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Novel Ordered Mesoporous Carbon Based Sulfonic Acid as an Efficient Catalyst in the Selective Dehydration of Fructose into 5-HMF: the Role of Solvent and Surface Chemistry

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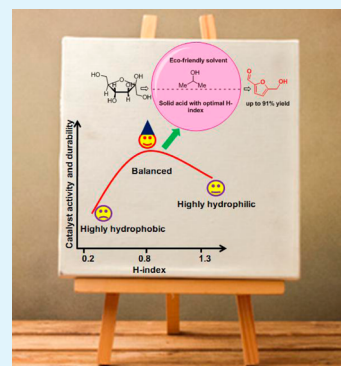
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S Supporting Information

ABSTRACT: Novel ionic liquid derived ordered mesoporous carbons functionalized with sulfonic acid groups IOMC-ArSO₃H and GIOMC-ArSO₃H were prepared, characterized, and examined in the dehydration reaction of fructose into 5-hydroxymethylfurfural (5-HMF) both in aqueous and nonaqueous systems. To study and correlate the surface properties of these carbocatalysts and some other SBA-15 typed solid acids with 5-HMF yield, hydrophilicity index (H-index) were employed in the fructose dehydration. Our study systematically declared that almost a criterion may be expected for application of solid acids in which by increasing H-index value up to 0.8 the HMF yield enhances accordingly. More increase in H-index up to 1.3 did not change the HMF yield profoundly. Although, it has been shown that the catalyst with larger H-index (~1.3) resulted in higher activity both in aqueous and 2-propanol systems, during the recycling process deactivation occurs because of more water uptake and the catalysts with optimum amount of H-index (~0.8) is more robust in the dehydration of fructose.

KEYWORDS: 5-hydroxymethylfurfural, ordered mesoporous carbon, nanocasting, hydrophilicity index, solid acid



1. INTRODUCTION

Climate change, high consumption of fossil resources, and growing concerns about energy and environmental issues made biomass as an important feedstock for the renewable production of fuels and platform chemicals.^{1–3} Recently, much effort has been paid to the conversion of biomass into 5-hydroxymethylfurfural (5-HMF), a versatile chemical platform and bridge intermediate in the biofuel and petrochemical industries, which can be synthesized through partial deoxygenating of hexose carbohydrates known as acid-catalyzed dehydration reaction.^{4–7} 5-HMF itself can be subjected to further structure functionalization via oxidation, reduction, hydrogenolysis, and condensation to provide numerous top value added derivatives, such as 2,5-diformylfuran (DFF) and 2,5-furandicarboxylic acid (FDCA), from which innovative renewably sourced product such as biopolymers, solvents, and fuel additives can be produced.^{8–12} However, the major side reactions in the process of preparing 5-HMF include its known acid-catalyzed rehydration into the corresponding levulinic acid (LA), formic acid (FA), and/or polymerization to give humin products.¹³ In the current research, it is known to a great extent that the distribution of products and in particular the selectivity toward HMF formation is highly dependent on the type (physicochemical properties) of the catalyst, reaction solvent, and temperature and development of new selective and effective protocols for this process has attracted broad research

activity.^{14–17} The first important issue in developing an economically and environmentally benign process for HMF formation is a green solvent in terms of easy separation, purity of the final product and low *E* factor [*E*-factor = total waste (kg)/product (kg)].^{2,18} Although from the standpoint of advance green and sustainable chemistry using water as a reaction solvent is a long-standing goal and thus often preferable, the difficulty in separating and purifying highly water-soluble HMF, the higher possibility of rehydrating HMF in water, and the deactivation of the acid catalysts are important issues that need to be respected.³ To address these concerns, a variety of solvent systems including nonaqueous,^{19–22} ionic liquids,^{23–26} and biphasic organic-aqueous solvents,^{27–31} has been developed in order to either minimize or inhibit the rehydration side reaction of HMF. However, separation and purification of HMF from high-boiling solvent and the use of expensive ionic liquids render these approaches less attractive for large scale applications. Thus, as a matter of fact finding readily available low boiling solvent for highly selective HMF production is one of the current interests. Recently, biomass derived solvents such as γ -valerolactone (GVL) and THF and also alcohols such as 2-propanol found broad applicability in

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biomass conversion.^{32–37} This advances is highly desirable for chemical community reducing concerns about biomass transformations in toxic and expensive solvents.

Another important route aiming at improving the sustainability of HMF production is the development of novel acid catalyst systems by emphasizing to concomitantly enhance (improve) the HMF selectivity, catalyst activity, durability, and ease of separation from the reaction media. Despite the high activity and selectivity which has been generally obtained for this transformation by homogeneous acid catalysts,^{25,26,38–40} heterogeneous (solid) catalysts,^{6,41–43} hold greater promise for use in large scale industrial applications because of the simple separation and recycling of the catalyst as well as the minimization of final product contamination with acidic wastes. This issue was further emphasized within one-pot transformation of cheap and available biomass feed such as cellulose and up to now, some great achievements have been attained in this area.^{44–46} In addition, in many circumstances it is possible to concomitantly tune both the surface physicochemical properties and acidity of solid acids in a designated manner, a feature that is very important for combining the benefits of an integrated purification strategy with the design of high performance catalyst in a molecular level. Among the possible strategies for heterogeneously catalyzed dehydration of hexoses to HMF, immobilization of acid catalysts on either SBA-15 type ordered mesoporous silicas^{31,47} or periodic mesoporous organosilicas (PMO's)^{48,49} in the form of supported sulfonic acid appears particularly attractive because it combines the advantage of conventional homogeneous catalyst with the unique properties of mesoporous material such as high specific surface area and pore volume, narrow pore size distribution, and high thermal stability. Furthermore, the high concentration of silanol groups in these silica-based materials may serve as handles for not only the covalent immobilization of active sites, they can provide a means of incorporating additional organic functionality on the catalyst surface, thus enabling to control (adjust) the surface hydrophobicity and in turn enhancing their performance (activity, selectivity, and durability) in varied acid-catalyzed chemical transformations.^{50–55}

