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Biopolymer templated porous TiO₂: An efficient catalyst for the conversion of unutilized sugars derived from hemicellulose

Sudipta De^a, Saikat Dutta^a, Astam K. Patra^b, Bharat S. Rana^c, Anil K. Sinha^c, Basudeb Saha^{a,*}, Asim Bhaumik^{b,**}

^a Laboratory of Catalysis, Department of Chemistry, University of Delhi, North Campus, Delhi 110 007, India

^b Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

^c Catalytic Conversion Process Division, Indian Institute of Petroleum, Dehradun 248 005, India

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ABSTRACT

An efficient procedure for the conversion of unutilized abundant sugar derivatives, such as D-mannose, Dgalactose and lactose, into platform molecule 5-hydroxymethylfurfural in aqueous and organic medium is reported. This process involves biopolymer sodium alginate templated porous TiO₂ nanocatalysts containing strong Lewis acidic sites as determined by pyridine-IR and temperature programmed desorption (TPD) of ammonia studies. Porous TiO₂ materials were characterized by XRD, SEM, HR-TEM and N₂ sorption techniques. Biopolymer templating pathway provided effective synthetic route for the TiO₂ nanomaterials, which contain considerable mesoscopic void space as revealed from the HR-TEM and N₂ sorption studies. Using this TiO₂ catalyst, improved HMF yields were obtained without using expensive ionic liquids as solvents. Hydrothermally obtained TiO₂ nanocatalysts showed maximum activity in Dmannose conversion to HMF, whereas nonporous TiO₂ is inactive in this reaction. Porosity (surface area), small particle size and strong acidic sites generated through biopolymer templating pathway are crucial for high catalytic activity.

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1. Introduction

The consumption rate of fossil fuels compared to the available resources and the calamity of global warming resulting increased CO₂ emissions are two major problems faced by humanity. These crises of entire planet require the right solution as a top priority. The effects of global warming and energy crisis have spurred many research projects focused on utilization of renewable biomass as carbon-neutral feedstock and their efficient conversion to fuels and chemicals by using active chemical catalysts [1]. Toward sustainability, the efficient utilization of cellulose required the development of new technologies for the efficient and selective conversion of cellulose [2] into platform molecule such as 5hydroxymethylfurfural (HMF) for a wide range of downstream applications [3-5]. In the recent years, considerable progress has been made to obtain fuels [6] and polyester building block chemicals [7,8] from HMF platform. Significant progresses have also been made in the synthesis of HMF from sugar derivatives and

** Corresponding author.

cellulose using ionic liquids-metal halide and other active catalysts [9–12]. Although HMF can be easily prepared from fructose by using a wide variety of catalysts [13,14], advances in the synthesis of HMF from glucose [15,16], cellulose [17,18] and hexoses have not been studied extensively. Transformation of C-2 epimers of glucose, such as D-mannose and D-galactose (Scheme 1), into HMF would be interesting since D-mannose and D-galactose are comparatively unutilized among the sugar derivatives and it should be noted that mannose-containing polymers can account for 10% of the dry weight of pine wood [19], while galactose can be as much as 2% of the carbohydrate in corn stover [20]. Even mannose and galactose are present in wood-biomass in small quantities. The conversion of these glucose epimers to platform chemical would be interesting study as the isomerization mechanism of glucose is a difficult transformation. In addition to these, lactose can also be considered as inexpensive renewable feedstock since it is an underutilized sugar derivative and several million tons of it can be obtain annually as a by-product from the dairy industry [21].

Recently, biopolymers have been shown to exert a remarkable degree of control over the nucleation and growth of crystalline metal oxides [22]. Alginate, for example, is the structural biopolymer found in seaweed and contains blocks of guluronate monomers (Scheme 2) that are readily cross-linked by strong electrostatic bonds to multivalent metal cations. High thermal stability and

^{*} Corresponding author.

E-mail addresses: bsaha@chemistry.du.ac.in (B. Saha), msab@iacs.res.in (A. Bhaumik).

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Scheme 1. Mono- and disaccharide precursors as HMF feedstock.

extended gel network structure in aqueous media made biopolymers capable of maintaining the pre-organized dispersion of metal cations to relatively high temperature i.e. influence the nucleation and growth of crystalline phases [23].

