



Dehydration of fructose to 5-hydroxymethyl furfural over ordered AISBA-15 catalysts



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ABSTRACT

5-Hydroxymethyl furfural is an important platform chemical. It is successfully synthesized from renewable carbohydrates using mesoporous AISBA-15 catalysts under biphasic conditions. Fine tuning of the catalyst acidity is important to drive the reaction to give good yields of furan compound. Al-SBA-15 catalysts with different Si/Al ratios were prepared and characterized by XRD, ^{27}Al MASNMR, SEM, TEM, N_2 sorption, ICP-OES and TPD of ammonia. Results show that part of aluminium is substituted into tetrahedral positions. The catalyst with lower acid site density but medium to strong acid strength favours selective formation of HMF. Under the optimized conditions, HMF selectivity was as high as 88% at 59 mol% conversion of fructose. Leaching of part of aluminium occurs under hydrothermal conditions, if solvent mixtures containing water are used, while activity can be retained if DMSO is used as solvent.

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1. Introduction

It is well accepted that present petroleum based chemicals need to be replaced with renewables as a result of the dwindling reserves of the former. Moreover, rapid ecological changes taking place as a result of fossil fuel use makes it imperative to replace them with renewable fuels to attain a sustainable and renewable society. In this context, effective utilization of biomass for the production of fuels and chemicals has emerged as an important area of research. Saccharides have attracted greater attention as a promising carbon based alternative source as it is a renewable chemical feedstock [1,2]. Hence, their conversion to useful chemicals has been intensely explored [3]. However, problems of low volatility, poor solubility in desired medium and polyfunctionality of carbohydrates is hindering their effective conversion to value added chemicals. This necessitates development of innovative methods and catalyst systems to facilitate and accelerate their utilization. Among the various transformations, the synthesis of 5-hydroxymethylfurfural (HMF) through dehydration of hexoses is extensively studied due to importance of HMF as a platform chemical [4]. The potential applications of HMF includes its selective oxidation to 2,5-furandicarboxylic acid which can be used as a replacement for terephthalic acid in the production of polyesters [5–8], its reduction to 2,5-dihydroxymethylfuran and 2,5-bis(hydroxymethyl)tetrahydrofuran [9,10], which can serve as alcohol components in the production of polyesters, its hydrogenolysis to

dimethyl furan, with excellent fuel properties to replace gasoline [11], its rehydration to levulinic acid an important chemical building block with versatile applications [12,13]. Moreover, numerous phenolic resins and polymerizable furanic compounds with promising properties have been prepared from HMF [14,15].

As a result of above described versatile applications, successful efforts were made to produce HMF using a variety of reaction systems e.g., ionic liquids [16–19], high boiling organic solvents like dimethylsulfoxide [20–23], water [24] and biphasic systems [25,26], using both homogeneous and heterogeneous catalysts. Ionic liquid based systems have emerged as excellent mode for selective formation of HMF but suffer from drawbacks such as mass transfer limitations and high cost. Reactions in water medium offer a green protocol for HMF preparation, but HMF yields are lower as rehydration to LA is favorable. Whereas, in DMSO, formation of LA is suppressed leading to high yields of HMF. However, this approach necessitates difficult and energy intensive product isolation procedures [25]. In this context, biphasic systems are superior in terms of high HMF yields and energy efficiency. Currently researchers are focusing on the use of mesoporous materials as catalysts or catalyst supports for such reactions, as the mesoporosity is found to be beneficial, especially when reactant/product molecules are bulky [27]. In addition to mesoporosity, moderate acidity, pore structure along with their good thermal stability offers further possibilities for designing a more efficient and environmental friendly process for the production of HMF.

Visualizing the above mentioned potential of mesoporous materials, we have explored aluminium incorporated SBA-15 for the dehydration of fructose to HMF. We have incorporated

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aluminium into SBA-15 by post synthesis methods. The acidity was tuned by varying the Al content in the sample to study its influence on the reaction. The synthesized materials were subjected to detailed characterization to help in understanding the reactivity and selectivity during dehydration of fructose. Various process parameters were also optimized for the dehydration reaction with an aim to improve the HMF selectivity and yield. Attempt was made to correlate the acidity with HMF yield.

2. Experimental

2.1. Materials

Fructose, glucose, sucrose, maltose, methyl isobutyl ketone (MIBK), 25% NH₃ solution, zirconium oxychloride (ZrOCl₂·8H₂O), dodecatungstophosphoric acid (hereafter TPA) and toluene were purchased from Loba Chemie Pvt. Ltd., aluminium chloride, tetraethyl orthosilicate (TEOS) and poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (average molecular weight, 5800), were procured from Sigma-Aldrich, USA. All the chemicals were of research grade and were used after drying following standard procedures. Zeolites NH₄⁺-mordenite (Si/Al = 10) and NH₄⁺-beta were (Si/Al = 19) obtained from Zeolyst International, USA. Zeolite NH₄⁺-ZSM5 (Si/Al = 23) was obtained from catalyst pilot plant, National Chemical Laboratory, India. These were calcined at 450 °C for 4 h in air before using for the reaction.

