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## **Conversion of xylose into furfural over MC-SnO<sub>x</sub> and NaCl catalysts in a biphasic system**

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20 **ABSTRACT**

21 Furfural is a promising platform chemical that can be catalyzed from lignocellulose  
22 biomass. In this study, a novel micro-mesoporous carbon supported tin oxide catalyst (MC-  
23 SnO<sub>x</sub>) was developed to convert xylose into furfural in a low sodium chloride (NaCl)  
24 concentration and acid-free biphasic system. The catalysts synthesized by annealing from  
25 400 °C to 600 °C for 3.5h were characterized by BET, SEM, XPS, XRD, NH<sub>3</sub>-TPD and  
26 FTIR techniques. The factor that mostly affected the catalytic performance was the acid  
27 concentration of the catalysts, and the best catalytic performance was achieved by MC-  
28 SnO<sub>x</sub> annealed at 450 °C. Further increasing the annealing temperature can cause reduction,  
29 volatilization and aggregation of Sn species, which can finally affect acid concentration  
30 and performance of the catalyst. In addition, a synergistic catalytic effect was found  
31 between MC-SnO<sub>x</sub> and NaCl and effectivity of low concentration of NaCl indicated the  
32 potential of applying seawater or wastewater containing NaCl as a low-cost reaction  
33 solvent and NaCl source. To balance the catalytic performance, cost, equipment safety and  
34 environmental concerns, a reasonable furfural yield of 53.9 % was achieved over the MC-  
35 SnO<sub>x</sub>-450 and NaCl (0.2 M) in biphasic system under mild conditions (180 °C and 20 min)  
36 with a good catalyst reusability.

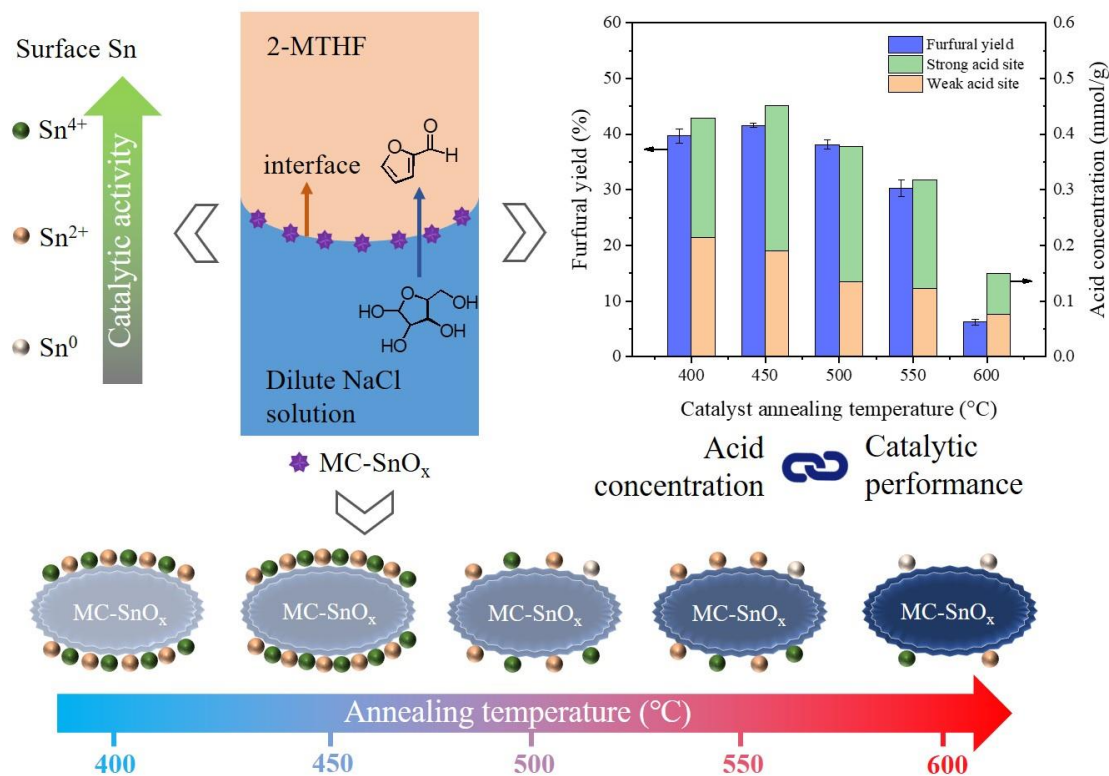
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38 **KEYWORDS:** Furfural, Annealing temperature, Sn reduction, Xylose conversion, Biphasic

39 solvent, Seawater

40

41 **Graphical abstract**



42

43 **1. Introduction**

44 Furfural is one platform chemical that can be derived from lignocellulose biomass in

45 large scale and can be converted to various useful chemicals to replace part of fossil derived

46 chemicals. Furfural and its conversion products can be used as various industrial raw

47 materials such as resin, adhesives, solvent, biofuel and so on (Bhaumik and Dhepe, 2016).  
48 Hence, furfural is believed as a kind of promising bio-based chemical (Wettstein et al.,  
49 2012). Currently, furfural is produced by a dilute acid catalytic hydrolysis process in  
50 industry. Biomass is first treated with dilute sulfuric acid or hydrochloric acid, and then the  
51 furfural is separated by high pressure steam (Choudhary et al., 2012). However, this  
52 method is not efficient enough and can produce massive acid wastewater, byproducts and  
53 cause severe equipment corrosion (Karinen et al., 2011). To overcome these disadvantages,  
54 many catalytic methods were developed to produce furfural.

