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*Published in:*  
Industrial and Engineering Chemistry Research

*DOI:*  
[10.1021/acs.iecr.9b06349](https://doi.org/10.1021/acs.iecr.9b06349)

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*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
2020

[Link to publication in University of Groningen/UMCG research database](#)

### *Citation for published version (APA):*

Qi, Z., Wang, Q., Liang, C., Yue, J., Liu, S., Ma, S., Wang, X., Wang, Z., Li, Z., & Qi, W. (2020). Highly efficient conversion of xylose to furfural in a water-MIBK system catalyzed by magnetic carbon-based solid acid. *Industrial and Engineering Chemistry Research*, 59(39), 17046–17056. <https://doi.org/10.1021/acs.iecr.9b06349>

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# Highly Efficient Conversion of Xylose to Furfural in a Water–MIBK System Catalyzed by Magnetic Carbon-Based Solid Acid

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Cite This: *Ind. Eng. Chem. Res.* 2020, 59, 17046–17056

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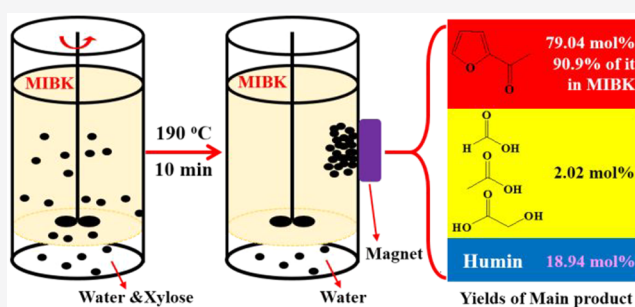
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**ABSTRACT:** In this work, the conversion of xylose to furfural (FF) was effectively achieved in a water–MIBK biphasic solvent system over a synthesized magnetic carbon-based solid acid catalyst (MMCSA). The effect of various reaction conditions was studied on the dehydration of xylose, and the highest FF yield of 79.04% was obtained. Byproducts in the reaction process were identified by high-performance liquid chromatography–mass spectrometry (LC-MS), which provides insights into the reaction pathway of the xylose conversion to FF over the current catalyst. The observed deactivation of the catalyst at high temperature (190 °C) was addressed by its regeneration with concentrated sulfuric acid (98 wt %). A comparable FF yield (73.74%) was achieved over the regenerated MMCSA. The possible deactivation–regeneration mechanism of this catalyst has also been proposed. Overall, this work provides a valuable basis for the efficient synthesis of FF by solid acid-catalyzed conversion of xylose or hemicellulose.



## 1. INTRODUCTION

Lignocellulosic biomass, a type of agricultural and forestry waste, is considered to be a promising renewable resource for the production of high value-added chemicals.<sup>1,2</sup> Among these, furfural (FF) is a key platform chemical that is widely used in the refining, plastics, pharmaceutical, and agrochemical industries.<sup>3,4</sup> FF is typically obtained through the dehydration and cyclization of reducing sugars generated from hemicellulose in lignocellulosic biomass.<sup>4–6</sup>

Industrial FF is obtained via a single-step catalyzed hydrolysis of corncob by dilute sulfuric acid in an aqueous medium, and the major bottleneck of such a process is that FF yield above 50% is difficult to reach.<sup>7,8</sup> Accordingly, various organic solvents have been attempted to replace water as the reaction medium,<sup>9,10</sup> which has closer properties to FF. Cai et al.<sup>9,10</sup> used a novel single-phase cosolvent system of tetrahydrofuran (THF), a single-step method for extracting FF directly from maple and corn stover using 1 wt % H<sub>2</sub>SO<sub>4</sub>, which easily and directly depolymerized the hemicellulose and cellulose. A FF yield of 86% was obtained, together with the yields of 5-hydroxymethylfurfural (HMF) and levulinic acid (LA) at 21% and 40%, respectively. However, an additional workup has to be considered since the mixed solution of FF, HMF, and LA is difficult to separate.

In order to improve the FF yield and address the facile separation of products from the reaction medium, a two-step method has been widely studied,<sup>11,12</sup> i.e., pretreatment of biomass to obtain a hemicellulosic sugar solution followed by

the acid-catalyzed conversion of the sugar solution to produce FF. Luo et al.<sup>11</sup> reported the synthesis of FF by first pretreating Pseudotsuga to obtain xylose hydrolysate in a  $\gamma$ -valerolactone (GVL)-H<sub>2</sub>O cosolvent at 160 °C and then by adding NaCl in GVL/THF system to achieve a furfural yield of 76.9%. Obviously, the two-step method can selectively produce furfural from biomass and has a better yield of furfural compared to the one-step method.

Besides the reaction procedure, research efforts have been focused as well on catalyst development. The utilization of liquid acid as a catalyst, though effective for the hydrolysis of lignocellulose, has many disadvantages such as low utilization rate of raw materials, high corrosiveness, difficulty in catalyst recovery, and serious environmental pollution.<sup>12,13</sup> New methods were therefore developed for preparing heterogeneous acids for the hydrolysis of lignocellulose into FF. Such solid acid catalysts have the promising properties of high selectivity toward FF, easy catalyst separation, and reusability.<sup>14</sup> Among these, carbon-based solid acids (such as those derived from biomass material via carbonization and sulfonation) are becoming increasingly popular, since they

**Special Issue:** Future of Biomass Utilization Technologies

**Received:** November 18, 2019

**Revised:** January 28, 2020

**Accepted:** January 30, 2020

**Published:** January 30, 2020



are economical and environmentally friendly and have good catalytic performance.<sup>15,16</sup> Laohapornchaiphon et al.<sup>17</sup> prepared a carbon-based solid acid catalyst (WH-PTSA-220) by one-step hydrothermal carbonization of water hyacinth in the presence of *p*-toluenesulfonic acid and used it for the dehydration of xylose. In the GVL solvent system, the optimum FF yield was 57% at 170 °C for 2 h. Although catalyst preparation was convenient and economical, the process had a low yield of FF. Zhang et al.<sup>18</sup> used 4-aniline sulfonic acid as a sulfonating agent to prepare a carbon-based solid acid catalyst for the conversion of xylose and corn stover to FF in GVL, and the highest FF yield of 78.5% was achieved at 170 °C in 30 min. Zhu et al.<sup>19</sup> prepared resorcinol–formaldehyde resin–carbon (RFC) with a good ordered mesoporous structure and applied it to catalyze the xylose conversion. They achieved an 80.5% FF yield at 99% xylose conversion under 170 °C in 25 min with 0.5 g of RFC. In brief, carbon-based solid acids have been widely used in the xylose dehydration to obtain FF and have achieved good results so far. However, most carbon-based solid acid catalysts studied still have to be improved in many aspects, including difficulty in separation and troublesome catalyst preparation (e.g., in the cases of SC–CCA and RFC catalysts).<sup>18,19</sup> Therefore, it is necessary to find solid acid catalysts that are facile to prepare, cost efficient, and promising to obtain high FF yields.

