One-step Preparation of Kraft Lignin Derived Mesoporous Carbon as Solid Acid Catalyst for Fructose Conversion to 5-Hydroxymethylfurfural

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A mesoporous carbon as solid acid catalyst was prepared from kraft lignin *via* one-step phosphoric acid activation. The catalyst was characterized by acid–base titration, N_2 adsorption–desorption, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and thermal gravity analysis (TGA). The results showed that the prepared solid acid catalyst had high thermal stability, large specific surface area (850 m^2/g), and a mesopore structure with the average pore diameter of 4.7 nm. The acid-base titration result of the catalyst revealed high surface acidity (5.36 mmol/g), indicating high catalytic activity. The prepared solid acid catalyst was used to catalyze dehydration of fructose to 5-hydroxymethylfurfural (HMF). The influence of reaction temperature and reaction time on HMF yield was investigated. The results indicated that a HMF yield of 80.1% was obtained with a reaction time of 3 h at 140 °C.

Keywords: Fructose; 5-Hydroxymethylfurfural; Dehydration; Solid acid catalyst; Lignin mesoporous carbon (LMC)

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INTRODUCTION

The progressive depletion of fossil resource reserves, the greenhouse gas emission by fossil transportation fuels, and environmental pollution caused by the utilization of fossil fuels and chemicals make renewable biomass feedstock the most interesting alternative to fossil feedstocks for the production of fuels, chemicals, and materials (Melero *et al.* 2012). 5-Hydroxymethylfurfural (HMF) is a key platform chemical that can be converted into more than 40 different products, such as fuels (Gawade *et al.* 2016), building block chemicals (Goyal *et al.* 2016), coating materials (Li and Zhang 2016), adhesives, fine-chemicals (Arias *et al.* 2016), and pharmaceutical intermediates (Seo and Han 2014). Furthermore, HMF can be obtained by the catalytic dehydration of biomass such as fructose, glucose, and polysaccharides (Argun and Onaran 2016; Li *et al.* 2016a; Cai *et al.* 2017). The dehydration of fructose has been performed by the use of mineral acids (HCl, H_2SO_4) as the catalysts (Chheda e*t al.* 2007; Pedersen *et al.* 2015). However, the use of mineral acids exhibit many drawbacks, such as their separation from biodiesel through deionized water washing, corrosive, nonrecyclable nature, and their disadvantage to environmental effects, which is unsuitable in the chemical industry. The design and preparation of a non-corrosive, environmentally friendly, low cost, and recyclable solid acid catalyst is critical to the development of a sustainable dehydration process for producing HMF from biomass.

Carbon-based materials, such as mesoporous carbons (MC), carbon nanotubes, and graphene oxide (GO), have been explored as green catalysts or supports for a number of sustainable chemical transformations (Shen *et al.* 2016; Wang *et al.* 2016). Graphene oxide was reported as an efficient catalyst for the dehydration of fructose to HMF (31% yield) at 100 °C for 24 h. The produced HMF was further reacted with ethanol to yield ethoxymethyl furfural (Mondal *et al.* 2014). The MCs also show a great potential as supports of catalyst due to the high specific surface areas and large pore diameters, such that large organic molecules have to access the well-dispersed active sites located inside the pores (Ji *et al.* 2016). However, conventional MC supported catalysts are disadvantageous due to a complicated preparation process and high cost. Conventional MCs are mainly made from phenolic resins, furfuryl alcohol, sucrose, polyacrylonitrile, and polydivinyl benzene *via* the template method. During this method, the template needs to be synthesized beforehand and to be removed by acid or base washing after the synthesis of MC, resulting in a high production cost, and a tedious and environmentally hazardous preparation process. Moreover, synthetic precursors are often expensive, which can increase the cost and energy consumption due to extensive processing and purification (Ren *et al.* 2016).