Along this line, we⁵³ and others⁴⁹ have discovered that anchoring of sulfonic acid functions on PMO possessing an appropriate density of additional organic functional groups results in versatile solid acids that provided the possibility of achieving high degree of selectivities in the biphasic (aqueous:organic) dehydration of fructose into 5-HMF or biodiesel synthesis through the adjusting the surface hydrophobic–hydrophilic balanced of the catalysts. Although these systems were shown to offer improved catalytic performance in the described reactions because of the inorganic and thus inherent hydrophilicity of silica framework in these materials their catalytic activity would tend to potentially decline by gradual adsorption of water through the processes (for example dehydration of hexose) in which water participates as product or reaction medium. Carbonaceous structures have somewhat higher chemical and in particular much higher hydrothermal stability as compared to silica-based materials. For this reason, we reasoned that the use of carbonaceous structures to covalently immobilize the sulfonic acid functionalities might indeed be an excellent alternative matrix which can be markedly enhance the durability of the resulting solid acid under harsh aqueous condition. Within this context, ordered mesoporous carbons have a special place and attracted considerable attention for application in various fields including catalysis

due to their unique structural as well as physicochemical properties.^{56–58}

We have recently shown that a novel ionic liquid derived mesoporous carbon (IFMC) exhibits excellent electrochemical^{59,60} and chemical properties. IFMC was also employed as a strong support for the activation and stabilization of Pd nanoparticles in aerobic oxidation of alcohols⁶¹ and Ullmann coupling reaction⁶² of aryl halides under mild reaction conditions. In continuation to this study, herein, we present the preparation and characterization of novel ionic liquid derived ordered mesoporous carbon (IOMC) based sulfonic acids for the selective dehydration of fructose into 5-HMF. This study was motivated by the fact that chemical composition over the surface of this type of carbons may provide a suitable hydrophobic–hydrophilic balance and play important role in selective production of HMF. In this way, we try to introduce a new correlation as a “rule of thumb” for the first time.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (EO = ethylene oxide, PO = propylene oxide), M_{av} = 5800) and tetraethyl orthosilicate (TEOS) were purchased from Aldrich. 1-Methylimidazole, 2-bromo-1-phenylethane, 2-butanol, sodium nitrite, dimethyl sulfoxide, hypophosphorous acid 50% solution, sulfuric acid (95–98%), hydrochloric acid (37%), and solvents were obtained from Merck Company, and methyl isobutyl ketone purchased from Daejung Company and used without purification.

2.2. Preparation of SBA-15. Briefly, 24 g of pluronic P123 was dissolved in 505 mL of H_2O and 101 mL of concentrated HCl at 35 °C.⁶³ Consequently, tetraethyl orthosilicate (TEOS) (54.2 g) was added to the solution. The mixture was stirred vigorously at 35 °C for 20 h followed by an aging step at 80 °C for 24 h. The solid material were separated by filtration, washed with deionized water, and dried at room temperature. The surfactant was removed by solvent extraction with anhydrous ethanol in a Soxhlet apparatus for 24 h.

2.3. Preparation of 1-Methyl-3-phenethyl-1H-imidazolium hydrogen sulfate (MPIHS). MPIHS was prepared according to standard methods and their purities were established before utilization by ^{13}C NMR and ^1H NMR. Briefly, a solution of dry toluene (50 mL), 1-methylimidazole (73.1 mmol), and 2-bromo-1-phenylethane (80.3 mmol) was refluxed for 24 h under an argon atmosphere. The resulting two phase reaction mixture was then allowed to cool at room temperature. The separated ionic liquid (IL) layer was washed with dry toluene and dried under vacuum. The anion-exchange reaction was carried out in dry methylene chloride containing 1 mmol of prepared IL and 1 mmol of H_2SO_4 . The solution was refluxed for 48 h until any hydrogen bromide byproduct was removed. After evaporation of the solvent under vacuum, 1-methyl-3-phenethyl-1H-imidazolium hydrogen sulfate (MPIHS) was isolated in >99% yield.

2.4. Preparation of Ionic Liquid Derived Ordered Mesoporous Carbon (IOMC). In a typical procedure, 1 mL of MPIHS was heated at 100 °C and 1 g of SBA-15 was slowly added to the ionic liquid to form a paste. Subsequently, the prepared SBA-15/IL paste was carbonized under argon (5 L min^{-1}) at 900 °C. In the next step, the SBA hard template was removed in a solution of sodium hydroxide (2 M) for 24 h at 50 °C. Filtration of the carbonized IOMC material and washing with deionized water up to neutralizing point and ethanol gives the final IOMC material in 10 wt % yield with respect to 1 g IL.

2.5. Preparation of Guanine-Rich Ionic Liquid Derived Ordered Mesoporous Carbon (GIOMC). The guanine-rich IOMC was prepared as follow: At first, 1 mL of MPIHS was heated at 100 °C and 0.1 g of guanine was added slowly and the mixture was stirred until dissolution of Guanine in IL. In the next step, SBA-15 (1 g) was added slowly to form a SBA-15/IL paste. As described above, the final composite was carbonized according to the above procedure. Subsequently, the hard template was removed in a sodium hydroxide (2 M) solution for 24 h at 50 °C. Filtration of the carbonized GIOMC material and washing with deionized water up to neutralizing point

and ethanol gives the final GIOMC material in ~ 10 wt % yield with respect to weight of IL and guanine.