Moreover, metal oxides with desired mesoporosity can be prepared by using various templates, such as block copolymers [24], amines [25], and surfactants [26]. Additionally, mesoporous TiO₂ nanoparticles prepared by salicylic acid and aspartic acid templating pathway were found to be effective catalysts for the conversion of hexoses into HMF in aqueous and organic media [27]. Metal binding and structure directing capacity of the biopolymer alginate with its ability to reduce metal salts to nanoparticles of desired mesoporous structures is something that yet to be explored. Herein, we report the synthesis method of porous TiO₂ nanospheres using alginate biopolymer as the structure directing agent. In the present synthesis, primary porous TiO₂ nanospheres was produced from titanium isopropoxide in aqueous media under alkali hydrothermal treatment method (Scheme 1). Apart from the full characterization of the porous TiO₂ material using HR-TEM, SEM and powder XRD, surface area and pore diameter analysis showed mesoporous nature of the material. Pyridine-IR and NH₃-TPD analyses showed the presence of strong Lewis acidic sites in the pores of the nanospheres of TiO₂. Consequently, the acidic TiO₂ nanomaterials were used as catalysts for the conversion of D-mannose, D-galactose and lactose into HMF under mild conditions in aqueous and organic media.

2. Experimental

D-mannose, D-galactose, lactose, sodium alginate, titanium isopropoxide were supplied by Sigma–Aldrich and were used without further purification. Dimethylacetamide (DMA), lithium chloride, 25% ammonia solution were supplied by Spectrochem, India. Unless otherwise stated, distilled water was used as aqueous phase. HR-TEM images were recorded on a JEOL DATUM Model No. JEM1011. A JEOL JEM 6700F field emission scanning electron microscope (FESEM) was used for the determination of the particle morphology of the TiO₂ nanoparticles. Fourier transform infrared (FT IR) spectra of the pyridine adsorbed samples were recorded on a



Scheme 2. Synthesis of HMF catalyzed by alginate derived TiO₂ NPs.

Perkin Elmer Spectrum 100 spectrophotometer. Temperature programmed desorption (TPD) of NH₃ studies in the temperature range 100–800 °C were employed for the quantitative estimation of surface acidity of the samples by using a Micromeritics ChemiSorb 2720 attached with a thermal conductivity detector. Powder X-ray diffraction of the TiO₂ nanoparticles for wide-angle was carried out in a Rigaku MiniFlex II XRD machine. Conversions of sugar derivatives (D-mannose, D-galactose, lactose) into HMF were performed in a CEM Matthews WC Discover microwave reactor, model no. 908010 DV9068, equipped with programmable pressure and temperature controller. ¹H NMR spectral analysis was performed on a JEOL JNM ECX-400 P 400 MHz instrument and data were processed using a JEOL DELTA program version 4.3.6. The yield of HMF was determined by UV–Visible spectrometric technique using a UV-SPECORD 250 analytikjena spectrophotometer.

Nitrogen sorption isotherms were obtained using a Beckmann Coulter SA3100 surface area analyzer at 77 K. Prior to the measurement, the samples were degassed at 393 K for 12 h.

2.1. Preparation of TiO_2 from titanium isopropoxide and sodium alginate

Sodium alginate (1.0 g) was dissolved in 300 mL water by stirring at 80 °C; to this was added titanium isopropoxide (14 mL) at room temperature under continuous stirring. The pH of the reaction mixture was adjusted to 10 by the dropwise addition of aqueous ammonia (25%) solution. Then the reaction mixture was then divided into three parts in equal volume and stored in freeze (0 °C), at room temperature and at 60 °C in hot oven for aging for 24 h in each case. The resultant solid was collected by repeated centrifugation (8000 rpm, 10 min) and washing with distilled water. The solid was dried in oven at 80 °C for overnight 8 h and then calcined at 300 °C in furnace for 4 h. TiO₂ materials prepared at room temperature, 0 °C, and under hydrothermal (60 °C) condition were designated as TiO₂-R, TiO₂-F, and TiO₂-H, respectively.