Lignin is the second most abundant natural polymer after cellulose, and kraft lignin (KL) is a byproduct of biomass pulping. Most KL is now directly burned to generate heat or electricity (Azadi *et al.* 2013), which is disadvantageous because the storage of heat or electricity is often complicated. In addition, the emission of flammable gas and ash could result in environmental problems. Only 1% of the annually produced lignin is being commercialized for its application in the preparation of chemicals and materials (Mahmood *et al.* 2016). Because KL has a high carbon content, it is a suitable precursor for the preparation of activated carbon and catalyst support (Li *et al.* 2016b). However, a review of the literature did not show that any research has been conducted on the synthesis of HMF using MC as solid acid catalyst from KL *via* the one-step non-template method. Therefore, in this work, a mesoporous carbon solid acid catalyst from KL was prepared *via* a one-step phosphoric acid (H_3PO_4) activation method. The prepared catalyst was characterized by acid-base titration, thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and the Brunauer-Emmett-Teller (BET) methods, and was used for the catalytic conversion of fructose into HMF.

EXPERIMENTAL

Materials

The technical KL was obtained from the Xuemei Paper Mill in Shandong Province (Shandong, China) and was de-ashed by the H_2SO_4 pretreatment method based on previous literature (Li *et al.* 2014). Fructose, H_3PO_4 (PA), and dimethyl sulfoxide (DMSO) were of analytical reagent grade and were purchased from Chendu Kelong Chemical Reagent Factory (Chendu, China). The HMF was chromatographic grade and was purchased from Sigma–Aldrich Chemical Company (Shanghai, China). High purity N_2 was obtained from the Mianyang Changjun Special Gases Factory (Mianyang, China).

Preparation of the LMC catalysts

The de-ashed KL was mixed with PA in a PA/KL mass ratio of 1:1, 2:1, 4:1 respectively, and impregnated for 12 h. The mixed samples were set on a stainless steel tubular reactor that was heated by a horizontal tubular electric furnace (LENTON, Sheffield, UK). The mixture was heated to 550 °C with a heating rate of 10 °C/min and maintained for 2 h under N_2 atmosphere. The mixture was cooled to below 50 °C before removal from the reactor. The reactor was purged with high purity N_2 at a constant flow rate (100 mL/min) during the entire activation process. The activated samples were washed with distilled water to remove residual chemical, and oven-dried at 105 °C to prepare the LMC solid acid catalysts.

Methods

Characterization of the as-synthesized catalysts

The total acid site density of the catalyst was measured using NaOH (0.01 mol/L) as titrant *via* acid-base titration, based on a method described in previous literature (Zhao *et al.* 2016). Titrations were performed three times for each condition, and the average number was reported.

The surface area, pore volume, and average pore diameter of the catalyst were determined from the corresponding N_2 adsorption-desorption isotherms obtained at -196 °C with an automatic instrument (TriStar II 3020 V1.03, Micromeritics, Norcross, MA, USA). Prior to the adsorption measurements, the sample was outgassed in a vacuum at 300 °C for 300 min. The specific surface area (A_{BET}) was determined by the BET method. The total pore volume (V_{t}) was calculated from the N_2 adsorption isotherm data at a relative pressure of 0.99. The micropore area (A_{micro}), micropore volume (V_{micro}), and the mesopore (external) surface area (A_{e}) were obtained from the *t*-plot method. The Barrett-Joyner-Halenda (BJH) method was employed for calculation of the average pore diameter.

The phosphorus content of the catalyst was analyzed by XPS (model: ESCALAB 250, Thermo-VG Scientific, West Sussex RH19 1UB, UK).

The surface morphology of the catalyst was imaged by using a scanning electron microscope (Model UItra55, Carl ZeissNTS GmbH, Oberkochen, Germany). Quantitative compositional analysis of catalyst was carried out with an energy-dispersive X-ray analysis (EDX) system attached to the electron microscope. Determination of the chemical composition was based on the average analytical data of individual particles

The weight loss behavior of catalyst was measured using a thermobalance (DTA-50, Shimadzu, Kyoto, Japan). The sample was heated to 900 °C at a heating rate of 10 °C/min under air flow.