In situ extraction of the target product from the aqueous reaction medium using an organic solvent represents one of the most promising strategies for FF production in high yields.<sup>20</sup> Hu et al.<sup>21</sup> studied the conversion of xylose to FF in 20 different solvents, demonstrating that dimethyl sulfoxide (DMSO) has a better effect. An optimum 75% of FF yield at 170 °C for 100 min was obtained. Although DMSO can better preserve FF, it took a long time (100 min) to produce the maximum yield. Moreover, the low efficacy of the downstream separation of FF from DMSO makes the procedure difficult to commercialize.<sup>22</sup> Therefore, it is desired to use a more efficient biphasic system. In this respect, water immiscible methyl isobutyl ketone (MIBK) as a low-cost extracting solvent has been reported favorable for the in situ extraction of FF from the catalytic aqueous phase.<sup>23–25</sup> Another major advantage of MIBK is that its boiling point differs from that of FF by 50 °C, making it conducive to the subsequent separation of FF.

Our group has previously synthesized the separable and stable magnetic carbon-based solid acid (MMCSA), which presents promising properties for the efficient hydrolysis of lignocellulose into xylose and the deconstruction of the structure of corncob at the optimized reaction temperature.<sup>26</sup> The good catalytic ability of MMCSA, along with its ability to obtain a rich xylose solution, makes it a potential catalyst candidate for FF production as well. In this work, a xylose solution was used as a model system to investigate the generation pathway and mechanism of FF from xylose catalyzed by MMCSA, both in the aqueous solution and a biphasic water–MIBK system. Since MMCSA was deactivated during a high-temperature reaction in the mixed reaction phase, a regeneration method of MMCSA was studied, and it was found that the catalytic ability of regenerated MMCSA is comparable to fresh MMCSA. This research has expanded the application of MMCSA and improved the entire system of biorefining under the catalysis of carbon-based solid acids.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** D-(+)-xylose (98 wt %, AR), FF (99 wt %, AR), and MIBK (>99.5 wt %, AR) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Sulfuric acid (98 wt %, GR) was obtained from Guangzhou Chemical Regent Factory (Guangzhou, China). Microcrystalline cellulose (GR) and iron(III) chloride (AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

**2.2. Preparation of MMCSA.** The catalyst preparation started with mixing 10 g of microcrystalline cellulose ( $\leq 120$  meshes) into a 1 L FeCl<sub>3</sub> solution (10 mmol/L) under continuous stirring at 400 rpm for 5 h, followed by heating of the mixture in a benchtop electric furnace (model ES-3618K, Guangzhou Yuecheng Factory, China) at 100 °C to evaporate the water. The remaining solid was then dried in an oven at 105 °C overnight. Thus, the obtained Fe-impregnated microcrystalline cellulose further underwent carbonization (350 °C, 1 h under N<sub>2</sub> protection), followed by sulfonation with sulfuric acid (98% w/w, solid–liquid ratio of 1:10, 130 °C, 10 h), and finally by washing with hot water (>80 °C) to obtain MMCSA.

The prepared MMCSA was an amorphous carbon consisting of –SO<sub>3</sub>H, –COOH, and phenolic –OH groups borne on nanographene sheets in a random fashion. The chemical formula of MMCSA is C<sub>0.505</sub>H<sub>0.3014</sub>O<sub>0.933</sub>S<sub>0.085</sub>Fe<sub>0.322</sub>, and more details about the preparation process and characterization of MMCSA can be found in our previous work.<sup>26</sup>

**2.3. Synthesis of FF from Xylose.** The synthesis of FF from xylose was carried out in a reactor equipped with a magnetic stirrer (Anhui Kemi Machinery Technology Co., Ltd., Anhui, China; model MS-100-C276), consisting of a 100 mL autoclave, an electric heating furnace, and a programmable temperature controller. Moreover, all parts of the autoclave that directly contacted the reactants were made of Hastelloy. A certain mass quantity or volume of xylose, water, MIBK (if present), and MMCSA were put into the autoclave which was then sealed and placed in an electric heating furnace. The reaction temperature was controlled by a programmable temperature controller, and the temperature of the reactant was directly measured with a thermocouple. The reaction was conducted at 120–200 °C for 5–60 min at a stirring rate of 500 rpm. After the reaction was complete, the autoclave was removed from the heating furnace and placed in cold air to be cooled to room temperature.

After the reaction, the hydrolysate was separated in a multibarrel automatic balance centrifuge (model TDZS-WS, Hunan Xiangyi Laboratory Instrument Development Co., Ltd., China) at 5000 rpm for 3 min. In the case of a biphasic solvent system, the MIBK phase and the aqueous phase were separated and centrifuged. The separated liquids were stored under refrigeration for later analysis, as indicated in Section 2.6.

In order to examine whether there was catalytic activity associated with the possible leaching of Fe ion and/or –SO<sub>3</sub>H from the catalyst in the reaction solution during the dehydration of xylose, additional experiments similar to those mentioned above were carried out under the optimized reaction conditions. In more detail, the xylose conversion to furfural was studied in the absence of MMCSA, using the biphasic system consisting of (i) water and MIBK or (ii) a –SO<sub>3</sub>H and Fe ion aqueous solution and MIBK; here, the –SO<sub>3</sub>H and Fe ion solution represented the hydrolysate which

was separated from the reaction system using MMCSA as the catalyst without addition of xylose. After the reaction, the reacting mixture was sampled, stored, and further analyzed as indicated in Section 2.6.

**2.4. Degradation of FF.** In order to better understand the pathway of MMCSA-catalyzed xylose conversion, experiments of the FF degradation were also carried out in the same 100 mL Hastelloy autoclave as described above. Before the reaction, FF, MMCSA, and a certain portion of the MIBK/water mixture were loaded into the reactor to achieve a FF concentration of 5.0 g/L. Then, experiments were carried out at a stirring rate of 500 rpm at 190 °C.

**2.5. Regeneration of MMCSA.** After the reaction, the MMCSA catalyst was separated from the reaction medium using a magnet, washed with deionized water, and dried in an oven at 105 °C for 4 h, followed by sulfonation with sulfuric acid (98% w/w, solid–liquid ratio at 1:10, 130 °C, 6 h). Subsequently, the catalyst was further washed with deionized water until the pH value of the effluent reached neutral and then finally dried in an oven at 105 °C for 12 h to complete the process. The regenerated MMCSA was used for the FF synthesis experiment under the optimal conditions (cf. Section 2.3).

**2.6. Analytical Methods.** The contents of monosaccharide, FF, and acids (formic acid, acetic acid, glycolic acid, etc.) were determined using high-performance liquid chromatography (HPLC; Waters 2695, Milford, USA) with a Shodex SH-1011 column coupled with a refractive index detector (Waters Corporation, 2414) and a photodiode array detector (Waters Corporation, 2998). The diluted sulfuric acid aqueous solution (0.005 M) was used as the mobile phase with a flow rate of 0.5 mL/min, and the column temperature was 50 °C. Before determination, all aqueous hydrolysates were filtered through 0.22- $\mu$ m aqueous filter membranes, and the MIBK phases were filtered through 0.22- $\mu$ m nylon filter membranes.

The byproducts during the xylose conversion process were also identified with high-performance liquid chromatography–mass spectrometry (LC-MS, Agilent 6540, USA). The high-performance liquid chromatograph was equipped with a HiP automatic sampler, a binary liquid pump, and a triple quadrupole mass spectrometer (QQQ). The mass spectrometer was operated under a double electrospray ionization (ESI) setting in a positive mode. The cracking voltage of the ion spray was 150 V, with a turbine temperature of 350 °C and gas flow rate of 10 L/min. The product was separated using an Agilent Extend-C18 reversed-phase column (1.8  $\mu$ m, 2.1 mm  $\times$  50 mm). The mixture of water and acetonitrile was used as the mobile phase at a flow rate of 0.15 mL/min.