55 Biphasic solvent systems are often used to enhance furfural yields. With  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  
56 sodium chloride (NaCl) in the aqueous phase and 2-methyltetrahydrofuran (2-MTHF) as  
57 the organic phase, a furfural yield of 71% was achieved with 98% furfural extracted  
58 (Vomstein et al., 2011). The advantages of the biphasic system are that furfural can be  
59 transferred to the organic phase and the reduction in the furfural concentration minimizes  
60 the degradation of furfural (Cai et al., 2014). Also, furfural can be recovered from the  
61 reaction solvent more easily (Sweygers et al., 2018). Among organic solvents, 2-MTHF  
62 displays promising application potential because of its good extraction ability (Wang et al.,  
63 2015), low toxicity (Lin et al., 2017), acid stability and recycle convenience (Li et al., 2016).

64 Chloride salts were found to have excellent catalytic efficiency. Researchers studied the  
65 catalysis influence of  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ , NaCl and HCl on furfural synthesis (Li et al., 2016).

66 FeCl<sub>3</sub> showed a similar catalysis effect with HCl in aqueous phase and NaCl also improve  
67 the synthesis of furfural when FeCl<sub>3</sub>, AlCl<sub>3</sub> or HCl are in the system. Other salts like SnCl<sub>4</sub>  
68 (Wang et al., 2015), ZnCl<sub>2</sub>, MnCl<sub>2</sub> (Jiang et al., 2018), CuCl<sub>2</sub> (Guenic et al., 2015), CrCl<sub>3</sub>  
69 (Choudhary et al., 2012), Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (Yang et al., 2017) and alkali halide (Enslow and Bell,  
70 2015) have been proven to have considerable promotion on furfural production. In addition,  
71 the salting out effect of chlorides also contribute to the higher yields due to more product  
72 can be extracted by the organic phase (Román-Leshkov et al., 2007). To realize greener  
73 conversion, researchers applied seawater to furfural production. However, in previous  
74 studies seawater itself cannot provide enough catalytic effect because of its low NaCl  
75 concentration. Systems containing concentrated seawater and other homogeneous catalysts  
76 were proven effective in xylose conversion into furfural (T. Guo et al., 2018; Vomstein et  
77 al., 2011).

78 However, high concentration of chlorides can also cause equipment corrosion at high  
79 temperatures. Thus, heterogeneous catalysts have been widely explored in furfural  
80 production. Heteropoly acids (X. Guo et al., 2018), polymeric solid catalyst (Agirrezabal-  
81 Telleria et al., 2012, 2011), metal oxides (H. Li et al., 2014), zeolites (Zhang et al., 2017)  
82 and carbon-based catalysts (Wang et al., 2017) have already been proven to be effective in  
83 furfural synthesis. The mechanism of xylose conversion into furfural has already been  
84 proposed as following one of 3 pathways (Yang et al., 2017): (1) xylose isomerizes to

85 xylulose intermediate and subsequently dehydrates to furfural, (2) xylose directly  
86 dehydrate into furfural and (3) xylose in a stepwise fashion dehydrates to furfural through  
87 a dicarbonyl intermediate. The second route is common in the homogeneous reactions  
88 catalyzed by strong acid (Nimlos et al., 2006). The third route has been proven in the  
89 research on Nb<sub>2</sub>O<sub>5</sub> catalysis (Gupta et al., 2017). Among the three routes, the first route is  
90 widely accepted in the presence of catalysts with both Brønsted and Lewis acid.

91 Among solid catalysts, tin and its oxide showed promising catalytic abilities and addition  
92 of SO<sub>4</sub><sup>2-</sup> can further promote catalytic performance: SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>- MMT (montmorillonite)  
93 (Qing et al., 2017) showed even higher furfural yield in solvents like toluene, methyl  
94 isobutyl ketone (MIBK) and cyclopentyl methyl ether (CPME) with addition of NaCl.  
95 SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>-diatomite (Jiang et al., 2018) was also found to have a maximum furfural yield  
96 of 68.9% in a  $\gamma$ -valerolactone ( $\gamma$ -GVL)–water system with 15 g/L ZnCl<sub>2</sub>. Waste like coal  
97 fly ash has been considered as a support for catalysts: Researchers (Gong et al., 2019)  
98 prepared SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CFA (coal fly ash) and achieved a good furfural yield of 84.7%  
99 in the NH<sub>4</sub>Cl-toluene biphasic system. As a kind of carbon-based material, bio-based  
100 materials which can be found from food and agriculture waste captured researchers'  
101 interest because of their characteristics of eco-friendly and low-cost. Rape pollen was used  
102 as raw material to produce SO<sub>4</sub><sup>2-</sup>/Sn-TRP (treated rape pollen) catalyst (Teng et al., 2020).  
103 High performance was observed in a prolonged reaction of xylose to furfural, which

104 reached a furfural yield of 82.79%. However, the sulfuric acid treatment process can  
105 discharge acid wastewater while providing catalytic activity to catalysts. Several recent  
106 studies reported the effectiveness of such bio-based/carbon-based tin oxide in biorefinery  
107 (Yang et al., 2017, 2019). Rare studies reported the application of carbon-supported tin  
108 oxide catalyst in furfural production. Since bio-based/carbon-based support has advantages  
109 of eco-friendly and low-cost and tin oxide displays promising performance, a greener bio-  
110 based/carbon-based tin oxide catalytic system is still deserved to develop.

