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Microwave assisted rapid conversion of carbohydrates into 5-hydroxymethylfurfural catalyzed by mesoporous TiO₂ nanoparticles

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ABSTRACT

Energy efficient and sustainable process for the production of 5-hydroxymethylfurfural (HMF) from carbohydrates is highly demanding. Here, direct conversion of carbohydrates into HMF has been investigated over self-assembled mesoporous TiO₂ nanoparticles (NPs) catalyst. Monosachharides D-fructose and D-glucose, disaccharides sucrose, maltose, cellobiose were successfully converted into HMF with variable yields in both aqueous and organic mediums under microwave-assisted heating conditions. The effects of solvent polarity, microwave absorbing ability, catalyst loading, reaction time, and substrate variations on the HMF yields have been studied. Pyridine-IR and NH₃-TPD analyses confirmed the presence of Lewis acidic sites, whereas N₂ sorption analysis revealed high BET surface area for the self-assembled mesoporous TiO₂ nanomaterials synthesized by using sodium salicylate as template. High surface area, Lewis acidity and uniform nanosphere-like particle morphology are responsible for high catalytic activity in the dehydration of carbohydrate substrates over this mesoporous TiO₂ nanomaterial, whereas commercially available TiO₂ is almost inactive for this dehydration reaction under similar conditions. The higher microwave energy absorbing ability (tan δ) of the DMSO and NMP resulted in higher HMF yield in organic solvents than water. Catalyst life-time analysis suggested that mesoporous TiO₂ NPs catalysts can be recycled for four catalytic cycles without appreciable loss of its catalytic activity.

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1. Introduction

Today the gap between the supply and demand of energy has reached into an alarming level, which motivated the researchers for new synthetic route and process development for utilizing renewable feedstock for chemicals and liquid fuels in order to reduce our dependence on petroleum sources and rising limit of CO_2 level in the atmosphere [1,2]. One compound that has been under particular scrutiny as a future platform chemical is 5-hydroxymethylfurfural (HMF), which is promising because of its identical carbon skeleton to those in most abundant cellulose and biomass-derived carbohydrates [3,4]. HMF is primarily considered a starting material for liquid transportation fuels [5,6] and polyester building block chemicals [7,8]. In this context a rapid progress has been witnessed in developing catalytic processes to convert biomass and carbohydrates into HMF [9–15]. More notably, multiple conditions are now established to enable dehydration of p-fructose to HMF in acidic water [9], sub- and supercritical water, water-acetone mixed solvents [10,11], organic solvents [12,13], multicomponent mixed solvents [14], and ionic liquids in combination with metal catalysts [15]. Biphasic continuous systems using porous solid acid catalysts and specially nanocatalysts have great potential in this context [16–19].

Among the approaches for the efficient synthesis of HMF from sugar derivatives, heterogeneous acid catalyst plays an important role. In the past, ion-exchange resin-activated carbon in water and Dowex-type ion-exchange resin in dimethyl sulfoxide (DMSO) were used as catalysts [20]. High conversion and selectivity of HMF has been reported in biphasic solvents using ion exchange resin under microwave-assisted heating conditions [21]. Microwave assisted dehydration of fructose with Amberlyst-15 catalyst in ionic liquid [BMIM][C1], or its combination with hydrotalcite exhibited high HMF yields [22–24].

Syntheses of HMF from hexoses in the presence of solid acid catalysts are known today [25]. ZrO₂ and TiO₂ catalyzed conversion of D-fructose and D-glucose into HMF in aqueous medium under microwave irradiation at 200 °C produced moderate HMF yields (38.1% and 18.6% respectively) [26,27]. Sulphated zirconia

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Scheme 1. Microwave-assisted dehydration of D-fructose into HMF catalyzed by self-assembled mesoporous TiO₂ NPs.

 (SO_4^{2-}/ZrO_2) was found to be effective catalysts for the HMF production from fructose under microwave heating at 180–200 °C [13]. Mixed metal oxide TiO₂–ZrO₂ under hot compressed water (HCW) acts as a good catalyst for glucose dehydration in sub-critical water [28].