2.2. Measurement of acid content of porous TiO₂ by temperature programmed FT IR and NH₃-TPD analyses

For the temperature programmed FT IR study, calcined sample was activated. Then 100 mg of this sample and 3 g of pyridine were taken separately in a 2 mL glass bottle and 70 mL polypropylene bottle, respectively. Then the glass bottle was kept inside the polypropylene bottle very cautiously. Here TiO₂ and pyridine were separated by glass contact and the polypropylene bottle was sealed with a cap. Then it was kept in the oven at 80 °C for 24 h. Then the temperature variation FT IR was studied with this pyridine adsorbed sample [28]. For the temperature programmed desorption (TPD) of ammonia studies, samples were activated at 300 °C and then the catalyst was cooled down to room temperature. Immediately ammonia was injected at room temperature in the absence of carrier gas flow. The temperature of the catalyst was then raised in a stepwise manner at a linear heating rate of 10°C/min. The desorption of ammonia in the temperature range 100-800 °C was analyzed by using a Micromeritics ChemiSorb 2720 containing a thermal conductivity detector.

2.3. Procedure of conversion of sugar into HMF in DMA-LiCl

In a typical experiment, a microwave tube was charged with p-mannose (25 mg), TiO₂ catalyst (10 mg) and DMA–LiCl (0.5 g, 10 wt% LiCl). The loaded microwave tube was placed in the microwave reactor. The reaction was continued for a desired time at $140 \,^{\circ}$ C. After completion of reaction for the desired time, the reaction mixture was allowed to cool to room temperature and HMF was extracted with diethyl ether. The purity of HMF was checked



Fig. 1. XRD profile of the TiO_2 samples (TiO_2-R, TiO_2-F and TiO_2-H) with indexed peaks.

by ¹H NMR spectroscopic method. The yield of HMF was measured by UV–Vis spectrophotometric technique.

2.4. Catalyst life-time study

A microwave tube was charged with D-mannose (100 mg), TiO₂-H catalyst (40 mg) and DMA–LiCl (2 g, 10 wt% LiCl). The mixture was heated for 5 min under microwave irradiation at 140 °C. After the reaction, the reaction mixture was cooled down to room temperature and filtered the catalyst. HMF component was extracted with diethyl ether. Spent catalyst was recovered, washed with distilled water and dried in oven at 80 °C for 12 h. The recovered catalyst was reused for next catalytic cycle using fresh DMA–LiCl solvent. The reusability of DMA–LiCl solvent was also tested by recycling the spent reaction mixture containing solvent and catalyst after extracting HMF with diethyl ether. Fresh solvent and TiO₂-H catalyst were not added in the later reaction.

2.5. Determination of HMF yield

The yield of HMF in the product solution was determined by UV–Visible spectrophotometric technique.

2.6. UV-Visible spectrophotometric method

The UV–Visible spectrum of pure HMF solution has a distinct peak at 284 nm with corresponding molar extinction coefficient (ε) value of $1.66 \times 10^4 \, {\rm M}^{-1} \, {\rm cm}^{-1}$. The percentage of HMF in each of the reaction product was calculated from the measured absorbance values at 284 nm and the extinction coefficient value. First, a standard HMF solution of 99% purity was analyzed for correlating the percentage of actual and calculated amount of HMF. Once a good correction was established, the extracted HMF product samples were run and the percentage of HMF yield was calculated. Repeated measurement of the same solution shows the percentage of error associated with this measurement was $\pm 3\%$.

3. Results and discussion

3.1. Characterization of porous TiO₂

The wide angle XRD patterns of the TiO_2 nanoparticles are shown in Fig. 1. This XRD result reveals that TiO_2 -H, TiO_2 -F and TiO_2 -R samples are composed of crystalline anatase phase. The crystalline planes corresponding to the peaks for anatase TiO_2 have been indexed in Fig. 1. All calcined samples show major peak at 2θ value of 25.3°, 37.8°, 48.0°, 53.7°, 54.9° and 62.5°, which corresponding to anatase (101), (004), (200), (105), (211) and (204) crystal planes (JCPDS 21-1272) [29]. The wide angle powder XRD results revealed that alginate template method produced highly stable and crystalline TiO₂ nanoparticles. Representative TEM images of porous TiO₂ nanoparticles (TiO₂-F and TiO₂-H) calcined at 300 °C are shown in Fig. 2. The HR TEM images are shown in Fig. 2(b) and (e). As seen in these figures that spherical tiny TiO₂ nanoparticle are assembled by forming self-aggregated (loose assembly) nanostructure for both the samples. Further, from the HR-TEM images, the (101) plane is quite clear in Fig. 2(b) and the planes (101) and (004) are also seen in Fig. 2(e). The selected area electron diffraction (SAED) patterns for both samples are shown in Fig. 2(c) and (f) suggested the diffraction spots for crystalline anatase TiO₂ phase. Thus XRD and TEM analyses show the phase purity and crystallinity of the TiO₂ nanoparticles.