The concentrations of Fe<sup>3+</sup> in the hydrolysates were determined by inductively coupled plasma emission spectrom-

**Table 1. Effects of Reaction Temperature and Time on Xylose Dehydration Reaction Performance<sup>a</sup>**

Temperature (°C)	Time (min)	Xylose conversion (%)	FF selectivity (%)	FF yield (%)
180	20	85.89	3.98	3.42
	30	89.78	5.98	5.37
	40	98.10	11.36	11.14
	50	93.95	14.21	13.36
	60	99.08	16.91	16.75
190	20	98.95	22.84	22.60
	30	99.04	21.56	21.36
	40	99.64	18.58	18.51
	50	98.96	18.04	17.85
	60	99.08	19.13	19.10
200	20	99.72	16.41	16.28
	30	99.48	19.83	19.65
	40	99.49	17.26	17.17
	50	99.41	15.05	14.96
	60	99.37	13.34	13.25

<sup>a</sup>Reaction conditions: 0.65 g of xylose, 40 mL of water, and 2 g of MMCSA catalyst.

etry (ICP, OPTIMA 8000, PerkinElmer, USA). The magnetic properties of MMCSA before and after use were examined using a vibrating sample magnetometer (VSM; 7410, Lakeshore, Colchester, USA). The Brunner–Emmet–Teller (BET) measurement was determined by N<sub>2</sub> isothermal adsorption–desorption behavior by an automatic specific surface and pore analyzer (ASIQMO002-2, Quantachrome, Boynton Beach, FL, USA).

**2.7. Calculation Methods.** The xylose conversion, FF yield, FF selectivity, and carbon balance were calculated as follows

$$\text{Xylose conversion rate (\%)} = \frac{X_0 - X_h}{X_0} \times 100\% \quad (1)$$

$$\text{Yield of FF (\%)} = \frac{X_f \times 150.1299}{X_0 \times 96.08} \times 100\% \quad (2)$$

$$\text{Selectivity of FF (\%)} = \frac{X_f \times 150.1299}{(X_0 - X_h) \times 96.08} \times 100\% \quad (3)$$

where  $X_0$  is the initial xylose mass,  $X_h$  is the xylose mass in the hydrolysate, and  $X_f$  is the FF mass in the hydrolysate.

The carbon balance of xylose conversion products was calculated according to the following equation

$$\text{Carbon balance (\%)} = \frac{5 \times X_f/96.08 + 5 \times X_h/150.1299 + X_a/46.03 + 2 \times X_b/60.05 + 2 \times X_c/76.05}{5 \times X_0/150.1299} \times 100\% \quad (4)$$

where  $X_a$  is the mass of formic acid in the hydrolysate,  $X_b$  is the mass of acetic acid in the hydrolysate, and  $X_c$  is the mass of glycolic acid in the hydrolysate.

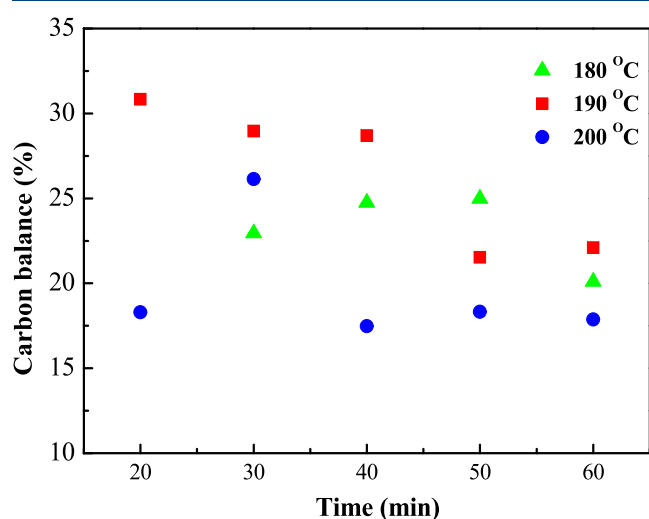
### 3. RESULTS AND DISCUSSION

**3.1. Dehydration of Xylose into FF in Aqueous Solution.** The xylose dehydration experiments were conducted first in the aqueous phase in a batch reactor setup,

where the influences of reaction temperature, reaction time, and the amounts of xylose, water, and catalyst on the reaction performance were investigated.

Some literature has studied the effects of catalysts on the dehydration of xylose at different temperatures in a range of 160–200 °C.<sup>18,19</sup> The results of preliminary experiments showed that xylose was consumed rapidly when the reaction temperature was above 180 °C (Table 1). Within this

temperature range, the conversion of xylose could reach more than 90% in 30 min, but the yield of FF is very low (less than 25%). Furthermore, from the carbon balances under three temperature points (Figure 1), it was found that all carbon



**Figure 1.** Carbon balance under the experimental conditions relevant to Table 1.

balances are low, indicating that less than 35% xylose was converted into FF and acids, although the xylose conversion was very high. It is possible that the degradation of FF and/or xylose to undetectable byproducts like humins occurred, a result consistent with the report of Wang et al.<sup>16</sup> that the acid-catalyzed dehydration of xylose to FF was limited by side reactions.

The influence of the catalyst dosage was investigated by altering the amount of MMCSA. The other reaction conditions were consistent with the previous experiments. The results are presented in Table 2, which shows that the increase in the

**Table 2.** Effect of MMCSA Catalyst Amount on Xylose Dehydration Reaction Performance<sup>a</sup>

Catalyst amount (g)	Xylose conversion (%)	FF selectivity (%)	FF yield (%)
2	98.95	22.84	22.60
3	99.08	14.94	14.80
4	99.56	6.78	6.75

<sup>a</sup>Reaction conditions: 0.65 g of xylose, 40 mL of water, 190 °C, and 20 min.

catalyst amount from 2 to 4 g resulted in a decreased FF yield and selectivity, with only a marginal increase in the xylose conversion (close to 100%), a result that might be due to the presence of sufficient acid sites for catalyzing undesired side reactions when the catalyst is overused. Zhang et al.<sup>18</sup> also reached similar conclusions.

The effects of water and xylose amounts on the FF production are presented in Tables 3 and 4, which reveal that adding more water or decreasing the amount of xylose loaded into the system (both leading to decreased xylose concentration) had only a slight influence on the xylose conversion, although the FF yield experienced an optimum. These results indicate the presence of an overall reaction order close to one regarding the xylose concentration, while the FF

**Table 3.** Effect of Water Volume on Xylose Dehydration Reaction Performance<sup>a</sup>

Water volume (mL)	Xylose conversion (%)	FF selectivity (%)	FF yield (%)
30	99.25	19.91	19.76
40	98.95	22.84	22.60
50	99.77	18.68	18.63

<sup>a</sup>Reaction conditions: 0.65 g of xylose, 2 g of MMCSA catalyst, 190 °C, and 20 min.

