The Catalytic Conversion of Fructose into 5-Hydroxymethylfurfural Over Acid-Functionalized KIT-6, an Ordered Mesoporous Silica

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Abstract

Well-ordered KIT-6 mesoporous silica was synthesized via a sol-gel process and functionalized with sulfonic acid groups. The catalyst was characterized using XRD, BET, TGA, SEM, TEM and pyridine FTIR spectroscopy techniques. The prepared catalyst was used to catalyze the conversion of fructose to 5-hydroxymethylfurfural (HMF) in DMSO. Various reaction parameters such as effect of reaction temperature, reaction time, catalyst loading, and solvent on HMF yield were investigated. A fructose conversion of 100% and 84.1% yield of HMF was obtained at 165 °C after 30 min in DMSO. The reaction is quite selective toward HMF. The catalyst was used several times without significantly losing its catalytic effect.

Keywords: Fructose; Mesoporous KIT-6; Catalytic conversion; HMF; Green chemistry

1. Introduction

In recent decades, the world has become more and more dependent on fossil resources including natural gas, coal and petroleum as the most important energy supplier and chemicals feedstock; due to such global demands, this dependence is increasing day after day. In addition, because of environmental pollution, global warming, diminishing reserves and high costs, many researchers have been motivated to probe sustainable alternative resources of fuel and chemicals [1-7]. At present, biomass with an approximately global production of about 1.0×10^{11} tons per year, which is also renewable and cheap, has received significant attention [8]. Sugars as derivatives of biomass are worthy feedstocks for the output of energy and chemicals including furan-based compounds [9,10]. Among them, 5-hydroxymethylfurfural (5-HMF), which has been put in the top 10 bio-based chemicals that could be made from biomass by the US DOE (Department of Energy) and it is identified as one of the most important platform chemicals [11]. HMF is procurable from acid-catalyzed triple dehydration of biomass-derived hexose carbohydrates such as sucrose, glucose, cellulose and fructose. It can be utilized as an intermediate with great potential applications for the synthesis of value-added chemicals and biofuels known as the "sleeping giants". Among them are furan-2,5-dicarboxylic acid (FDCA), which may be used as an alternative to terephthalic acid, and 2,5-diformylfuran (DFF), a versatile compound as an initiator for the synthesis of pharmaceuticals and 2,5-dimethylfuran (DMF), which is extremely valuable due to its high energy density [12-16]. Beside, fructose is often preferred among hydrocarbon resources for the production of HMF, because of its relatively easier dehydration and conversion to furanic ring. As a result, satisfactory results have been achieved using fructose [17] (Scheme 1).

Scheme 1. Conversion of fructose to 5-HMF

Many investigations for the dehydration of fructose into HMF were conducted by using a wide range of hetero- and homogeneous acidic catalysts. Mineral acids [18,19], metal chlorides [20-22], organic acids [23] and ionic liquids [24-26] are some of the homogeneous catalysts. Although these types of catalysts are inexpensive and in some cases, they have been used to obtain high yields of HMF, because of their toxicity and difficult separation from the product, further application of them is limited, especially in an industrial scale. Heterogeneous catalysts have more advantages as compared to the homogeneous ones (such as recyclability of catalyst, ease of the separation of product and less corrosiveness), making them more efficient and suitable for industrial purposes [27-30]. Therefore, according to this view, various heterogeneous acid catalysts have been employed to this end. Nijhuis *et al.* investigated the dehydration of fructose to HMF with a high selectivity by zeolites and ion-exchange resin [31]. Metal phosphates are some other solid acids [32,33]. Also, Carlini *et al.* obtained a 40.2% yield of 5-HMF for 6.0 wt.% aqueous solution of fructose by using vanadyl phosphate (VOP) [34]. Recently, many efforts have been made for the synthesis of HMF using mesoporous solid sulfonic acids. Ordered mesoporous silica (OMSs) are a type of solid catalysts with many

applications in chemistry [35, 36]. OMS- based sulfonic acids with high surface area and tunable mesopore diameter could be very efficient for the dehydration process [37-41]. Guo *et al.*, using SBA-15-SO₃H as an OMS functionalized organo-sulfonic acid, reported high efficiency in the selective synthesis of HMF. They obtained the high conversion of fructose (around 100 %) and HMF selectivity (nearly 81%) [42]. Jiang *et al.* used sulfonated MCM-41 and obtained 83.26% for the conversion of fructose and 51.83% for the yield of 5-Hydroxymethylfurfural [43].

