### Accepted Manuscript

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PII: DOI: Reference:	S0926-860X(19)30063-8 https://doi.org/10.1016/j.apcata.2019.02.008 APCATA 16978		
To appear in:	Applied Catalysis A: General		
Received date: Revised date: Accepted date:	<ul><li>13 October 2018</li><li>1 February 2019</li><li>5 February 2019</li></ul>		

Please cite this article as: Gan L, Lyu L, Shen T, Wang S, Sulfonated lignin-derived ordered mesoporous carbon with highly selective and recyclable catalysis for the conversion of fructose into 5-hydroxymethylfurfural, *Applied Catalysis A, General* (2019), https://doi.org/10.1016/j.apcata.2019.02.008

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### Sulfonated lignin-derived ordered mesoporous carbon with highly selective and

### recyclable catalysis for the conversion of fructose into 5-hydroxymethylfurfural

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### **GRAPHICAL ABSTRACT**



### HIGHLIGHTS

- Sulfonic acid-functionalized well-ordered lignin-derived mesoporous carbon (LDMC-SO<sub>3</sub>H) was synthesized using phenolation treatment and soft-template method followed by sulfonation.
- LDMC-SO<sub>3</sub>H showed superior catalytic activity in fructose dehydration to 5-HMF in terms of fructose conversion (100.0%), 5-HMF yield (98.0%) and selectivity (98.0%).
- LDMC-SO<sub>3</sub>H possessed superior reusability and stability in terms of 5-HMF yield during six cycle runs.
- The well-ordered mesostructure and the suitable hydrophobic/hydrophilic balance of the surfaces of LDMC-SO<sub>3</sub>H might play vital roles in the efficient catalytic dehydration of fructose to 5-HMF.

#### ABSTRACT

Sulfonic acid-functionalized lignin-derived mesoporous carbon (LDMC-SO<sub>3</sub>H) was prepared using phenolation and evaporation induced self-assembly method followed by sulfonation. The obtained LDMC-SO<sub>3</sub>H bearing sulfonic acid density of 0.6528 mmol/g possessed a well-ordered two-dimensional hexagonal mesoporous characteristics. A 5-hydroxymethylfurfural (5-HMF) yield of 98.0% with a full fructose

conversion was obtained using LDMC-SO<sub>3</sub>H as catalyst at 140 °C for 2 h in DMSO. Reactive kinetics studies revealed that fructose conversion in DMSO without catalyst or catalyzed by LDMC-SO<sub>3</sub>H may obey pseudo-first-order kinetics, and the activation energy of latter (72 kJ/mol) was much lower than that of former (114 kJ/mol). Adsorption kinetics studies indicated that almost no 5-HMF adsorbed onto LDMC-SO<sub>3</sub>H probably had a great contribution to the high selectivity of up to 98.0%, while the fructose adsorption on LDMC-SO<sub>3</sub>H was a diffusion-controlling adsorption process with more following Bangham kinetic model and Weber-Morris kinetic model owing to the characteristics of ordered mesostructure of LDMC-SO<sub>3</sub>H. Moreover, LDMC-SO<sub>3</sub>H exhibited superior reusability and stability in catalytic performance with a 5-HMF yield higher than 88.0% in six runs probably due to the synergistic effect of mesopore structure with a special surface and -SO<sub>3</sub>H groups with a relatively high content. These research results will contribute to a better understanding of structure-performance relationship of LDMC-SO<sub>3</sub>H used as an efficient catalyst in the fructose-to-5-HMF transformation as well as the high-value utilization of lignin in the field of catalysis.

Keywords: Kraft lignin, Mesoporous carbon, Solid acid catalyst, Kinetics analysis, Green chemistry

#### **1** Introduction

5-hydroxymethylfurfural (5-HMF) has been considered as an important biomass-derived green platform compound possessing highly reactive substructures including furan ring, hydroxymethyl group and aromatic aldehyde. Its derivatives can be utilized widely as perfume, pharmaceutical intermediate, fuel additive, and a substitute for benzene series applied in the synthesis of new polymer materials [1]. Therefore, the research on the dehydration of biomass to prepare 5-HMF using hetero- and homogeneous acidic catalysts has drawn much attention in the world [2].

Ordered mesoporous carbons (OMCs), have received worldwide attention owing to their remarkable properties such as mesoscopic structures, high surface area and good chemical stabilities, thus becoming a kind of important material with potential application prospects in the fields of catalyst support [3], adsorption [4], drug delivery [5] and supercapacitor electrode [6]. In recent years, combining the advantages of mesoporous carbon, the acid-functionalized OMCs have been empolyed in the acid catalyzed dehydration of fructose to produce 5-HMF owing to its excellent catalytic performance with high reaction selectivity and stability [7,8]. Gallo et al [7] studied the activity and stability of sulfonated ordered mesoporous carbons (OMCs-SO<sub>3</sub>H) for the conversion of fructose to 5-HMF. It was found that OMCs-SO<sub>3</sub>H showed comparable selectivity and up to 3 times more stable than commercial Nafion SAC-13. Wang et al [8] investigated the dehydration of fructose to 5-HMF using OMC-SO<sub>3</sub>H as catalyst, and result showed that a high HMF yield of 89.4% in DMSO was obtained at 120 °C within 30 min. Furthermore, no apparent loss of the activity of OMC-SO<sub>3</sub>H was observed after it was reused 3 times. Conventionally, nanocasting method technique was widely used in synthesis of ordered mesoporous carbons. However, compared to its disadvantages of complex process and environmental pollution, soft-template method using sacrificial amphiphilic surfactants for synthesizing ordered mesoporous carbons has been adopted and further

developed in recent years [9]. So far, owing to the excellent properties of good solubility in surfactant solution, capability to interact with surfactant and self-assembly, stable three-dimensional rigid structure and relatively high carbon content, phenolic-formaldehyde based resins mainly including formaldehyde cross-linked phenol, resorcinol and phloroglucinol have been selected widely as carbon precursors applied in soft-template synthesis of ordered mesoporous carbons [10].

The application of recyclable heterogeneous catalyst derived from renewable feedstock for chemical productions is considered as one of the core principles of green chemistry [11]. As is known, lignin is a natural biomass resource possessing obvious advantages of high carbon content, low cost, environmental friendliness and sustainable utilization, which has been used widely as a superior carbon precursor in the preparations of carbon materials such as activated carbon [12] and char [13]. In the meanwhile, lignin is the only natural biopolymer consisting of plenty of aromatic rings or phenolic hydroxyl groups in its three-dimensional network structure. Thus, to reduce the reliance on crude oil resources to some extent, lignin can be employed as a promising natural substitute for phenols to crosslink with formaldehyde to synthesize phenol resins [14]. However, the poor solubility and chemical activity of lignin restricted its addition amount during the synthesis process of phenol resin utilized as adhesive. In recent years, thermochemical technology has been adopted widely to improve the solubility and reactivity of lignin via phenolation treatment, which make it more suitable for the synthesis of lignin-phenol-formaldehyde (LPF) resin [15,16].