2.6. Preparation of Sulfonated Ordered Mesoporous Carbon (IOMC-ArSO₃H and GOMC-ArSO₃H). Functionalization of prepared carbon material (IOMC and GIOMC) was carried out by reacting with 4-benzene-diazoniumsulfonate in the presence of hypo-phosphorous acid. This functionalization was performed in two steps: first is the preparation of diazonium salt and second step is chemical reduction of this salt over carbon material. In a typical procedure, 12.99 g (0.075 mol) of *p*-sulfanilic acid was dispersed in 750 mL HCl (1 M). To the well-stirred suspension in an ice–water bath (4 °C), was drop-wisely added a 10% excess of 1 M aqueous solution of NaNO₂ (82.5 mL). The solid *p*-sulfanilic acid was slowly dissolved and a clear solution was obtained after all of NaNO₂ solution was added. The final mixture was stirred for 45 min at the same temperature. The white precipitate was filtered off and washed by small amount of cold water, and dried under reduced pressure. For modification of IOMC material: the prepared 4-benzene-diazonium-sulfonate (12 g) was added into a solution of water:ethanol (200:200 mL) at 5 °C. Then, 1.2 g of IOMC was put into this solution and after mixing 200 mL of hypo-phosphorous acid (50 wt %) was added. The mixture was stirred at 5 °C for 30 min and another 200 mL of H₃PO₂ aqueous solution was added. Finally, the sulfonic acid functionalized IOMC carbon material (denoted as IOMC-ArSO₃H) was filtered and washed thoroughly with water and acetone, and dried in an oven at 80 °C.

2.7. Catalytic Procedure for the Conversion of Fructose into 5-HMF. In a home-designed stainless steel reactor with 25 mL total volume, 75 mg (0.42 mmol) fructose, 2 mol % catalyst, and either biphasic solvent, (0.5 mL H₂O/4.5 mL CH₃NO₂), [water (0.3 mL), DMSO (0.7 mL)/2-butanol (0.6 mL), MIBK (1.4 mL)], or nonaqueous 2-propanol (2 mL), were charged. The reactor was transferred to an oil bath (140 °C) to perform dehydration of fructose into 5-HMF. For semilarge scale HMF production, 750 mg fructose and IOMC-ArSO₃H catalyst (2 mol % = 90 mg) in 10 mL of 2-propanol were reacted in the same reaction conditions. After completion of the reaction, the catalyst was simply centrifuged and the resulting solution was analyzed by HPLC for conversion and HMF yield calculation.

All analysis were performed using KNAUER system equipped with UV K-2600 and RI K-2301 refractive index detectors.

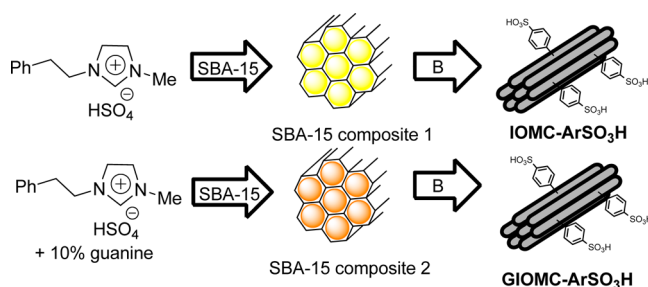
2.7.1. For Biphasic Reaction Mixture. For calculation of reaction conversion (Fructose consumption) in biphasic reaction mixtures, portions of the aqueous phase (20 μ L) were drawn out and accordingly analyzed by means of a Eurokat H C-54-1181H column, using H₂SO₄ (5 mM) as the mobile phase at a flow rate of 1 mLmin⁻¹ and a column temperature of 30 °C. For estimation of 5-HMF yield in biphasic system, a portion of aqueous (50 μ L in 2 mL methanol) and organic phases (50 μ L in 1 mL CH₃OH) was separately drawn out and accordingly analyzed by means of a Nucleosil-100 C18 column, using a 7:3 v/v (water:CH₃CN) eluent at a flow rate of 0.6 mLmin⁻¹ and a column temperature of 30 °C using a UV detector (282 nm).

2.7.2. For Reaction in 2-Propanol. For calculation of fructose conversion in 2-Propanol solvent system, a 20 μ L aliquot was drawn out and accordingly analyzed by means of a Eurokat H C-54-1181H column, H₂SO₄ (5 mM) as the mobile phase at a flow rate of 1 mLmin⁻¹ and a column temperature of 30 °C. To determine the 5-HMF yield in *i*-PrOH system, a 50 μ L of the mixture was drawn out and diluted with methanol (1 mL) and then analyzed using essentially the same method as described for organic phase analysis in biphasic systems. It was assumed that the volume changes are negligible after the dehydration reaction for all experiments. Fructose conversion was calculated as moles of fructose reacted per mole of fructose fed based on external fructose standard. Also, HMF yield was calculated as moles of HMF produced based on HMF external standard. In the case of 2-propanol as the solvent system, solvent was evaporated under reduced pressure, and the product was analyzed by means of NMR and IR.

3. RESULTS AND DISCUSSION

Novel ordered mesoporous carbons were first prepared through a two-stage carbonization of either 1-methyl-3-phenethyl-1*H*-imidazolium hydrogen sulfate (MPIHS) or 10% mixture of guanine/MPIHS in the presence of SBA-15 as hard template to give the corresponding IOMC and GIOMC respectively, following to our reported procedure with some modification.⁶¹ We prefer to employ the term IOMC rather than IFMC because, in the process of preparing IOMC, we did not use any diluting solvent and this resulted in much better ordered structure in the materials. Both IOMC and GIOMC samples were then further functionalized with arenesulfonic acid groups by chemical reduction of sulfanilic acid diazonium salt following the reported protocol by Wang et al.⁶⁴ to give the corresponding sulfonic acid supported carbons denoted as IOMC-ArSO₃H and GIOMC-ArSO₃H, respectively (Scheme 1).

Scheme 1. Schematic Representation of Ordered Mesoporous Carbon Solid Acid Preparation^a



^aB is three steps: (1) carbonization, (2) hard template removal, and (3) carbon sulfonation.

The structural parameters of all prepared materials were then measured by means of N₂ adsorption–desorption analysis at -196 °C. To do this, samples were first outgassed at 200 °C for 6 h prior to analysis. All described materials are characterized by type IV adsorption isotherms with sharp one-step capillary condensation, indicating the mesoporous structure with narrow pore size distribution. Also, acid capacity of functionalized solid carbons was measured according to standard acid–base titration of ion-exchanged materials in which 50 mg of each catalyst was suspended into 50 mL of NaCl (2 M) for 24 h.⁵¹ The characterization details of prepared materials were depicted in Table 1.