111 In this study, we have prepared a novel mesoporous carbon-supported tin oxide catalyst  
112 (MC-SnO<sub>x</sub>) without acid treatment process, which has proven to have a reasonable catalytic  
113 performance with low concentration of NaCl. Characteristics of acid-free process and  
114 potential of applying seawater or wastewater containing NaCl enable greener production  
115 of furfural. Comprehensive characterization was conducted to construct the structure-  
116 performance relationship between MC-SnO<sub>x</sub> catalyst and furfural production. In addition  
117 to factors like catalyst loading, NaCl concentration, reaction temperature and time,  
118 temperature of catalyst's annealing process impacts most on furfural production. The  
119 probable mechanism of Sn species content and contribution variation at different annealing  
120 temperature was investigated and a catalytic activity order of Sn species was concluded.  
121 Finally, the reusability of MC-SnO<sub>x</sub> catalyst was studied and proven good. The results are



122 meaningful for further development of carbon-supported tin oxide catalysts in furfural  
123 production.

124

## 125 **2. Materials and methods**

### 126 *2.1. Materials*

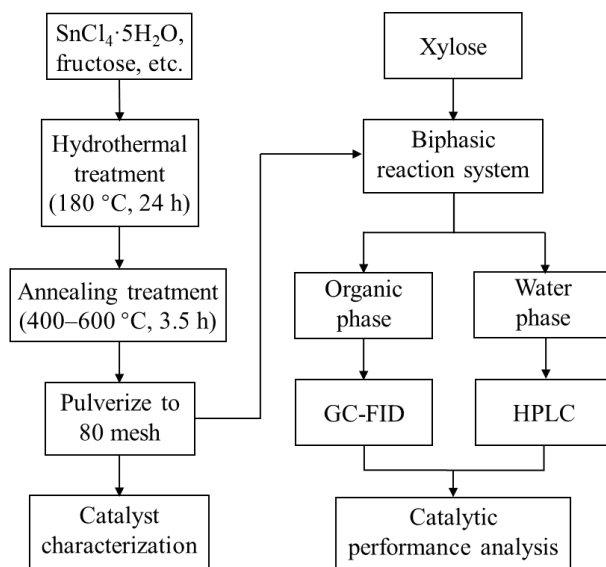
127 Furfural ( $\geq 99.5\%$ ), D-xylose (98%) and D-fructose (99%) were supplied by Aladdin  
128 Reagent Corporation. 2-methyltetrahydrofuran (2-MTHF) ( $\geq 99\%$ ),  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$   
129 (analytical grade) and NaCl ( $\geq 99.5\%$ ) were brought from Shanghai Titan Scientific Co.,  
130 LTD, Sinopharm Chemical Reagent Co., Ltd and Shanghai Dahe Chemicals Co. LTD,  
131 respectively. Pluronic P-123 ( $M_w=5800$ ,  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ) and Pluronic F-127 ( $M_w=2600$ ,  
132  $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ ) were purchased from Sigma Aldrich. All reagents were used without  
133 further purification.

134

### 135 *2.2. Synthesis of MC-SnO<sub>x</sub> catalysts*

136 The synthesis method of MC-SnO<sub>x</sub> catalysts refers to previous study ([Zhang et al., 2019](#)),  
137 and the basic process is shown in Fig. 1. P-123 and F-127 were used as composite template  
138 in the preparation. Briefly, 8.7 g  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , 2 g fructose, 1 g P-123 and 3 g F-127 were  
139 dissolved in 70 mL ultrapure water and stirred at room temperature for 2 h. The solution  
140 was then sealed in a stainless reactor with 100 mL polytetrafluoroethylene lining and

141 heated in the oven at 180 °C for 24 h. The mixture was centrifuged and the residual was  
 142 washed by ultrapure water to neutral pH value, then residual was dried in oven at 80 °C  
 143 overnight. The as-prepared samples were annealed at the temperature from 400 °C to  
 144 600 °C with a heating rate of 2 °C /min in a tube furnace for 3.5 h in a nitrogen atmosphere.  
 145 Finally, the MC-SnO<sub>x</sub> catalysts was ground and pulverized to 80 mesh before use. In the  
 146 following sections, MC-SnO<sub>x</sub>-X is used to represent catalysts annealed at certain  
 147 temperature. For example, MC-SnO<sub>x</sub>-400 is the MC-SnO<sub>x</sub> catalyst annealed at 400 °C.