For the same consideration, lignin also can be a superior carbon precursor for synthesis of mesoporous carbon. To our best knowledge, some studies were performed on the synthesis of lignin-derived mesoporous carbon (LDMC). Among them, the research group led by Naskar studied on LDMC synthesis and its applications involving drug delivery and supercapacitor electrode material [17-20]. However, these LDMCs were short of orderliness and the whole process was time-consuming (more than 7 days). Furthermore, only

the KL fraction extracted by methanol was employed in LDMC synthesis, thus leading to the underutilization of KL. More recently, using lignin extracted from soft wood or straw as carbon sources, Qin et al [21] found that the low-molecular-weight lignin bearing more hydroxyl groups was favorable to the formation of highly ordered mesoporous carbon as well as its utilization as catalyst support. Song et al [22] synthesized LDMC for supercapacitors using a nano-sized MgO template coupled with soft template. Besides, Chen et al [23] synthesized NiO-containing mesoporous carbon materials derived from sodium lignosulphonate (LS) using sol-gel method. Using LS as carbon source and cetyltrimethylammonium bromide as template agent, Zhao et al [24] prepared mesoporous carbon by hydrothermal and template method. Considering the sustainable development and environmental protection, either KL or LS, being a renewable biomass resource and the largest reservoir of natural aromatic polymer recovered from pulping spent liquor, is a very promising carbon precursor for LDMC synthesis. KL is separated from spent liquor of kraft pulping, which is the most dominant chemical method in pulp and paper industry. Compared to the water-soluble LS, the industrial applications of KL in large quantity are restrained by its poor solubility to a great extent. Therefore, finding an innovative approach for efficient utilization of KL in LDMC synthesis is more urgent and valuable.

Herein, firstly, to overcome the obstacles of complex super-molecular structure and poor solubility of KL, thus increasing the overall utilization of KL and the synthesis efficiency of LDMC as well as reducing its preparation cost, a well-ordered mesoporous carbon was synthesized using KL as raw material via soft-template method as shown in Scheme 1. Thus, we creatively present a reasonable synthesis route via using KL degradation products liquefied in phenol under alkaline condition followed by crosslinking with formaldehyde as carbon precursor. Compared to the results described by Naskar et al [17,19], KL could be used fully as much as possible, and the preparation time was shortened largely (about 3 days). Furthermore,

KL could be degraded into fragments with lower molecular weight and more phenolic hydroxyl groups were engrafted onto structure after phenolation treatment [16], thus facilitating the formation of LDMC [21]. Secondly, LDMC prepared in the present work was utilized as catalyst support for the synthesis of carbonaceous solid acid catalyst using traditional sulfonation method. The sulfonic acid-functionalized lignin-derived mesoporous carbon (LDMC-SO<sub>3</sub>H) was fully characterized by small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM) and Brunauer-Emmett-Teller (BET) to confirm the formation and stability of ordered mesoporous structure. The catalytic performance of LDMC-SO<sub>3</sub>H was investigated in the fructose dehydration to 5-HMF. Finally, to clarify the catalytic mechanism when using LDMC-SO<sub>3</sub>H as catalyst in fructose-to-5-HMF transformation, the studies on reaction kinetics and adsorption kinetics onto LDMC-SO<sub>3</sub>H were carried out, respectively. This study will not only provide an efficient solid acid catalyst for the conversion of fructose to 5-HMF, but also propose a new strategy for the high value-added utilization of KL in the field of catalysis as well as apply a sustainable approach for the synthesis of OMC.

#### **2** Experimental

#### 2.1 Materials

KL and Pluronic F127 were purchased from Sigma-Aldrich Chemical Co. Phenol, formaldehyde (an aqueous solution of 37%), sodium hydroxyl (NaOH), concentrated hydrochloric acid (HCl) and concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) were purchased from Xilong Chemical Co. Ltd, China. Fructose and dimethyl sulphoxide (DMSO) were purchased from Sinopharm Chemical Reagent Co. Ltd, China. 5-HMF (95%) and 5-HMF (HPLC solvent) were purchased from Aladdin Industrial Inc. All chemicals in this work were used as received without further purification.

#### 2.2 Preparations of LDMC and LDMC-SO<sub>3</sub>H

Typically, 10.0 g of KL, 30.0 g of phenol, 2.0 g of NaOH and 50 mL of 50 v% ethanol solution were added into a three-necked, round-bottomed flask provided with a mechanical stirrer, and KL was phenolated in alkaline medium at 160 °C for 2 h. Then, 10.0 mL of 37 wt% formaldehyde solution was added dropwise, and the mixture was stirred and heated at 70 °C for 60 min (donated as LPF solution). After cooling reaction mixture to room temperature, the pH value of LPF solution was adjusted to 7.0 using 2.0 mol/L HCl solution. Afterward, solvent was removed by reduced pressure distillation, and the final LPF product was dissolved in ethanol to precipitate salt.

Pluronic F127 was dissolved in 20 mL ethanol under magnetic stirring at 40 °C, which was added into the above ethanol solution containing LPF prepolymer, further stirred for 12 h. The solution was transferred onto a Petri dish, the solvent of ethanol evaporated gradually at room temperature for 8 h to form a transparent membrane first, and then the membrane was further thermo-polymerized at 100 °C for 24 h in oven. The obtained materials were scraped from the dishes and carbonized in a tube furnace under nitrogen atmosphere with the heating profile being heating to 400 °C at a rate of 1 °C/min and then heating up to 900 °C at a rate of 2 °C/min followed by maintenance at 900 °C for 60 min. Finally, LDMC was obtained after being cooled to room temperature in nitrogen flow.

The as-synthesized LDMC was added into the concentrated sulfuric acid (m/v, 1 g/20 mL) and sulfonated under nitrogen atmosphere at 180 °C for 12 h. After cooling to room temperature, the black slurry was washed with hot water (>80 °C) until no detection of  $SO_4^{2-}$  in the filtrate, then the sulfonated product was dried at 60 °C in oven for 8 h to obtain LDMC-SO<sub>3</sub>H.

#### 2.3 Characterization

Thermal gravimetric analyses (TGA) and differential thermal analyses (DTA) of F127, LPF and the

mixture of F127 and LPF were carried out on Shimadzu DTG-60H thermogravimetric analyzer in a temperature range of 30-800 °C under nitrogen atmosphere at a constant heating rate of 10 °C/min. Fourier transform infrared spectroscopy (FTIR) spectra of KL and LDMC-SO<sub>3</sub>H were recorded on a Nicolet iS50 FTIR spectrometer for KBr pellets in a range of 4000-400 cm<sup>-1</sup> and 32 scans per sample. X-ray diffraction (XRD) pattern of LDMC was recorded on Rigaku Smart Lab X-ray diffractometer with Cu K $\alpha$  radiation source at 40 kV and 30 mA from 10 to 80 ° (2 $\theta$ ) at a scanning speed of 4 °/min. The regular mesopore arrangement in a 2 $\theta$  range of 0.6-5° was identified by using SAXS profile recorded by the Rigaku Smart Lab X-ray diffractometer with Cu K $\alpha$  radiation at 40 kV and 40 mA with a scanning speed of 1 °/min. The pore textural properties of LDMC and LDMC-SO<sub>3</sub>H were investigated by nitrogen adsorption–desorption at -196 °C in a Micromerities ASSP 2020 gas adsorption analyzer. The specific surface area (*S*<sub>BET</sub>) was calculated using BET method, and the pore size distribution curve was obtained from adsorption branch by using BJH method and DFT model. TEM image of LDMC-SO<sub>3</sub>H was obtained using a FEI Tecnai G2 F20 200 kV field emission transmission electron microscope.

