production of chemicals and fuels [1–4]. Biomass is inexpensive, renewable and abundant in nature. 5-Hydroxymethyl-2-furfural (HMF) is considered an important signature chemical among other chemical intermediates derived from the biomass [5–7]. Other useful intermediates, including the bio-based polymers (2,5-diformylfuran and 2,5-furandicarboxylic acid), fuels (2,5-dimethylfuran) and solvents such as levulinic acid, can be prepared by the selective oxidation, reduction and rehydration of HMF, respectively [8,9]. HMF is synthesized from the dehydration of mono-/di-/polysaccharides (such as fructose, glucose, sucrose, cellobiose, cellulose, etc.) [10–13]. The use of fructose as substrate is not economical because of its low availability and high cost. Glucose which is the main component of biomass has been considered more desirable substrate. The formation of HMF from glucose requires an initial isomerization to fructose, followed by the dehydration of fructose. The synthesis of HMF from hexose has been performed using a variety of acid catalysts such as inorganic materials [3,14], organic acids [15] and metal chlorides [16], and heterogeneous catalysts, e.g. zeolites [17,18], ion-exchange resins [19,20], heteropoly acid salts [21], sulfated [22] and phosphoric acid-treated metal oxides [23]. Extensive efforts have been made to improve the yield of HMF by adopting different kinds of reaction methods and solvent systems such as ionic liquids or aqueous/bi/multiphase organic solvent systems [10,11]. Metal phosphates (such as Al, Ti, Zr and Nb) have also been employed as heterogeneous acid catalysts for the conversion of sugars into HMF due to the presence of the Lewis (metal sites) and Brønsted (protonated phosphate group) acidic sites [24]. It has been reported that the Lewis acidic sites on the solid catalyst promotes the isomerization of glucose to fructose, via intermolecular hydride shift, while the Brønsted acidic sites helps in the dehydration of fructose to HMF [25–27]. Benvenuti et al. [28] performed a comparative study of the catalytic activity of various form of Zr-/Ti-phosphates (layered and cubic forms) for the conversion of fructose to HMF in aqueous media and suggested cubic zirconium pyrophosphate and γ-titanium phosphate as the best catalysts among the investigated samples. On the other hand, Asghari et al. [29] investigated the catalytic performance of the crystalline and amorphous forms of zirconium phosphate under sub-critical water conditions for the dehydration of fructose to HMF. To the best of our knowledge, the use of the mesoporous zirconium phosphate as catalyst in the preparation of HMF from hexoses has not been reported so far.

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In this work, the catalytic activity of mesoporous zirconium phosphate (ZrP) for the formation of HMF from fructose, glucose and sucrose was investigated. This material was prepared by hydrothermal method at low temperature using CTAB as a cationic pore directing agent. It has a mesoporous structure with a very high surface area (407 m^2/g). Due to the high surface area, this catalyst exhibited excellent catalytic performance for hexose transformation to HMF with high yield. We have also studied the effect of various factors such as solvents, reaction time, temperature and reaction systems on its catalytic activity in the formation of HMF. The catalyst was regenerated by heat treatment and exhibited acceptable performance after re-use.

2. Experimental

2.1. Chemicals

All chemicals required for the synthesis of catalyst and catalytic reactions were purchased from Alfa Aesar, Acros Organics, Sigma Aldrich and BDH companies.

2.2. Catalyst synthesis

The zirconium phosphate (ZrP) catalyst was synthesized according to a literature procedure with slight modification [30]. Briefly, hydrothermal treatment involving an in situ generated zirconium carbonate complex, di-ammonium hydrogen orthophosphate and hexadecyl trimethyl ammonium bromide (CTAB) in a basic medium was carried out. CTAB is a micelle-forming agent that is used in the process to add porosity to the catalyst. The white zirconium carbonate was precipitated out upon mixing of a dilute aqueous solutions of ammonium carbonate (Alfa Aesar, ACS, NH_3 30.0+%) (3 g dissolved in 200 mL of DI H_2O) and zirconium oxychloride (Alfa Aecar, 98%) under continuous stirring. After complete precipitation, the solid residue was collected by repeated centrifugation and washings with water until the complete removal of chloride ions. The chloride-free precipitate was mixed in an aqueous solution of ammonium carbonate and vigorously stirred until a clear solution was obtained. Finally, this solution was diluted to 175 mL using distilled water. A 50 mL aqueous solution of 6.5506 g di-ammonium hydrogen orthophosphate, $[(NH_4)_2HPO_4]$ (ACS, 98% min.) was added to the clear solution at a fixed flow rate (5 mL min^{-1}) to make a 225 mL solution of 1% (w/v). The aqueous solutions containing CTAB (Amresco, high-purity grade) was placed in a 1000 mL thick-wall glass bottle and stirred continuously for 12 h at room temperature, then at 80 °C for 2 days and finally at 90 °C for 1 day in the same glass bottle. The reaction mixture was left for another day in a Teflon-lined stainless steel reactor (Parr bomb) that was kept in a pre-heated hot air oven at 135 °C. After cooling, the white precipitate reaction mass was centrifuged, washed thoroughly with distilled water and dried in a hot air oven at 80 °C for 12 h. The dried samples were calcined in a high-temperature furnace at 550 °C for 6 h to get pure mesoporous zirconium phosphate. Synthesis was carried out using a molar ratio of $Zr^{4+}/PO_4{}^{3-}/CTAB/H_2O$: 1:2:0.25:1000.