148 **Fig. 1.** Diagram of catalyst preparation and furfural production processes

149

### 150 2.3. Conversion of xylose to furfural

151 As shown in Fig. 1, the catalytic conversion from xylose to furfural was conducted in a  
 152 25 mL Hastelloy reactor. A biphasic rate of 1:1 (v/v) was selected because of its prior

153 performance (Qing et al., 2017; Wang et al., 2019). In a typical run, 5 mL aqueous solution  
154 containing 20 g/L xylose (some with NaCl) and 5 mL 2-MTHF organic solvent were mixed  
155 with MC-SnO<sub>x</sub> catalysts in the reactor. Then the reactor was heated up to target temperature  
156 (160–180 °C) while stirring at 700 rpm. The reactor can reach the target temperature no  
157 longer than 10 min as shown in Fig. S1. When reaction completed, the reactor was cooled  
158 in tap water to room temperature quickly. Needle filters equipped with filter paper were  
159 used to separate catalysts. Water phase and organic phase was then separate after quick  
160 stratification. All samples were filtered by a 0.22 μm syringe filter before analyzing.

161

#### 162 *2.4. Catalysts characterization*

163 Catalysts' specific surface area were analyzed by a Quantachrome Quantasorb SI  
164 Brunauer-Emmett-Teller (BET) analyzer. The surface composition and structure of MC-  
165 SnO<sub>x</sub> catalysts were analyzed by a VEGA3 (TESCAN) scanning electron microscopy  
166 (SEM) instrument with a Bruker XFlash Detector 610M energy dispersive spectroscopy  
167 (EDS) system. X-ray photoelectron spectroscopy (XPS) was used to analyze the state of  
168 the developed catalysts with an RBD-upgraded PHI 5000C ESCA system (Perkin Elmer).  
169 The crystal structures of the catalysts were analyzed by a Bruker advance D8 powder X-  
170 ray diffraction (XRD) analyzer equipped with a Cu-Kα radiation (40 kV, 35 mA) at a scan  
171 rate of 5 °/min. The spectra were scanned over a 2θ range from 5 to 90°. A Thermo Fisher

172 Nicolet iS5 Fourier Transformed Infrared (FTIR) spectrometer with a spectral resolution  
173 of  $4\text{ cm}^{-1}$  was employed to characterize the functional groups of MC-SnO<sub>x</sub> catalysts.

174 The ammonia-temperature-programmed desorption (NH<sub>3</sub>-TPD) was employed to  
175 analyze acid properties of MC-SnO<sub>x</sub> catalysts on a TP 5080 (Tianjin Xianquan) analyzer.  
176 Before adsorption of NH<sub>3</sub>, the samples were treated at 450 °C for 30 min in the nitrogen  
177 atmosphere. Then catalysts were exposed to ammonia at 50 °C for 1 h and stabilized at the  
178 same temperature for 30 min before the run. Afterwards, the sample tube was heated to  
179 500 °C at a rate of 10 °C/min. The desorption of NH<sub>3</sub> was detected by a thermal  
180 conductivity detector.

181

## 182 2.5. Product analysis

183 After separation of organic and water phase, furfural concentrations in organic phase  
184 were analyzed by a gas chromatograph (Shimadzu GC-2010 plus) equipped with a flame  
185 ionization detector (FID) and a HP-5ms column (30 m, 0.25 mm i.d., 0.25 μm film  
186 thickness). Nitrogen was used as the carrier gas with a flow rate of 1 mL/min. The injector  
187 was set at 240 °C and the detector was maintained at 250 °C. Initially, the column oven  
188 was maintained at 100 °C for 3 min, then the temperature was increase to 200 °C at a rate  
189 of 10 °C/min and kept for 10 min.

190 For samples of water phase, a HPLC (Agilent 1260) equipped with an Agilent Hi-plex  
191 H column (diameter 7.7 mm, length 300 mm, particle size 8  $\mu\text{m}$ ), a UV detector at a  
192 wavelength of 280 nm and a refractive index detector (RID) were employed to determine  
193 the concentrations of furfural and xylose. 5 mmol/L  $\text{H}_2\text{SO}_4$  solution was used as mobile  
194 phase and the flow rate was 0.6 mL/min. The column oven and RID were maintained at  
195 60  $^\circ\text{C}$  and 55  $^\circ\text{C}$ , respectively.

196 Furfural yield and selectivity contained furfural production in both water phase and  
197 organic phase. Furfural yield, D-xylose conversion and furfural selectivity were calculated  
198 by the following equations:

$$199 \quad \text{Furfural yield (\%)} = \frac{\text{Moles of furfural in the product (mol)}}{\text{Moles of initial xylose (mol)}} \times 100 \quad (1)$$

$$200 \quad \text{D - xylose conversion (\%)} = \frac{\text{Moles of xylose in reactant consumed (mol)}}{\text{Moles of initial xylose (mol)}} \times 100 \quad (2)$$

$$201 \quad \text{Furfural selectivity (\%)} = \frac{\text{Moles of furfural in the product (mol)}}{\text{Moles of xylose in reactant consumed (mol)}} \times 100 \quad (3)$$

202

### 203 **3. Results and discussion**

#### 204 *3.1. Characterization of MC-SnO<sub>x</sub> Catalyst*

205 [Table 1](#) and [Fig. S2](#) shows surface area and pore volume properties of MC-SnO<sub>x</sub> catalysts.