Using elemental analysis on an Elementar Vario Micro elemental analyzer, the sulfur contents of KL and LDMC-SO<sub>3</sub>H were measured to be 1.84 wt% and 2.30 wt%, respectively. The loading amounts (mmol/g) of -SO<sub>3</sub>H group in LDMC-SO<sub>3</sub>H was estimated using the acid-base back titration on a WDDY-2008J automatic potentiometric titrator (China). Firstly, 50 mg of LDMC-SO<sub>3</sub>H was added into 20 mL, 2 mol/L NaCl aqueous solution, then the mixture was stirred at room temperature for 12 h and was centrifuged. The filtrate was titrated with 0.01 mol/L NaOH aqueous solution. As a result, the loading amount of -SO<sub>3</sub>H group was determined to be 0.6528 mmol/g in this work.

#### 2.4 Fructose conversion into 5-HMF

The dehydration reaction of fructose was carried out in a 25 mL digestion tube. 200 mg of fructose,

20 mg of catalyst and 2 mL of DMSO were added into the digestion tube. The mixture was shaken intensively (200 rpm) in shaking table by purging with nitrogen for 2 min. Subsequently, the reaction was heated at desired reaction temperature for certain time. After reaction, the reactor was cooled to the room temperature immediately. The suspension was then filtered using 0.22 µm filter membrane, and the remaining amount of fructose and 5-HMF yield in filtrate were determined using high performance liquid chromatography (HPLC).

For the recycling experiments, 200 mg of fructose, 17.5 mg of LDMC-SO<sub>3</sub>H and 2 mL of DMSO were added to a digestion tube. The mixture was heated at 140 °C for 120 min under nitrogen atmosphere. After the reaction, LDMC-SO<sub>3</sub>H was readily recovered by filtering, washing with ethanol three times and dried at 80 °C overnight. The recovered LDMC-SO<sub>3</sub>H was used to catalyze the dehydration of fructose into 5-HMF over ten successive reactions by adding fresh fructose (200 mg) and DMSO solvent (2 mL) in each run.

#### 2.5 Analysis of product

The concentration of 5-HMF was measured by HPLC analysis performed on an Elite P-1201 (Dalian, China) equipped with a UV-Vis detector ( $\lambda$ =284 nm) and an Agilent ZORBAX Eclipse Plus C18 analysis column (Ø4.6 × 250 nm). The mixture solution of methanol and water (1/4, v/v) was used as the mobile phase at a flow rate of 0.8 mL/min, and the column temperature was maintained at 50 °C. In the meanwhile, the concentration of fructose was tested by HPLC analysis performed on an Agilent 1260 Infinity II equipped with a refractive index detector and an Agilent ZORBAX carbohydrate analysis column (Ø4.6 × 250 mm). The mixture solution of acetonitrile and water (3/1, v/v) was used as the mobile phase at a flow rate of 1.0 mL/min, and the column temperature was maintained at 50 °C. The amounts of fructose and 5-HMF were calculated according to the external standard curves constructed with authentic standards.

Finally, yield of 5-HMF (Y), fructose conversion (x) and reaction selectivity (S) were calculated based on the Eqs. (1)-(3), respectively.

$$Y(\%) = \frac{n_H c_H V M_F}{m M_H} \times 100 \tag{1}$$

$$x(\%) = (1 - \frac{n_F c_F V}{m}) \times 100$$
(2)

$$S(\%) = \frac{Y}{x} \times 100 \tag{3}$$

where  $c_F$  and  $c_H$  are the concentrations of fructose and 5-HMF (mg/mL) determined by HPLC; *m* is the original amount of fructose (mg) before reaction; *V* is the volume of solution (mL);  $M_F$  and  $M_H$  are the molecular weights of fructose and 5-HMF (mg/mol);  $n_F$  and  $n_H$  are the times of volume dilution for fructose and 5-HMF, respectively.

In addition, the important byproduct of levulinic acid generated from the further acid catalyzed degradation of 5-HMF was determined using gas chromatography (GC) performed on an Agilent 7890N GC equipped with a flame ionization detector and an Agilent 19091N-116 HP-INNOWax chromatographic column ( $60 \text{ m} \times 0.32 \text{ mm} \times 0.25 \text{ }\mu\text{m}$ ). Nitrogen was used as carrier gas. The 10  $\mu$ L of sample was injected and the injector temperature was set at 250 °C in split mode with split ratio of 20:1. The GC oven temperature was programmed from 100 °C (3 min) to 220 °C (10 min) at 30 °C/min. The detector temperature was maintained at 250 °C.

#### 2.6 Batch adsorption experiments

Adsorption kinetic experiments of fructose and 5-HMF on LDMC-SO<sub>3</sub>H were carried out in a series of 25 mL digestion tubes. 200 mg of fructose, 20 mg of catalyst and 2 mL of DMSO were added into the digestion tube at 45±0.2 °C. All digestion tubes were placed in a thermostatic orbital shaker (THZ-C-1, Qiangle Lab Instruments, China) and agitated continuously at a constant speed of 150 rpm for different

contact time. The suspension was then filtered using 0.22  $\mu$ m filter membrane, and the molar concentrations of fructose remaining and 5-HMF in filtrate were determined using HPLC mentioned above. The amounts adsorbed of fructose (*q*<sub>Ft</sub>) and 5-HMF (*q*<sub>Ht</sub>) were determined using the following Eqs. (4),(5):

$$q_{\rm F_t} = \frac{(c_{\rm F_0} - c_{\rm F_t}) \times 180.16 \times V}{m_{\rm L}}$$
(4)

$$q_{\rm H_t} = \frac{(c_{\rm H_0} - c_{\rm H_t}) \times 126.11 \times V}{m_{\rm L}}$$
(5)

where  $q_{\text{Ft}}$  and  $q_{\text{Ht}}$  are the amounts adsorbed of fructose and 5-HMF after adsorption at different contact time (mg/g),  $c_{\text{F0}}$  and  $c_{\text{H0}}$  are the initial molar concentrations of fructose and 5-HMF (mol/L),  $c_{\text{Ft}}$  and  $c_{\text{Ht}}$  are the molar concentrations of fructose and 5-HMF after a certain adsorption time (mol/L), V is the volume of DMSO added into adsorption system (mL) and  $m_{\text{L}}$  is the mass of LDMC-SO<sub>3</sub>H as adsorbent (g).

#### **3 Results and discussion**

#### 3.1 Sulfonic acid-functionalized LDMC

To ensure an appropriate carbonization temperature for removing soft temple (F127) completely during the preparation process of catalyst, the pyrolysis analyses of main substances involved in experiments were conducted by means of the methods of TGA and DTA, and the results were shown in Fig. 1. It can be seen from Fig. 1a that all of the LPF, F127 and their compound start to lose weight at 190 °C. Especially for F127, its weight loss increases dramatically at 315 °C, and then becomes gentle at 410 °C, finally leading to zero in weight. In the meantime, the DTA curve in Fig. 1b further exhibits the maximum weight loss rate of F127 pyrolysis occurs at 380 °C, highlighting the complete removal of F127 at temperature higher than 400 °C. While the weight loss rate of LPF pyrolysis is relatively stable in the temperature range from room temperature to 1000 °C. Furthermore, it is also observed in Fig. 1b that the

maximum weight loss rate of the pyrolysis of compound of LPF and F127 appears at 395 °C, which is close to the result of F127, thus suggesting the weight loss of compound is mainly caused by F127 combustion. Thus, F127 can be removed absolutely at the selected carbonization temperature of 900 °C in this experiment.