Despite recent developments in heterogeneous catalysts for dehydration of carbohydrates to HMF, it remains a challenge to develop a more energy efficient heterogeneous catalyst and process for efficient conversion of carbohydrates to HMF. Porous TiO₂ with high surface area and unique particle morphology, which can be synthesized through the templating pathways [29,30] can be an efficient solid acid catalyst in this context as surface Lewis acidity together with high surface area could play crucial role in this dehydration reaction. Herein, we first report the use of selfassembled mesoporous titania nanoparticles synthesized by using sodium salicylate as template in efficient catalytic dehydration of carbohydrates into HMF under microwave-assisted heating in various solvents such as water, water–MIBK (methylisobutyl ketone), NMP (*N*-methylpyrollidone), and DMSO (dimethyl sulfoxide) in morderate to good yield in very short reaction time (Scheme 1).

2. Experimental

Fructose, glucose, sucrose, cellobiose, and maltose monohydrate were purchased from Sigma–Aldrich and were used without further purification. MIBK, DMSO and NMP were purchased from Spectrochem, India. Self-assembled mesoporous TiO₂ was prepared by following the literature procedure using sodium salicylate as template [30]. As-synthesized mesoporous TiO₂ samples were calcined at 500 °C for 6 h to remove the template molecules and this sample was used for all the characterizations except the TPD analysis, where the sample was activated at 800 °C for 3 h before ammonia adsorption. Unless otherwise stated, freshly distilled water was used as aqueous phase for reactions in aqueous and aqueous–organic phase.

The catalytic reactions for carbohydrate substrates dehydration to 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. HMF yields were determined by using a UV-visible spectrophotometer (UV-SPECORD 250 analytikjena spectrometer) monitoring the absorbance of the product solution at 284 nm (corresponding to λ_{max} of HMF with $\varepsilon = 1.66 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). A JEOL JEM 6700F field emission scanning electron microscope was used for the determination of the particle morphology of the TiO₂ NPs. Fourier transform infrared (FT IR) spectra of the pyridine adsorbed samples were recorded by using a Perkin Elmer Spectrum 100 spectrophotometer. For the temperature programmed desorption (TPD) of ammonia studies, sample was activated and then ammonia was injected at room temperature in the absence of carrier gas flow. The temperature was then raised in a stepwise manner at a linear heating rate of 10°C/min. The desorbed ammonia in the temperature range 100-800 °C was analyzed by using a Micromeritics ChemiSorb 2720 attached with a thermal conductivity detector.

In a typical microwave-assisted reaction, desired amount of carbohydrate substrates and catalyst were charged in a microwave tube containing of 2 mL solvent. The tube was placed in the microwave reactor. The microwave power was set to 300 W. Desired temperatures and time was set. After the reaction, the tube was allowed to cool to room temperature. The reaction mixture was then analyzed (after separating the reactant) by using NMR and spectrophotometric techniques.

The recycling efficiency of the catalyst was determined by using dehydration of fructose as a representative reaction. In this study, 5 wt% fructose solution in water was mixed with 100 mg mesoporous TiO₂ sample in a microwave tube. The tube was placed in the microwave reactor and the mixture was heated for 5 min at 120 °C using 300W microwave power. After the reaction, the tube was cooled down to room temperature and liquid was collected by decanting the tube. The solid residue left in the tube was collected and washed several times with distilled water and dried in oven for 3 h at 100 °C. The dried catalyst was re-used for three more cycles by following the above method and HMF yields were determined from each run. The yield of HMF was determined by both ¹H NMR and UV-visible spectrophotometric techniques. For ¹H NMR spectroscopic analysis, HMF was extracted from the reaction mixture with diethyl ether. Pale yellow oily HMF was obtained after removing the solvent in vacuum at room temperature.

2.1. ¹H NMR method

For quantifying the yield of HMF using ¹H NMR spectroscopic technique, known concentration of mesitylene (internal standard) was added into the HMF product solution in DMSO- d_6 . The percentage of HMF yield was calculated by using the integrated values of the aldehyde proton (δ = 9.58 ppm) of HMF and three aromatic ring protons of mesitylene (δ = 6.79 ppm). First, standard HMF solution of 99% purity was analyzed for correlating the percentage of actual and calculated amount of HMF. Once good correction was established, extracted HMF product samples were run and the percentage of HMF yield was calculated.

