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Synthesis of 5-Hydroxymethylfurural from Carbohydrates using Large-Pore Mesoporous Tin Phosphate

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A large-pore mesoporous tin phosphate (LPSnP-1) material has been synthesized hydrothermally by using Pluronic P123 as the structure-directing agent. The material is composed of aggregated nanoparticles of 10–15 nm in diameter and has a BET surface area of 216 m²g⁻¹ with an average pore diameter of 10.4 nm. This pore diameter is twice as large as that of mesoporous tin phosphate materials synthesized through the surfactant-templating pathways reported previously. LPSnP-1 shows excellent catalytic activity for the conversion of fructose, glucose, sucrose, cellobiose, and cellulose to 5-hydroxymethylfurfural (HMF) in a water/methyl isobutyl ketone biphasic solvent to give maximum yields of HMF of 77, 50, 51, 39, and 32 mol%, respectively, under microwave-assisted heating at 423 K. Under comparable reaction conditions, LPSnP-1 gives 12% more HMF yield than a small-pore mesoporous tin phosphate catalyst that has an identical framework composition. This confirms the beneficial role of large mesopores and nanoscale particle morphology in catalytic reactions that involve bulky natural carbohydrate molecules.

This opened up the possibility to use rich transition metal

chemistry in the vast field of heterogeneous catalysis. Later

Tian et al. reported a self-adjusting synthetic process for differ-

Introduction

The discovery of mesoporous materials based on FSM^[1] (Folded Sheet Mesoporous) and MCM^[2] (Mobil Composition of Matter) in the early 1990s made a breakthrough in the field of materials research not only by solving the pore-size limitation of zeolite chemistry but also because of the introduction of a generalized supramolecular templating approach that gave total control over pore-size tuning. These materials showed pore diameters in the range of 2-4 nm if a cationic surfactant such as cetyltrimethyl ammonium bromide (CTAB) was used as the template. Although the use of different swelling agents can expand the pore dimensions of these materials.^[3] the use of block copolymers as structure-directing agents (SDAs)^[4] extended the pore size up to 30 nm. Large mesopores are essential for some specific applications such as biomolecule immobilization,^[5] biocatalysis,^[6] protein adsorption and separation,^[7] catalytic reactions that involve bulky natural products,^[8] etc. Initially, most research concentrated on MCM-based mesoporous silica materials until Stucky and co-workers proposed a generalized synthesis route for large-pore mesoporous metal oxides.^[9]

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ent porous transition metal oxides and phosphates with a variety of pore sizes.^[10] Among the different types of porous materials, metal phosphates are of great importance for their application in catalysis,^[11] ion exchange,^[12] conductivity,^[13] optoelectronics,^[14] Li-ion batteries,^[15] etc. A low surface area and small pore size are, in general, the main drawbacks of metal phosphates for their successful utilization in different catalytic reactions. As tin phosphates show excellent catalytic^[16] and electrochemical^[17] properties, much effort has been devoted to the synthesis of porous tin phosphate materials with high surface areas.^[18] However, the large particle size and small pore opening of tin phosphate materials remain a problem as they hinder the accessibility of the framework pores for different catalytic processes that involve bulky natural products. Here we report a facile hydrothermal synthesis of large-pore mesoporous aggregated tin phosphate nanoparticles (LPSnP-1) by using Pluronic P123 as the SDA. This material showed a high thermal stability and excellent catalytic activity for the production of 5-hydroxymethylfurural (HMF) from naturally abundant carbohydrates in an aqueous medium. HMF, one of the top ten bio-based platform chemicals, has received significant attention as it can be used to produce a broad range of chemicals and liquid transportation fuels.^[19] As a result of the versatile applications of furfurals, rapid progress in the development of efficient catalytic processes for the conversion of carbohydrates and biomass has been witnessed over recent years, although sustainable and economically viable routes for their production in scalable quantities are yet to be developed. Several homogeneous Brønsted acidic mineral acids and ionic liguids, Lewis acidic metal chlorides and bifunctional Brønsted/ Lewis acidic catalytic materials have been employed for the production of HMF in single and biphasic solvent systems.^[20] Although these homogeneous catalysts gave moderate to high yields of HMF, the separation of catalysts and product purification remains a major challenge. To overcome these challenges, several heterogeneous Lewis and bifunctional Lewis/ Brønsted acidic materials have been developed and tested as solid catalysts.^[20b, c] Among several groups, Watanabe and coworkers have used an anatase TiO₂ catalyst for fructose and glucose conversion to HMF with 38 and 7.7% yield, respectively.^[21] Zhao et al. used a heteropoly acid, Cs_{2.5}H_{0.5}PW₁₂O₄₀, catalyst for HMF production.^[22] More recently, self-assembled mesoporous TiO₂ nanospheres prepared through templating pathways and a hierarchically porous titanium phosphate (MTiP-1) that has different Lewis acidity and pore size have been synthesized and tested for HMF production.^[23] However, analysis of the acidity-catalytic activity relationship for the reported mesoporous materials suggests that the catalytic activity of the acid catalysts is not simply dependent on the total acidity of the material. Although the acid density of the catalyst is an important parameter to determine catalytic effectiveness, other material properties such as pore size, surface area, and particle morphology can also play important roles to determine the overall activity. The pore diameter of the present material is twice as large as that of mesoporous tin phosphates synthesized by using block copolymers as SDAs in an alcoholic medium reported previously.^[10] Herein, we first report a largepore tin phosphate material, LPSnP-1, which shows a BET surface area of $216 \text{ m}^2\text{g}^{-1}$ and pore diameter of 10.40 nm. The large mesopores and interparticle voids present in the material are expected to be beneficial for the production of HMF from the natural biopolymer carbohydrate substrates.