Dehydration reaction of fructose and HMF analysis

In a typical reaction, 0.5 g of D-fructose, 5 mL of DMSO, and 0.2 g of LMC solid acid catalyst were charged into the reactor. The reaction mixture was heated to 140 °C in an oil bath and agitated with an electromagnetic stirrer to keep the catalyst particles suspended for the desired time. After reaction, the solid acid catalyst was removed from the reaction mixture *via* centrifugation. Each sample was diluted with distilled water and then analyzed by high performance liquid chromatography (HPLC). The HMF was used for qualitative and quantitative analyses. The HPLC analysis was performed on a Hitachi L-2000 series system (Hitachi High-Tech, Tokyo, Japan) equipped with Diode array detector (DAD), Cosmail 5QC18-PAQ column (4.6 mm by 250 mm), with a mobile phase with a methanol to water ratio ($CH_3OH{:}H_2O$) of 10:90, at a flow rate of 1.0 mL/min. The column temperature was set at 30 °C, and the wavelength was set at 280 nm. Fructose conversion, HMF yield were defined as follows:

$$Fructose\ conversion\ (\%) = [1 - \frac{moles\ of\ \ fructose\ in\ \ product}{initial\ \ moles\ of\ \ fructose}] \times 100 \tag{1}$$

$$HMF\ \ yield\ \ (\%) = \frac{moles\ of\ \ HMF\ \ produced}{initial\ \ moles\ of\ \ fructose} \times 100 \tag{2}$$

All reaction experiments were duplicated and data shown were the average values within ±3% errors.

Recycling experiment

The reusability of the prepared solid acid catalyst was investigated. After the first reaction (condition: 5 g of D-fructose, 50 mL DMSO, 2 g of LMC solid acid catalyst, 140 °C of reaction temperature, and 120 min of reaction time), the solid acid catalyst was recovered by centrifugation, washed with acetone, and oven-dried at 60 °C. The recovered catalyst was used for the next run under the same reaction condition.

RESULTS AND DISCUSSION

Catalyst Characterization

Figure 1 shows the N_2 adsorption–desorption isotherms of the solid acid catalysts obtained by various PA to KL impregnated ratio. The N_2 sorption–desorption isotherms shapes of the solid acid catalyst activated at PA to KL mass ratio of 1:1 can be interpreted as a type I, indicating that the catalyst is microporous network system. However, isotherms shapes activated at PA to KL ratio of 2:1 and 4:1 were a characteristic type IV curve with a noticeable hysteresis loop at the broadened capillary condensation steps at a relative pressure (P/P_0) in the range of 0.4 to 0.9. This loop demonstrated the presence of mesopore structure, and the N_2 adsorption capacities and mesoporosity developments increased with PA to KL mass ratio increasing.

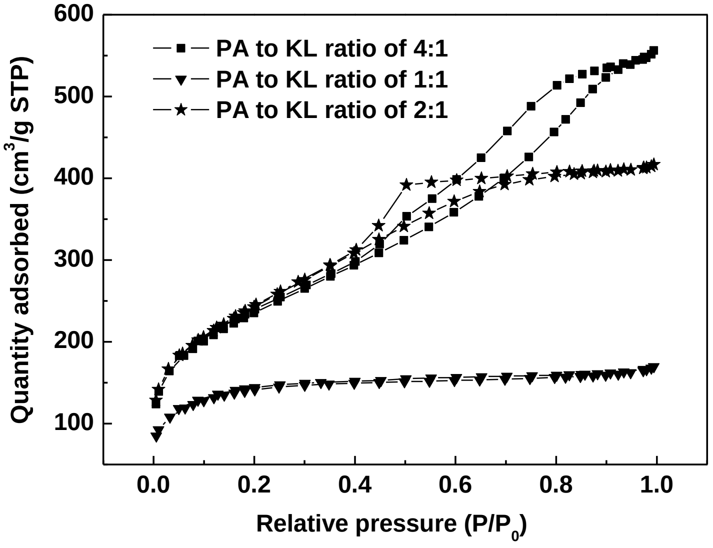

Fig. 1. Nitrogen adsorption-desorption isotherms of solid acid catalysts obtained by various PA to KL impregnated mass ratio