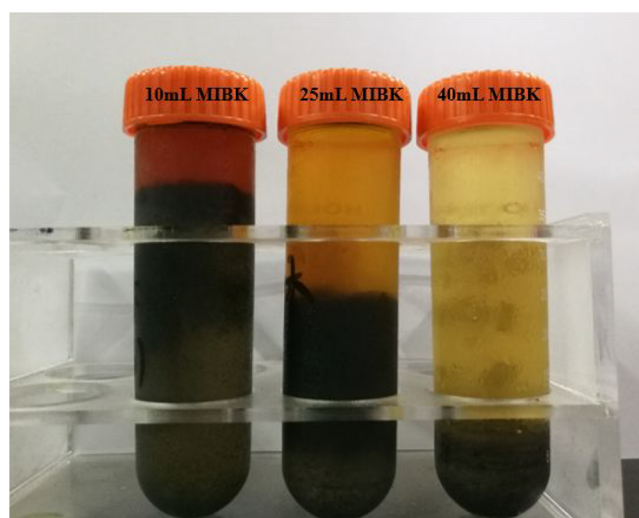
**Table 4.** Effect of Xylose Amount on Xylose Dehydration Reaction Performance<sup>a</sup>

Xylose amount (g)	Xylose conversion (%)	FF selectivity (%)	FF yield (%)
0.40	99.51	12.16	12.10
0.65	99.21	23.72	23.56
0.90	98.95	22.84	22.60
1.15	97.20	22.96	22.32

<sup>a</sup>Reaction conditions: 40 mL of water, 2 g of MMCSA catalyst, 190 °C, and 20 min.

formation seems to be favored at intermediate xylose concentrations.

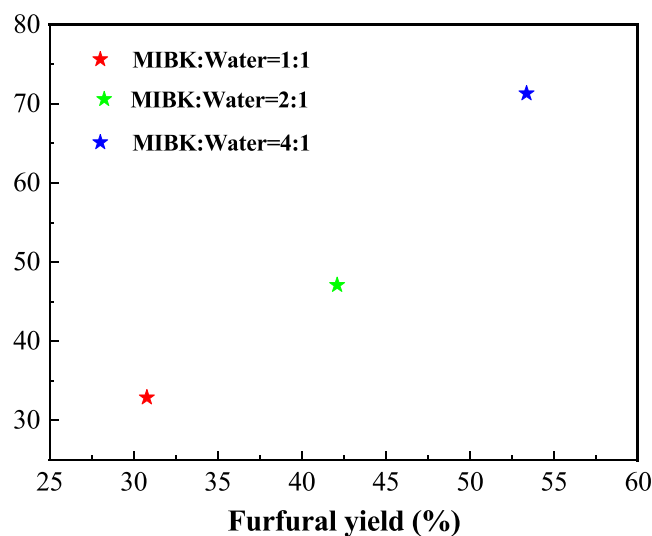
**3.2. Dehydration of Xylose into FF in the Water–MIBK System.** 3.2.1. *Effect of MIBK Dosage on Xylose Dehydration.* Some literatures have explored the advantages of using MIBK as the extracting organic solvent in improving the FF yield.<sup>23,24,27,28</sup> As can be seen from Figure 2, with the



**Figure 2.** Photos of the reaction mixture in the presence of different amounts of MIBK.

addition of MIBK, an obvious stratification phenomenon occurred after the dehydration experiment. Through analysis, the ratio of the FF product in MIBK to that in water was almost 10:1. Interestingly, the entire MMCSA amount resided in the aqueous phase, which thus did not affect the recovery of FF in the MIBK phase. From the results of Table S1, it is seen that by keeping the xylose concentration and the catalyst-to-xylose weight ratio constant, an increased MIBK-to-water volume ratio did result in an increased FF yield, while the xylose conversion was unchanged. An FF yield of 57.43% at a xylose conversion of almost 100% was obtained at an MIBK-to-water volume ratio of 4:1. This suggests that the addition of

MIBK increased the FF yield by extracting it from the aqueous phase, which is consistent with the literature results.<sup>27,28</sup> The carbon balance data (Figure 3) also proved that with increased

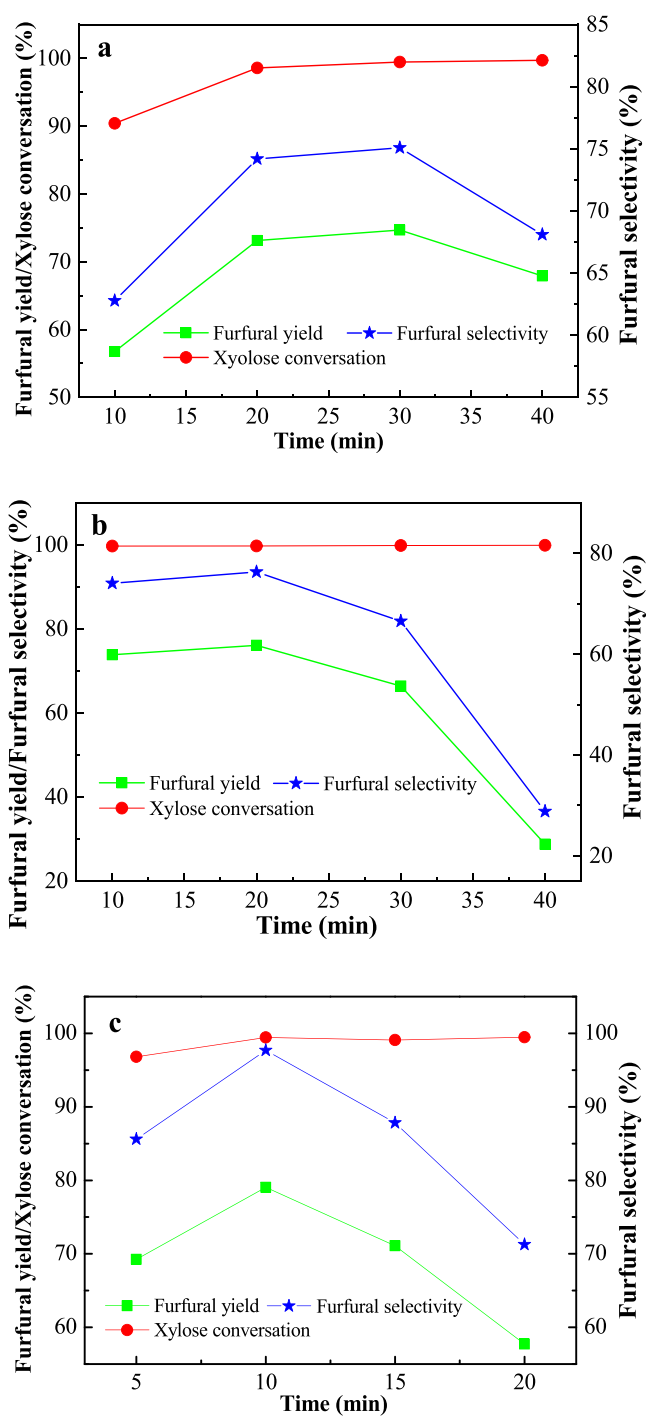


**Figure 3.** Carbon balance under experimental conditions relevant to Table S1.

MIBK-to-water volume ratios (and thus higher FF yields), fewer byproducts were formed from FF due to its effective transfer into the organic phase.