2.2. Catalyst preparation

2.2.1. Synthesis of SBA-15

Mesoporous siliceous SBA-15 was synthesized according to the procedure reported by Stucky and co-workers [28]. About 4 g of amphiphilic triblock copolymer, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (average molecular weight, 5800) was dispersed in 30 mL of water, to which 120 g of 2 M HCl solution was added to get a homogeneous solution. To this solution, 8 g of TEOS was added slowly under stirring. This mixture was continuously stirred at 40 °C for 24 h and transferred to a Teflon-lined autoclave for crystallization at 100 °C for 2 days. The solid obtained after crystallization was filtered, washed with distilled water and dried at 100 °C for 12 h. The crystalline material was then calcined in flowing air at 550 °C for 6 h in order to decompose and remove the tri-block copolymer to yield mesoporous SBA-15.

2.2.2. Synthesis of AISBA-15

A post-synthesis route similar to the procedure reported by Luan et al. [29] was employed for the preparation of AISBA-15. In a typical synthesis, anhydrous AlCl₃ was dissolved in dry ethanol (25 mL). To this solution, SBA-15 (1 g) was added and refluxed for 10 h under stirring. The material was then filtered, washed repeatedly with dry ethanol and dried at room temperature followed by calcination at 550 °C for 5 h to give Al-SBA15 catalysts. By varying the AlCl₃ content, a series of AISBA-15 catalysts (with Si/Al ratio ranging 10–40) were prepared.

2.2.3. Synthesis of 15 wt% TPA on ZrO₂

This catalyst was prepared by wet impregnation method following the procedure described elsewhere [30]. The support zirconium oxyhydroxide was prepared by adding 5 wt% NH₃ solution to 0.5 M solution of ZrOCl₂·8H₂O, drop wise under continuous stirring till a final pH of 9.5 was obtained. The precipitate was filtered, washed repeatedly (till free from chloride ions), dried at 110 °C for 14 h and crushed to get white zirconium oxyhydroxide powder. To methanolic solution of TPA, zirconium oxyhydroxide was added and stirred for 12 h at room temperature. The solvent was

evaporated to dryness, dried at 80 °C overnight and calcined at 750 °C to get 15 wt% TPA/ZrO₂.750 (hereafter 15TZ750).

2.3. Characterization

The specific surface area of the catalysts was measured by N₂ physisorption at liquid nitrogen temperature using a Quantachrome Nova-1200 surface area analyzer and standard multi point BET analysis method. Samples were degassed at 300 °C in vacuum for 2 h before N₂ physisorption measurements. Pore volumes were calculated using the t-plot method of De Boer. The BJH method and the corrected Kelvin equation was used to determine the pore size distributions from the adsorption and desorption branches of the isotherms [31].

Low-angle X-ray diffraction patterns were collected in the 2θ range 0.5–5°, with a Philips X'pert Pro diffractometer using Ni filtered CuK_α (λ = 1.5406 Å, 40 kV, 30 mA), radiation, with an X'celerator detector, using the real time multiple strip (RTMS) detection technique, at a scan rate of 0.5° min⁻¹.

The acidity of the catalysts was investigated by temperature-programmed desorption of NH₃ (NH₃-TPD) using a Micromeritics Autochem-2920 instrument. Prior to TPD run, the sample was activated at 450 °C in He flow (40 mL min⁻¹) for 1 h. Subsequently, the temperature was brought down to 80 °C and NH₃ was sorbed by exposing the samples to a stream of 10% NH₃ in He (30 mL min⁻¹) for 0.5 h. The temperature was then raised to 100 °C and flushed with He for 1 h at 100 °C to remove the physisorbed NH₃. The desorption of NH₃ was carried out in He flow (40 mL min⁻¹) by increasing the temperature to 550 °C at 10 °C min⁻¹, while monitoring the concentration of NH₃ desorbed using a thermal conductivity detector.

Scanning electron microscopy of the samples was carried out using Quanta 200, 3D instrument model of FEI. The samples were prepared by dispersing them ultrasonically in isopropyl alcohol, transferring a portion onto silicon wafers which were dried and subjected to gold coating in vacuum.

Transmission electron microscopy of the samples was carried out using FEI Technai TF-30 instrument operating at 300 kV. The samples for TEM measurements were prepared by placing a droplet of the sample suspension, prepared in isopropyl alcohol using ultrasonication on a carbon coated copper grid by leaving them for drying at room temperature.

²⁷Al Magic-angle spinning (MAS) NMR spectra were recorded on a Bruker DSX300 spectrometer at 7.05 T magnetic field. The sample was rotated at 6000 Hz at the magic angle, while collecting the spectral data. A delay of 2 s was maintained between two 45° pulses. External Al(H₂O)₆³⁺ was used as a reference.

2.4. Catalytic activity

The dehydration reaction was carried out in 300 mL Parr (SS 316) autoclave with a Teflon liner. In a typical reaction, 1 g of fructose was dissolved in 10 mL of Millipore water, to which 50 mL of MIBK and freshly activated catalyst were added. The closed vessel was purged with nitrogen and the reaction was conducted at the desired temperature, while stirring the mixture constantly at 500 RPM. At the end of reaction, the aqueous phase was filtered using nylon 0.22 μm filter and the filtrate was analyzed using HPLC, equipped with RI detector and H⁺ Aminex column (305 mm × 7.8 mm) with 0.1% H₃PO₄ as the mobile phase at a flow rate of 0.6 mL min⁻¹. The organic phase was analyzed by Varian 3800 gas chromatograph, equipped with flame ionization detector and a HP-5 capillary column (50 m × 0.32 mm × 1.05 μm film thickness). The products were identified by GC-MS and compared with authentic samples.

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