The porous structure parameters of the solid acid catalysts are shown in Table 1. The highest BET surface area of catalysts was 878 m^2/g at PA to KL mass ratio of 2:1. However, the total volume and average mesopore diameter increased with PA to KL ratio. The average mesopore diameter of the catalyst activated at a PA to KL ratio 4:1 is 4.7 nm calculated from these adsorption isotherms data by BJH method. This large pore diameter of the catalyst makes it suitable for applications where large organic molecules have to access the well dispersed active sites located inside the pores.

Table 1. Textural Characteristics of Catalysts Obtained from KL by H_3PO_4 Activation at Various Impregnated Mass Ratio of PA to KL

Ratio of PA to KL	A_{BET} (m^2/g)	A_{micro} (m^2/g)	A_e (m^2/g)	V_t (cm^3/ g)	V_{micro} (cm^3/ g)	D (nm)
1:1	497.7	215.3	282.4	0.25	0.09	3.2
2:1	878.4	57.8	820.6	0.63	0.02	3.3
4:1	849.8	90.1	759.7	0.84	0.03	4.7
D: average mesopore diameter calculated from adsorption data by BJH method.						

The pore size distribution of the solid acid catalysts are shown in Fig. 2. When catalyst was prepared at PA to KL mass ratio of 1:1, the incremental mesopore (2 to 500 nm) volume of catalyst was negligible. However, with the PA to KL mass ratio increase, the total pore volume and mesopore volume increased, and the pore diameter widened. This result was also consistent with the results of Fig. 1 and Table 1. The catalysts obtained at various PA to KL ratio were used to check the catalytic activity of fructose dehydration to HMF. The catalyst obtained at PA to KL mass ratio of 4:1 had the highest catalytic activity with HMF yield of 72.3% under reaction conditions of 0.5 g D-fructose, 5 mL DMSO, 0.2 g of LMC solid acid catalyst, and 60 min. So, the catalyst activated at PA to KL mass ratio of 4:1 was used to study further.

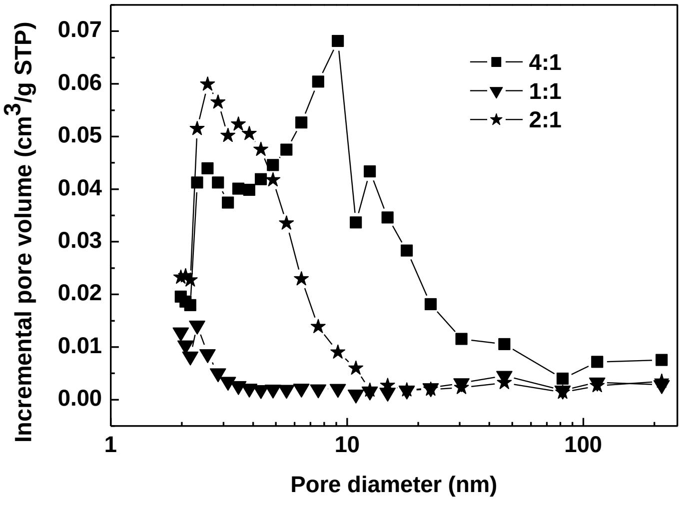

Fig. 2. Pore size distribution of LMC catalysts obtained from various PA to KL mass ratio

The surface morphology of the prepared LMC catalyst is shown in Fig. 3. As observed, the catalyst contained an irregular, heterogeneous micron grade particles with particle size about 2 to 20 μm. The micron particles was composed of many rough nanospheres with large interparticle voids, confirming a heterogeneous structure and a high mesoporosity. EDX measurement was made to determine the chemical composition of the LMC catalyst, and quantitative analysis of different elements showed that the catalyst contained 73.55 wt % C, 18.66 wt % O, 6.59 wt % P, and 1.2 wt% Ca.