2.2. UV-visible spectrophotometric method

The UV–visible spectrum of pure HMF solution has a distinct peak at 284 nm with corresponding extinction coefficient (ε) value of 1.66 × 10⁴ M⁻¹ cm⁻¹. The yield of HMF was determined by measuring the absorbance of HMF product solution at 284 nm and the extinction coefficient value. Repeated measurement of the same solution showed the percentage of error associated with this measurement was ±0.3%. The yield of HMF obtained from two different methods (¹H NMR and UV–visible) for the same reaction product agreed very well and the result was within ±5% error.

3. Results and discussion

Self-assembly of tiny mesoporous TiO₂ nanospheres used as catalyst was prepared utilizing sodium salicylate (SS) as a template by following the literature procedure [30]. This material is composed of very tiny uniform spherical nanoparticles of 12–20 nm in size. N₂ sorption analysis revealed high surface area ($326 \text{ m}^2 \text{ g}^{-1}$) and large pore volume ($0.3 \text{ cm}^3 \text{ g}^{-1}$, not shown). FT IR spectra of the pyridine adsorbed mesoporous TiO₂ NPs show two characteristic bands at 1588 and 1439 cm⁻¹ (Fig. 1). The band at 1439 cm⁻¹ could be attributed to the adsorbed pyridine at the Lewis acid site (PyL) [31,32]. This band showed no sign to disappear with increase in the desorption temperature. This result suggested the presence of



Fig. 1. FT IR spectra of mesoporous TiO_2 NPs (a) and pyridine desorbed samples at 523 K (b), 423 K (c), 323 K (d) and 298 K (e).

considerably strong Lewis acid sites in our mesoporous TiO₂ NPs. Further, in Fig. 2 we have plotted the temperature programmed desorption of NH₃. As seen from Fig. 2 that the desorption temperature range is very high (400–800 °C with peaks at *ca*. 650 and 744 °C). Total acidity of this mesoporous TiO₂ NPs corresponds to *ca*. 0.4 mmol g⁻¹. Hence this strong surface acidity of the self-assembled TiO₂ NPs could be effectively utilized in the dehydration of carbohydrates.

Several solid metal oxides such as nanoparticulate of ceria (CeO₂), commercial alumina (Al₂O₃), commercial SiO₂, commercial anatase TiO_2 , and mesoporous TiO_2 nanoparticles synthesized here were screened for the catalytic dehydration of fructose in aqueous medium under identical microwave-assisted heating conditions. Among these metal oxides, except our self-assembled mesoporous TiO₂ NPs, others can rarely be considered as catalysts for HMF production in aqueous or organic medium. As shown in Table 1, in the presence of other metal oxides as catalyst only 1.0–3.4% HMF have been produced (reaction conditions: fructose = 100 mg, catalyst = 50 mg, $T = 120 \circ C$, reaction time = 5 min and solvent = water). Commercial anatase TiO₂ was also ineffective to catalyze the dehydration of fructose, suggesting the nanostructure of our mesoporous TiO₂ NPs plays crucial role in this catalytic reaction. In contrast to the catalytic activity of the metal oxides listed in Table 1, mesoporous TiO₂ nanoparticulate material with



Fig. 2. Temperature programmed desorption of ammonia over mesoporous TiO₂ nanoparticles.

Table 1

Catalytic activity of various metal oxides in the dehydration reaction under MW conditions.

Entry	Metal oxides	Loading (mg)	HMF yield (%)
1	CeO ₂ NPs (6-10 nm)	50	1.0
2	Al ₂ O ₃ (commercial)	50	1.8
3	TiO ₂ (commercial)	50	3.4
4	SiO ₂ (commercial)	50	1.2

Fructose = 100 mg; metal oxides = 50 mg; $T = 120 \circ C$; solvent = water; $t = 5 \min$.

well-defined nanosphere like particle morphology [see the SEM images of the reused catalysts below] catalyzed the fructose dehydration and produced 34.3% HMF in water under microwave-assisted heating at 120 °C in 5 min (Table 2, entry 2). To test this catalytic effectiveness further, control experiments were performed for fructose dehydration without mesoporous TiO₂ catalyst, which produced only trace amount of HMF under identical reaction conditions (Table 2, entry 1). Thus, high yield of HMF in the presence our prepared mesoporous TiO₂ nanoparticulate material again validated its catalytic effectiveness as discussed above.