Results and Discussion

Material synthesis and characterization

As part of our continuous efforts to produce different types of efficient catalysts for the synthesis of HMF, our aim was to design a large-pore mesoporous tin phosphate solid-acid catalyst that will be suitable to accommodate bulky natural carbohydrates. Pluronic P123 was used as the SDA to produce a large-pore mesoporous tin phosphate material. A previous report of the synthesis of mesoporous tin phosphate by using P123 as the SDA in ethanolic solution showed the highest pore diameter of 5.2 nm together with a low BET surface area of $122 \text{ m}^2\text{g}^{-1}$.^[10] It is known that the micellar radius and core size of P123 decrease steadily with an increase in the concentration of ethanol in a mixed solvent with water.^[24] Therefore, we chose water as the solvent to synthesize large-pore mesoporous tin phosphate. Orthophosphoric acid was preferred over other phosphate sources because of its ability to maintain the low solution pH required for micelle formation^[25] in aqueous medium through H bonding and the effect of the phosphate ion to increase the micelle size according to the Hofmeister anion series.^[26] A low solution pH also ensures the very slow precipitation that is crucial for the proper interaction between the organic and inorganic phases to lead to a mesostructured material. The gel formed initially was aged at 373 K for 72 h under hydrothermal conditions to ensure the extended crosslinking of the material. Finally, the as-synthesized material was calcined at 973 K for 5 h to remove the template, and this calcined large-pore tin phosphate material was labeled as LPSnP-1. Although thermogravimetric analysis (TGA) showed that the template could be removed at a much lower temperature (Figure S1), 973 K was applied to verify the thermal stability of the material because the catalyst must be stable enough for repeated use under microwave conditions at high temperature. A schematic representation of the formation of LPSnP-1 is shown in Scheme 1. To verify the catalytic effectiveness of the large-pore catalyst, in which a large number of catalytic sites are expected to be exposed, for comparison we synthesized



Scheme 1. Schematic representation of the synthesis of LPSnP-1.

a small-pore mesoporous tin phosphate material by following a previously reported procedure.[18c] The FTIR spectrum of LPSnP-1 shows that bands in the region ~2950 and ~2870 cm⁻¹ that correspond to the C–H stretching vibration of hydrocarbons are absent (Figure S2). The band at 1460 cm⁻¹ that corresponds to the C-H bending vibration of methylene groups of surfactant molecules was also absent in the calcined material, which indicates the complete removal of the template molecules upon calcination. The FTIR spectrum of the assynthesized material before calcination is also shown for comparison. The sharp band centered around 1095 cm⁻¹ corresponds to the asymmetric Sn–O–P stretching vibration, which indicates the presence of a phosphate framework in LPSnP-1.^[23b] The narrow band at 760 cm⁻¹ is attributed to the asymmetric vibration of bridging P-O-P bonds, and the two bands at 610 and 530 cm⁻¹ correspond to the bending vibration of PO_2 .^[17b] The broad bands around ~3400 and 1630 cm⁻¹ are attributed to asymmetric O-H stretching and bending vibrations of the adsorbed water molecules. The FTIR spectrum of the small-pore catalyst shows a similar kind of bonding, which is consistent with a previous report (Figure S3).^[18c] From energy dispersive spectroscopy (EDS) equipped with SEM it is seen

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that the ratio of Sn to P in LPSnP-1 remains nearly 1:1 in the final product (Table S1).