Also, in the process of the dehydration of fructose into HMF, the selection of a suitable solvent is of great importance. Although using the water as solvent has been extensively investigated due to environmental and economical reasons, because of the lack of selectivity, it leads to the emergence of by-products such as formic acid (FA), insoluble humins and levulinic acid (LA) [44,45]. Thus, researchers attempting to examine some organic solvents (e.g. IL, MIBK, DMF, DMAc, NMP and DMSO) have tried to enhance the HMF yield instead of water. Among the organic solvents mentioned, dimethylsulfoxide (DMSO), with favorable features such as low viscosity and a high boiling point, can be more beneficial for industrial applications. On the other hand, previously published studies have shown good solubility for fructose in DMSO and the formation of furan ring is preferred in DMSO [46-48].

With regard to the described strategies, as this type of catalyst (KIT) is more hydrothermally stable for the conversion of biorenewables [49], in the present work, for the first time, we used KIT-6 (a highly ordered mesoporous silica with cubic Ia3d symmetry) functionalized propyl-sulfonic acid groups as a heterogeneous solid acid catalyst and investigated the impact of KIT-6-Pr-SO₃H on the dehydration of fructose through the selective synthesis of 5-HMF in DMSO.

2. Experimental section

2.1. Materials

HMF (as a standard sample for HPLC analysis), D-Fructose, tetraethyl orthosilicate (TEOS, 98%), 3-mercaptopropyltrimethoxysilane (MPTMS), triblock copolymer Pluronic P123 (EO20PO70EO20, Mw =5800), Dimethylacetamide (DMAc), N-Methyl-2-pyrrolidone (NMP), dimethylformamide (DMF) and DMSO were purchased from Sigma–Aldrich. On the other hand, n-butanol was obtained from Merck and all other chemicals, which were of an analytical grade, were applied without further purification.

2.2. Synthesis of mesoporous KIT-6

The KIT-6 mesostructured silica was synthesized by following the procedures published by Kleitz *et al.* [50]. For this purpose, 7 g of Pluronic P123, a triblockcopolymer used as a surfactant, was dissolved in a mixture of 253 g of deionized water and 13.7 g of HCl (35%). After the surfactant was completely dissolved, 7 g of n-BuOH was added to the homogeneous solution under stirring at 35 °C. After 1 h of vigorous stirring, 15.05 g of TEOS (tetraethyl orthosilicate) was added to the solution and the stirring of the mixture was continued for 24 h at the same temperature. Thereafter, the mixture was transferred in a closed polypropylene bottle and heated (in an air oven) under 100 under static conditions. After that, the white solid product obtained was hot filtered without any washing and dried at 100°C overnight. Finally, KIT-6 was obtained by the calcination at 550°C for 6 h.

2.3. Preparation of functionalized mesoporous KIT-6

After the surfactant was removed by calcination, the calcined KIT-6 was functionalized with sulfonic acid groups. For this propose, 1 g of parent KIT-6 was added to a mixture of 30 ml of dry toluene and 1 ml of MPTMS and then refluxed under stirring at 130°C for 24h. The obtained

thiol functionalized precipitate was filtered and extracted for 12 h in methanol using a soxhlet system and then the material was placed in an oven to dry at 80°C overnight. In the next step, the thiol groups were oxidized into -SO₃H groups by 50 ml of H₂O₂ under stirring for 24 h at room temperature. The functionalized product was filtered and then washed twice with methanol and oven dried at 80°C overnight. (Figure 1).

Figure 1. Schematic representation of preparation of KIT-6-PrSO₃H

2.4. Characterization techniques

Surface areas were computed by using the Brunauer- Emmett- Teller (BET) equation. The pore size distribution (PSDs) of the samples was obtained from the desorption branches of the isotherms by applying the Barrett–Joyner–Halenda (BJH) model and the collected pore volumes were measured from the amount of N₂ gas adsorbed at P/P₀ = 0.98. N₂ adsorption/desorption isotherms measurement was undertaken at liquid nitrogen temperature (77 K) on a Quantachrome Autosorb-iQ. Prior to the measurement, the materials were degassed at 120 °C for 4 h. The low angle X-ray powder diffraction (XRD) patterns of KIT-6 were obtained on a Brucker D8 Advance diffractometer by using Co-K α radiation (i = 40 mA and V = 40 kV). Thermo-gravimetric analysis (TGA) of the functionalized KIT-6 was performed using a STA 503 TA instrument (Hullhorst, Germany) analyzer. The samples were heated from room