**3.2.2. Effects of Reaction Temperature and Time.** Through the preceding experiments, it was found that the addition of MIBK can significantly increase the yield of FF in an otherwise simple aqueous phase as the reaction medium, making it necessary to explore the optimal yield of FF catalyzed by MMCSA in the water–MIBK system. Therefore, the effect of reaction temperature and time on the FF yield was investigated. Table S2 shows that at temperatures below 140 °C the xylose conversion was low, as were the FF selectivity and yield. At a temperature of 160 °C, a significant FF yield of 55% could be achieved, but the reaction time was relatively long: 3 h. Therefore, it is necessary to explore higher temperatures toward identifying a better reaction performance. Figure 4 shows that the conversion of xylose was over 90%, sometimes even close to 100% as the temperature was raised to 170 °C and above. Moreover, the FF yield and selectivity first increased and then decreased with the increase in the reaction time. The highest FF yields, corresponding to the operating conditions of 170 °C in 30 min, 180 °C in 20 min, and 190 °C in 10 min, are 74.69%, 76.09%, and 79.04%, respectively. The higher the temperature is, the shorter is the time to achieve the maximum yield, which is consistent with the literature findings.<sup>17</sup> It can be concluded that the optimum reaction conditions (0.1625 g of xylose and 0.5 g of catalyst in 40 mL of MIBK and 10 mL of deionized water at 190 °C for 10 min) produced the highest yield of FF at 79.04%.

A comparison of the catalytic performance of MMCSA in the xylose conversion to FF with those of other catalysts under the respective optimized reaction conditions is listed in Table S. Liu et al.<sup>29</sup> obtained a 74.12% yield of furfural from xylose catalyzed by diluted sulfuric acid in a fixed bed reactor and gas phase neutralization. Our furfural yield level is similar to that from sulfuric acid catalysis. Although a similar or slightly higher FF yield was obtained from SC–CCA and S-RFC,<sup>18,19</sup> the



**Figure 4.** Effect of reaction time on xylose degradation at 170 °C (a), 180 °C (b), and 190 °C (c).

homogeneous mixture of GVL and water in use made it hard to separate FF. Furthermore, the expensive solvent GVL greatly increases the operating costs. When compared with other solid acid catalysts,<sup>28,30</sup> this study obtained higher xylose conversion and FF yield. The current results confirm the superior performance of MMCSA in the production of furfural from xylose. Qi et al.<sup>26</sup> have proved that MMCSA has a good catalytic ability for the production of xylose through an environmentally friendly sustainable saccharification process within a certain reacting strength. Thus, MMCSA represents a promising common solid catalyst for use in both the upstream

**Table 5. Comparison of Catalytic Activity of MMCSA and Other Catalysts in Production of FF from Xylose**

Catalyst (g)	Solvent system	Xylose conversion (%)	FF yield (%)
<sup>a</sup> H <sub>2</sub> SO <sub>4</sub>	Water–NaCl	–	74.12
<sup>b</sup> SC–CCA <sup>18</sup>	GVL	100	78.5
<sup>c</sup> S-RFC	GVL–water	99	80.5
<sup>d</sup> H-MOR <sup>28</sup>	MIBK–water	92.3	57.4
<sup>d</sup> ZrP	MIBK–water	87.6	63.7
<sup>d</sup> H-ZSM-5 <sup>28</sup>	MIBK–water	70.5	44.6
<sup>e</sup> RHC <sup>30</sup>	DMSO	–	75.8
MMCSA This work	MIBK–water	99.45	79.04

<sup>a</sup>Catalyst, 2 mol/L; xylose, 10 wt %; water–NaCl, 80 g; 170 °C.

<sup>b</sup>Catalyst, 0.2 g; xylose, 0.4 g; GLV, 16.5 mL; 170 °C; 30 min.

<sup>c</sup>Catalyst, 0.5 g; xylose, 0.8 g; GLV, 32 mL; water, 4 mL; 170 °C; 25 min.

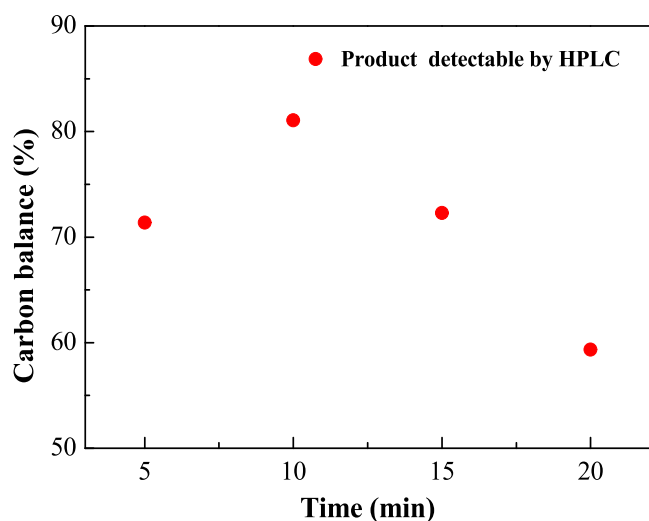
<sup>d</sup>Catalyst, 0.2 g; xylose, 2 g; MIBK, 30 mL; water, 18 mL; 180 °C; 180 min.

<sup>e</sup>Catalyst, 1.0 g; xylose, 0.8 g; DMSO, 20 mL; 160 °C; 640 min.

<sup>f</sup>Catalyst, 0.5 g; xylose, 0.1625 g; MIBK, 40 mL; water, 10 mL; 190 °C; 10 min.

biomass pretreatment and downstream sugar valorization, which contributes to a simplified biorefinery process.

**3.3. Mechanism Analysis of Xylose Dehydration into FF.** It is well known that FF has an aldehyde group and a furan ring structure. Of these, the aldehyde group is more susceptible to acetalization, acylation, aldol condensation, etc., and the furan ring can undergo alkylation, hydrogenation, oxidation, halogenation, ring opening, and nitration.<sup>4,6,31</sup> Figure 5 shows

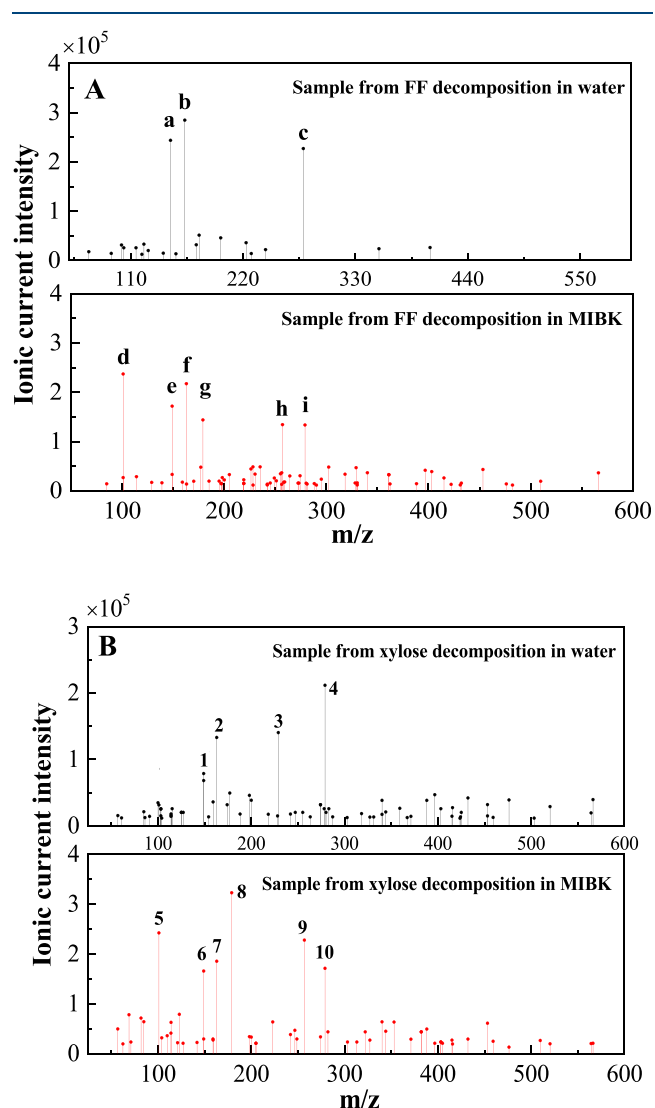


**Figure 5.** Carbon balance detectable by HPLC under optimal reaction conditions.

that the total yield of known products (i.e., FF, formic acid, acetic acid, and glycolic acid detected by HPLC) was about 81.06% during the xylose dehydration over the current catalyst in the water–MIBK system at 190 °C for 10 min, indicating that nearly 18.94% unknown soluble byproducts were produced from xylose conversion. In order to identify the side reactions in the reaction process, the degradation byproducts of xylose in the water–MIBK biphasic system were determined by LC-MS.