Powder X-ray diffraction

The powder X-ray diffraction (PXRD) pattern of LPSnP-1 has only one peak in the small-angle region (Figure 1). The peak position corresponds to the distribution maximum of the adjacent pore center to pore center distance, and the peak at $2\theta =$



Figure 1. Small-angle PXRD pattern of LPSnP-1.

 0.66° indicates an interpore distance of 13.40 nm. From the wide-angle PXRD pattern, it is clear that there are no distinct characteristic peaks and the material is amorphous (Figure S4). The small-angle PXRD pattern of the small-pore mesoporous catalyst shows a single peak at $2\theta = 2.15^{\circ}$, which indicates an interpore spacing of 4.10 nm (Figure S5).

Microstructural analysis

From the SEM images shown in Figure 2a and b it is seen that the material is composed of aggregated spherical nanoparticles. Magnified views of the TEM images presented in Figure 2c and d show that there are small spherical nanoparticles of 10-15 nm in diameter aggregated throughout the specimen that give rise to large mesopores in the material. A low solution pH during the synthesis of the material helps to avoid uncontrolled precipitation and polymerization of the inorganic species and prevents the formation of large aggregates. The advantage of aggregated small nanoparticles is that they give better access to the internal mesoscopic void spaces, which improves mass transport throughout the material and helps to improve the catalytic activity.^[23b] The TEM images of the smallpore catalyst show the presence of mesopores of approximately 3 nm in diameter (Figure S6). The porous channels indicate the presence of a fraction of ordered pores in this material.

N₂ adsorption-desorption

The N_2 adsorption-desorption isotherms of LPSnP-1 are shown in Figure 3. LPSnP-1 shows a type IV isotherm with an H1-type

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Figure 2. a) and b) SEM and c) and d) TEM images of LPSnP-1.



Figure 3. N_2 adsorption-desorption isotherm of LPSnP-1. Inset: pore size distribution obtained by using the NLDFT method.

hysteresis loop, which are characteristic of mesoporous materials. The H1 hysteresis loop with parallel and nearly vertical branches is also common for materials in which approximately spherical particles are agglomerated in a fairly uniform fashion.^[27] For mesoporous solids, multilayer adsorption is followed by capillary condensation in a high relative pressure region.[28] Similar to the N₂ adsorption isotherms for SBA-15 samples, the isotherm of LPSnP-1 showed a hysteresis loop with sharp adsorption and desorption branches. An H1 hysteresis loop with a sharp adsorption branch is indicative of high pore size uniformity.^[27] This is also supported by the narrow pore size distribution pattern of the material shown in the inset of Figure 3. The pore size was calculated by using an adsorption-branch model in nonlocal density functional theory (NLDFT). Capillary condensation for this material occurred in the high relative pressure range from 0.7–0.85, which indicates the presence of large mesopores because capillary condensation pressure is a function of pore diameter.^[29] The material shows a BET surface area of 216 m²g⁻¹ with a pore volume of 0.59 cm³g⁻¹. The pore size distribution plot shows only one sharp peak at 10.40 nm. The N₂ adsorption–desorption isotherm of the smallpore tin phosphate is shown in Figure S7, which shows a type IV isotherm typical of materials with small mesopores.^[18c] The pore size distribution pattern (from NLDFT) presented in the inset of Figure S7 shows that the material possesses mesopores of approximately 3 nm in diameter. This material exhibits an almost comparable BET surface area to that of LPSnP-1of 221 m²g⁻¹ with a much lower pore volume of 0.18 cm³g⁻¹.

Acidity measurement

The acidic sites of these materials were quantified by an NH₃ temperature-programmed desorption (TPD) measurement. The NH₃ desorption profiles of different tin phosphate samples are shown in Figure S8a and b. The large-pore material shows desorption peak maxima at very high temperatures of 860 and 990 K. The high-temperature desorption of NH₃ indicates the presence of very strong acidic sites in the material,^[30] which indicates that it is suitable for different acid-catalyzed reactions. The concentration of the acid sites is 2.2 mmol g^{-1} for LPSnP-1. The NH₃-TPD profile (Figure S8b) of the small-pore material shows comparatively low-temperature desorption peaks, which indicate the presence of weaker acidic sites. The acid-site concentration is 0.7 mmolg⁻¹ for the small-pore tin phosphate. The higher acid-site concentration of LPSnP-1 could be attributed to a high external surface area because of the tiny nanoparticle morphology, large pore size, and high pore volume that expose a larger number of acid sites at the surface of the material.