More experiments were designed for optimizing the reaction conditions and HMF yields at variable substrate to catalyst ratios and in different solvents. As shown in Table 2, these experiments produced variable yields of HMF in the range of 25-54%. These results clearly indicates that mesoporous TiO₂ is an effective catalyst for HMF synthesis from fructose. In an earlier report, anatase-TiO₂ catalyzed fructose dehydration reaction claimed to produce 33.5% HMF at 200 °C in hot compressed water [26,27]. It is to point out that such a high temperature conversion reported by Oi et al. [27] is energy consuming and not sustainable. It is pertinent to mention that, from the present study maximum 36% HMF yield was achieved in aqueous phase using mesoporous TiO₂ catalyst at a considerably lower temperature (120 °C). This justifies that the microwave-assisted process described herein is more sustainable. To our knowledge, this is the first report of using mesoporous TiO₂ material as an effective catalyst for the rapid conversion of carbohydrates into HMF under mild microwave assisted heating conditions.

The promising catalytic activity of the mesoporous TiO₂ NPs for fructose dehydration has prompted us to test the effectiveness of this catalyst for HMF synthesis from glucose and other disaccharides such as sucrose, cellobiose and maltose in aqueous and in organic solvents under microwave heating. The reaction conditions of glucose, sucrose, cellobiose and maltose dehydration reactions and corresponding HMF yields in different solvents are summarized in Table 3. Under comparable reaction conditions and 2:1 weight ratio of glucose to TiO₂, 22.1% and 35.5% HMF yields were achieved from glucose dehydration in water and DMSO, respectively. The similar reactions performed in NMP and water-MIBK biphasic solvents produced 29.6% and 25.9% HMF, respectively. The data presented in Table 3 shows a variation in HMF yields (%) as a function of the polarity of the solvents for the glucose conversion to HMF. Under identical reaction conditions, sucrose dehydration reaction produced less HMF than that of glucose dehydration reaction. Using 1:1 substrate to catalyst weight ratio, the sucrose dehydration reaction produced 15.1% and 20.5% HMF in water and DMSO, respectively. The NMP and water-MIBK solvents mediated sucrose dehydration reactions produced 14.9% and 13.9% HMF. The cellobiose dehydration reaction produced 14.5% and 18.7% HMF in water and DMSO, respectively. An earlier report claimed 41% HMF yield from cellobiose using a biphasic [BMIM]Cl-MIBK solvents and CrCl₃ catalyst [33]. This difference in HMF yields can be attributed to the strong Lewis acidic nature of the chromium chloride catalyst in comparison to the surface acidity of the mesoporous TiO₂ catalyst. Moreover, HMF yields in ionic liquids are superior to that in water or

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Microwave-assisted	l fructose	dehydration	to HMF	with meso	porous TiO ₂	catalyst. ^a
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Entry	Fructose (mg)	TiO ₂ NPs (mg)	Solvent (mL)	t(min)	HMF yield (%)		
					UV-vis	NMR	Isolated
1	100	-	Water (2)	5	0.8		
2	100	100	Water (2)	5	34.3	32.3	31.9
3	100	50	Water (2)	5	33.5	32.7	32.8
4	100	25	Water (2)	5	30.4	29.5	30.0
5	100	10	Water (2)	5	25.6		
6	50	25	Water (1)	2	27.2		
7	50	25	Water (1)	10	35.0	33.5	
8	50	25	Water (1)	15	36.3	34.9	
9	50	50	DMSO(1)	5	54.1	52.6	53.2
10	100	50	DMSO(2)	5	53.4	51.4	51.7
11	100	25	DMSO(2)	5	50.8	49.1	
12	100	10	DMSO(2)	5	48.3	47.3	
13	100	5	DMSO(2)	5	40.5		
14	50	25	DMSO(1)	2	41.8 ^b		
15	50	25	DMSO(1)	10	53.7		
16	50	25	DMSO(1)	15	54.0	52.8	53.2
17	50	-	DMSO(1)	5	20.3		
18	150	75	Water-MIBK (1/2)	5	40.2	38.0	38.4
19	50	25	NMP(1)	5	36.5		
20	50	25	Acetonitrile (1)	5	29.3		
21	100	10	Water (2)	10	27.4		
22	100	10	Water (2)	20	27.9		
23 ^c	100	25	DMSO(2)	5	49.1		
24 ^d	100	25	DMSO (2)	5	48.3		