206 The specific surface area increased gradually from 331.4 m<sup>2</sup>/g to 387.4 m<sup>2</sup>/g when  
207 annealing temperature rose from 400 to 500  $^\circ\text{C}$ , which can be attributed to improvement  
208 of higher annealing temperature. MC-SnO<sub>x</sub>-400, has the lowest micropore surface area of

209 107.7 m<sup>2</sup>/g and micropore volume of 47 cm<sup>3</sup>/kg, which is only 41.5% and 43.9% of those  
 210 of MC-SnO<sub>x</sub>-500. There are similar differences between MC-SnO<sub>x</sub>-400 and MC-SnO<sub>x</sub>-500  
 211 in other properties. It can be concluded that MC-SnO<sub>x</sub>-400 has less micropore structure  
 212 and MC-SnO<sub>x</sub>-500 has most, consistent with the measured pore distributions (Fig. S2).  
 213 MC-SnO<sub>x</sub>-400 has abundant mesopore structure, leading to the largest average pore  
 214 diameter and the highest total pore volume among the catalysts.

**Table 1**

Surface areas and porosities of MC-SnO<sub>x</sub> catalysts.

| Catalyst Annealing<br>temperature (°C) | S <sub>BET</sub> <sup>a</sup><br>(m <sup>2</sup> /g) | S <sub>micro</sub> <sup>b</sup><br>(m <sup>2</sup> /g) | V <sub>total</sub> <sup>c</sup><br>(cm <sup>3</sup> /kg) | V <sub>micro</sub> <sup>d</sup><br>(cm <sup>3</sup> /kg) | Average pore<br>diameter (nm) |
|--|--|--|--|--|-------------------------------|
| 400                                    | 331.4  | 107.7  | 474  | 47   | 5.7                           |
| 450                                    | 342.8  | 194.6  | 423  | 81   | 4.9                           |
| 500                                    | 387.4  | 259.3  | 409  | 107  | 4.2                           |
| 550                                    | 360.4  | 178.8  | 433  | 75   | 4.8                           |
| 600                                    | 381.4  | 196.5  | 421  | 81   | 4.4                           |

<sup>a</sup> Specific surface area calculated by Brunauer-Emmett-Teller (BET) equation.

<sup>b</sup> Specific surface area of micro-pores calculated by density functional theory (DFT) method.

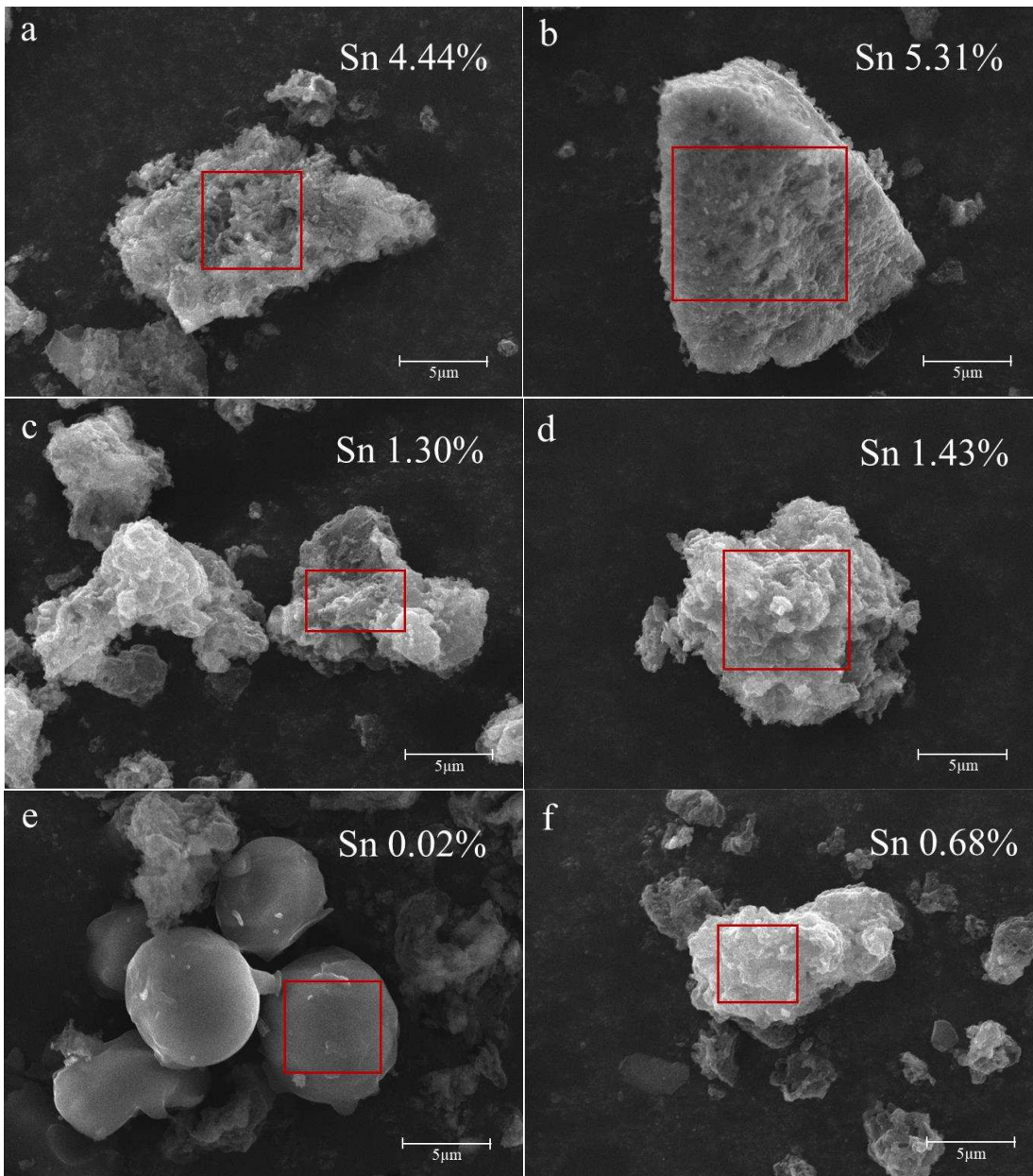
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<sup>c</sup> Total pore volume determined at  $P/P_0=0.99$ .