temperature to 800 °C with 10 °C/min ramp rate under nitrogen atmosphere. Sulfur loading in KIT-6-Pr-SO₃H catalyst was estimated for sulfonic acid density by elemental analysis on a Leco CHNS model 932 elemental analyzer. The surface topography and the morphology of the parent and functionalized KIT-6 were recorded using scanning and transmission electron images (SEM and TEM) on a Philips XI30 microscope and Philips CN120 instruments, respectively. A JASCO FT/IR-680 PLUS spectrometer was used to record the IR spectra before and after the adsorption of pyridine on KIT-6-Pr-SO₃H.

2.5. Catalytic reactions

Dehydration reaction of fructose to HMF in DMSO as a solvent was done using KIT-6-Pr-SO₃H as the catalyst under various conditions. As a general procedure, 1 mmol of fructose and 5 mL of solvent were added in a round bottom flask (10 mL) provided with a screw top of Teflon and then 50 mg of catalyst was added into the mixture. The reaction was vigorously stirred and heated for the given time and temperature. The starting time of the reaction was taken when the temperature of the bath was set to the desired point. Upon completion, the reaction flask was transferred to an ice–water bath and then the reaction mixture was centrifuged, the catalyst was separated, and the liquid phases were diluted with deionized water before analysis. Samples were analyzed by high performance liquid chromatography (HPLC), using a RIGOL liquid chromatograph equipped with a solvent organizer (L-3140), a quaternary gradient pump (L-3240), a column oven (L-3400) using a Merck C18 reversed-phase column (125 mm × 4.6 mm, 5µm), and UV-vis detector (L-3500). The mobile phase consisted of 10% MeOH in water (with a flow rate of 1 mL.min⁻¹) and the column temperature was maintained at at 30 °C. HP 1090-II liquid chromatograph (now Agilent, Palo Alto, CA, USA) equipped with a RIE- 6A shimadzu

refractive was employed for the conversion of fructose. HMF yield, fructose conversion, and product selectivity were defined as follows:

$$\text{HMF yield (\%)} = \left[\frac{\text{moles of HMF produced}}{\text{initial moles of fructose}} \right] \times 100$$

$$\text{Fructose conversion (\%)} = \left[1 - \frac{\text{mass of fructose in product}}{\text{initial mass of fructose}} \right] \times 100$$

$$\text{HMF selectivity (\%)} = \left[\frac{\text{HMF yield}}{\text{Fructose conversion}} \right] \times 100$$

3. Results and discussion

3.1. Catalyst characterization

The textural parameters of KIT-6 and KIT-6-PrSO₃H materials were analyzed based on the nitrogen gas porosimetry. Figure 2 shows the N₂ adsorption–desorption isotherms and pore size distributions, revealing a type IV curve, according to the International Union of Pure and Applied Chemistry (IUPAC) classification, with H1 hysteresis loops typical of mesoporous structures. The isotherms shown in the figure imply that N₂ adsorption/ desorption curves of the modified catalyst were similar to those of the parent sample, thereby confirming that the mesoporous structure was preserved after modification. The results listed in the Table 1 indicated a decrease in the surface area, PSDs and pore volume of KIT-6-PrSO₃H, as compared with KIT-6. All of these decreases after loading demonstrated that PrSO₃H groups were also loaded in the pores of KIT-6. The acid functional groups present in the sulfonated sample were confirmed by CHNS elemental analyzer for measuring the sulfur content; it was illustrated that the propyl sulfonic acids were successfully anchored on into the

pores. Also, CHNS analysis of the spent catalyst was carried out, indicating a slight decrease in sulfur content due to the leaching of the active sites (see Table 1).