T = 120 °C (water), 130 °C (water/MIBK), 120 °C (acetonitrile), 140 °C (NMP and DMSO).

^a Microwave power 300 W.

^b Fructose conversion was 61.0%.

^c Microwave power 100 W.

^d Microwave power 200 W.

DMSO. When maltose monohydrate was used as a substrate, HMF yields were slightly lower than that obtained from other two disaccharides, cellobiose and sucrose. In case of DMSO solvent mediated reaction, the slight difference in HMF yields from maltose can be explained due to the presence of water of crystallization associated with the maltose molecular structure, which could inhibit its dehydration into HMF.

Microwave-assisted HMF synthesis from fructose using mesoporous TiO₂ catalyst has been studied by varying catalyst concentrations for optimizing the reaction conditions and maximizing the HMF yield. A plot showing the catalyst loadings *versus* HMF yield (%) is shown in Fig. 3. When fructose solution (100 mg in 2 mL water) was treated with 5 mg of TiO₂ for 5 min under microwave-assisted heating at 120 °C, an HMF yield of 19.0% was obtained. To improve the HMF yield, catalyst loading was increased to 10 mg for same fructose concentration (100 mg in 2 mL water), which resulted an increase in HMF yield to 25.6%. Further increase in catalyst loading to 25 mg resulted slight improvement in HMF yield to 28.4%. To test the effect of more catalyst loading, 50 mg and 100 mg of mesoporous TiO_2 were used, which produced 33.5% and 34.3% HMF, respectively. Further increase in catalyst loading beyond 1:1 weight ratio of substrate to catalyst showed no significant increase in HMF yield. The DMSO solvent mediated fructose dehydration reaction showed similar trend of HMF yield on catalyst loading. Maximum 54.1% HMF was obtained in DMSO solvent mediated reaction in comparison to 34.3% in water.

Since, maximum HMF yields from fructose were obtained with a catalyst/substrate ratio of 1:1, results with a low loading of catalyst (catalyst to substrate ratio 1/10) would be more favourable to demonstrate the catalytic activity against run time. The additional experiments using fructose as substrate with 1/10 catalyst–substrate ratio in water showed a small increase in HMF yield from 25.6% to 27.9% (Table 2, entry 5, 21, and 22) upon increasing the run time of reaction from 5 min to 20 min.

Table 3

Results of glucose, sucrose, maltose, and cellobiose dehydration to HMF catalyzed by mesoporous TiO₂ NPs.

Entry	Substrate (mg)	TiO ₂ NPs (mg)	Solvent (mL)	<i>T</i> (°C)	<i>t</i> (min)	HMF yield (%)	
1	Glucose (100)	50	Water (2)	120	2	22.1	
2	Glucose (100)	50	DMSO(2)	140	5	35.5	
3	Glucose (50)	50	DMSO(1)	140	5	37.2	
4	Glucose (50)	50	NMP(1)	140	5	29.6	
5	Glucose (150)	75	Water/MIBK (1/2)	130	5	25.9	
6	Glucose (50)	50	Water (1)	120	5	24.8	
7	Sucrose (50)	50	Water (1)	120	10	15.1	
8	Sucrose (100)	50	DMSO(2)	140	5	20.5	
9	Sucrose (100)	50	DMSO(1)	140	5	21.0	
10	Sucrose (50)	50	NMP(1)	140	5	12.0	
11	Sucrose (150)	75	Water-MIBK (1/2)	130	5	14.9	
12	Sucrose (50)	50	Water (1)	120	5	13.9	
13	Cellobiose (100)	100	Water (2)	120	5	14.5	
14	Cellobiose (100)	100	DMSO(2)	140	5	18.7	
15	Maltose (100)	100	Water (2)	120	5	10.7	
16	Maltose (100)	100	DMSO(2)	140	5	14.1	



Fig. 3. The effect of HMF yield on catalyst loading for the microwave assisted fructose dehydration in water and DMSO. Reaction conditions: fructose = 100 mg, TiO₂ = 5-100 mg, T = $120 \degree \text{C}$, t = $5 \degree \text{min}$.