<sup>d</sup> Micropore volume calculated using t-plot method.

215

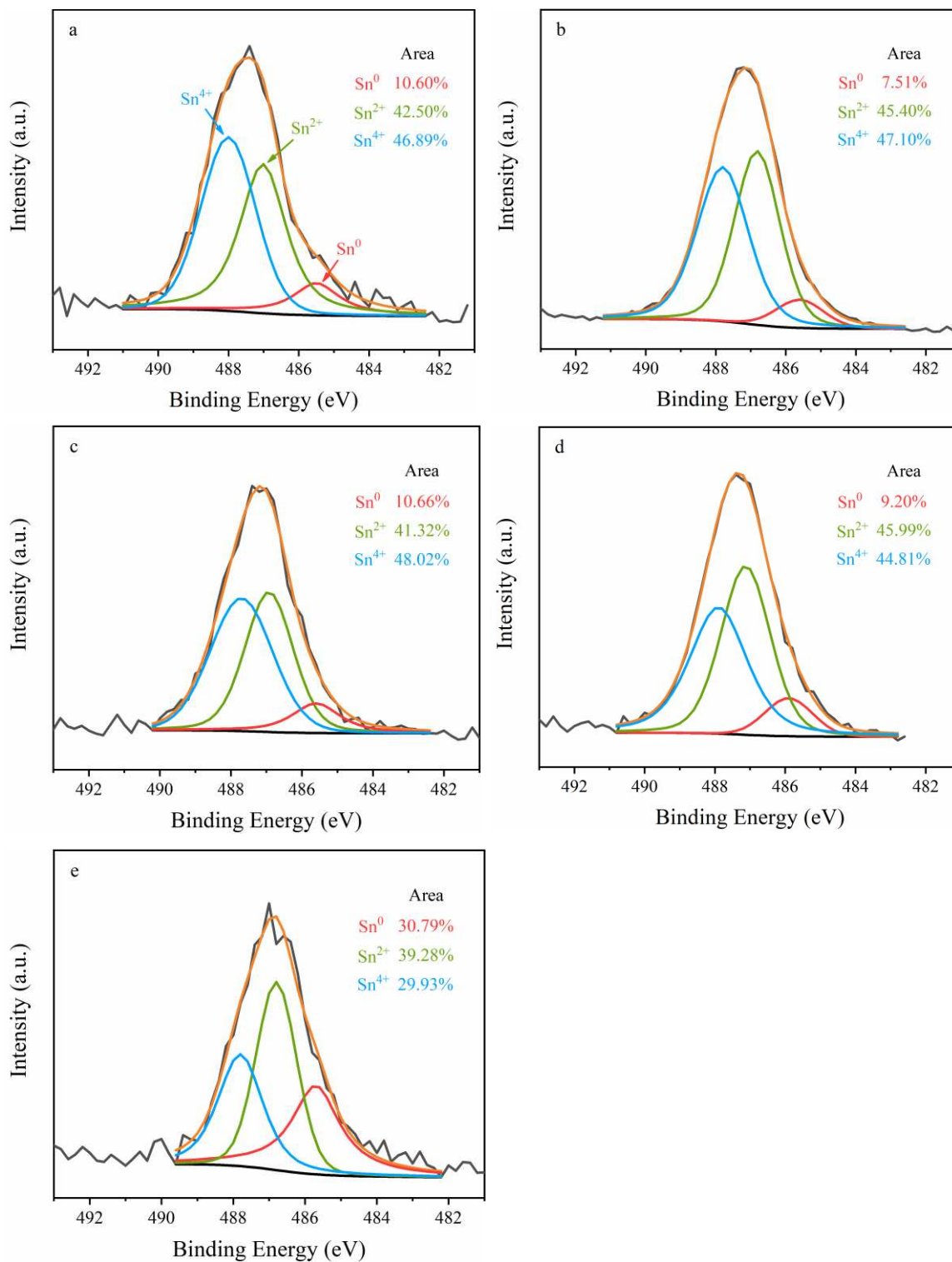
216 SEM images (see Fig. 2) demonstrate morphology and surface Sn proportion of MC-  
217 SnO<sub>x</sub> catalysts. Fig. 2a, 2b, 2c, 2d and 2f captured irregular sharp particles of catalysts  
218 annealed at temperature from 400 °C to 600 °C. Ravine and pit structures were found on  
219 the surface of these catalyst particles. EDS mapping results indicate that MC-SnO<sub>x</sub>-450 has  
220 the highest tin concentration on the surface of 5.31% (atomic ratio). With further increase  
221 of annealing temperature, the Sn content decreased sharply to MC-SnO<sub>x</sub>-600 catalyst's  
222 0.68%. However, another kind of globular particles are found in MC-SnO<sub>x</sub>-600 (Fig. 2e).  
223 It can be noted that these particles had relatively smooth surface and very low levels of Sn  
224 content on their surface (only 0.02%). These globular particles were commonly found in  
225 MC-SnO<sub>x</sub>-600 (Fig. S3). EDS mapping images (Fig. S4) proved that highly dispersed Sn  
226 species exist on the surface of catalysts' particles, which confirms successful hybridization  
227 of Sn species with MC in the catalysts.