Therefore, the catalyst possessed high specific surface area and external surface area. This result was also consistent with the results of Fig. 1 and Table 1.

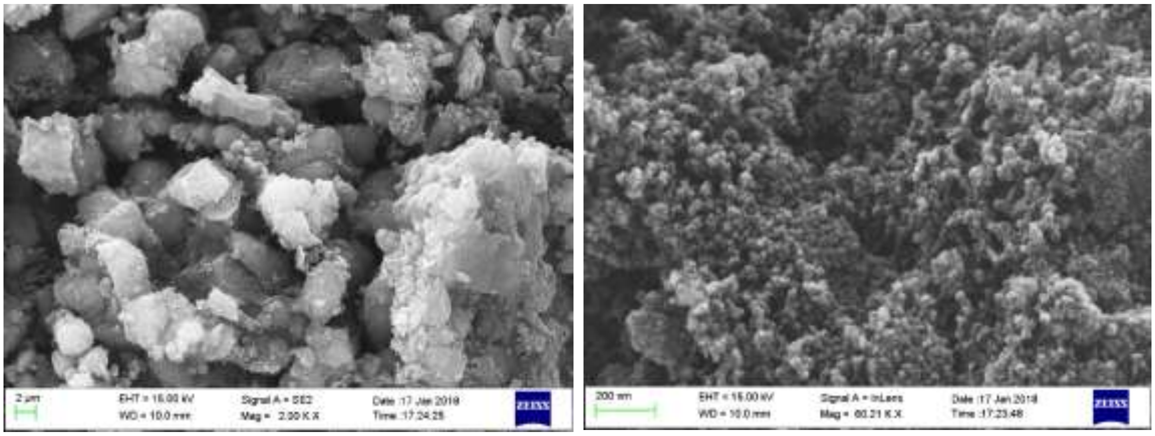

Fig. 3. SEM micrographs of the LMC catalyst with two different magnifications (2000 and 60210)

X-ray photoelectron spectroscopy was used to investigate the electronic states and content of *P* in the solid acid catalyst. As shown in Fig. 4(a), for P 2p energy level, the peak at 135.4eV can be attributed to the oxidized *P* species such as P = O or P = OOH (Sun *et al.* 2012; Villa *et al.* 2013). The binding energy of O_{1s} (533.4eV) and C_{1s} (284.8eV) are characteristics of C-O type surface moiety. The atom composition of catalyst is estimated to consist of roughly 65.25% C, 31.26 O, 6.09% P and 2.41% Si *via* area estimation. This result of P content calculated from XPS was slight different from EDX (6.59% P). The total acid site density estimated by acid-base titration using 0.01 mol/L NaOH as titrant was up to 5.36 mmol/g, which was remarkably high and indicated that the prepared catalyst had high catalytic activity. Fig. 4(b) shows the FTIR spectrum of LMC catalyst. The band at about 1168 cm^{-1} and a band at 1124 cm^{-1} are possibly caused by P = OOH deformation mode. A band at 2923 cm^{-1} could be due to the O−H stretching vibration of the $-PO_3-OH$ groups. Associated with the result reported by Alam *et al.* (2014), the prepared LMC catalyst may mainly contain Brønsted acid sites.