Table 1. Physicochemical properties of KIT-6 and KIT-6-PrSO₃H

Samples	$S_{\text{BET}}(\text{m}^2 \cdot \text{g}^{-1})$	PSD (nm)	$V_{\text{Total}}(\text{cm}^3 \cdot \text{g}^{-1})$	S Content (mmol S.g ⁻¹)
KIT-6	493	5.9	0.75	—
KIT-6-PrSO ₃ H	445	5.4	0.6	1.640 (Spent catalyst: 1.53)

Figure 2. Nitrogen adsorption–desorption isotherms and pore size distribution (inset) of KIT-6 (orange curves) and KIT-6-PrSO₃H (blue curves).

The powder XRD patterns of samples in figure 3 show three peaks corresponding to the (1 0 0), (1 1 0) and (2 0 0) diffractions at 0.98° (intense), 1.72° (weak) and 1.98° (weak) for KIT-6, respectively. This showed that the sample had a highly ordered mesostructure with a three-dimensional cubic Ia3d symmetry (Fig 3a). XRD patterns of the KIT-6-Pr-SO₃H after the grafting process (Fig 3b) and the catalyst in the second recycling (Fig 3c) showed that the long-range structural order was kept, but the intensity of XRD peaks was decreased and the 200 peak became invisible. The decrease in the intensity of XRD peaks was because of the decreased

scattering contrast between walls and channels after functionalization, as viewed for KIT-6 after surface modification.

Figure 3. low-angle XRD patterns of KIT-6 (a), KIT-6-Pr-SO₃H (b) and second recycling of the catalyst (c)

To determine the thermal stability of KIT-6-Pr-SO₃H, TGA analysis was employed. The curve of weight loss, as presented in figure 4, exhibited two distinguished weight reductions: (I) a lower weight loss across 50 and 150°C because of water removal, and (II) elimination of propyl sulfonic groups in a temperature range between 200-600°C with a higher weight loss.

Figure 4. TGA thermogram of KIT-6-Pr-SO₃H

Figure 5(a) and (b) shows the representative TEM images. These TEM images displayed an ordered cubic Ia $\bar{3}$ d symmetric mesostructure with well-ordered cubic pores arrays. The TEM observations indicated that ordered mesostructure of KIT-6 was retained even after incorporating the MPTMS via post-grafting. Thus, the remaining long range cubic ordered mesopores corroborated the results of N₂ adsorption and XRD. Also, as figure 5(c) and (d) depicts, the corresponding pore size distribution histogram was compatible with the results of BET analysis.

Figure 5. TEM images of KIT-6 (a) and KIT-6-Pr-SO₃H (b). Histograms (c) and (d) indicate the corresponding pore size distributions.

The morphology of samples was obtained using SEM (see Fig 6). The SEM images depicted the typical rock-like morphologies with accumulated particles between 50 - 400 nm, as generally seen for KIT-6 [51,52]. As shown in the figure, the samples were shaped and sized irregularly. No recognizable change in the surfaces was seen after and before Pr-SO₃H grafting.

Figure 6. SEM images of KIT-6 (a) and KIT-6-Pr-SO₃H (b)

The acidic properties of the samples were determined by FTIR spectroscopy of adsorbed pyridine measurements. The infrared spectrum in the 1400 to 1700 cm⁻¹ region was determined for pyridine adsorbed on acidic solids [53]. Spectra of the sample KIT-6-PrSO₃H before and after the adsorption of pyridine is given in figure 7. The results of the adsorption of pyridine on KIT-6-PrSO₃H obviously showed three signals at wavenumbers 1485, 1545 and 1639 cm⁻¹, indicative of pyridinium ions coordinated to Brönsted acidic sites.

Figure 7. FTIR spectra of KIT-6-PrSO₃H. (a) Before pyridine adsorption and (b) after pyridine adsorption.

3.2. Catalytic study

Mesoporous KIT-6 functionalized by propyl sulfonic acid groups as an acid catalyst was evaluated in the reaction upon the dehydration of fructose to HMF in DMSO. In the first step, the impact of the temperature on the catalytic activity was assessed. The reaction was conducted in experimental conditions including 50 mg of catalyst, 1 mmol of fructose, 5 mL DMSO and 30 min of the reaction time. The results showed that fructose conversion was increased with raising temperature, such that fructose was completely converted, achieving 100% at 180°C (Fig 8); but as shown in the figure 8, the temperature effect on the conversion was not prominent.