To get more insight into structural pattern of these modified carbon materials, they were further studied using transmission electron microscopy (Philips CM 200 FEG microscope, TEM) images (Figure 1).

As it can be clearly seen in Figure 1, these materials feature a 2D ordered mesoporous hexagonal structure in good agreement with nitrogen adsorption–desorption analysis data. Moreover, in order to understand the thermal stability of these materials we next analyzed the prepared mesoporous carbons by means of thermal gravimetric analysis and it was found that these materials are highly stable with a little weight loss up to 400 °C under nitrogen atmosphere (Figure 2, IOMC and GIOMC).

It was observed that this weight loss is more pronounced for functionalized carbon solid acids because of destroyed surface sulfonic acid functional groups. To assess the surface physicochemical properties, all sulfonic acid supported

Table 1. Characterization of Solid Mesoporous Materials

entry	material	S_{BET} (m^2g^{-1}) ^a	V_p (cm^3g^{-1}) ^b	W (nm) ^c	H-index ^d	acidity (mmolg^{-1}) ^e	S (mmolg^{-1}) ^f
1	SBA-15	1004	1.2	6.4			
2	IOMC	765	0.6	2.5			
3	IOMC-ArSO ₃ H	636	0.4	2.2	0.83	0.90	1.1
4	GIOMC	1050	0.9	3.3			
5	GIOMC-ArSO ₃ H	665	0.6	4.7	1.28	0.40	0.7
6	Recycled-IOMC-ArSO ₃ H	288	0.4	4.0		0.56	
7	Recycled-GIOMC-ArSO ₃ H	383	0.4	3.4		0.28	
8	SBA-15-PrSO ₃ H	682	0.92	6.2	0.81	1.2	
9	SBA-15-Ph-PrSO ₃ H	349	0.62	5.4	0.21	0.8	
10	SBA-15-ArSO ₃ H	573	0.90	9.2	0.42	0.9	
11	SBA-15-Ph-ArSO ₃ H	507	0.83	9.2	0.36	0.5	

^aSpecific surface area was determined based on BET method. ^bTotal pore volume was measured thorough BET method at $P/P_0 = 0.99$. ^cPore diameter was measured by NLDFT method. ^dHydrophilicity index = amount of adsorbed water/amount of N₂ adsorbed at ($P/P_0 \approx 0.92$). ^eAcid capacity was calculated by standard base titration (acidity of recycled catalysts after 4th run was calculated). ^fS content was measured according to CHNS analysis.

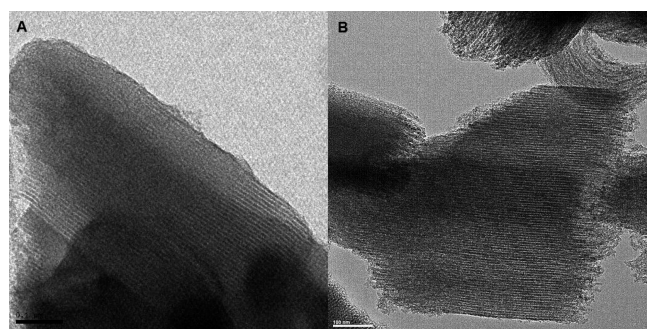


Figure 1. TEM images of carbon materials prepared by nanocasting method: IOMC-ArSO₃H (A) and GIOMC-ArSO₃H (B). The scale bar is 100 nm.

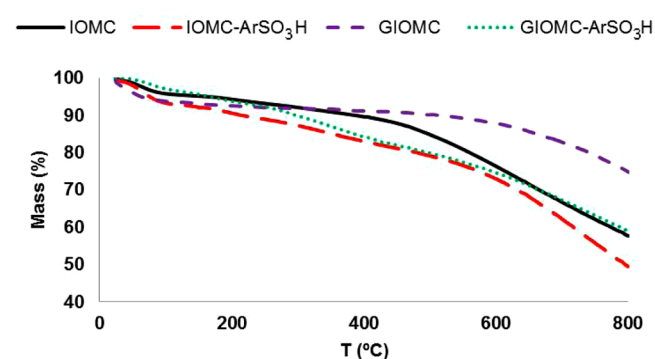


Figure 2. Thermal gravimetric analysis (TGA) of ordered mesoporous carbons prepared by nanocasting method.

materials were also studied by water sorption analysis at 25 °C. The information regarding this study will be discussed later in the manuscript. Moreover, CHN analysis disclosed that GIOMC-ArSO₃H material has 8% nitrogen content whereas IOMC-ArSO₃H has lower content of 5% nitrogen, which is truly shown the effect of guanine additive in enhancing the nitrogen content of the final mesoporous carbon. Very recently, we demonstrated that among different types of mesoporous silica functionalized sulfonic acid catalysts capable to catalyze the dehydration of fructose into 5-HMF under aqueous condition, the catalyst having an optimum hydrophilicity (i.e., SBA-15-PrSO₃H) as evidenced by its water-adsorption behavior

provided a mean of faster desorption of HMF from the catalytic surface, thus suppressing its side rehydration reaction.⁴⁷

In contrast, hydrophobic MCM-41 and SBA-15 supported sulfonic acids showed lower HMF yield and selectivity. Following this preliminary study, we noticed that Thommes and co-workers have nicely introduced an advanced hydrophilicity index (H-index) that is capable of identifying differences in surface chemistry between porous materials regardless to their chemical composition.⁶⁵ This index is a comparison of the adsorption isotherms of an adsorptive which is sensitive to surface chemistry (water) with the adsorption isotherm of an adsorptive which completely wets the adsorbent surface (nitrogen). These indices can be measured according to formula $[\text{H-index} = V_p(\text{water})/V_p(\text{nitrogen})]$, where $V_p(\text{water})$ and $V_p(\text{nitrogen})$ are, respectively, the volume of water and nitrogen in liquid form at a $P/P_0 = 0.92$. The V_p values were calculated from Gurvich rule by assuming that the pores are filled with the liquid adsorptive at this pressure (Figure 3, see also Supporting Information for calculation details).⁶⁵

Encouraged by this report, we were initially interested to compare our previously reported SBA-type mesoporous sulfonic acids by calculating their H-indices. Figure 3 demonstrates individual comparison of water (dash line) with N₂ (solid line) sorption isotherm for the described SBA-15 based sulfonic acids. A direct comparison between the H-indices and HMF yield are also demonstrated in Figure 4a.