The total ion chromatogram corresponding mass spectra (LC-MS) of products from xylose and FF degradation under optimal conditions (0.5 g of catalyst in 40 mL of MIBK and 10 mL of deionized water, 190 °C, 10 min) were studied. As

shown in Figure 6, the mass–charge ratios of the main MS ion fragment peaks were mostly between 50 and 300, indicating



**Figure 6.** Mass spectrogram corresponding to total ion flow diagram from xylose and FF degradation. Sample from FF decomposition (A). Sample from xylose decomposition (B).

that the masses of most of the byproducts were in this range: i.e., the main polymers produced during the reaction were dimer, trimer, and tetramer. van Zandvoort et al.<sup>32</sup> studied the reaction of glucose, fructose, and xylose to produce humins with molecular weights of 270–650 g/mol. Their results indicated that the polymer produced during the reaction was humins or its precursor. Therefore, the substance detected by HPLC-MS here should be the precursor of soluble humins.

Table S3 lists the main ion peaks ( $m/z$ ), excimer ions, and molecular formulas of xylose degradation products at different reaction times in the water–MIBK system, detected by high-performance liquid chromatography–mass spectrometry (corresponding to Figure 6). There are three main ion peaks: protonation peak  $[M+H^+]$ , loss of water molecule  $[M+H^+ - H_2O]$ , and sodium ion peak  $[M+Na^+]$ .

In Table S3, the substances with the molecular formulas of  $C_8H_4O_3$  and  $C_{16}H_{22}O_4$  are interfering ions often appearing in LC-MS. Furthermore, the substance with the formula  $C_6H_{12}O$

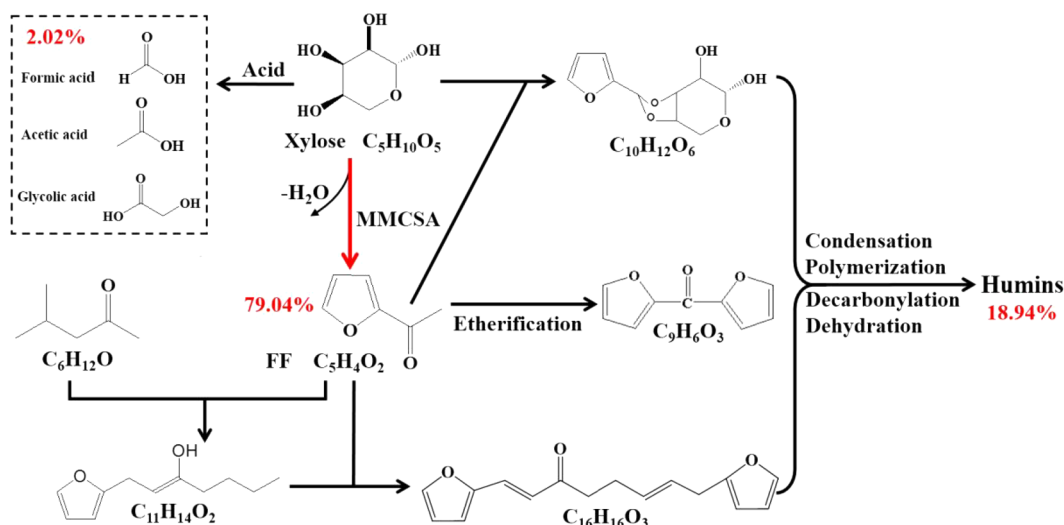


Figure 7. Proposed reaction pathway during the conversion of xylose in the water–MIBK biphasic system over MMCSA.

is MIBK, and  $C_9H_6O_3$  is a condensation product of FF itself.  $C_{11}H_{14}O_2$  is an aldol condensation product of FF and MIBK, and  $C_{16}H_{16}O_3$  is a further condensation product of  $C_{11}H_{14}O_2$  and FF. Pholjaroen et al.<sup>28</sup> proved that  $C_{11}H_{14}O_2$  and  $C_{16}H_{16}O_3$  were formed during the reaction of FF with MIBK. By comparison with the xylose conversion test results,  $C_{10}H_{12}O_6$  in Table S3 is the reaction product of xylose and FF, which is consistent with the literature findings.<sup>33,34</sup>

From the byproducts detected by HPLC and LC-MS, the reaction pathway of xylose in the water–MIBK system can be inferred. As shown in Figure 7, under the catalysis of MMCSA, xylose was mainly converted to FF (e.g., at a yield of 79.04% under 190 °C in 10 min; cf. Figure 1(c)), with an inappreciable total yield of formic acid, acetic acid, and glycolic acid (e.g., at 2.02%). This implies that under such conditions, nearly 18.94% unknown soluble byproducts were produced in the reaction. Specifically, FF could be condensed to difuran-2-methyl ketone, and a part of FF could react with xylose to form a dimer. In addition to these known reactions, FF might react with MIBK to form dimers, and then, dimers react with MIBK to produce trimers, which may be the precursor of solid humins. The formation of humins has been detected by LC-MS according to the molecular weight range from 200 to 600 g/mol as shown in Figure 6, which is consistent with some published researches.<sup>32,35</sup>

### 3.4. Characterization of Fresh and Recycled MMCSA.

Long-term durability is an important property of solid acid used in biomass pretreatment and conversion. To investigate this, after the FF production experiment, MMCSA was separated using an external magnet, and the collected MMCSA was reused as a catalyst in the following FF production experiment. After five reuse cycles, the FF yield decreased gradually from 79.04% to 26.03% (Figure 8), indicating that the activity of the catalyst had changed obviously. At the same time, the results reveal that the decrease in the catalyst activity was most pronounced after the first use, and the subsequent decline was slow.

To find the cause of catalyst deactivation, the acid amount and acid group content of the (reused) catalyst were analyzed first. The results are shown in Figure 9. It was found that the total amount of acid gradually decreased from 3.23 to 1.65 mmol g<sup>-1</sup> after five reuses. Among these, the decline of the

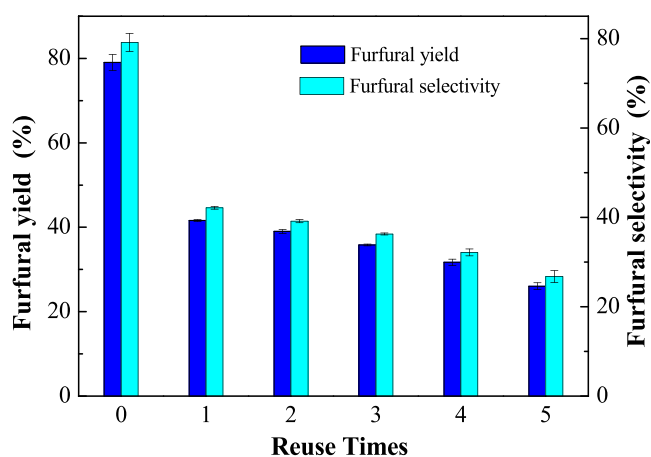


Figure 8. Reusability of MMCSA in FF production experiment.