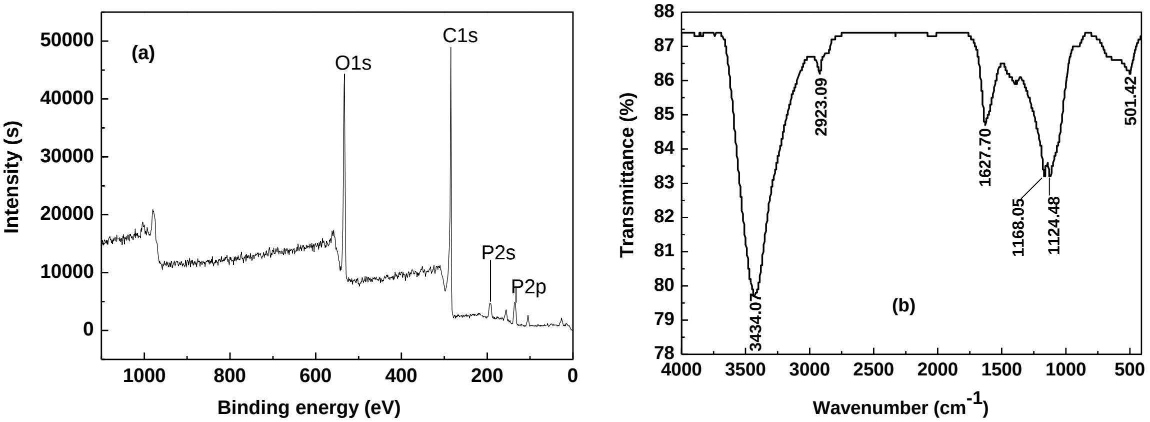

Fig. 4. XPS spectra (a) and FTIR spectra (b) of the solid acid catalyst

The TGA plot of the solid acid catalyst in air atmosphere is presented in Fig. 5. The catalyst showed an obvious weight loss below 100 °C, which was mainly due to the loss of a small amount of adsorbed water. In the temperature range of 100 °C to 400 °C, the weight loss of the catalyst did not show obvious change. With further increase in temperature, the catalyst demonstrated dramatic weight loss. The composition of the residue determined by X-ray fluorescence spectrometer is the ash, main SiO_2, and a small amount of CaO, Fe_2O_3, and Al_2O_3. The TGA analysis also showed that the solid acid catalyst was physically stable up to 400 °C.

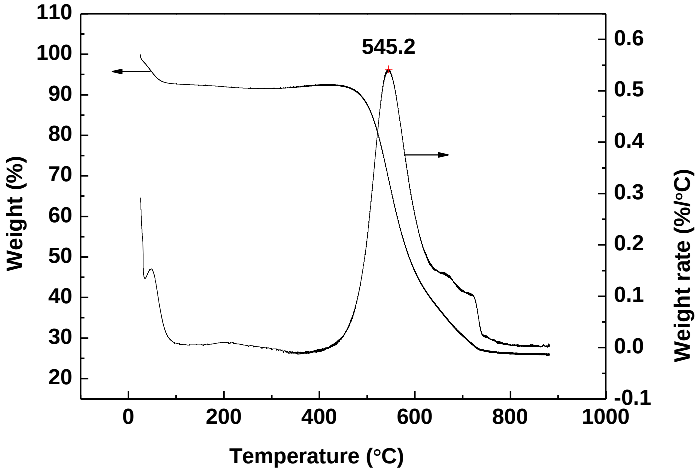

Fig. 5. TGA profile of the solid acid catalyst in air atmosphere

Catalytic Activity during Dehydration of Fructose by the LMC Catalyst

Figure 6 shows the temperature dependence of the fructose conversion and HMF yield on the solid acid catalyst. The fructose conversion increased from 58.6% at 120 °C to almost 100% at 160 °C. The HMF yield first increased to a maximum at 140 °C (78.2%) and then rapidly decreased. This trend could have been due to the formation of undesired byproducts, such as levulinic acid, humins, and coke, as indicated by the dark color of the reaction solution although these products were not quantified due to analytical issues which is in line with the results reported by Hafizi *et al.* (2016).