Although the maximum conversion was obtained at 180°C, as compared to 165°C, a decrease was observed in the HMF yield and selectivity due to the quick formation of solvable polymers and humins on the catalyst surface. Actually, the catalyst change of colour to brown was after some minutes of reaction at the highest temperature. Therefore, at the same time, the maximum selectivity and yield were achieved at 165 °C. For this reason, 165 °C was chosen as the optimal reaction temperature to consider the impact of other parameters on the catalytic process.

Figure 8. Influence of reaction temperature on the dehydration reaction of fructose. Reaction conditions: fructose 1 mmol, DMSO 5 mL, temperature = 165°C, catalyst weight = 50 mg, and time = 30 min.

The next step, the impact of the reaction time in the catalytic consideration, was assessed at 165°C. The results are shown in figure 9. The data revealed that fructose conversion was very fast, reaching to 79.9 % only in 5 minutes, whereas for yield and selectivity, the increasing trend

was continued up to 30 minutes and after this time, a decreasing trend was observed. So selectivity and yield toward the formation of HMF were uniformly increased with the reaction time, obtaining the maximum value of 77.8 % and 74.2 % after 30 min, respectively. However, in the higher reaction times, it was difficult to improve the formation of HMF, owing to the formation of humins and some of the soluble polymers. Therefore, this reaction time (30 min) was investigated as the optimal time to consider the effect of other factors on the catalytic reaction.

Figure 9. Influence of reaction time on the dehydration reaction of fructose. Reaction conditions: fructose 1mmol, DMSO 5 ml, temperature = 165°C, and catalyst weight = 50 mg.

The impact of catalyst amount was evaluated at 165°C for 30 min in the catalytic reaction. Changing amounts of catalyst (15-75 mg) indicated that with increasing KIT-6-Pr-SO₃H loading, the fructose conversion was hardly improved, perhaps because of the higher activity and the role of catalyst during the conversion of fructose in the solvent (Fig 10). Also, as shown in the figure, HMF yield and selectivity were monotonously enhanced with the increase in the dosage of catalyst, achieving a maximum value close to 84.1 % and 88.5 % respectively, with 75 mg of the catalyst. This means that in the presence of higher amounts of catalyst, the probability of the transformation of substrate into undesired products such as humins was decreased.

Figure 10. Influence of catalyst weight on the conversion, selectivity and yield of HMF among the dehydration reaction of fructose. Reaction conditions: fructose 1mmol, DMSO 5 ml, temperature = 165°C, time = 30 min.

To thoroughly investigate the advantage in the catalytic performance of KIT-6-Pr-SO₃H, we also compared and evaluated the catalytic fulfillment of two other solid acid catalysts including Amberlite-IRC-120 ion-exchange resin and Al-MCM-41 for the dehydration of fructose to HMF using similar experimental conditions (at 165°C for 30 min, with 75 mg of catalyst), though for these catalysts, the mentioned conditions might not be not optimal for their performance (some other references are listed for more comparison). The results are summarized in Table 3. When applying Amberlite-IRC-120 as the catalyst, the yield of HMF was 68.6 %, and the conversion of fructose was 100%. The tested Al-MCM for the dehydration of fructose alos gave the conversion of 100% and the HMF yield of 59.4%. The data demonstrated that the KIT-6-Pr-SO₃H had superior catalytic activity for the dehydration process amongst solid acid catalysts examined, achieving an HMF yield of 84.1% and the complete conversion of fructose.

Table 2. Comparison of HMF yields for different solid acid catalysts.

Catalyst	Substrate	Solvent	T (°C)	Time	HMF Yield(%)	References
Sulfonated CS ^a	Fructose	DMSO	160	1.5h	90	55
Sulfated zirconia	Fructose	Acetone/DMSO	180	20min	72.8	56
MASZN-3 ^b	Fructose	DMSO	110	3h	73.7	57
Al-MCM-41	Glucose	Water/ MIBK	195	150min	36	54
Nb ₂ O ₅	Fructose	DMSO	120	2h	86.2	58
SBA-15-Pr-SO ₃ H	Fructose	THF/Water	130	24h	60	35
SBA-15-Pr-SO ₃ H	Fructose	Water/ MIBK	140	30min	69.75	59
MCM-41-PrSO ₃ H	Fructose	Water/ MIBK	140	30min	59.52	59
Al-MCM-41	Fructose	DMSO	165	30 min	59.4	This work

Amberlite-IRC-120	Fructose	DMSO	165	30 min	68.6	This work
KIT-6-Pr-SO ₃ H	Fructose	DMSO	165	30 min	84.1	This work