At carbonization temperature of 900 °C, the XRD pattern in Fig. 2 of as-prepared LDMC is characterized mainly by two peaks appeared around at 22° and 43°, respectively. The former broad diffraction peak corresponds to the (002) reflection of graphite, illustrating the composition of non-regular multi-ring aromatic carbon thin layers. And the latter peak with less intense is attributed to the (110) and/or (100) planes of graphite, suggesting an occurrence of graphitic structure in LDMC.

Fig. 3 illustrates the FTIR spectra of KL and LDMC-SO<sub>3</sub>H. The FTIR spectrum of KL displays the typical structural characteristics of KL. A strong and broad peak is observed around 3420 cm<sup>-1</sup>, which is originated from O-H stretching, illustrating the presence of a large amount of aliphatic hydroxyl group and phenolic hydroxyl group in KL structure. The absorption bands located around 1600 and 1515 cm<sup>-1</sup> are assigned to vibrations of aromatic rings in lignin. More absorption bands are observed at 1450 cm<sup>-1</sup> (deformation vibration of the CH- group in the aromatic ring), 1370 cm<sup>-1</sup> (symmetric deformation vibrations of C-H in methoxyl groups), 1270 and 1230 cm<sup>-1</sup> (stretching vibrations of guaiacyl rings), 1130 cm (vibrations of syringyl ring) and 1030 cm<sup>-1</sup> (deformation vibrations of the C-H bonds in the guaiacyl ring and C-O bonds) [25]. Furthermore, it is found that the intensity of the absorption band at 1515 cm<sup>-1</sup> is greater than that at 1600 cm<sup>-1</sup>, and the intensity of the absorption band at 1270 cm<sup>-1</sup> is also greater than that at 1230 cm<sup>-1</sup>, as well as there is an intensive absorption band at 1030 cm<sup>-1</sup>, all of which are very typical for the FTIR spectrum of softwood lignin containing more guaiacyl units [26]. For LDMC-SO<sub>3</sub>H, there occurs a strong and broad adsorption peak around 1084 cm<sup>-1</sup> originating from S=O bond (~1190 cm<sup>-1</sup>) and C-S

bond (~1040 cm<sup>-1</sup>) in its FTIR spectrum, confirming a successful introduction of -SO<sub>3</sub>H group into LDMC structure after sulfonation.

Fig. 4 shows the SAXS patterns of LDMC prepared by the method of solvent evaporation induced self-assembly (EISA) and the sulfonated LDMC after sulfonation treatment. The SAXS patterns of the synthesized carbon materials from Fig. 4 reveal the well resolved (100) ( $2\theta$ =1.0°) and the (110) and (200) peaks, indicating an existence of ordering at long range distance associated with the two-dimensional (2D) hexagonal symmetry (p6m mesostructure) [27]. Because the N<sub>2</sub> adsorption-desorption isotherms at a low relative pressure of approximately 0.01-0.04 is considered as exhibiting microporous characteristics [21], Fig. 5 depicts the  $N_2$  adsorption-desorption isotherms in the relative pressure at P/P<sub>0</sub> >0.05 and pore size distribution of LDMC before and after sulfonation. Fig. 5a reveals that carbon samples are characterized by a broad hysteresis loop at a high relative pressure (P/P<sub>0</sub>>0.4). The isotherm is type IV, a typical mesoporous material. Meanwhile, a narrow peak in pore size distribution occurs at about 3.42 nm shown in Fig. 5b. Notably, there is no obvious difference in SAXS pattern between LDMC and LDMC-SO<sub>3</sub>H (Fig. 4), and the same result occurs in the results of BET measurement as shown in Fig. 5. Furthermore, seen from Table 1, the specific surface area and the mesopore volume ( $V_{\text{meso}}$ ) reflecting textural properties of mesopore in LDMC are similar to those of LDMC-SO<sub>3</sub>H, indicating a good maintenance of mesoporous structure in carbon material after sulfonation treatment. Compared with the lignin-derived solid acid (LPC-SO<sub>3</sub>H) prepared via incomplete carbonization (at 450 °C) followed by sulfonation in our previous work [28], there is no obvious structural shrinkage for LDMC-SO<sub>3</sub>H after the treatment of concentrated sulfuric acid probably due to its higher crystallinity after carbonization at high temperature (900 °C used in this work) shown in Fig. 2.

The morphology and microstructure of LDMC-SO<sub>3</sub>H inspected by transmission electron microscopy

is shown in Fig. 6. It is observed clearly that LDMC-SO<sub>3</sub>H exhibits hexagonally arranged and stripe-like patterns, further authenticating a well-ordered 2D hexagonal mesoporous characteristics [27].

#### 3.2 Conversion of fructose into 5-HMF

To evaluate the catalytic performance, LDMC-SO<sub>3</sub>H was used as solid acid catalyst for the dehydration of fructose into 5-HMF in DMSO. Fig. 7 exhibits the influences of reaction temperature and time on the dehydration of fructose into 5-HMF in terms of fructose conversion, 5-HMF yield and reaction selectivity with LDMC-SO<sub>3</sub>H and without catalyst (blank tests). Seen from Fig. 7a,c,e, it is observed that fructose conversion, 5-HMF yield and selectivity increase with prolonging reaction time in the absence of catalyst, reflecting a certain catalytic reactivity of DMSO (solvent) in the conversion process of fructose. Furthermore, higher temperature more exacerbates this change trend. However, by comparing the experimental results between dehydration fructose to 5-HMF with LDMC-SO<sub>3</sub>H (Fig. 7b,d,f) and those without catalyst (Fig. 7a,c,e), it is found that LDMC-SO<sub>3</sub>H can accelerate the conversion of fructose significantly. For example, the fructose conversion increases from 53.0% to 92.2% with adding LDMC-SO<sub>3</sub>H (catalyst load of 10 wt%) at 140 °C for 60 min. More importantly, it is found that in the absence of catalyst, the 5-HMF yield (8.1%) and selectivity (10.3%) are very low at the initial reaction time, and low temperature can prolong this initial period dramatically. It is widely believed that the dehydration of glucose or fructose to 5-HMF catalyzed by an acid catalyst is via an open-chain or a cyclic furanose intermediate pathway [29]. A key intermediate in the dehydration reaction of fructose to 5-HMF in DMSO at 150 °C without catalyst was identified by Amarasekara et al [30]. It was found that there was a synergistic catalysis between DMSO solvent and acid catalyst for this reaction. In this work, it is proposed that due to the longer time spent on the dehydration of fructose to intermediates in the absence of catalyst compared to that in the present of LDMC-SO<sub>3</sub>H as catalyst, 5-HMF is not formed during the first period of time. In other word, the

prepared LDMC-SO<sub>3</sub>H can accelerate the intermediate reactions to shorten the time for generating 5-HMF from fructose in DMSO solvent.