Catalysis

The catalytic effectiveness of LPSnP-1 was investigated for the dehydration reactions of carbohydrates (fructose, glucose, sucrose, cellobiose) in water/methyl isobutyl ketone (MIBK) biphasic solvent under microwave-assisted heating conditions. All reactions were performed in aqueous medium using MIBK as an organic phase in a biphasic solvent system for the concurrent extraction of HMF into the organic phase as it is formed in the aqueous phase. A preliminary reaction for the dehydration of 0.25 mmol fructose with 10 mg LPSnP-1 catalyst at 423 K produced 36 mol% HMF in 5 min. Separate experiments at various reaction times from 10-20 min showed an increase in the HMF yield from 36-77 mol%. This total amount of HMF is the sum of the HMF obtained from both the organic and aqueous phases. The distribution of the HMF product analyzed in the organic and aqueous phases as a function of reaction time is shown in Table S2. The color of the extracted organic product was pale yellow, which is an indication that a significant amount of black humin oligomer^[31] did not form under these conditions. A clean ¹H NMR spectrum of the product solution in CDCl₃ further confirmed the purity of HMF as The quantitative conversion of fructose (98%) was recorded in 20 min by analysis of the aqueous phase by using the phenol–sulfuric acid method.^[33] The continuation of the reaction for 30 min revealed a loss in the HMF yield, which indicates that the rehydration of HMF to the side products could occur for reactions performed over a longer time (Figure 4). Therefore, subsequent experiments were performed over 20 min. A blank experiment without catalyst showed the formation of only 3% HMF and confirmed the true catalytic pathway for these reactions.



Figure 4. Conversion of fructose and yields of HMF as a function of time for the reaction between fructose (0.25 mmol) and LPSnP-1 (10 mg) at 423 K under microwave irradiation.

The dehydration of fructose to HMF was studied at various catalyst loadings to optimize the reaction conditions and maximize the HMF yield. The loading of LPSnP-1 varied from 5–20 mg, and the other reaction parameters were constant: [fructose] = 0.25 mmol, T=423 K, t=20 min. The results presented in Figure 5 show that the yield of HMF increases from 3 to 77% upon increasing the catalyst loading from 0 to 10 mg. A further increase in catalyst loading from 10 to 20 mg showed a slight increase in the HMF yield from 77 to 81%. This suggests that an optimal HMF yield can be achieved by using



Figure 5. Dependence of HMF yield on catalyst loading for the dehydration of fructose (0.25 mmol) at 423 K under microwave irradiation, t = 20 min.

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proton signals for side products levulinic and formic acids^[32] were not present (Figure S9).

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10 mg of catalyst for 0.25 mmol of fructose substrate, and subsequent experiments were performed with 10 mg of catalyst.

The effect of temperature on the yield of HMF from fructose was studied by performing fructose dehydration reactions at various temperatures from 393–433 K. Under comparable reactions conditions with 0.25 mmol of fructose, 10 mg of catalyst, and 20 min reaction time, the yield of HMF increased from 40 mol% at 393 K to 77 mol% at 423 K. A further increase of the temperature to 433 K resulted in a slight decrease in the yield to 71 mol%, which suggests that possible side reactions, namely, rehydration and oligomerization, of HMF in the aqueous medium could be predominant at higher temperatures. A plot of the HMF yield as a function of the reaction temperature is shown in Figure 6.



Figure 6. Effect of the reaction temperature on fructose conversion and HMF yield by using LPSnP-1 as the catalyst. Reaction conditions: 0.25 mol fructose in 1 mL water and 2 mL MIBK; 10 mg LPSnP-1, t=20 min under microwave heating.

Although fructose is the preferred feedstock for HMF production, its occurrence in nature is limited. This drives our interest to use a more abundant carbohydrate, glucose, as the raw material for HMF synthesis. Therefore, the dehydration of glucose with LPSnP-1 was performed in water/MIBK at 413 and 423 K. The results shown in Table 1 (entries 1 and 2) reveal the formation of 34 and 50 mol% HMF at 413 and 423 K, respectively, over 20 min. These yields are significantly lower than those obtained from fructose under similar reaction conditions. The lower HMF yield from glucose can be attributed to the mutarotation and isomerization of glucose before the dehydration step can occur.^[20c, 32]