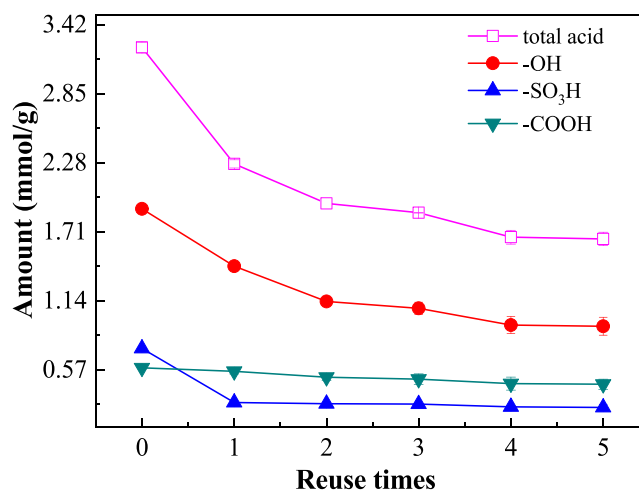


Figure 9. Changes in the acid amounts of different groups in MMCSA during repeated tests.

–OH group amount is initially fast (from an initial 1.89 mmol g<sup>-1</sup> to 1.43 mmol g<sup>-1</sup> after the second use and then to 1.13 mmol g<sup>-1</sup> after the third use) and then slowed in the successive runs. The initial amount of –SO<sub>3</sub>H was 0.75 mmol g<sup>-1</sup>, which



decreased rapidly after the first use (by 66.67%), and then, it remained stable.

–COOH decreased little and was almost stable throughout the process. It can be concluded accordingly that the removal of the phenolic –OH group was more responsible for the total acid amount decrease over multiple reuses. A previous study by Qi et al.<sup>26</sup> showed that the phenolic hydroxyl group of MMCSA decreased only slowly at 120 °C during the repeated corncob hydrolysis experiments. In addition, the desulfonation results are consistent with the previous studies by Asakura et al.,<sup>36</sup> who reported that –SO<sub>3</sub>H on the sulfonic acid cation exchange resin is thermally stable in the aqueous phase at 120 °C. Gong et al.<sup>37</sup> reported a carbon-based solid acid WCSA prepared from waste newspapers, which was recycled for a hydrolysis test of cellulose at 150 °C; –SO<sub>3</sub>H and –OH groups also fell off. Therefore, the –SO<sub>3</sub>H and –OH groups could be removed under high temperature conditions.

Figure 9 also reveals that the significant decrease in the FF yield only in the first reuse could be mainly due to the decrease of –SO<sub>3</sub>H over the catalyst as observed in Figure 8. This is also based on the observation that the –OH group was still decreasing after the second reuse, but –SO<sub>3</sub>H already remained at a relatively stable level. As a result, the FF yield was no longer significantly changed, supporting that the shedding of –SO<sub>3</sub>H from the catalyst surface was the main reason for its activity decrease. Researchers also have proved that –SO<sub>3</sub>H acted as the catalytic site in a similar solid acid catalyst, and –OH acted only as the binding site.<sup>38</sup> It is therefore necessary to regenerate the current catalyst (i.e., to recover the –SO<sub>3</sub>H groups) to improve its reusability.

Moreover, to investigate whether the good catalytic activity was caused by the solid catalyst itself, or by the removed –SO<sub>3</sub>H group at the reaction condition acting as a homogeneous catalyst, the furfural production experiments both in the water–MIBK system with or without MMCSA and in the –SO<sub>3</sub>H and Fe ion aqueous solution–MIBK system were conducted under the optimal condition (190 °C for 10 min). The –SO<sub>3</sub>H and Fe ion solution was the hydrolysate which was separated from MMCSA after the reaction (0.5 g of MMCSA reacted at 190 °C in 10 mL of deionized water for 10 min without addition of xylose). As Figure S2 shows, the furfural yields were 17.15% and 36.51%, respectively, much lower than the 79.04% furfural yield obtained in the water–MIBK system with MMCSA. Thus, it is confirmed that although the –SO<sub>3</sub>H groups removed from MMCSA during the reaction have a certain effect on the furfural yield, the catalytic effect of the soluble –SO<sub>3</sub>H groups is much weaker than that of MMCSA. It is the MMCSA itself that plays a major role on the high furfural yield.

The Fe ion was detected in the liquid after the degradation reaction by ICP analysis, indicating that Fe was also leached from the catalyst during the reaction. According to the concentration of Fe in liquid (as shown in Table S4) and the original Fe content in MMCSA,<sup>26</sup> the leaching rate of Fe was 4.48% after the first time use. The saturation magnetization intensity value of MMCSA after the first time use is 2.87 Am<sup>2</sup>/kg (Figure S1), which is lower than the original MMCSA.<sup>26</sup> The result indicated that although the leaching rate of Fe from MMCSA was small during the catalytic reaction, it still influenced the stability of saturation magnetization intensity value of MMCSA.

The pore size distribution of the fresh and used MMCSA is shown in Figure S3. The pore size distribution indicated that

the pore in the catalyst before and after use was mainly composed of mesopores, and there was no obvious changes.

**3.5. Regeneration of Recycled MMCSA and Its Reusability.** To regenerate MMCSA, it was sulfonated in concentrated sulfuric acid (cf. Section 2.5), similar to the regeneration of other carbon-based solid acids.<sup>39,40</sup> The regenerated MMCSA was used in the furfural production experiment under the optimal conditions. As shown in Figure 10, in the first use, MMCSA catalyzed the hydrolysis of xylose

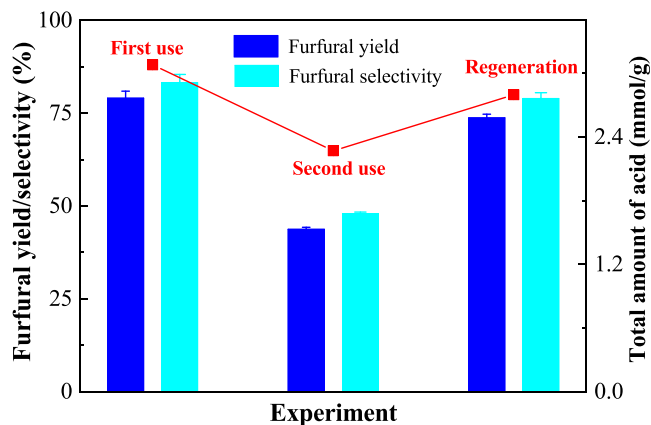


Figure 10. Hydrolysis experiment results before and after regeneration of MMCSA.

to obtain a yield of 79.04% furfural, but in the second use, only 43.74% of the furfural yield was obtained. Satisfactorily, the regenerated MMCSA catalyzed the hydrolysis of xylose to obtain a furfural yield of 73.74%, while the selectivity of furfural did not decrease appreciably. Moreover, it was found that the total amount of acid over the catalyst decreased from 3.08 to 2.27 mmol g<sup>-1</sup> after the first use, but could be returned to 2.80 mmol g<sup>-1</sup> after generation via the sulfonation treatment.