FE SEM images (Fig. 3) of TiO₂ samples are composed of tiny spherical nanoparticles. The self-assembled structure of TiO₂ nanoparticles for samples prepared hydrothermally and at room temperature are observed from their respective FE SEM images (Fig. 3a and b). Both samples are composed of uniform tiny spherical nanoparticles and there are inter-particle voids of *ca*. 10 nm. A closer look at these SEM images revealed that porous TiO₂-F and TiO₂-R synthesized at lower temperatures have relatively smaller particle size (*ca*. 8–10 nm), whereas high temperature synthesized TiO₂-H material composed of relatively larger particles of *ca*. 15 nm size.

The mesoporosity of the TiO₂ materials was investigated from the N₂ adsorption/desorption study. The isotherms of TiO₂ materials obtained by using sodium alginate as template are shown in Fig. 4. Isotherms for TiO₂-H (Fig. 4), TiO₂-F, and TiO₂-R (ESI Fig. S4) could be classified as type IV isotherm corresponding to the mesoporous materials based on their behavior at high P/P_0 . Hydrothermally prepared TiO₂-H material shows high surface area among them. BET surface area of TiO₂-H, TiO₂-R and TiO₂-F samples were 124.0 $m^2 g^{-1}$, 74.0 $m^2 g^{-1}$ and 50.2 $m^2 g^{-1}$. Pore volumes of these samples were 0.44 ccg^{-1} , 0.21 ccg^{-1} and 0.44 ccg^{-1} , respectively. In these isotherms, between P/P_0 of 0.05–0.70 the N₂ adsorption gradually increases for all the samples. The sharp uptake in N₂ adsorption observed at higher P/P_0 (0.70–0.85) indicating the presence of large mesopore in these samples [30]. The pore size distributions of the samples, measured using the Non Local Density Functional Theory (NLDFT) method (using N₂ adsorption on silica as a reference), suggested that the TiO₂-H synthesized at 60 °C has a larger pore (ca. 11.68 nm, Fig. 4b) than TiO₂-R and TiO₂-F materials. TiO₂-F has an average pore dimension ca. 9.2 nm. Similar decrease in dimension of pores was also observed for our TiO₂ nanoparticles synthesized by using sodium salicylate as template [29].

Temperature programmed FT IR spectroscopy is one of the most important analytical tools for characterizing the Lewis acidic property of the materials using a Lewis base like pyridine as probe molecule. From Fig. 5 and ESI Fig. S5, it is clearly observed that all the pyridine adsorbed mesoporous TiO₂ materials show two characteristic bands at 1587 and 1443 cm⁻¹. The band at 1443 cm⁻¹ could be attributed to the adsorbed pyridine at the Lewis acid site [29] and with increase in desorption temperature this band showed slow decrease in intensity due to removal of pyridine from the TiO₂ surface. This result suggested the presence of considerably strong Lewis acid site in our self-assembled porous TiO₂ nanoparticles. From the NH₃-TPD study, we measured quantitatively the surface acidity of the porous materials. The NH₃-TPD results of our porous TiO₂ samples are shown in Table 1. All three porous TiO₂ materials possess three types of acidic sites: weak, medium and strong [31,32]. As seen from the table that surface acidity decreases in the order TiO_2 -R > TiO_2 -H > TiO_2 -F. Thus, although the hydrothermally



Fig. 2. TEM image of typical nanostructure of TiO₂-F (a), HR-TEM images of typical nanostructure of TiO₂-F showing (101) crystalline planes (b), selected area electron diffraction (SAED) pattern of the calcined mesoporous TiO₂-F (c) and the nanostructure of hydrothermally synthesized materials TiO₂-H (d), HR-TEM images of typical nanostructure of TiO₂-H showing (101) and (004) crystalline planes (e), selected area electron diffraction (SAED) pattern of the calcined mesoporous TiO₂-H (f).

prepared porous TiO₂-H material has highest surface area, strong acid sites of this sample are lower.