| Table 1. from glue solvent. F 20 min, w | The catalytic effect cose, cellobiose, s Reaction condition vater = 1 mL, MIBK | tiveness of L ucrose, and s: substrate = 2 mL. | PSnP-1 for the produ cellulose in water/l =0.25 mmol, catalys | uction of HMF MIBK biphasic t = 10 mg, t = |
|--------------------------------------------------|-----------------------------------------------------------------------------------------|---------------------------------------------------------|---------------------------------------------------------------------|--------------------------------------------------|
| Entry | Substrata | T | Conversion | |

| Entry | [0.25 mmol] | [K] | [%] | [mol %] |
|-------|-------------|-----|-----|---------|
| 1 | glucose | 413 | 74 | 34 |
| 2 | glucose | 423 | 80 | 50 |
| 3 | cellobiose | 423 | 94 | 39 |
| 4 | sucrose | 423 | 96 | 51 |
| 5 | cellulose | 423 | - | 32 |

The scope of this investigation was further extended to examine the dehydration of cellobiose (a dimer of glucose units), sucrose (a dimer of fructose and glucose units), and cellulose (a polysaccharide that consists of a linear chain of several glucose units through a H-bonded network) with the LPSnP-1 catalyst. In the case of cellobiose, the reaction steps are believed to involve (i) the hydrolysis of cellobiose to glucose, (ii) the isomerization of glucose to fructose, and (iii) the dehydration of fructose. A reaction between 0.25 mmol of cellobiose and 10 mg of catalyst in MIBK/water biphasic solvent produced 39% HMF (entry 3, Table 1) with 94% conversion in 20 min at 423 K. Although the conversion of cellobiose was nearly 94%, the phenol-sulfuric acid analysis of the aqueous phase of the reaction solution revealed the presence of a large amount of unconverted reduced sugars in the solution. Previous reports on cellobiose dehydration with homogeneous GeCl₄ and CrCl₃ catalysts showed the formation of 41 and 50% HMF,^[34] respectively, in pure or mixed 1-butyl-3-methylimidazolium chloride ionic liquid. Compared to these reported HMF yields that use toxic and inseparable Lewis acidic salts in a toxic ionic liquid, the present catalysis that uses the nontoxic and recyclable LPSnP-1 catalyst in aqueous medium that enables a 39% yield of HMF is impressive and advances green chemistry applications. Under comparable reaction conditions, sucrose dehydration with LPSnP-1 produced a maximum of 51% HMF in 20 min at 423 K (entry 4, Table 1). The higher yield of HMF from sucrose, a disaccharide of glucose and fructose units, can be explained by the hydrolysis of sucrose to fructose and glucose units, both of which are concurrently dehydrated to HMF. In the case of cellulose, a lower yield of HMF (32%) was recorded, which could be because of the lower solubility and hydrolysis of pure cellulose in an aqueous medium because of the presence of a strong H-bonded network in its structure.^[35] Nevertheless, we performed a control experiment for cellulose conversion without a catalyst to evaluate the effect of the catalyst on cellulose hydrolysis to glucose and the subsequent dehydration of glucose to HMF. Under comparable reaction conditions with 0.25 mmol cellulose, 423 K, and 20 min reaction time, the blank experiment produced no HMF in water/MIBK (water = 1 mL, MIBK = 2 mL) under both microwave and oilbath heating. This is perhaps an indication that cellulose hydrolysis takes place on the catalyst surface and cellulose cannot break down to glucose without a catalyst. A comparison of the HMF yields from different substrates is presented in Figure 7.

Effect of NaCl on the HMF yield

The partitioning of HMF into the extracting organic phase of the biphasic solvent system increases in the presence of NaCl in the reactive aqueous phase.^[36] This effect was observed in fructose dehydration in an aqueous/organic biphasic medium catalyzed by boric acid upon addition of NaCl and similar alkali metal salts.^[37] To investigate the salting-out effect in the present study, the dehydration reaction of 0.25 mmol of glucose was performed with 10 mg of LPSnP-1 in biphasic aqueous/MIBK solvent at 423 K by using various amounts of NaCl. The

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Figure 7. Comparison of HMF yields obtained from different substrates (0.25 mmol) and LPSnP-1 (10 mg) in water/MIBK at 423 K for 20 min. (F=fructose, G=glucose, S=sucrose, Cb=Cellobiose, C=cellulose)

| Table 2. Effect of NaCl on the HMF yield for glucose dehydration with |
|----------------------------------------------------------------------------|
| LPSnP-1. Reaction conditions: glucose = 0.25 mmol, catalyst = 10 mg, $t =$ |
| 20 min, water = 1 mL, MIBK = 2 mL, s = 423 K. |