As can be seen, by increasing the H-index from 0.21 for SBA-15-Ph-PrSO₃H up to 0.81 for SBA-15-PrSO₃H, the HMF selectivity (and of course the HMF yield) was gradually improved to reach a maximum value of 75% selectivity at 93% fructose conversion in water-organic biphasic solvent system (~70% HMF yield). It is noticeable that the rate enhancement is more pronounced by increasing H-index up to 0.42 under these conditions over SBA-type solid acid catalysts. At this stage one question arose: Is it possible to suggest that under the same reaction conditions an H-index around 0.8 for a catalyst should be an optimum value of hydrophilicity for obtaining higher HMF selectivity during the dehydration of fructose in aqueous solutions? To check the validity of this issue, we next managed to calculate the H-index for the present mesoporous carbon-based sulfonic acids in a similar way to that accomplished for SBA-type mesoporous sulfonic acids (Figure 3 E, F). In this way, the H-index values were estimated to be 0.83 and 1.28 for IOMC-ArSO₃H and GIOMC-ArSO₃H, respectively.

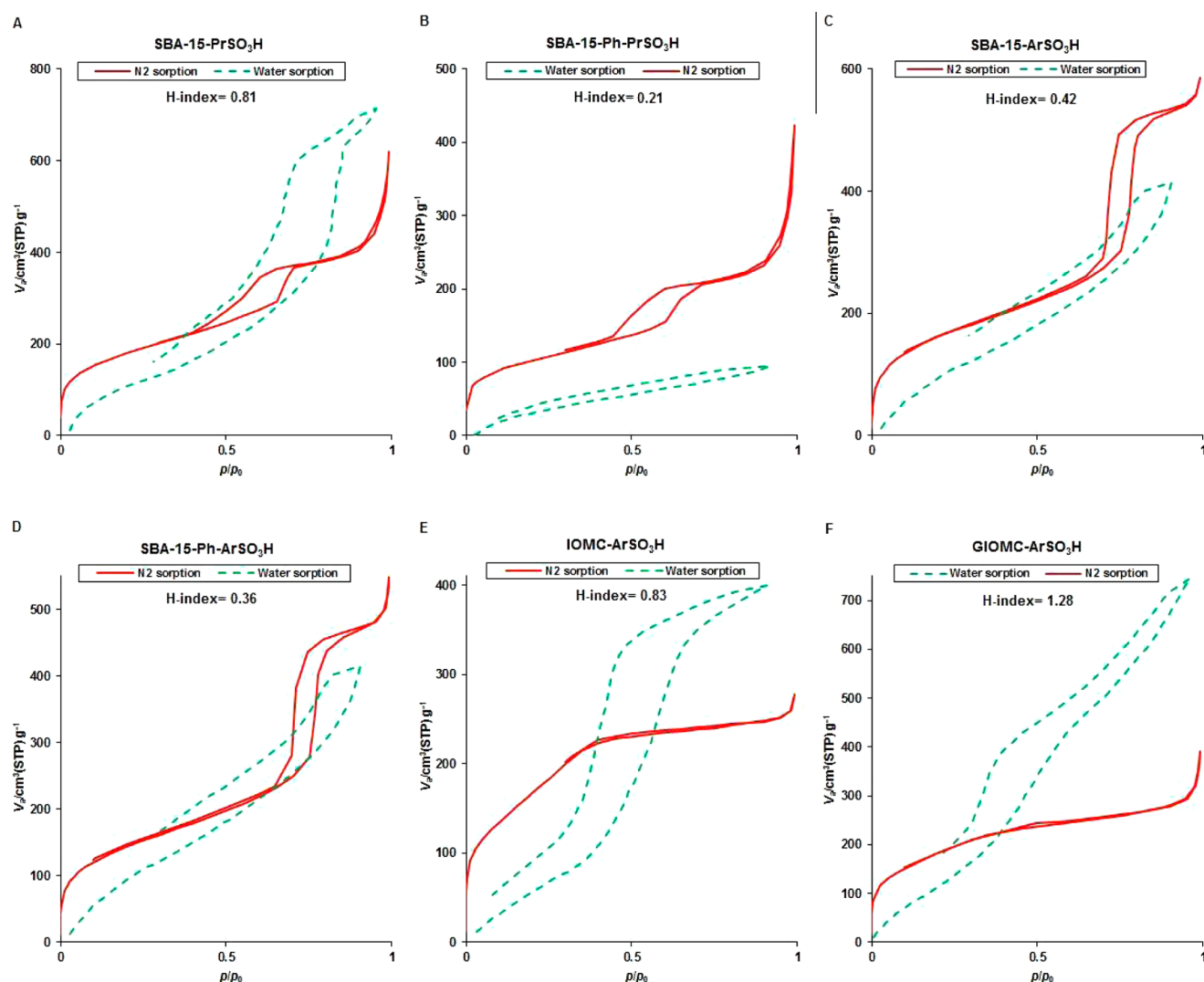


Figure 3. Hydrophilicity indices, N_2 (solid red line), and water adsorption–desorption (dashed green line) of SBA-15- $PrSO_3H$ (A), SBA-15- $Ph-PrSO_3H$ (B), SBA-15- $ArSO_3H$ (C), SBA-15- $Ph-ArSO_3H$ (D), IOMC- $ArSO_3H$ (E), and GIOMC- $ArSO_3H$ (F).