In the meanwhile, it was observed obviously in Fig. 7b that the conversion of fructose increases with prolonging time until it reaches a high equilibrium conversion and is even completely transformed. Notably, increasing reaction temperature can shorten the reaction time required to achieve the equilibrium conversion or the full conversion of fructose. Within the scope of experiments, fructose conversion, 5-HMF yield and selectivity reach the maximum values of 100.0%, 98.0% and 98.0% when reaction temperature and time are 140 °C and 120 min, respectively. It is particularly noteworthy that 5-HMF yield as well as reaction selectivity increase dramatically to the maximum values first but then decline gradually with time. Research over the years has revealed that in addition to the main reaction of dehydration of fructose into 5-HMF, the transformation process of fructose catalyzed by acids is complicated owing to the simultaneous existence of side reactions including tandem and/or parallel reactions [2,31,32]. With prolonging reaction time to some extent, side reactions could occur under enough reaction time. For example, the accumulation of 5-HMF produced from fructose-to-5-HMF transformation will accelerate the further degradation of 5-HMF to other substances with smaller molecular weight such as levulinic acid [32-35], thus leading to the gradual decreases in 5-HMF yield and reaction selectivity. Under the experimental conditions of reaction temperature and time of 140 °C and 120 min, 5-HMF yield and selectivity are only 8.1% and 10.3% without catalyst, but both of them increase dramatically to the maximum 5-HMF yield (98.0%) with adding LDMC-SO<sub>3</sub>H (catalyst load of 10 wt%). It is suggested that LDMC-SO<sub>3</sub>H can accelerate the fructose conversion and has highly selective catalysis for the conversion of fructose to 5-HMF in DMSO within 120 min. And when reaction time is prolonged from 120 min to 180 min, some 5-HMF is rehydrated to levulinic acid (4.0 mol%), thus slightly decreasing 5-HMF yield from the maximum value of 98.0% to 93.8% (Fig. 7d), which

basically corresponds to the stoichiometry of rehydration reaction of 5-HMF to levulinic acid. In addition, based on the mass balance of 5-HMF, a small amount of 5-HMF (about 0.2 mol%) is probably transformed into the insoluble humins.

#### 3.3 Reaction kinetics study

Kinetics study of fructose dehydration into 5-HMF using LDMC-SO<sub>3</sub>H as a catalyst was investigated. Previous studies have certified the assumption that the conversion of fructose into 5-HMF is inclined to obey a pseudo-first order reaction process when fructose is dehydrated into 5-HMF (the sole and stable degradation product) with high selectivity [11,36]. Thus, under experimental conditions, the rate of fructose conversion can be expressed as follows (Eq. (6)) according to the first order reaction:

$$\frac{\mathrm{d}c_{\mathrm{F}}}{\mathrm{d}t} = -kc_{\mathrm{F}} \tag{6}$$

which, integrated, lead to Eq. (7):

$$kt = \ln \frac{c_{\rm F_0}}{c_{\rm F_t}} = \ln \frac{1}{1 - x_{\rm t}}$$
(7)

where *k* is the pseudo-first-order rate constant of fructose dehydration at a certain reaction temperature (min<sup>-1</sup>); *t* is the reaction time (min); and  $x_t$  is the conversion of fructose at a certain reaction time (%).

Results of the data fitting are listed in Table 2. The correlation coefficient  $R^2$  shows relatively good linearity at different reaction temperature, which supports the hypothesis of pseudo-first order reaction for the dehydration of fructose into 5-HMF. Furthermore, as listed in Table 2, the obtained rate constant (*k*) of fructose-to-5-HMF transformation increases when the reaction temperature increases from 120 to 160 °C, thus quantitatively confirming an obvious promotion of fructose conversion into 5-HMF via raising reaction temperature. In addition, the reaction rate constant follows Arrhenius equation (Eq. (8)), and its logarithmic form is shown as Eq. (9).

$$k = A e^{\left(-\frac{E_a}{RT}\right)} \tag{8}$$

$$\ln k = -\frac{E_{\rm a}}{RT} + \ln A \tag{9}$$

where *A* is the pre-exponential factor (min<sup>-1</sup>) and  $E_a$  is the activation energy (kJ/mol). Results of the data fitting for the plot of (ln *k*) as a function of (1/*T*) based on the Arrhenius equation are also listed in Table 2. As shown in Table 2, the obtained  $E_a$  and *A* for the fructose conversion without catalyst and with LDMC-SO<sub>3</sub>H as catalyst are 114 kJ/mol,  $3.13 \times 10^{12}$  min<sup>-1</sup> and 72 kJ/mol,  $7.04 \times 10^7$  min<sup>-1</sup>, respectively. It further affirms that the addition of LDMC-SO<sub>3</sub>H as catalyst can decrease the reaction activation energy and promote the efficient conversion of fructose significantly, and it is suggested that the synthesized LDMC-SO<sub>3</sub>H in this work has a comparable efficiency as a catalyst for fructose dehydration to 5-HMF in DMSO over other efficient porous solid acids reported in literature [11], such as sulfonic acid-functionalized metal-organic frameworks (55 kJ/mol), HZSM-5 (Si/Al=25) (70 kJ/mol), bifunctional catalyst prepared by sulfonic acid- and ionic liquid-functionalization over mesoporous silica nanoparticles (68 kJ/mol) under the reaction conditions of temperature of 120 °C, time of 60 min and catalyst load of 60 wt% in DMSO.

Fig. 8a exhibits the comparison of catalytic performance of different catalysts including three typical commercial solid acids of HZSM-5, Amberlyst 15 and phosphotungstic acid (PTA) for the conversion of fructose into 5-HMF under the previous optimized conditions. As shown in Fig. 8a, fructose conversion (100%), 5-HMF yield (98.0%) and reaction selectivity (98.0%) obtained with LDMC-SO<sub>3</sub>H as catalyst are much higher than those with HZSM-5 as catalyst. In the meanwhile, the catalytic performance of LDMC-SO<sub>3</sub>H for production of 5-HMF from fructose dehydration is comparable to that of Amberlyst 15 or PTA, highlighting a good prospect for catalytic application of LDMC-SO<sub>3</sub>H in the conversion of fructose into 5-HMF. Furthermore, to verify the behavior of catalyst, the effect of reaction time on the fructose conversion reaction with three different catalyst (Amberlyst 15, PTA and LDMC-SO<sub>3</sub>H) were investigated, and the

results are shown in Fig. 8b. Seen from Fig. 8b, the reaction time to reach the maximum fructose conversion and 5-HMF yield is within 40 min using PTA as catalyst, which is shorter than that using Amberlyst 15 or LDMC-SO<sub>3</sub>H as catalyst, highlighting the catalytic efficiency of PTA. Notably, it is observed that although the variation trend of fructose conversion with reaction time using Amberlyst 15 is similar to that using LDMC-SO<sub>3</sub>H, the 5-HMF yield obtained using Amberlyst 15 is much lower than that using LDMC-SO<sub>3</sub>H during the experimental time (~120 min). As is known, both of Ameberlyst 15 and PTA have very high acid density [37]. In addition, Bispo et al [38] proposed that when the loading of -SO<sub>3</sub>H group on sulfonic acidfunctionalized periodic mesoporous organosilicas was not less than 0.56 mmol/g, other particular factors such as the problem of acid sites accessibility might also influence the activity of catalyst. Therefore, the result in this work implies that the ordered mesoporous structure of LDMC-SO<sub>3</sub>H bearing less acid sites (0.6528 mmol/g of -SO<sub>3</sub>H group density) compared to Ameberlyst 15, could presumably contribute a lot to promote the conversion of fructose into 5-HMF via providing pore channels for the acid sites accessibility. 3.4 Catalytic mechanism