| Entry | Substrate | m _{NaCl} [g] | HMF yield ^[a] [mol %] | | |
|-------------------------------------|-----------|--------------------------|-------------------------------------|--|--|
| 1 | glucose | 0.0 | 50 | | |
| 2 | glucose | 0.1 | 61 | | |
| 3 | glucose | 0.5 | 62 | | |
| [a] Determined by NMR spectroscopy. | | | | | |

results tabulated in Table 2 show a significant improvement in HMF yield (by 11 mol%) upon the addition of 0.1 g of NaCl into the reaction mixture owing to the higher partitioning of HMF into the organic phase. A further increase in NaCl from 0.1 to 0.5 g resulted in only 1 mol% improvement in yield, perhaps because the maximum partition coefficient was achieved in the presence of 0.1 g of NaCl.

Catalyst comparison

In a recent publication, Ordomosky et al. have shown that the conversion of fructose to HMF takes place inside the pore of acidic zeolite materials and hence the pore diameter plays an important role to determine the overall catalytic effectiveness in addition to the acid density.^[38] Zeolite materials with a subnanometer pore diameter (5.6-7.0 Å) were more effective for higher fructose conversion and HMF selectivity than aluminosilicate materials without micropores. To further test the effect of the pore diameter of the mesoporous catalysts on HMF yields, we studied fructose dehydration with the large-pore (10.40 nm) tin phosphate nanoparticles LPSnP-1 (prepared by using Pluronic P123 as the SDA) and the small-pore (~3 nm) tin phosphate catalyst (prepared by using CTAB as the SDA). Both experiments were performed in water/MIBK biphasic solvent system (water-to-MIBK volume ratio = 2) under conventional oil-bath heating to demonstrate the practical applicability of this method for large-scale reactions. A reaction between 20 mg of LPSnP-1 and 0.5 mmol of fructose at 403 K produced 27% HMF. Notably, the same reaction under microwave-assisted heating produced 49% HMF at 403 K. The lower HMF yield under oil-bath heating than that under microwave-assisted heating is consistent with previous data.^[32] However, the effect of microwave heating may be different for soluble sugars and cellulose biopolymer because of the involvement of an additional hydrolysis step in cellulose conversion. To test this hypothesis, we performed cellulose conversion under oil-bath heating by adopting the experimental conditions of entry 5 in Table 1. This reaction produced only 7% HMF under oil-bath heating compared to 32% HMF under microwave heating (entry 5, Table 1). These results indicate that the effect of microwave heating on this biopolymer is significant, perhaps because microwave heating facilitates biopolymer hydrolysis. Under comparable reaction conditions, the small-pore catalyst produced only 15% HMF from fructose, which is significantly lower than that observed with the large-pore tin phosphate catalyst. The higher catalytic activity of LPSnP-1 is a result of the higher acid-site concentration on the surface of the material and large pore openings that facilitate the flow of reactants and products inside the porous channels. A similar observation has been reported by Ordomosky et al. who prepared a series of heterogeneous materials with different pore diameters and different Lewis and Brønsted acid densities for fructose dehydration.[39] The results showed that the catalytic activity for fructose conversion was correlated to the strength of the Lewis acidity of the catalysts. However, mordenite zeolite that contained the highest acid density exhibited the lowest fructose conversion, which could be because of the small pore diameter of this material in which bulky sugar molecules face diffusion limitations.

Catalyst recyclability

The reusability of the LPSnP-1 catalyst was examined for glucose dehydration in water/MIBK solvent by performing a reaction between 0.25 mmol of glucose and 10 mg of LPSnP-1 in water/MIBK solvent that contained 0.1 g of NaCl at 423 K for 20 min. After 20 min, an aliquot was collected for analysis, and the solid catalyst left in the tube was collected and reused for four more cycles on addition of fresh substrate and solvent. Fresh catalyst was not added to compensate for any loss of the catalyst during recovery. The organic and aqueous phases of the reaction solution of each run were analyzed separately to quantify the total amount of HMF formation. The loss of activity of the catalyst, in terms of HMF yield, after five cycles was only ~4% (Figure 8).



Figure 8. Recyclability study of the LPSnP-1 catalyst for the production of HMF from glucose.