The reaction time for the dehydration of carbohydrates was varied to optimize the HMF yield. The yield of HMF was monitored as a function of reaction time from 2 min to 15 min for a set of experiments with variable catalyst to substrate ratios in aqueous and DMSO medium under microwave-assisted heating conditions. As plotted in Fig. 4, maximum yield of HMF recorded within 5 min for most of the reaction. When these reactions were continued for a longer period of time, ca. 15 min, no significant increase in HMF yield was observed. The similar trend in HMF yield was recorded at different catalyst to substrate ratios as well. Curves a and b in Fig. 4 represents the dehydration of fructose at 2:1 substrate to catalyst ratio in water and DMSO, respectively. Curve b shows the formation of 52.9% HMF in 5 min in DMSO. Extending the reaction time to 15 min resulted only 1% increase in HMF yield. In aqueous media, 32.1% HMF was obtained in 5 min reaction time which increased to 36.3% in 15 min. An increase in HMF yield was also noted for the conversion of glucose and sucrose in water and DMSO under essentially identical reaction conditions (Fig. 4, curves c-e and f-h) upon



Fig. 4. Results of carbohydrate dehydration to HMF with TiO₂ NPs catalysts at various substrates to catalyst ratios in water at 120 °C. (unless otherwise mentioned.) Reaction conditions: (a) fructose: TiO₂ = 2:1; (b) fructose: TiO₂ = 1:2, DMSO, 140 °C; (c) glucose: TiO₂ = 1:1; (d) glucose: TiO₂ = 1:2; (e) glucose: TiO₂ = 1:4; (f) sucrose: TiO₂ = 1:1; (g) sucrose: TiO₂ = 1:2; (h) sucrose: TiO₂ = 1:4.



Fig. 5. Results of TiO₂ NPs catalyzed conversion of fructose, glucose, and sucrose to HMF in different solvents. Reaction conditions: substrate = 100 mg, TiO₂ = 100 mg, $T = 120 \degree C$, t = 5 min.

continuing the reaction for a longer time. The results suggest that the kinetics of HMF formation is rapid in initial 2 min reaction time followed by a slower rate of reaction.

Microwave-assisted dehydration reaction of sugar substrates (fructose, glucose, sucrose, cellobiose, and maltose) were carried out in aqueous, biphasic aqueous-MIBK, NMP, and DMSO medium. Details of the reaction conditions and corresponding HMF yields are summarized in Tables 2 and 3. Under comparable reaction conditions, mesoporous TiO₂ catalyzed fructose dehydration in water, NMP, water–MIBK, and DMSO produced 34.3%, 36.5%, 40.2%, 54.1% HMF, respectively. Similar trend of increased HMF yields were observed for glucose and sucrose as substrates. The higher yield of HMF obtained in DMSO is attributed to the large tangent (tan δ) value of DMSO (0.825) than that of water (0.123) and NMP (0.275). The higher tan δ value of DMSO corresponds to its higher microwave energy absorbing ability than that of water [34]. In DMSO, more electromagnetic energy is converted into heat energy at a given frequency and temperature which resulted to improved



Fig. 6. HMF yield *versus* reusability of the TiO₂ catalyst in water and DMSO for microwave-assisted fructose dehydration reaction. Reaction conditions: fructose = 100 mg, TiO₂ = 100 mg, T = 120 °C, t = 5 min, water or DMSO = 2 mL.



Fig. 7. The FE-SEM images of mesoporous TiO_2 nanospheres after first (a) and fourth (b) catalytic cycles for the microwave assisted dehydration of fructose.