In the next stage, we compared the ability of both IOMC- $ArSO_3H$ and GIOMC- $ArSO_3H$ to actually catalyze the dehydration of fructose under a set of similar reaction conditions, with the aim of finding whether the H-index could influence their catalytic performance and HMF yields. Initially, we tested the dehydration of fructose using both catalysts under the same reaction condition ($140\text{ }^\circ\text{C}$, H_2O (0.5 mL)/ CH_3NO_2 (4.5 mL), 30 min) reported in our previous paper⁴⁷ (Table 2, entries 1, 2).

Interestingly, both IOMC- $ArSO_3H$ and GIOMC- $ArSO_3H$ catalysts were able to furnish 5-HMF in high yields of 80% and 83%, respectively. To get better insight into this observation, we next managed to conduct fructose dehydration in the presence of both catalysts under somewhat milder aqueous and nonaqueous conditions to consider the effectiveness of these catalysts over water containing and nonwater containing systems. Therefore, the performance of our catalysts was compared in widely used biphasic [water (0.3 mL), DMSO (0.7 mL)/2-butanol (0.6 mL), MIBK (1.4 mL)] system. This study confirms the superior catalytic activity of GIOMC- $ArSO_3H$ catalyst with 42% rather than IOMC- $ArSO_3H$ with 24% HMF yield (Table 2, entries 3, 4). Therefore, it may be suspected as a “rule of thumb” that a catalyst with higher H-index would

finally result in higher fructose conversion and give more HMF yield in aqueous systems. However, it is well-known that the use of nitromethane, DMSO, MIBK are not sustainable, either from an environmental or economical point of view. Therefore, it is necessary to replace these solvents with greener alternatives. With the aim of improving the sustainability and green feature of the process and HMF yield and its separation from the reaction mixture, we next switched our attention to use alcohol solvent system. Recently, alcohol mediated solvent systems were shown to be effective for solubility of sugars and their conversion into HMF while minimizing the impact on environment.^{35,66–68} Using 2-propanol as a green solvent is highly desirable enabling isolation of HMF by simple evaporation of the solvent (bp 2-propanol $\sim 83\text{ }^\circ\text{C}$). It is noteworthy that fructose solubility in this solvent is 6.7 mg mL^{-1} at $30\text{ }^\circ\text{C}$.⁶⁹ However, this solubility is significantly enhanced by increasing the temperature similar to our condition where 150 mg fructose was found to be easily dissolved in 2-propanol (2 mL) at $140\text{ }^\circ\text{C}$.

In this context, it was gratifyingly revealed that the dehydration of fructose is more favorably progressed using both catalysts in 2-propanol solvent and 87% and 91% HMF were obtained in the case of IOMC- $ArSO_3H$ and GIOMC-

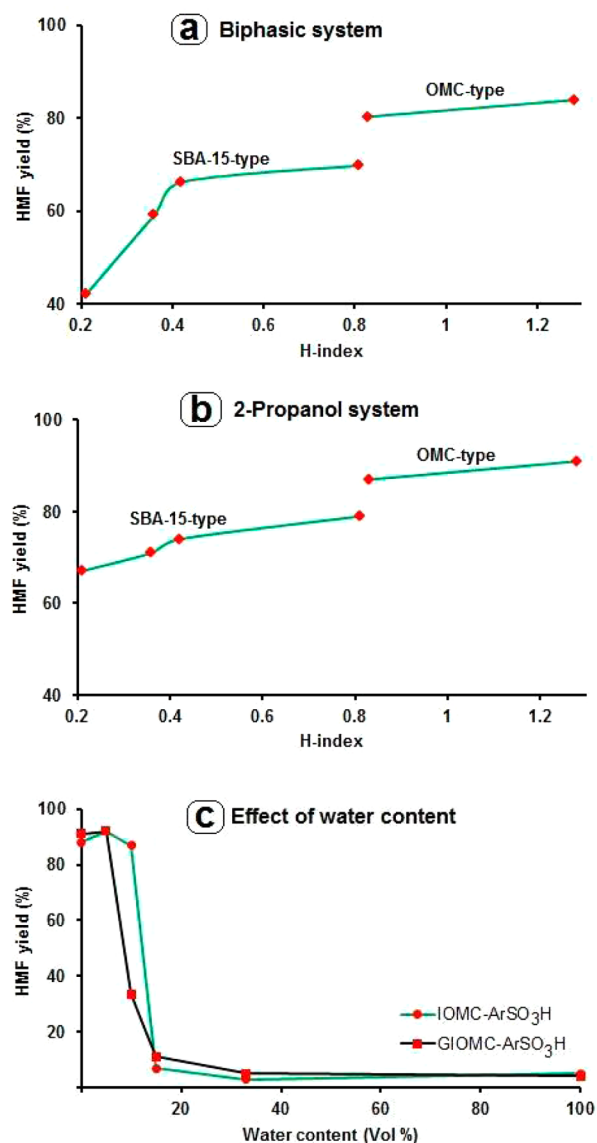


Figure 4. Correlation between HMF yield and H-index for solid acids in biphasic system (a) (1 mmol of fructose, 2 mol % catalyst, 0.5 mL of water, 4.5 mL of CH₃NO₂, 140 °C, 30 min) and in nonaqueous system and (b) (0.42 mmol of fructose, 2 mol % catalyst, 2 mL of 2-propanol, 140 °C, 30 min). (c) Effect of water content on HMF yield in 2-propanol (2 mL) over IOMC-ArSO₃H and GIOMC-ArSO₃H catalysts (2 mol %) at 140 °C for 30 min.