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Conclusions

Large-pore mesoporous aggregated tin phosphate nanoparticles (LPSnP-1), which have a pore diameter of 10.40 nm and acid-site concentration of 2.2 mmolg⁻¹, have been synthesized under hydrothermal conditions by using Pluronic P123 as the structure-directing agent. This material shows excellent catalytic activity for the conversion of fructose, glucose, sucrose, cellobiose, and cellulose to 5-hydroxymethylfurfural (HMF) in water/methyl isobutyl ketone (MIBK) biphasic solvent to give maximum yields of 77, 50, 51, 39, and 32 mol%, respectively, under microwave-assisted heating at 423 K. The water/MIBK biphasic solvent saturated with NaCl in the reactive aqueous phase gave an 11% higher HMF yield from glucose because of the better partitioning of HMF into the organic phase. Temperature dependence experiments revealed a decrease in HMF selectivity above 423 K, which suggests that HMF rehydration and oligomerization reactions take place at higher temperatures. Under comparable reaction conditions, the tin phosphate catalyst with a 10.40 nm pore size produced 12% more HMF than the corresponding catalyst with a smaller pore size (3 nm) and lower acidity (0.7 mmol g^{-1}), which suggests that the pore size and the surface acidity of the catalyst play important roles in the conversion of carbohydrates to HMF.

Experimental Section

Materials and instrumentation

Tin(IV) chloride (SnCl₄:5 H₂O, M_r =350.60) was purchased from Loba Chemie. Orthophosphoric acid (H₃PO₄, M_r =98.00, 85% in water) was purchased from Merck. CTAB (M_r =364.45) was purchased from Sisco Research Laboratories. Pluronic P123, catalytic substrates (fructose, glucose, sucrose, cellobiose, and cellulose), and MIBK were purchased from Sigma–Aldrich India and were used as received. Pure HMF and levulinic acid (LA) samples were purchased from Sigma–Aldrich India. Unless otherwise mentioned, distilled water was used in catalyst synthesis and as the aqueous phase of the biphasic solvent system in the catalytic reactions.

PXRD patterns of the catalysts were recorded by using a Bruker D-8 Advance diffractometer operated at 40 kV and 40 mA, calibrated with a standard Si sample, using Ni-filtered CuK_{α} ($\lambda = 0.15406$ nm) radiation. A JEOL JEM 6700F field emission scanning electron microscope was used to determine the morphology of powder samples and for EDS analysis. EDS analysis was performed on a randomly chosen area on the surface of the material. The pore structure of the catalyst was explored by using a JEOL JEM 2010F TEM operated at an accelerating voltage of 200 kV. FTIR spectra of as-synthesized and calcined tin phosphate materials were recorded by using a Nicolet MAGNA-FT IR 750 Spectrometer Series II. N2 adsorptiondesorption isotherms were obtained by using a Quantachrome Autosorb 1C at 77 K, and the pore size of the materials were estimated by using the NLDFT method (with reference to N₂ sorption at 77 K for the equilibrium model on silica with cylindrical pore geometry and adsorption branch model) by using the software package supplied with the instrument. TGA and differential thermal analysis (DTA) of the samples were preformed from 300-1073 K by using a TA Instruments thermal analyzer TA-SDT Q-600. NH₃-TPD analysis was conducted by using an ALTAMIRA acidity analyzer in the temperature range 373-1173 K by using a thermal conductivity

detector. The catalytic conversion of carbohydrates to HMF was performed by using a CEM Matthews WC Discover Microwave reactor (model: Discover System, no. 908010 DV9068) at the standard operating frequency of a microwave synthesis reactor (2.45 GHz, power 250 Watt). ¹H NMR spectra were recorded by using a JEOL JNM ECX-400 P 400 MHz instrument, and the data were processed by using the JEOL DELTA program version 4.3.6. The yield of HMF was measured by ¹H NMR spectroscopy and UV/Vis spectrophotometry. UV/Vis spectra were recorded by using a UV-SPECORD 250 analytikjena spectrometer. The conversion of starting substrates was determined by using the reported phenol–sulfuric acid method.^[33]

Catalyst preparation

P123 (1 g) and H_3PO_4 (1.15 g, 10 mmol) were dissolved in H_2O (15 g), and this mixture was stirred for 2 h. Tin chloride pentahydrate (3.5 g, 10 mmol) dissolved in H_2O (5 g) was added to the H_3PO_4 solution. A white colloidal precipitate was formed slowly. The whole mixture was stirred for another 3 h and kept inside a polypropylene bottle at 373 K for 72 h. The white material was collected by filtration and dried at RT. Finally, the mesostructured material was calcined at 973 K for 5 h, and this calcined sample was labeled as LPSnP-1.