228 **Fig. 2.** SEM images and EDS mapping results of particles of (a) MC-SnO<sub>x</sub>-400, (b) MC-  
229 SnO<sub>x</sub>-450, (c) MC-SnO<sub>x</sub>-500, (d) MC-SnO<sub>x</sub>-550, (e) globular MC-SnO<sub>x</sub>-600, and (f)  
230 irregular MC-SnO<sub>x</sub>-600. Sn element content information (atomic ratio) was achieved by  
231 EDS mapping of the area that framed in red boxes.  
232

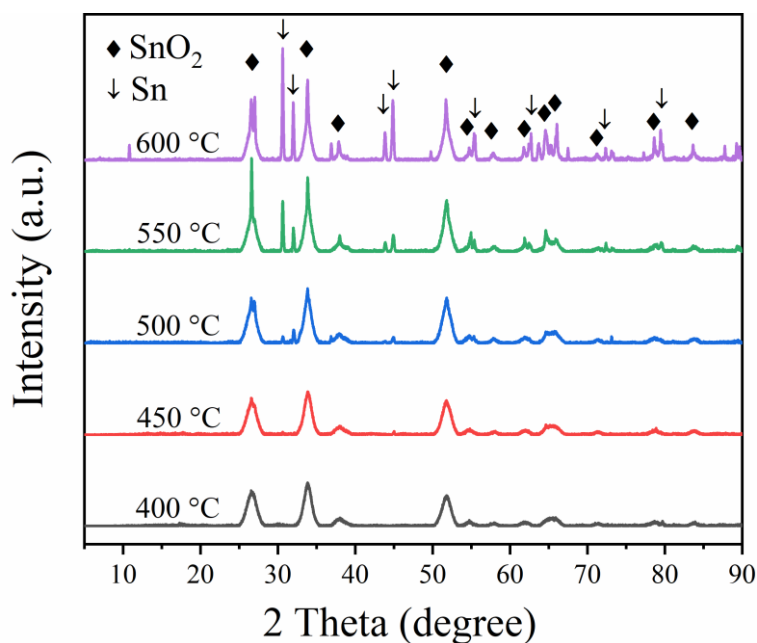


233 The X-ray photoelectron spectroscopy characterization of Sn in the catalysts is shown in  
234 [Fig. 3](#). The fitting curves consist of three subpeaks in the XPS spectra of Sn 3d<sub>5/2</sub>. The  
235 resolved peaks at binding energies of ~485.6 eV, ~487.0 eV, ~487.8 eV originate from the  
236 Sn<sup>0</sup>, Sn<sup>2+</sup> and Sn<sup>4+</sup> states, respectively. However, the binding energies for all peaks of Sn  
237 appear higher than the reference values ([Quackenbush et al., 2013](#); [Zhu et al., 2016](#)). The  
238 increase of binding energies is probably caused by strong interactions between Sn species  
239 and the carbon-based support ([Ma et al., 2011](#)). MC-SnO<sub>x</sub> catalyst annealed at 400 °C, has  
240 10.60% Sn<sup>0</sup>, 42.50% Sn<sup>2+</sup> and 46.89% Sn<sup>4+</sup> species. When the annealing temperature rose  
241 to 600 °C, there remained only 29.93% Sn<sup>4+</sup> and the proportion of Sn<sup>0</sup> increased to 30.79%.  
242 It can be concluded that more Sn converted to lower valence species such as Sn<sup>0</sup> and Sn<sup>2+</sup>  
243 at higher annealing temperature, which indicates that reduction reactions become more  
244 significant with increasing annealing temperature.



245 **Fig. 3.** X-ray photoelectron spectroscopy (XPS) Sn 3d<sub>5/2</sub> spectra of (a) MC-SnO<sub>x</sub>-400, (b)  
 246 MC-SnO<sub>x</sub>-450, (c) MC-SnO<sub>x</sub>-500, (d) MC-SnO<sub>x</sub>-550, (e) MC-SnO<sub>x</sub>-600 catalysts.

247 MC-SnO<sub>x</sub> catalysts' XRD patterns were shown as Fig. 4. Peaks of tin dioxide can be  
248 found in all samples, which proved SnO<sub>2</sub> synthesis in the catalysts after annealing (Bellayer  
249 et al., 2009). For catalysts that were annealed at 550 °C and 600 °C, more peaks of metallic  
250 Sn appeared. The formation of metallic Sn was more significant in MC-SnO<sub>x</sub>-600 than  
251 MC-SnO<sub>x</sub>-550, suggesting that reduction reaction of Sn species became more intense when  
252 annealing at 600 °C. This result is in accordance with that of XPS analysis (see Fig. 2).  
253 Table S1 shows average crystallite sizes calculated by Scherrer formula. Both metallic Sn  
254 and tin dioxide grew larger in size with increasing annealing temperature.