3.2. Catalytic activity of porous TiO₂

The catalytic activity of the alginate templated porous TiO₂ nanoparticulate materials was investigated for the conversion of mannose, lactose and galactose into HMF at varying reaction conditions. As shown in Table 2, dehydration reaction of 25 mg mannose with 10 mg TiO₂-H catalyst produced 29% HMF under microwave irradiation for 0.5 min in DMA-LiCl medium at 140 °C. The yield of HMF increased from 29% to 42% upon continuing the same reaction for 2 min. A further increase of reaction time from 2 min to 5 min showed only 2% improvement in HMF yield. At lower temperature (120 °C), the yield of HMF decreased from 42% to 35%. The variation of TiO₂-H catalyst loading from 2 mg to 20 mg for the dehydration of fixed amount of mannose (25 mg) showed an improvement in HMF yields from 27% to 45%. A blank experiment without catalyst resulted in only 9% HMF in 2 min as compared to 36% HMF with 5 mg catalyst for mannose dehydration reaction. Once the catalytic activity of TiO₂-H material in DMA-LiCl solvent was realized, we have tested environmentally benign water-MIBK biphasic solvent. The catalyst was also effective in water-MIBK solvent, giving 26% HMF from mannose in 5 min at 120 °C. The yield of HMF increased from 12% to 26% upon increasing the reaction time from 0.5 min to 5 min

followed by almost a plateau up to 15 min. A control experiment without catalyst resulted in only 4% HMF in 5 min as compared to 26% with catalyst, confirming the true effectiveness of the catalyst. Commercial anatase TiO₂ was ineffective to catalyze the dehydration of mannose (yield less than 2%). This anatase TiO₂ sample has BET surface area and acidity of $48 \text{ m}^2 \text{ g}^{-1}$ and 0.01 mmol/g [33], which are much lower than the biopolymer template porous TiO₂ samples. This result suggests that mesoporosity together with strong surface acidic sites generated through biopolymer templating pathway are crucial for the catalytic efficiency. The higher yield of HMF in DMA-LiCl solvent than that in water-MIBK can be interpreted by facile hydrolysis of lactose in DMA-LiCl due to the presence of highly ion-paired chloride ions in DMA-LiCl. Previous literature report has shown moderate HMF yields from mannose dehydration using 6 mol% CrCl₂ catalysts in organic or ionic liquid solvent solvents [34]. In the present reaction, we avoided using chromium halide catalyst due to their toxicity and environmental pollution. Nevertheless, the investigated solid acid catalyst showed promising results in environmentally benign solvent.

Lactose is another potential substrate for HMF synthesis. However, due to the presence of a large number of hydroxyl groups, lactose has lower solubility than mannose. It is reported that only 20% HMF yield was obtained from the lactose dehydration reaction with chromium chloride/lithium halide/6 mol% H₂SO₄ catalytic systems [34]. Given the toxicity issue of chromium salt and

Table 1		
Surface	acidity	diffe

ladie I		
Surface acidity differ	ent porous TiO ₂ samples	estimated from NH ₃ -TPD studies

Sample name	Total acidity (mmol/g)	Weak acidity (mmol/g)	Medium acidity (mmol/g)	Strong acidity (mmol/g)
TiO ₂ -R	1.216	0.480	0.218	0.518
TiO ₂ -F	0.95	0.353	0.156	0.441
TiO ₂ -H	1.11	0.427	0.267	0.416

Table 2

HMF synthesis from D-mannose, D-galactose and lactose with TiO₂ obtain via alginate templating route.