The XPS spectrum of MMCSA showed that S was on the catalyst surface before and after the regeneration (Figure 11). The peak at a binding energy of 168 eV is ascribed to S 2p of

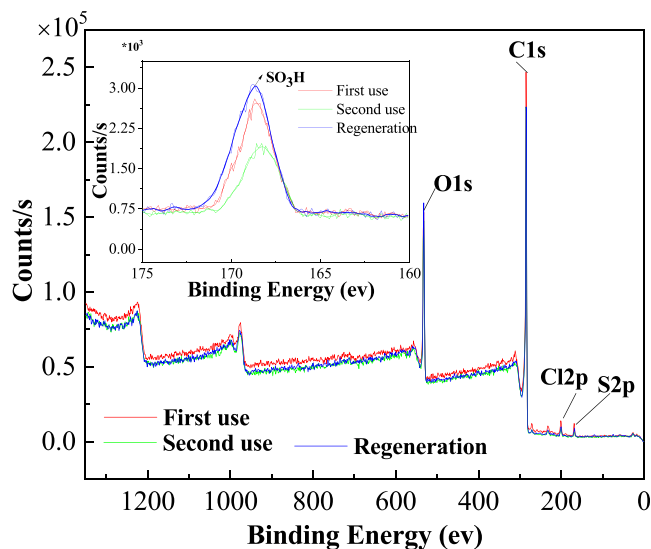
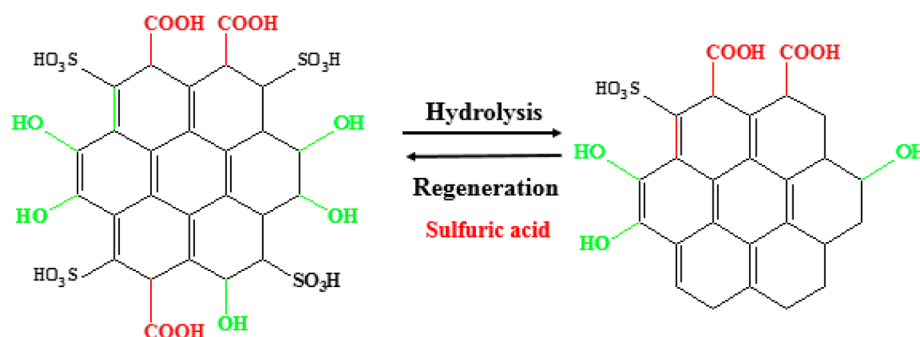


Figure 11. X-ray photoelectron spectroscopy of MMCSA before and after regeneration.



**Figure 12.** Schematic diagram of the deactivation and regeneration process for MMCSA. The schematic diagram does not represent the real amount and distribution of the functional groups.

$-\text{SO}_3\text{H}$ ,<sup>41</sup> which also indicates that  $-\text{SO}_3\text{H}$  in MMCSA detached during hydrolysis, and after sulfonation,  $-\text{SO}_3\text{H}$  was regained in MMCSA. Combined with the above results (cf. Section 3.4),  $-\text{SO}_3\text{H}$  leaching is the main reason for the decrease in the furfural yield, which is consistent with the literature results.<sup>42,43</sup> Fortunately, such leaching could be mitigated via a simple sulfonation of MMCSA with concentrated sulfuric acid. The consistent results have been also demonstrated,<sup>39</sup> implying that MMCSA can be regenerated by a simple procedure. Based on these, the catalyst deactivation and regeneration process of MMCSA was proposed. As shown in Figure 12, MMCSA is an amorphous carbon composed of a nanographene sheet with phenolic  $-\text{OH}$ ,  $-\text{COOH}$ , and  $-\text{SO}_3\text{H}$  acid groups supported in a random manner.<sup>26</sup> In the process of furfural production, some acid groups (like  $-\text{SO}_3\text{H}$ ,  $-\text{COOH}$ ,  $-\text{OH}$ ) in MMCSA will fall off partially, which significantly reduces the catalytic activity. After further sulfuric acid sulfonation, the deactivated MMCSA was regenerated by a reintroduced acid group (mainly  $-\text{SO}_3\text{H}$ ).

**3.6. Integrated Biorefinery Process from Corncob Conversion under MMCSA Catalysis.** Figure S4 shows an integrated biorefinery process from corncob conversion under MMCSA catalysis. Our group has synthesized MMCSA and used it to pretreat the corncob process, which could effectively improve the enzymatic digestibility (95.2%), and the total sugar yield reached 90.4%.<sup>26</sup> In this work, we further realized the efficient conversion of xylose to furfural in a water–MIBK system over the same MMCSA catalyst (a best furfural yield of 79.04% was obtained in the first use, and comparable yields were achievable after a simple regeneration). These efforts also indicate the great potential of MMCSA in the field of biorefinery, which would contribute to a simplified overall process.

## 4. CONCLUSIONS

In this work, the conversion of xylose to furfural was effectively achieved using the magnetic carbon-based solid acid catalyst (MMCSA), bearing  $-\text{SO}_3\text{H}$ ,  $-\text{COOH}$ , and phenolic  $-\text{OH}$  acid groups, which was synthesized based on the impregnation–carbonization–sulfonation procedure detailed in our previous work.<sup>26</sup> The hydrolysis conditions were optimized to obtain a highest FF yield of 79.04%, with 0.1625 g of xylose and 0.5 g of catalyst in 10 mL of deionized water and 40 mL of MIBK at 190 °C for 10 min. Moreover, byproducts in the reaction process were identified by LC-MS, which provided a reference for analysis of the reaction pathway of xylose to FF catalyzed by MMCSA. Although MMCSA was deactivated at

high temperatures (190 °C), the recycled MMCSA can be regenerated by concentrated sulfuric acid (98 wt %), and the yield of FF is up to 73.74%, which is comparable to the initial result catalyzed by MMCSA. The results of this work indicate that MMCSA can be used not only for the comprehensive utilization of lignocellulose to produce fermentable sugars but also for the excellent production of platform compounds, under reasonable control of the reaction conditions, indicating a great commercial potential for the catalyst.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.9b06349>.

Effects of MIBK/water volume ratio, reaction temperature and time for xylose dehydration, main MS fragment ions of products during conversion of xylose and FF, ion concentration of Fe in hydrolysate of reaction, VSM and BET analyses of MMCSA, and comparison of xylose dehydration and integrated biorefinery process of corncob under MMCSA catalysis. (PDF)

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## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported financially by the National Natural Science Foundation of China (51676193, 51861145103, and 2171101430), National Key Research and Development Program of China (2018YFC1901201), Youth Innovation Promotion Association, CAS (2017401), and Municipal Science and Technology Program of Guangzhou (201804010187). Qiong Wang would like to thank the International Cooperation and Exchange Project between the National Natural Science Foundation of China (NSFC) and the Dutch Research Council (NWO) (21811530627). Jun Yue would like to thank NWO for financially supporting his scientific visit at Guangzhou Institute of Energy Conversion to carry out collaborative research (Project No. 040.21.006). Xiaohan Wang would like to thank the Foundation of State Key Laboratory of Coal Combustion (FSKLCCA1804).

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