It has been reported that mass transfer limitations often result in a reduced selectivity for exothermic reactions, but the similar result was also found in the dehydration of fructose into 5-HMF as an endothermic reaction [11]. To confirm the contribution of pore channels of the lignin-derived mesoporous carbon to the heterogeneous catalytic system, adsorption studies of fructose and 5-HMF onto LDMC-SO<sub>3</sub>H in DMSO solvent were carried out, respectively. Fig. 9 illustrates the adsorption kinetic curves of fructose and 5-HMF on LDMC-SO<sub>3</sub>H under the experimental conditions of LDMC-SO<sub>3</sub>H of 20 mg as adsorbent, DMSO of 2 mL, initial concentration of fructose or 5-HMF of 100 mg/mL and adsorption temperature of 45 °C. Interestingly, it is observed that there are different stages occurred during adsorption process. In the first stage, a small amount of fructose is adsorbed gradually onto LDMC-SO<sub>3</sub>H during the initial 50 min. And

then, the adsorbed amount of fructose increases dramatically with prolonging adsorption time to 90 min in the second stage. Finally, in the third stage, the adsorption kinetic curve of fructose on catalyst reaches a platform within the experimental range of adsorption time from 90 to 240 min, and the equilibrium adsorption capacity of fructose on LDMC-SO<sub>3</sub>H is determined to 691.4 mg/g. However, compared to fructose, 5-HMF is barely adsorbed onto catalyst during its whole adsorption process, highlighting an obvious difference in adsorption behavior on LDMC-SO<sub>3</sub>H between fructose and 5-HMF.

Based on the data shown in Fig. 7, the fructose conversion without catalyst (42.8%) is lower than that with LDMC-SO<sub>3</sub>H (82.7%) at 30 min; at the same time, the former 5-HMF yield is close to zero, but the latter 5-HMF yield is obtained to 46.9%. It is suggested that although fructose can be converted in DMSO at high temperature, the fructose-to-5-HMF transformation only quickly occurs on the LDMC-SO<sub>3</sub>H when fructose is gradually adsorbed onto LDMC-SO<sub>3</sub>H in the first adsorption stage. With prolonging time from 60 to 120 min, the 5-HMF yield without catalyst varies slightly from 1.0% to 8.1% which can be neglected, but the 5-HMF yield in the presence of LDMC-SO<sub>3</sub>H increases dramatically from 77.7% to 98.0%. Interestingly, it is found that the difference in 5-HMF yield increases significantly (from 46.8% at 30 min to 76.7% at 60 min to 89.9% at 120 min), which accords with the result that larger amount of fructose is adsorbed onto LDMC-SO<sub>3</sub>H and contacts its acid sites for achieving higher 5-HMF yield in the second adsorption stage mentioned above. It can be inferred that the yield of 5-HMF increases significantly at the initial reaction stage until reaching the maximum value (98.0%), which is probably due to the increasing adsorbed amount of fructose onto LDMC-SO<sub>3</sub>H. The result also demonstrates that the dehydration process of fructose to intermediates can be sped up dramatically and 5-HMF can be obtained quickly through the contact between fructose and LDMC-SO<sub>3</sub>H, highlighting the efficient catalytic activity of LDMC-SO<sub>3</sub>H in the dehydration of fructose to 5-HMF.

In addition, because LDMC-SO<sub>3</sub>H can hardly adsorb 5-HMF within the experimental time range of 0~240 min, the 5-HMF generated during the dehydration process of fructose can be removed away from the acid sites of LDMC-SO<sub>3</sub>H into DMSO solvent instantaneously, thus enhancing the reaction selectivity significantly via greatly reducing the further acid catalyzed degradation of 5-HMF into byproducts [32-35]. Moreover, due to the more hydrophobic nature of HMF than fructose, it can be speculated reasonably that the as-prepared LDMC-SO<sub>3</sub>H has a suitable hydrophobic/hydrophilic balance of the surfaces, which is more favorable for the faster departure of the generated 5-HMF, thus retarding the rehydration of 5-HMF to byproducts and improving selectivity significantly [39].

To further clarify the correlation between mesoporous structure of LDMC-SO<sub>3</sub>H and its catalytic mechanism for fructose-to-5-HMF transformation, four adsorption kinetic models including pseudo-first-order, pseudo-second-order, Weber-Morris (intra-particle diffusion) and Bangham (two-constant rate) equations were employed to fit the adsorption kinetic curve of fructose on LDMC-SO<sub>3</sub>H shown in Fig. 9. The linear fitting results are illustrated in Fig. 10.

The integral expression of pseudo-first-order kinetic model proposed by Lagergren as Eq. (10):

$$\log(q_{\rm F_e} - q_{\rm F_t}) = \log q_{\rm F_e} - \frac{k_1}{2.303}t \tag{10}$$

where  $k_1$  is the pseudo-first-order rate constant (min<sup>-1</sup>) and  $q_{Fe}$  is the equilibrium amount adsorbed of fructose after equilibrium adsorption (mg/g). Value of  $k_1$  was calculated from the slope of the plots of 2.303×log ( $q_{Fe}/(q_{Fe}-q_{Ft})$ ) versus *t* (Fig. 10a). The pseudo-second-order rate equation can be followed as Eq. (11):

$$\frac{t}{q_{\rm F_t}} = \frac{1}{k_2 q_{\rm F_e}^2} + \frac{t}{q_{\rm F_e}}$$
(11)

$$h = k_2 q_{\mathrm{F_o}}^2 \tag{12}$$

where  $k_2$  is the pseudo-second-order rate constant (g/(mg·min)), h expresses the initial adsorption rate

 $(mg/(g \cdot min))$  (Eq. (12)). Values of  $k_2$  and  $q_{Fe}$  were calculated from the plots of  $t/q_{Ft}$  versus t (Fig. 10b).

In general, the adsorption process onto porous adsorbents includes four major steps: (a) external diffusion in bulk liquid-phase, (b) boundary layer diffusion, (c) intra-particle (pore) diffusion within particle and (d) adsorption on active sites [40]. Among them, adsorption occurs instantaneously and its effect on adsorption rate can be neglected. Thus, the main resistances to mass transfer are liquid film diffusion (including steps (a) and (b)) and intra-particle diffusion. To further predict the rate-limiting step of adsorption process, Weber-Morris model (intra-particle diffusion model) is suggested, which can be described by the following Eq. (13):

$$q_{\rm F_t} = k_{ip} t^{0.5} + C \tag{13}$$

where  $k_{ip}$  is the intra-particle diffusion rate constant (mg/(g-min<sup>0.5</sup>)), *C* is a constant being closely related with the thickness of boundary layer (mg/g). If  $C \neq 0$ , indicates that intra-particle diffusion is not the only controlling step and more than one diffusive resistance are involved in the adsorption process. Notably, multilinearities can be observed from the linear plot of  $q_{Ft}$  versus  $t^{0.5}$  (Fig. 10c) and the plots do not pass through the origin, demonstrating that the intra-particle diffusion controls the adsorption process but not the only rate-limiting step. In other words, the mass transfer in adsorption process is mainly influenced and controlled by liquid film diffusion and intra-particle diffusion. As defined in Eq. (13), the slopes of the first linear section ( $k_{i1}$ ) and the second linear section ( $k_{i2}$ ) are the diffusion rate constants for different adsorption stages.