ArSO₃H, respectively (Table 2, entries 5 and 6). In contrast to aqueous systems which lead to byproducts, such as levulinic acid, formic acid, and humins, this system did not produce any detectable indicated side-products. Instead, a very small amounts of *i*-propyl ether of HMF (*i*-PrHMF₂, 5-(isopropoxymethyl)furan-2-carbaldehyde) were produced in <7% possibly via direct etherification of 5-HMF with 2-propanol (Figure S33–S35). We think that these excellent HMF yields over ordered mesoporous carbon acids are highly linked to nonaqueous alcohol system which is able to simultaneously dissolve both fructose and HMF in one-phase solvent system. Thus, to find whether the addition of water would deteriorate the final HMF yield, the dehydration of fructose over both carbon-based solid acids were examined in 2-propanol with different water content. It is also important to note while no apparent change in catalytic performances of

Table 2. Dehydration of Fructose over Ordered Mesoporous Solid Acid Carbons^a

entry	fructose (mmol)	catalyst	solvent (ml)	conversion (%) ^b	HMF yield (%) ^b
1	1	IOMC-ArSO ₃ H	H ₂ O/CH ₃ NO ₂ (0.5:4.5)	93	80
2	1	GIOMC-ArSO ₃ H	H ₂ O/CH ₃ NO ₂ (0.5:4.5)	96	84
3	0.42	IOMC-ArSO ₃ H	H ₂ O/DMSO:2-butanol/MIBK (0.3/0.7:0.6/1.4)	65	24
4	0.42	GIOMC-ArSO ₃ H	H ₂ O/DMSO:2-butanol/MIBK (0.3/0.7:0.6/1.4)	73	42
5	0.42	IOMC-ArSO ₃ H	2-propanol (2)	99	87
6	0.42	GIOMC-ArSO ₃ H	2-propanol (2)	99	91
7	0.42	SBA-15-PrSO ₃ H	2-propanol (2)	97	79
8	0.42	SBA-15-Ph-PrSO ₃ H	2-propanol (2)	98	67
9	0.42	SBA-15-ArSO ₃ H	2-propanol (2)	98	74
10	0.42	SBA-15-Ph-ArSO ₃ H	2-propanol (2)	99	71
11 ^c	0.42	SBA-15	2-propanol (2)	nd ^d	4
12 ^c	0.42	IOMC	2-propanol (2)	nd ^d	< 1
13 ^c	0.42	GIOMC	2-propanol (2)	nd ^d	< 1
14	4.20	IOMC-ArSO ₃ H	2-propanol (10)	99	85

^aReaction conditions are 2 mol % catalyst, 140 °C, and 30 min.

^bFructose conversion and HMF yield are calculated based on HPLC method (see Supporting Information for more information). ^c10 mg of solid supports were examined in fructose dehydration. ^dNot determined.

either IOMC-ArSO₃H or GIOMC-ArSO₃H has been occurred in the presence of H₂O vol % less than 10%, the situation has been markedly altered in the presence of higher percentage of water. In this case, it was revealed that upon the addition of 10–15% water to the fructose dehydration reaction using these catalysts, the yields of 5-HMF dramatically dropped to less than 10% (Figure 4c). Notably, this study also revealed that IOMC-ArSO₃H with H-index of 0.8 (higher surface hydrophobicity) exhibited to some extent more water resistivity as compared to that of GIOMC-ArSO₃H (H-index = 1.3, more hydrophilic) in the presence of 10–15% water (at ~12% H₂O). Although, at this stage there is no precise explanation for the reduction of HMF yield in single-phase aqueous/organic solvent system, but it might be originated from the intrinsic property of fructose dehydration process in which three water molecules are generated during the reaction. The additional water that gradually formed in the same phase with the reactant could most likely slow down the dehydration of fructose. It is also not surprising to speculate that in the presence of water higher than 15 vol % in 2-propanol, the water molecules could diffuse in the pore system of relatively hydrophilic carbon mesostructure and strongly block the catalytic active sites through solvation. This finding clearly highlights the importance of H-index to foresight the activity and stability of a solid acid catalyst in water medium fructose dehydration. This means that although by increasing H-index the HMF yield enhanced, in large scale the by-produced water gradually poison the catalyst. Thus, here it may

be possible to conclude that an optimum H-index around 0.8 is more desirable resulting in both high HMF yield and durability of the catalyst.

Encouraged by these results, we then decided to compare the efficiency of other solid acids like SBA-15 type sulfonic acids in 2-propanol solvent over the same reaction conditions to find the effectiveness of the H-index as a rule of thumb in this system (Table 2, entries 7–10). Along this line, four different SBA-15 type sulfonic acid catalysts with H-index ranging from 0.21 to 0.81 were also examined in 2-propanol giving 65–79% HMF yields in the same reaction condition (Table 2, entries 7–10, Figure 4b). However, it is clear in 2-propanol system the changes in HMF yields are not significant and comparable (but still measurable) to those observed in biphasic water/organic solvent systems (Figure 4a). That means in biphasic water/organic solvent systems the HMF yields were more substantially enhanced by increasing the H-index values from 0.21 to 0.42 (42–66% HMF yields) and then less profoundly changed upon further increasing in H-index to 0.81 (69% HMF yield). Moreover, to find the effectiveness of sulfonic acid catalysts in fructose dehydration, bare solid SBA-15, IOMC, and GIOMC supports were examined in this reaction and it was found that these supports are inactive as catalysts and no HMF was produced in the same conditions (Table 2, entries 11–13).

These observations suggest that, under aqueous and biphasic organic/aqueous conditions the fructose molecules are mostly present in water phase and should more favorably diffuse in the interior of mesochannels of the catalyst with higher hydrophilicity (higher H-index). This model may explain the inferior catalytic performance (fructose conversion and HMF selectivity) in the case of mesoporous solid sulfonic acids with high hydrophobicity, that is, H-index value lower than 0.8 in aqueous and 2-propanol systems (Figure 4a and b). In the same way, it is thereby reasonable to speculate that solvents such as 2-propanol can not only effectively dissolve the starting fructose but it may also provide a means of their fast diffusion into the mesochannels of hydrophobic, as well as hydrophilic solid acids, a feature that is most likely related to amphiphilic nature of 2-propanol. On the basis of this model, the use of 2-propanol also increases the partitionation of 5-HMF product in the solvent system as compared with those systems employing water as reaction solvent, thereby increases the departure rate of 5-HMF as soon as they generated from the catalyst surface pore system and suppressing its side reactions arising from extended residence in close proximity to the active sites. On the basis of this unprecedented observation, the present study offers a new pathway to design novel solid acid catalysts having suitable surface physicochemical properties (H-index > 0.8) for achieving high degree of conversion and selectivity in HMF production in a specific reaction media while emphasizing the elements of green and sustainability of the process.