HMF yield in comparison to that of NMP and water. The results of HMF yields (%) as a function of different solvents is shown in Fig. 5. The higher yield of HMF in water-MIBK biphasic solvent than that in water is due to the thermodynamic phenomenon of the biphasic solvent in which HMF can easily accumulates in the organic phase after its formation in aqueous phase, and thereby drives the dehydration reaction equilibrium towards the HMF side. Maximum HMF yield (54.1%) from fructose was obtained over mesoporous TiO₂ catalyst in DMSO likely due to its high microwave absorption ability $(\tan \delta)$. To study the direct influence of the microwave energy on the catalytic performances of TiO₂, fructose dehydration process in DMSO was carried out by varying microwave power at 100, 200, and 300 W independently with a 4:1 fructose to catalyst ratio for 5 min at 140 °C. No significant difference in HMF yield (Table 2, entry 11, 23, and 24) was evident upon varying microwave power. These results demonstrates that minimum 100W microwave energy to be sufficient for the significant reaction progression using TiO₂ catalyst as observed in the case of HCl-catalyzed microwave-assisted fructose dehydration in aqueous media [9].



Fig. 8. Comparative HMF yields obtained from a range of carbohydrate substrates from TiO_2 catalyzed dehydration in water and DMSO. Reaction conditions: sugar = 100 mg, TiO_2 = 100 mg, T = 120 °C, t = 5 min.

The reusability of the TiO_2 NP catalyst was examined for fructose dehydration reaction in aqueous and organic media by recycling the solid catalyst after oven drying for each run. A plot of the catalyst cycle number *versus* HMF yields for fructose dehydration is shown in Fig. 6. The results show that the loss of activity of the catalyst in terms of HMF yield is only 2% in fourth catalytic cycles (34.3% HMF in first cycle and 32.0% HMF yield in fourth cycle). The catalyst life-time study in DMSO solvent also showed about 2% decrease in HMF yield in fourth catalytic cycles (Fig. 6). FE-SEM images of the reused TiO₂ NPs after first and fourth recycling are shown in Fig. 7(a) and (b), which reveals that small uniform nanosphere-like particle morphology has been retained after fourth reaction cycle.

We have studied a range of carbohydrate substrates to examine the catalytic performance of mesoporous TiO₂ NPs in producing the HMF. A decreasing trend of HMF yields from 34.3% to 10.4% is observed from fructose to maltose monohydrate in aqueous medium at 120 °C in 5 min reaction time (Fig. 8). It is interesting to note that maltose is a disaccharide formed from two units of glucose joined with an $\alpha(1 \rightarrow 4)$ bond, which is structurally similar to cellobiose. In this study, we have obtained higher yield of HMF from cellobiose in comparison to that from maltose. This could be probably due to the water inhibition effect of the hydrated maltose monohydrate. Similar trend of HMF yields were observed in DMSO. In DMSO, fructose and glucose dehydration reactions produced maximum 54.1% and 37.2% HMF, respectively under identical reaction conditions. This decrease in HMF yield from fructose to maltose agreed well with the reported data of CrCl₂ catalyzed dehydration of several carbohydrate substrates [35].

4. Conclusion

From our experimental observations we can conclude that the self-assembled mesoporous nanoparticulate TiO_2 material can be utilized as catalyst for the microwave-assisted conversion of carbohydrates into HMF in aqueous and organic media. These self-assembled spherical TiO_2 NPs catalyzed fructose dehydration reaction produced maximum 34.3% and 54.1% HMF in water and DMSO, respectively. Moderate yield of HMF (37.2%) was also obtained from glucose as substrate in DMSO. Optimized reaction conditions were established by varying the catalyst loading, reaction time, substrates to catalyst weight ratios and solvents. The presence of strong Lewis acidic sites in TiO₂ NPs surface was determined by pyridine-IR and NH₃-TPD studies. Catalyst life-time study showed the catalyst retained its activity after four repeating cycles in terms of HMF yields. The ability of mesoporous TiO₂ NPs catalyst to convert a range of carbohydrate substrates into HMF in aqueous and organic media under microwave heating promises the opportunity for utilizing this catalyst for the conversion of abundant and inexpensive cellulosic biomass into a renewable energy source.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2011.09.037.

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