2.3. Instrumentation

Powder X-ray diffraction analysis of the catalyst was carried out using Panalytical Empyrean Diffraction System with an operating voltage set to 40 kV and current of 45 mA using Cu Kα radiations ($\lambda = 1.542$ Å). X-ray diffraction patterns were recorded at 0.01°/min step in 5–90° range using 8 s residence time. Fourier transform infrared (FT-IR) spectra of zirconium phosphate and pyridine-absorbed sample were recorded on Perkin Elmer (Model spectrum 100). The field-emission scanning electronic microscope (FESEM) images were collected on FEI Quanta 3D FEG operated at an accelerating voltage of 5 kV. The specific surface area and pore volumes were obtained by means of N_2 adsorption and desorption studies on a Nova 2200 operated at 77 K. The specific surface area was determined by using Brunauer–Emmette–Teller (BET) method and the pore volume by John-Teller method. The catalyst was degassed at 300 °C for 16 h prior to the surface area measurements.

2.4. Synthesis of HMF

The reactions were performed in a thick-walled glass pressure tube. In a typical experiment, sugar, catalyst, aqueous phase (saturated NaCl solution) and diglyme were placed in the glass reactor vessel, respectively. The aqueous phase and diglyme were used in the volume ratio of 1:3. The glass reactor vessel was sealed and placed in a pre-heated oil bath at a set temperature with continuous stirring. After the set time, the reaction mixture was cooled down in an ice bath and then transferred into a centrifuged tube. The reaction mixture was separated from the catalyst by centrifuging it. The solid catalyst was washed with water and acetone, respectively, and dried in a hot air oven at 100 °C. The analysis of liquid layer was performed by means of high-performance liquid chromatography (HPLC) using a Agilent 1100 series instrument and C18 reversed-phase column of dimensions 250 mm × 4.6 mm × 5.0 μm. The product solution containing HMF was run using a mobile phase of acidic water and methanol (0.05% H_2SO_4 (10%) + MeOH (90%)) at a flow rate of 1 mL min^{-1}. The HMF peak was identified by its retention time in comparison with the standard sample. The actual concentration of HMF was determined from the calibration plot (see supplementary data, Fig. S1). The results are tabulated in Table 1. The HPLC chromatograms are shown for a few selective reactions in supplementary data (Figs. S2–S4). The proton NMR of the crude product in the case of the dehydration reaction of fructose to HMF (entry #3 in Table 1) is also shown as a reference in Fig. S5.

3. Results and discussion

3.1. Catalyst characterization

The powder XRD pattern of the calcined ZrP sample shows two broad peaks in 2θ ranges of 10–40° and 40–70° and suggests its amorphous nature (Fig. 1a). The FT-IR spectra of the sample before and after calcination are shown in Fig. 2a. The as-synthesized sample exhibits a broad peak at 1000–1200 cm^{-1} that is due to $-PO_4$ stretching vibration and shifts towards higher wave numbers (ca. 55–65 cm^{-1}) after calcination. The bands at 3375 and 1630 cm^{-1} are attributed to the asymmetric OH stretching and bending of water molecule, respectively. The bands at 1471 and 2800–3000 cm^{-1} are due to the C–H stretching of the surfactant that disappear after calcinations. A similar pattern of powder XRD and FT-IR of mesoporous zirconium phosphate has been reported by Sinhamahapatra *et al.* [31]. The surface acidity of ZrP has been determined by FT-IR using pyridine as a probe molecule. Pyridine forms pyridinium ions with proton (Brønsted acid sites) and is coordinated to electron-deficient metal centers (Lewis acid centers) [31]. Fig. 2b shows the FT-IR of zirconium phosphate before and after adsorption of pyridine. The band at ~1545 cm^{-1} is assigned to pyridinium ion, confirming the presence of Brønsted acid sites. The Brønsted acidity arises as a result of the presence of geminal P(OH) groups [32]. A peak at around ~1445 cm^{-1} is due to the pyridine attached to a Lewis acid center. The band at 1490 cm^{-1} is a combination band between two separates bands at 1545 and 1445 cm^{-1}, corresponding to Brønsted and Lewis acid sites, respectively.