In an attempt, a new semilarge scale experiment for production of HMF was conducted using 750 mg (4.2 mmol) fructose, IOMC-ArSO₃H catalyst (2 mol % = 90 mg), in 10 mL 2-propanol under otherwise the same reaction condition. It was found that the reaction was almost completed within 30 min and after usual work up and removal of the solvent under reduced pressure pure HMF product was obtained in 85% isolated yield (Table 2, entry 14). The stability and activity of ordered mesoporous carbon supported sulfonic acids (IOMC-ArSO₃H and GIOMC-ArSO₃H) were

then investigated in fructose dehydration using 0.83 mmol fructose (Figure 5).

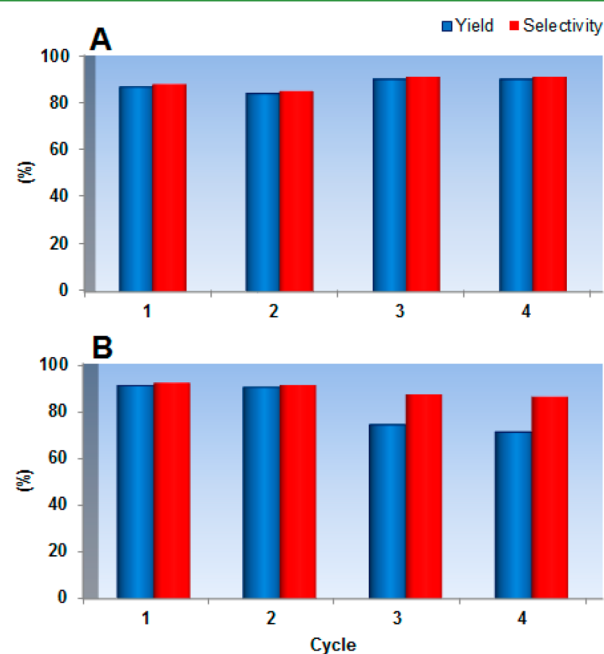


Figure 5. Reusability of IOMC-ArSO₃H (A) and GIOMC-ArSO₃H (B) in fructose dehydration in 2-propanol, 140 °C, and 30 min.

To recycle the catalyst, the catalyst was centrifuged from the reaction, washed with water and 2-propanol and dried for the next cycle at 80 °C. Although, IOMC-ArSO₃H catalyst showed good stability for at least 4 runs in terms of fructose conversion, HMF yield, and selectivity, the GIOMC-ArSO₃H catalyst was slightly deactivated which might be due to the more water uptake in this catalyst as discussed in water content experiments (Figures 4c and 5). By this observation, we concluded that although solid acid catalysts with H-indices higher than 0.8 are good candidates in fructose dehydration, large H-index catalyst has more tendencies for water adsorption in fructose dehydration and finally result in lower activity during recycling and large scale HMF production. Thus, an optimal H-index around 0.8 is more preferable in fructose dehydration. Finally, the textural properties of our catalysts were further examined by N₂ sorption analysis. Both recycled catalysts showed type (IV) isotherm with H2 hysteresis loop which indicates that the parent structure of mesoporous carbons have survived in this reaction (Table 1 and Supporting Information). However, the BET surface area and pore volume were significantly reduced which could be related to the adsorption of unreacted fructose and other byproducts during the recycling process. After fourth reaction run, recycled catalysts acidity was measured and it was observed that majority of both catalyst centers (~70%) survived in this reaction (Table 1). These results are comparable and even superior with other carbon sulfonic acid catalysts such as carbon nanotubes supported sulfonic acids from both activity-durability and in terms of using green 2-propanol solvent.⁷⁰ We are currently working on to develop novel surface tuned catalysts for more complicated carbohydrates transformation such as glucose and polysaccharides.

4. CONCLUSION

Novel ionic liquid derived ordered mesoporous carbons functionalized with sulfonic acid groups IOMC-ArSO₃H and GOMC-ArSO₃H were prepared, characterized, and examined in the dehydration reaction of fructose into 5-hydroxymethylfurfural (5-HMF) in aqueous and nonaqueous systems. To correlate the surface properties of catalysts with HMF yield, H-indices were calculated for these catalysts and also for some SBA-15 type ordered mesoporous silica acid catalysts in order to quantify surface hydrophilicity–hydrophobicity nature of the materials. It has been shown that almost a criterion may be expected for both ordered mesoporous carbon and silica solid acids in which by increasing H-index value up to 0.8 the HMF yield enhances. However, additional increasing in H-index up to 1.3 did not change the HMF yield profoundly. This observation highlights the notion that while the solid acid catalysts with H-indices higher than 0.8 (i.e., GIOMC-ArSO₃H with H-index of ~1.3) could result in superior fructose conversion into 5-HMF, it has in contrary more tendency to be deactivated through water adsorption in fructose dehydration, recycling, and particularly in large scale HMF production. Thus, the catalysts with H-index around 0.8 seem to be more preferable in fructose dehydration from the standpoint of catalyst durability.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b03985.

Additional experimental data including the sorption data, pore size distribution, TEM images, TGA, H-indices calculations, recycling data, HPLC and GC analyzes, ¹H NMR, ¹³C NMR, and IR spectra of prepared materials (PDF)

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Author Contributions

B.K. was the supervisor and proposed the initial idea of the project. B.K. and H.M.M. designed the experiments and cowrote the manuscript. H.M.M. performed most of experiments and analyzed the experimental data. H.B. conducted the original preparation and characterization of IOMC and GIOMC. H.V. conducted all TEM analyses and thoroughly discussed the results with the rest of authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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