To compare the catalytic activities, a small-pore mesoporous tin phosphate catalyst was synthesized according to a previously reported procedure by using CTAB as the SDA.^[18c]

HMF production

The dehydration reactions of carbohydrates, fructose, glucose, cellobiose, cellulose, and sucrose, were performed under microwave irradiation by filling the substrate, solvent, and catalyst into a 10 mL microwave tube. In a typical experiment, substrate (0.25 mmol) and LPSnP-1 (10 mg) were added into a microwave tube that contained water (1 mL) and MIBK (2 mL). A small magnetic stirrer bar was inserted into the tube to mix the reaction mixture during the reaction. The loaded tube was then placed into the microwave reactor preset at the desired temperature, typically 393-423 K, for the desired time. After the set reaction time, the temperature of the reaction mixture was cooled to RT, and the organic phase was transferred into a round-bottomed flask. The aqueous phase was washed repeatedly with diethyl ether to extract organic components, which was combined with the organic layer. The solvent was removed by using a rotary evaporator, and the oily organic product was dissolved in CDCl₃ for ¹H NMR spectroscopy. The aqueous phase was analyzed separately by UV/Vis spectrophotometry to determine any residual organic components.

Catalyst life-time study

The recycling efficiency of the LPSnP-1 catalyst was determined by using the dehydration of glucose as a representative reaction. In this study, glucose (45 mg, 0.25 mmol) and LPSnP-1 (10 mg) were charged into a microwave tube that contained water (1 mL) and MIBK (2 mL). The tube was placed in the microwave reactor and the mixture was heated for 20 min at 423 K by using 250 W microwave power. After the reaction, the tube was cooled to RT, and the liquid decanted from the tube. The solid residue left in the tube was collected and dried. The dried catalyst was reused for five more cycles following the above method, and HMF yields were determined from each run. The yield of HMF was determined by anal-

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ysis of the oily product obtained from the organic phase by using ¹H NMR spectroscopy and the aqueous phase by UV/Vis spectrophotometry.

Determination of HMF yields

The yield of HMF was determined by analysis of both the organic and aqueous phase by using ¹H NMR and UV/Vis spectroscopy, respectively. For ¹H NMR spectroscopy, HMF was extracted from the reaction mixture with diethyl ether. Pale yellow oily HMF was obtained after the removal of the solvent by using a rotary evaporator. The organic and aqueous phases were analyzed separately to quantify the total HMF yield [mol%].

¹**H NMR spectroscopic method**: To quantify the yield of HMF by using ¹H NMR spectroscopy, a known concentration of mesitylene (internal standard) was added into the HMF product solution in CDCl₃. The percentage HMF yield was calculated by using the integrated values of the aldehyde proton (δ = 9.58 ppm) of HMF and the three aromatic ring protons of mesitylene (δ = 6.73 ppm; Figure S9). First, a standard HMF solution of 98% purity was analyzed to correlate the percentage of the actual and calculated amounts of HMF. Once a good correction was established, extracted HMF product samples were measured and the percentage HMF yield was calculated. Repeated measurements of the same solution show that the percentage of error associated with this measurement was ±5%.

UV/Vis spectrophotometric method: The presence of any remaining HMF in the aqueous phase after diethyl ether extraction was measured by using UV/Vis spectrophotometry. The UV/Vis spectrum of pure HMF (Figure S10) has a distinct peak at 284 nm with a corresponding extinction coefficient (ϵ) of $1.66 \times 10^4 \, \text{m}^{-1} \, \text{cm}^{-1}$. The amount of HMF in the aqueous phase of each of the reaction product was calculated from the measured absorbance values at 284 nm and the extinction coefficient. Repeated measurement of the same solution showed that the percentage of error associated with this measurement was $\pm 3 \, \%$.

Test for Lewis acidity

For NH₃-TPD analysis, the catalyst sample (\approx 100 mg) was loaded into a U-tube glass cell and was initially flushed with a He gas flow at 723 K for 2 h, cooled to 423 K, and then saturated with NH₃ for 30 min at a rate of 20 mL min⁻¹. After exposure to NH₃, the catalyst sample was purged with He to flush out the excess NH₃. The temperature was then increased at a linear heating rate of 10 K min⁻¹ in the range of 373–1173 K. The amount of desorbed NH₃ was monitored by using the computer program supplied with the instrument.

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FULL PAPERS

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Synthesis of 5-Hydroxymethylfurural from Carbohydrates using Large-Pore Mesoporous Tin Phosphate



Sugar to fuel: A large-pore mesoporous tin phosphate material is synthesized hydrothermally by using Pluronic triblock copolymer as the template. This material shows high thermal stability and catalyzes naturally abundant carbohydrates in the aqueous phase to 5-hydroxymethylfurfural, which is a potential bio-based platform chemical to produce a broad range of chemicals and liquid transportation fuels.