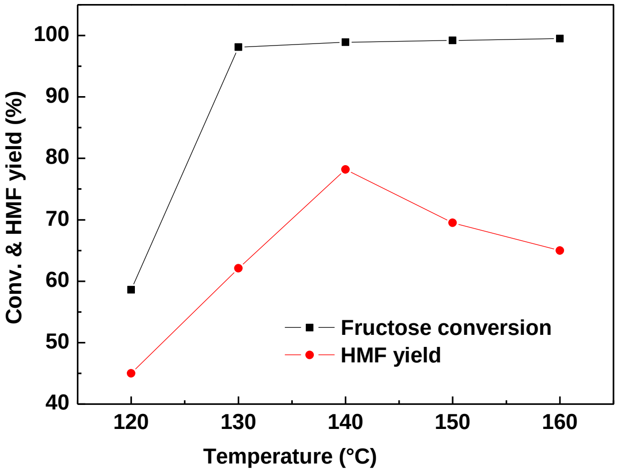

Fig. 6. Effects of reaction temperature on the fructose conversion to HMF; reaction conditions: 0.5 g D-fructose, 5 mL DMSO, 0.2 g of LMC solid acid catalyst, and 120 min

Figure 7 plots the fructose conversion and HMF yield *versus* reaction time at 140 °C. As shown, the fructose conversion kept quickly increasing to almost 100% along with the reaction time increasing to 2 h, indicating the catalyst was highly active for the dehydration of fructose. The HMF yield can increase to 70.7% only after 30 min of reaction time. Then, the HMF yield slightly increased to 80.1% as the reaction time increased to longer than 3 h. Further increase in reaction time led to an obvious decrease in HMF yield. This can be attributed to the further reaction of the products into byproducts, for example, levulinic acid, formic acid, and humins (Moreno-Recio *et al.* 2016).

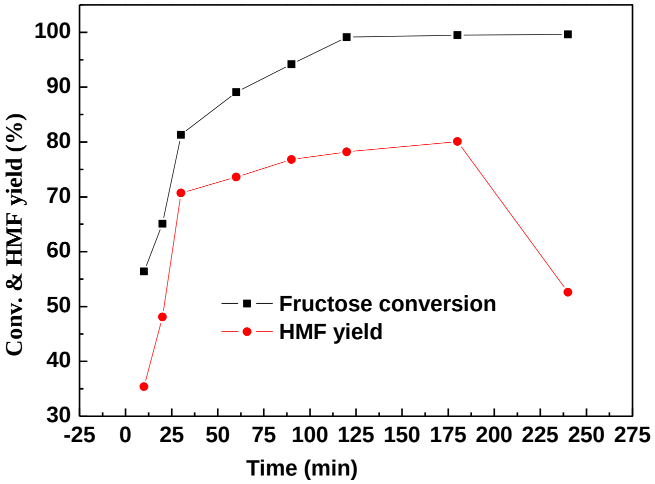

Fig. 7. Effects of reaction time on the fructose conversion to HMF; reaction conditions: 0.5 g D-fructose, 5 mL DMSO, 0.2 g of LMC solid acid catalyst, reaction temperature 140 °C

The catalytic performance of the prepared LMC catalyst was compared with other carbon-based solid acid catalysts for fructose dehydration to HMF and the results were shown in Table 2. As shown, the LMC in this work showed a better activity than SAC and SMC, and slight worse than SCHOP. The SBC catalyst has a highest activity under the similar reaction conditions. However, considering that LMC is produced from waste kraft lignin by one-step carbonization and phosphorylation, and therefor has features of lower cost and environmental friendly character, the LMC can be regarded as a promising solid acid catalyst candidate for the dehydration of fructose to HMF.

Table 2. Comparison of Catalytic Performance for Various Carbon-Based Solid Acid Catalysts Used in Fructose Dehydration to HMF

Catalyst	Fructose Conv. (%)	HMF yield (%)	Solvent	*T* (°C)	Time (h)	Reference
LMC	98.2	62.1	DMSO	130	2	this work
SCHOP ^{a}	100	64.0	DMSO	130	2	Wang *et al.* 2017
SMC ^{a}	100	58.0	DMSO	130	2	Wang *et al.* 2017
SAC ^{a}	97.5	52.0	DMSO	130	2	Wang *et al.* 2017
SBC ^{b}	97.9	87.8	DMSO	130	1	Shen *et al.* 2106
CS-2 ^{c}	97	77	DMSO	140	0.5	Zhao *et al.* 2016

a: SCHOP, SMC and SBC are three sulfonated hierarchically ordered pores, mesopores, and micropores carbon, respectively; b: Sulfonated bamboo-derived carbon prepared by simultaneous carbonization and sulfonation; c: sulfonated carbon by glucose carbonization and subsequent H_2SO_4 sulfonation.