Entry	Substrate (mg)	Catalyst (mg)	Solvent (0.5 g)	<i>T</i> (°C)	t (min)	HMF yield (%)
1	Mannose, 25	TiO ₂ -H, 10	DMA-LiCl	140	0.5	29
2	Mannose, 25	TiO ₂ -H, 10	DMA-LiCl	140	2	42
3	Mannose, 25	TiO ₂ -H, 10	DMA-LiCl	140	5	44
4	Mannose, 25	TiO ₂ -H, 10	DMA-LiCl	120	5	35
5	Mannose, 25	TiO ₂ -H, 2	DMA-LiCl	140	2	27
6	Mannose, 25	TiO ₂ -H, 5	DMA-LiCl	140	2	36
7	Mannose, 25	TiO ₂ -H, 20	DMA-LiCl	140	2	45
8	Mannose, 25	_	DMA-LiCl	140	2	9
9	Mannose, 25	_	Water-MIBK	120	5	4
10	Mannose, 25	TiO ₂ -H, 10	Water-MIBK	120	0.5	12
11	Mannose, 25	TiO ₂ -H, 10	Water-MIBK	120	2	18
12	Mannose, 25	TiO ₂ -H, 10	Water-MIBK	120	5	26
13	Mannose, 25	TiO ₂ -H, 10	Water-MIBK	120	10	29
14	Mannose, 25	TiO ₂ -H, 10	Water-MIBK	120	15	27
15	Lactose, 25	TiO ₂ -H, 10	DMA-LiCl	140	5	35
16	Lactose, 25	TiO ₂ -H, 10	Water-MIBK	120	5	11
17	Lactose, 25	TiO ₂ -H, 10	Water-MIBK	120	10	14
18	Galactose, 25	TiO ₂ -H, 10	DMA-LiCl	140	5	27
19	Galactose, 25	TiO ₂ -H, 10	Water-MIBK	120	5	6
20	Galactose, 25	TiO ₂ -H, 10	Water-MIBK	120	10	10

DMA-LiCl contains 10 wt% LiCl; Water:MIBK = 1:1 (v/v).

hazardousness of H_2SO_4 , the present work of lactose dehydration reaction was carried out using mesoporous TiO_2 -H catalyst in water-MIBK and DMA-LiCl solvents. DMA-LiCl solvent is known to form DMA•Li⁺ macrocations, resulting in highly ion-paired chloride ions [26]. When lactose (25 mg) dehydration reaction was carried out using 10 mg TiO_2-H catalyst in DMA-LiCl (10 wt% LiCl) solvent at 140 °C for 5 min, 35% HMF yield was obtained. Under comparable reaction conditions, lactose dehydration with TiO_2 -H catalyst produced 11% less HMF than that obtained from mannose. The involvement of an additional hydrolysis step in lactose dehydration process accounted for lower HMF yield from lactose. When lactose dehydration was carried out in water–MIBK solvent, a significantly less HMF yield was recorded; 11% from lactose versus 26% from mannose. The yield slightly improved to 14% upon



Fig. 3. FE-SEM image of calcined (300 $^\circ$ C) mesoporous TiO_2 samples prepared under hydrothermal condition and at low temperature: (a) TiO_2-H and (b) TiO_2-F.



Fig. 4. N₂ adsorption (\bullet)-desorption (o) isotherm of the calcined TiO₂-H (a) measured at 77 K and the representative pore size distribution using NLDFT method is shown (b).



Fig. 5. (a) FT IR spectra of mesoporous TiO₂-H (298 K) and pyridine desorbed TiO₂ sample at (298 K, 323 K, 423 K, and 523 K).



Scheme 3. Isomerization of galactose to tagatose and further dehydration to HMF.

continuing the reaction for 10 min. The scope of present investigation was further extended for galactose substrate. In the case of galactose, its isomerization to ketose results in the formation of tagatose intermediate [35], the C-4 epimer of fructose (Scheme 3). Inefficient dehydration of tagatose intermediate to HMF is the reason of low HMF yields from galactose [35]. The dehydration reactions of galactose with TiO_2 -H catalyst were carried out in both DMA-LiCl and water–MIBK solvents. As shown in Table 1, HMF yields from galactose was about 4–8% lower than that obtained from lactose dehydration under comparable reaction conditions. A comparison of HMF yields from all substrates in both solvents is pictorially shown in Fig. 6.

3.3. Effectiveness of TiO_2 NPs prepared under different synthesis method

The effectiveness of the TiO_2 NPs prepared under different synthesis conditions was examined as acid catalysts for the



Fig. 6. A comparison of HMF yields obtained from dehydration reactions of mannose, lactose and galactose using TiO₂-H catalyst.