^a Sulfonated Carbon Sphere

^b Mesoscopically assembled sulfated zirconium nanostructures

In the catalytic reactions, solvents usually play an important role and hence in this study, the influence of the solvent on the HMF formation from fructose was examined. The results are shown in Table 3. Among the solvents examined, the best results for HMF formation were obtained in DMSO, offering superior catalytic performance. By adding DMF into DMSO (w/w = 3:7), the yield of HMF was considerably decreased to 57%, proving that the DMF solvent was unfavorable for the dehydration of fructose to HMF. When the reaction was performed in NMP, the yield of HMF was 44.4%. It should be noted that in the optimal condition (165°C and 30 min), no yield of HMF for 2-propanol and DMAc was obtained. So the reaction was continued until 2.5 h for both solvents and the yield of 15.2 % and 39.6 % was obtained, respectively. However, the present research illustrated that the DMSO had excellent solvent action in promoting HMF formation from the dehydration of fructose, and the separation of the solvent from the product was difficult. Hence, more investigation is required to find a more suitable solvent. A plausible mechanism for this DMSO-induced fructose dehydration using KIT-6-Pr-SO₃H can be seen in Scheme 2.

Scheme 2. Plausible reaction mechanism.

DMSO is a polar solvent. The oxygen end of the bond is nucleophilic while the sulfur end is electrophilic. According to the proposed mechanism, the initiation step starts with proton transfer from solid Brønsted acid (KIT-6-Pr-SO₃H) to DMSO. In the next step, the OH group at the anomeric centre of fructose attacks the electrophilic (S atom) centre of protonated DMSO, leading to the formation of the covalent bond between S and O atoms. This step is accompanied

by proton transfer from the hydroxyl group of the anomeric centre to oxygen atom in DMSO. In the next steps, by the entrance of other DMSO molecules and the elimination of three water molecules, 5-HMF could be achieved.

Table 3.
Effect of solvent on the fructose conversion and yield of HMF

Entry	Substrate	Solvent	Temp. (°C)	Time	Conversion (%) ^a	Yield (%) ^a
1	Fructose	DMSO	165	30 min	100	84.1
2	Fructose	DMF/DMSO	165	30 min	93.6	57
3	Fructose	NMP	165	30 min	99	44.4
4	Fructose	2-propanol	165	2.5 h	96.7	15.2
5	Fructose	DMAc	165	2.5 h	95.9	39.6

The catalyst stability is of utmost significance for the applied use; therefore, the reusability test of KIT-6-Pr-SO₃H was carried out. The results are depicted in figure 11. To this end, the catalyst was separated from the reaction by centrifugation, washed with the mixture of water and acetone, and dried in the oven at 60°C; then it was reused in the same reaction conditions. From figure 11, it could be understood that the catalyst was reused at least for five successive catalytic runs with a slight decrease of the yield to HMF. The reason could be the active-site obstruction by humins or the leaching of active acidic species [52, 45]. The loss of activity of the catalyst in terms of product yield was only about 4% after five subsequent runs (71.4% HMF in 1th run and 67.6% HMF in 5th run). This obviously showed that the catalytic performance of the KIT-6-Pr-SO₃H was retained in the successive runs. So the catalyst system could have high reusability and

sulfated mesoporous KIT-6 characterized herein could be a very efficient and resistant solid acid catalyst in the biomass dehydration process.

Figure 11. Recycling of KIT-6-Pr-SO₃H for dehydration of fructose to HMF. Reaction conditions: fructose 1 mmol, DMSO 5 ml, temperature = 165°C, time = 30 min, catalyst weight = 50 mg.

Conclusions

In this study, the catalytic activity of well-ordered sulfonated mesoporous KIT-6 silica materials in the selective conversion of fructose to HMF under various reaction conditions was examined. The suitable condition for the production of HMF from 1 mmol of fructose was obtained when 75 mg catalyst was used at 165 °C for 30 min in DMSO as the solvent. At this condition, 84.1 % yield of HMF was obtained. Our results demonstrated that solvents had a remarkable effect on

the product distribution. It was found the catalytic activity of sulfonated mesoporous KIT-6 remained unchanged after five cycles. This method could be used to facilitate the cost-efficient conversion of biomass materials into biofuels and bio-based products.

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