The Bangham kinetic model is expressed as Eq. (14), which is often known as the two-constant rate equation and usually employed to describe the mechanism of pore diffusion in the complex heterogeneous diffusion process [41,42].

$$\ln q_{\rm E} = \ln \nu + k_{\rm b} \ln t \tag{14}$$

where  $k_b$  is the rate constant (mg/(g·min)) and v is also a constant indicating the adsorption intensity.  $k_b$  and v can be determined from the linear plot of ln  $q_{Ft}$  versus ln *t* (Fig. 10d).

Seen from Fig. 10, comparing the correlation coefficients ( $R^2$ ) of four adsorption kinetic equations, the adsorption process of fructose onto LDMC-SO<sub>3</sub>H more follows the Bangham kinetic model ( $R^2$  = 0.90337) and the Weber-Morris kinetic model ( $R^2$  = 0.81561 for the first adsorption stage,  $R^2$  = 0.90580 for the second adsorption stage). Furthermore, for Weber-Morris model, the calculated value of  $k_{i1}$  (12.61999) is much lower than that of  $k_{i2}$  (252.3087), highlighting that the adsorption rate of fructose onto LDMC-SO<sub>3</sub>H is more controlled by liquid film diffusion (as rate-limiting step) in its initial adsorption process (the first stage). Based on the combination of the comprehensive analyses above and the structural characteristics of LDMC-SO<sub>3</sub>H, it is suggested that the adsorption kinetic fitting results conform to the diffusion-controlling adsorption of reactant onto porous catalyst during the heterogeneous catalysis process. Both of liquid film diffusion and intra-particle (pore) diffusion contribute to the adsorption mechanism of fructose on LDMC-SO<sub>3</sub>H. Moreover, the mass transfer rate of fructose may be increased via accelerating stirring to decrease the resistance of liquid film and/or enlarging pore size as well as porosity of catalyst to facilitate the intra-particle (pore) diffusion.

Combining the analyses of reaction kinetics and adsorption kinetics above, the catalytic mechanism of LDMC-SO<sub>3</sub>H in the dehydration of fructose into 5-HMF with high conversion and selectivity is proposed as shown in Scheme 2. As can be seen, the well-ordered mesostructure provides LDMC-SO<sub>3</sub>H with larger area for grafting more -SO<sub>3</sub>H groups to improve the fructose contact with acid sites and the suitable paths (pore channels) for the diffusion of the fructose and the generated 5-HMF, which contributes to the high catalytic performance of LDMC-SO<sub>3</sub>H in the conversion of fructose to 5-HMF.

3.5 Stability in catalytic performance

Besides catalytic activity, the stability of catalyst is another vital property for demonstrating its catalytic performance under the background of green and sustainable chemistry. To investigate the reusability of LDMC-SO<sub>3</sub>H in the dehydration of fructose to 5-HMF in DMSO, a ten-run experiment was performed, and the results are shown in Fig. 11. Notably, under the conditions of catalyst load of 8.75 wt% (mass ratio of catalyst to fructose), reaction temperature and time of 140 °C and 2 h, the fructose conversion decreases slightly from 98.0% to 95.8% along with a decrease in 5-HMF yield from 92.1% to 88.2% in former six runs owing to the existence of minor deactivation of catalyst, but both of fructose conversion and 5-HMF yield have obvious decreases in later four runs. First of all, compared to other sulfonic acid-functionalized porous materials used as catalyst in fructose-to-5-HMF transformation in DMSO listed in Table 3 [2,8,11,43], the as-prepared catalyst in this work exerts better stability in catalytic performance in terms of 5-HMF yield with a high 5-HMF selectivity (>90%) in former six runs. The effect of catalyst load on the catalytic performance in fructose dehydration to 5-HMF is investigated, and the corresponding result demonstrated in Fig. S1 shows that 5-HMF yield does not decrease linearly with decreasing catalyst load.

As shown in Fig. S1, when catalyst load decreases from 8.75 wt% to 3.75 wt%, 5-HMF yield decreases slightly from 91.9% to 88.1%, the variation curve is relatively smooth. However, with further decreasing catalyst load from 3.75 wt% to 1.25 wt%, 5-HMF yield decreases from 88.1% to 74.7%, and even decreases to 8.1% in the absence of solid catalyst. Interestingly, 5-HMF yield increases significantly from 8.1% (without adding anything) to 34.3% with adding LDMC before sulfonation, suggesting that LDMC without –SO<sub>3</sub>H groups also exerts the catalytic performance in fructose dehydration to 5-HMF probably because LDMC with an ordered mesostructure provides mesopore channels with special surfaces for the dehydration reaction of fructose in DMSO. Yang et al [44] indicated that the hydrophobicity of functionalized silica nanoparticles was beneficial to both of 5-HMF yield and selectivity. Inagaki et al [45]

proposed that the catalyst with orderly arranged hydrophobic-hydrophilic surfaces could enclose the guest molecules or clusters with structural orientation in its pores, thus leading to an increase in the activity and selectivity. Similarly, for LDMC-SO<sub>3</sub>H in this work, the structure with suitable hydrophobic/hydrophilic balance of its surfaces can be beneficial to a large amount of capture of the fructose as well as a fast departure of the 5-HMF produced from fructose dehydration reaction within the pore channels of catalyst, which finally improves catalytic activity and reaction selectivity. Thus, it is suggested that the high 5-HMF yield and selectivity in fructose dehydration is a synergistic effect of mesopore structure with a special surface and -SO<sub>3</sub>H groups with a relatively high content in LDMC-SO<sub>3</sub>H.

The deactivation of functionalized solid acid in fructose dehydration to 5-HMF could be due to the obstruction of insoluble humins generated in side reaction or the leaching of active acid sites after repeated catalytic cycles [2,44]. As discussed in *3.2 Conversion of fructose into 5-HMF*, there is almost no humins produced under the optimized conditions. Therefore, the loss of -SO<sub>3</sub>H groups (acid sites) may be the main reason for the deactivation of LDMC-SO<sub>3</sub>H, which has a much more obvious effect on the catalytic performance in later four runs than that in former six runs in our work (Fig. 11), thus resulting in a nonlinear variation trend for ten-run experiment. It is proposed that when the content of -SO<sub>3</sub>H group in LDMC-SO<sub>3</sub>H is not very low, the problems of acid sites accessibility and reaction interface probably also influence the catalytic performance of catalyst, which is similar to the description by Bispo et al [38]. Conversely, the density of -SO<sub>3</sub>H group in LDMC-SO<sub>3</sub>H is the key factor affecting its catalytic performance in the conversion of fructose to 5-HMF.