Fig. 7. A comparison of the catalytic activity of TiO_2 NPs prepared under three synthesis conditions for the synthesis of HMF from D-mannose. (For interpretation of the references to color in the text, the reader is referred to the web version of the article.)

conversion of mannose to HMF in both DMA-LiCl and water-MIBK under microwave assisted heating. All reactions in DMA-LiCl and water-MIBK solvents were carried out at 140 °C and 120 °C, respectively. The effectiveness of three catalysts (TiO₂-H, TiO₂-R, TiO₂-F), in terms of HMF yields, is compared in Fig. 7. As seen, the effectiveness of all three catalysts was comparable in both solvents. In the case of DMA-LiCl solvent mediated reactions, the yields were in the range of 42–44% (red bars, Fig. 7). Further, TiO₂-H sample possess lower concentration of strong Lewis acid sites although it possess highest surface area among these three samples. If we see the HMF yields under similar reaction conditions this hydrothermally prepared porous TiO₂ showed marginally better catalytic activity than other two samples. Although, this TiO₂ sample has higher surface area but surface acidity, specially strong acid sites, which could be actually responsible for catalytic conversion of the utilized sugars to HMF is lower than the materials synthesized at room temperature and at 0 °C (Table 1). Apart from this, TiO₂-F and TiO₂-R samples synthesized at lower temperature have relatively smaller particle size (\sim 8–10 nm), whereas that for porous TiO₂-H is \sim 15 nm. Thus the advantage of high surface area of porous TiO₂-H could have been nullified by the bigger particle size and relatively smaller number of strong acid sites, and thus it did not show much improvement in HMF yield over other porous TiO₂ samples.

3.4. Catalyst recyclability

The reusability of the mesoporous TiO₂-H catalyst was examined for D-mannose dehydration reaction in DMA–LiCl by recycling the spent catalyst. Prior to recycle the catalyst for the next run, the reaction mixture was filtered and HMF component was extracted from the reaction mixture with diethyl ether. The solid TiO₂-H catalyst was recovered by filtration, washed with distilled water and dried. The catalyst was reused for four catalytic cycles. After fourth cycle, the loss of catalyst activity in HMF yields was about 6% (Fig. 8, Table S1).

From the perspective of renewable chemistry, recyclability of both catalyst and solvent is highly desirable. In order to address the practical application of the current method of HMF synthesis, both catalyst and DMA–LiCl solvent were recycled for mannose (500 mg) dehydration reaction with TiO₂-H catalyst (50 mg) under conventional oil-bath heating conditions at 140 °C. The reaction produced 39% HMF in 45 min in the first cycle (Table S2). In the consecutive second and third cycles, the reaction produced 34% and 32% HMF, respectively, which are much lower than those under microwave heating conditions. Although DMA–LiCl solvent



Fig. 8. Recyclability study of TiO₂-H catalyst for D-mannose dehydration reaction. Reaction conditions: D-mannose = 100 mg, TiO₂-H = 40 mg, T = 140 °C, and t = 5 min.

perhaps mixed with resulting water from the dehydration reaction, the loss in activity of the used catalyst in spent solvent was not significant, in terms of HMF yield.

4. Conclusion

In conclusion, we have successfully prepared porous TiO_2 nanoparticulate catalysts via biopolymer alginate templating pathway under hydrothermal conditions and compared the structural characteristics of the TiO_2 materials obtained from the processes. Three different TiO_2 catalysts have been employed to catalyze the transformation of unutilized sugar derivatives, namely D-mannose, D-galactose, and lactose to useful platform chemical HMF in DMA-LiCl under microwave irradiation at $140 \,^{\circ}$ C, which produced maximum 44% yield. The hydrothermally prepared TiO_2 showed considerable mesoporosity. Substrate screening in the catalytic studies revealed that D-mannose is the best candidate to produce HMF in maximum yield. TiO_2 -H retains its catalytic activity for four cycles suggesting potential of our TiO_2 nanomaterials in the biomass conversion.

Supporting information

Recycling results of the conversion of carbohydrates to HMF under microwave and oil bath heating conditions (Tables S1–S2), representative ¹H and ¹³C NMR spectra, UV–Vis spectrum and N₂ sorption isotherms, pyridine adsorbed FT IR spectra (Figs. S1–S5) have been provided.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2012.06.002.

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