Stability and Recycling of Solid Acid Catalyst

To examine the stability of the solid acid catalyst, the reusability test of the solid acid catalyst was carried out under the reaction conditions of 5 g of D-fructose, 50 mL DMSO, 2 g of LMC solid acid catalyst, 140 °C reaction temperature, and 120 min reaction time. The catalyst was separated from the reaction system by centrifugation, washed with acetone, and oven-dried at 60 °C. Then, the catalyst was reused in the same reaction conditions. The results of stability and reusability of the catalyst are shown in Fig. 8. There was a slight decrease in the HMF yield after the first run. The solid acid catalyst was recycled at least five cycles without noticeable loss of activity, and the yield of HMF was still 78.3% after the fifth run. The fifth used catalyst was titrated by 0.01 mol/L NaOH to determinate the acid density, and remained 4.84 mmol/g. In addition, the amount of phosphorus in after fifth used catalyst was 5.37% measured by XPS with only slight decrease.

The slight decrease in HMF yield could be ascribed to the slight leaching of phosphorus, and formation of humins or intermediates that were adsorbed in the acid site of the solid acid catalyst (Yang *et al.* 2016).

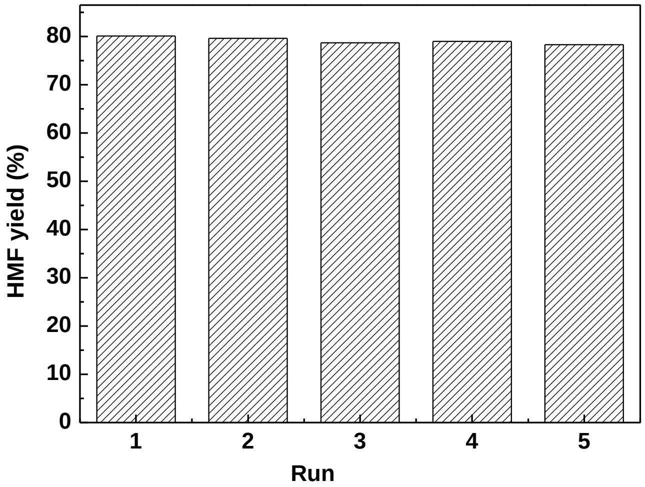

Fig. 8. Catalyst recycling experiments; conditions: 5 g of D-fructose, 50 mL DMSO, 2 g of LMC solid acid catalyst, 140 °C reaction temperature, and 120 min reaction time

CONCLUSIONS

1. Phosphoric acid activated mesoporous carbon from KL was prepared and successfully employed as solid acid catalyst for the dehydration of fructose to HMF.
2. The solid acid catalyst displayed high activity and the HMF yield could reach 80.1%. The catalyst displayed a good reusability as well. The remarkable catalytic performance was attributed to the mesopore structure of the carbon catalyst, which makes the catalytic active sites easily accessible for fructose molecules and the synergic effect between the surface acidic groups.
3. These results provide new possibilities to develop green catalytic processes for the conversion of biomass to biofuels and process chemicals.

ACKNOWLEDGMENTS

This work was supported by the Key Research and Development Plan of the Science & Technology Department of Sichuan Province (2018SZ0301), the Doctor Foundation of Southwest University of Science and Technology (14zx7155), and the Innovation Team Building Fund Project of Sichuan Provincial Biomass Modified Materials Engineering Research Center in China (14tdgc02).

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Article submitted: September 24, 2017; Peer review completed: December 29, 2017; Revised version received: April 17, 2018; Accepted: April 24, 2018; Published: April 30, 2018.
DOI: 10.15376/biores.13.2.4428-4439