#### **4** Conclusions

In summary, owing to the characteristics of lignin chemical structure, sulfonic acid-functionalized well-ordered mesoporous carbon derived from kraft lignin was prepared successfully by adopting the

methods of phenolation, EISA and sulfonation. Compared with other solid acid catalysts reported, the asprepared LDMC-SO<sub>3</sub>H exhibited superior catalytic performance in the conversion of fructose into 5-HMF. A high 5-HMF yield of up to 98.0% with a full fructose conversion was obtained under the conditions of fructose of 200 mg, LDMC-SO<sub>3</sub>H of 20 mg (catalyst load of 10 wt%), DMSO of 2 mL, reaction temperature and time of 140 °C and 2 h. Results revealed that the conversion reaction of fructose catalyzed by LDMC-SO<sub>3</sub>H in DMSO solvent might obey pseudo-first-order kinetics with an observed activation energy of 72 kJ/mol which was lower than the activation energy of 114 kJ/mol for the reaction in the absence of catalyst. Interestingly, it was found that LDMC-SO<sub>3</sub>H was inclined to adsorb fructose rather than 5-HMF, which probably contributed a lot to the efficient catalysis with a high selectivity of 98.0% for fructose-to-5-HMF transformation. Moreover, adsorption kinetic analysis indicated that the adsorption of fructose onto LDMC-SO<sub>3</sub>H more followed Bangham kinetic model and Weber-Morris kinetic model, which accorded with the result of diffusion-controlling adsorption on porous catalyst, further discovering the probable catalytic mechanism of LDMC-SO<sub>3</sub>H in the dehydration of fructose into 5-HMF besides its sulfonic acid groups as Brønsted acid sites. Most importantly, LDMC-SO<sub>3</sub>H possessed superior reusability with excellent stability of the relatively high 5-HMF yield for fructose dehydration in DMSO.

### Declarations of interest: none

#### Acknowledgements

The authors gratefully acknowledge the financial support by the National Natural Science Foundation of China (grant No. 21706085).

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#### **Captions of Schemes and Figures**

Scheme 1 Schematic illustration of the synthesis process of LDMC-SO<sub>3</sub>H derived from kraft lignin.

Scheme 2 Proposed schematic illustration of the correlation between the mesostructure of LDMC-SO<sub>3</sub>H

and its catalytic mechanism for fructose-to-5-HMF transformation.

Fig. 1 Pyrolysis behaviors of LPF, F127 and the compound of LPF and F127.

Fig. 2 XRD pattern of LDMC prepared via carbonization at 900 °C.

Fig. 3 FTIR spectra of KL and LDMC-SO<sub>3</sub>H.

Fig. 4 SAXS patterns of LDMC before and after sulfonation treatment.

Fig. 5 (a) N<sub>2</sub> adsorption-desorption isotherms and (b) pore size distribution of LDMC and LDMC-SO<sub>3</sub>H.

Fig. 6 TEM image of LDMC-SO<sub>3</sub>H.

**Fig. 7** Effects of reaction temperature and time on the dehydration of fructose to 5-HMF: without catalyst (a, c and e) and with adding LDMC-SO<sub>3</sub>H (20 mg) as catalyst (b, d and f). Reaction conditions: fructose (200 mg) and DMSO (2 mL).

**Fig. 8** (a) Effect of catalyst type on the conversion of fructose into 5-HMF (reaction conditions: temperature (140 °C), time (2 h), initial concentration of fructose (100 mg/mL), catalyst (20 mg) and DMSO (2mL)); (b) Effect of reaction time on the dehydration of fructose to 5-HMF with adding different catalyst (reaction conditions: temperature (140 °C), initial concentration of fructose (100 mg/mL), catalyst (20 mg) and DMSO (2mL)).

**Fig. 9** Comparison of adsorption capacity on LDMC-SO<sub>3</sub>H changed with time between fructose and 5-HMF. Conditions: temperature (45 °C), initial concentration of fructose or 5-HMF (100 mg/mL), LDMC-SO<sub>3</sub>H (20 mg) and DMSO (2 mL).

Fig. 10 Four kinetic models plot for the adsorption of fructose onto LDMC-SO<sub>3</sub>H. (a) pseudo-first-order

kinetic equation, (b) pseudo-second-order kinetic equation, (c) Weber-Morris (intra-particle diffusion) equation, (d) Bangham (two-constant rate) equation.

**Fig. 11** Recycling experiments of LDMC-SO<sub>3</sub>H for the dehydration of fructose to 5-HMF. Reaction conditions: fructose (200 mg), LDMC-SO<sub>3</sub>H (17.5 mg), DMSO (2 mL), reaction temperature and time (140 °C and 2 h).

### Table 1

Sample	$S_{\rm BET}{}^{ m a}$	$V_{ m meso}{}^{ m b}$	$D^{\mathrm{b}}$
	(m <sup>2</sup> /g)	$(\text{cm}^3/\text{g})$	(nm)
LDMC	260.0	0.075	3.42
LDMC-SO <sub>3</sub> H	261.7	0.067	3.42

Textural properties of LDMC before and after sulfonation treatment.

<sup>a</sup> The specific surface area was calculated using BET model.

<sup>b</sup> The mesopore volume and the pore diameter were determined using DFT model.

### Table 2

The first-order kinetic parameters for fructose conversion in DMSO without catalyst and that catalyzed by LDMC-SO<sub>3</sub>H.

No catalyst			LDMC-SO <sub>3</sub> H			
T (K)	$k_1 ({ m min}^{-1})$	$R^2$	T (K)	$k_1 (\min^{-1})$	$R^2$	
393.15	0.00532	0.92477	393.15	0.01484	0.96397	
403.15	0.00520	0.82036	403.15	0.03116	0.93070	
413.15	0.01020	0.93288	413.15	0.04473	0.96371	
423.15	0.02610	0.97370	423.15	0.08857	0.95693	
433.15	0.02660	0.96243	433.15	0.11333	0.85419	
$k_1 = 3.13 \times 10^{12}$	exp (-114/RT)	0.97641	$k_1 = 7.04 \times 10^7$	exp (-72/RT)	0.97590	

### Table 3

Comparison of catalytic performance in fructose dehydration to 5-HMF in DMSO between sulfonated porous materials.

Catalyst	Temperature (°C)	Time (min)	Catalyst load <sup>a</sup> (wt%)	Fructose conversion (%)	5-HMF yield (%)	Stability
KIT-6-Pr-SO <sub>3</sub> H [2]	165	30	28	100.0	84.1	71.4% 5-HMF in the 1 <sup>st</sup> run and 67.6% 5-HMF in 5 <sup>th</sup> run
OMC-SO <sub>3</sub> H [8]	120	15	33	98.7	89.4	Deactivated to <85.0% 5-HMF after 3 runs
MIL-101(Cr)-SO <sub>3</sub> H [11]	120	60	60	100.0	91.0	Deactivated from 90.0% 5-HMF in 1 <sup>st</sup> run to 85.0% 5- HMF in 5 <sup>th</sup> run
MLC-SO <sub>3</sub> H [43]	130	40	50	100.0	81.1	Deactivated from 81.1% 5-HMF in 1 <sup>st</sup> run to 74.6% 5- HMF in 5 <sup>th</sup> run
LDMC-SO <sub>3</sub> H (this work)	140	120	10	100.0	98.0	Deactivated from 92.1% 5-HMF in 1 <sup>st</sup> run to 88.2% 5- HMF in 6 <sup>th</sup> run and to 72.8% 5-HMF in 10 <sup>th</sup> run

<sup>a</sup>Catalyst load means the mass ratio of catalyst to fructose.



Scheme 1



Scheme 2



Fig. 1



Fig. 2



Fig. 3



Fig. 4

ACCEPT CRIPT 









**Fig. 7** 



Fig. 8



Fig. 9



Fig. 10



Fig. 11