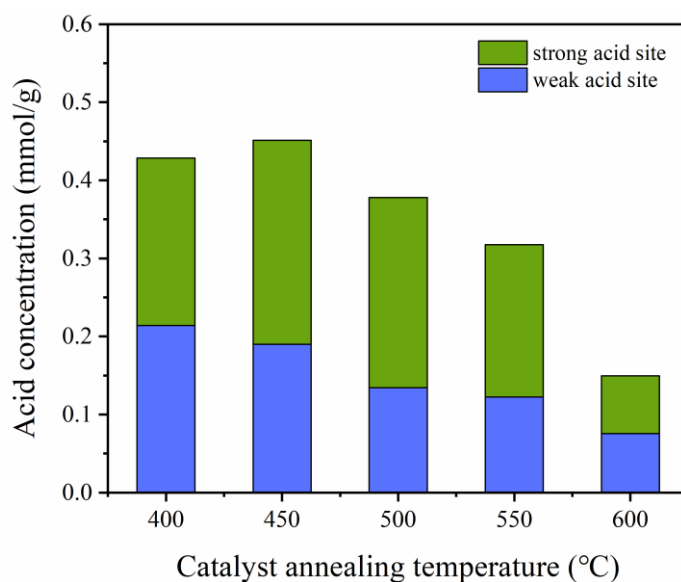
255 **Fig. 4.** X-Ray diffraction (XRD) pattern of MC-SnO<sub>x</sub> catalysts.

256

257 NH<sub>3</sub>-TPD was employed to analyze acid site strength and distribution in the catalysts.

258 Fig. S5 depicts NH<sub>3</sub> desorption profile of MC-SnO<sub>x</sub> catalysts. The distribution of acid site

259 was determined by NH<sub>3</sub> desorption temperature. In general, NH<sub>3</sub> peaks below 250 °C  
260 represent desorption of partially ionic NH<sub>4</sub><sup>+</sup> species which are absorbed by weak Brønsted  
261 acid sites on catalysts, while desorption peaks between 250 °C and 500 °C are caused by  
262 strong Brønsted acid sites and coordinated NH<sub>3</sub> bound Lewis acid sites, which are both  
263 considered as strong acid sites (Zhang et al., 2019; Zhao et al., 2016). Due to the limitations  
264 of catalyst annealing and pretreatment temperature, strong acid sites were calculated and  
265 compared based on peaks between 250 °C and 450 °C. Fig. 5 displays calculated acid site  
266 concentration of the catalysts. Total acid site concentration rose from 0.43 mmol/g to 0.45  
267 mmol/g when annealing temperature increased from 400 °C to 450 °C. Further increasing  
268 of annealing temperature caused acid site concentration to come down quickly. When  
269 preparing the catalyst at 600 °C, acid site concentration remained only 33% of that in MC-  
270 SnO<sub>x</sub>-450.



271 **Fig. 5.** Acid concentration of MC-SnO<sub>x</sub> catalysts calculated from NH<sub>3</sub>-TPD profiles.

272 *3.2. Impact of annealing temperature on catalyst characteristics*

273 Since the MC-SnO<sub>x</sub> catalysts synthesis consists of two steps: (1) hydrothermal treatment  
274 to produce catalyst precursor containing Sn element; and (2) annealing preparation at  
275 different temperature to obtain activated MC-SnO<sub>x</sub> catalyst, the key step that significantly  
276 influence the catalytic effect was step (2).

277 The difference of acid site abundance is induced by the tin species distribution and  
278 content variation. Increasing the annealing temperature can accelerate the reduction  
279 reaction of tin oxide. This reduction reaction was probably caused by reducing ambient CO  
280 produced in the high-temperature reaction of carbon-rich support. [Fig. S6](#) demonstrates an  
281 oxygen-containing functional groups decrease with increasing annealing temperature,  
282 indicating the emission of CO or CO<sub>2</sub> could form a reducing atmosphere at higher  
283 temperature. In the metallurgical industry, iron concentrate is roasted in an atmosphere of  
284 CO and CO<sub>2</sub> to remove tin element and this process is called selective reduction  
285 volatilization ([G. Li et al., 2014](#); [Su et al., 2016](#)), which has similar conditions with that in  
286 the annealing process in catalyst preparation. Thus, it is supposed that similar reduction  
287 and volatilization of Sn species happen in the annealing process, which follows the results  
288 of XPS and EDS. With an increase of annealing temperature, Sn<sup>4+</sup> species react with  
289 reductive substance like C and CO produced during annealing process ([Ma et al., 2011](#))  
290 and transform into lower valence species such as Sn<sup>0</sup> and Sn<sup>2+</sup>. Lower valence Sn species

291 are further volatilized and cause decreases of surface Sn content. Similar reduction reaction  
292 between tin oxide and carbon-based support in the annealing process were found in the  
293 catalyst preparation for glucose isomerization reaction (Yang et al., 2020, 2019) and  
294 conversion of cellulose into acetol (Liu et al., 2019). According to the mechanism of xylose  
295 conversion into furfural mentioned in section 1, the amount of acid sites plays a dominant  
296 role in influencing the conversion of xylose to furfural. The variation of Sn content and  
297 valence further change the acid sites of catalysts and finally influence catalytic  
298 performance of them.

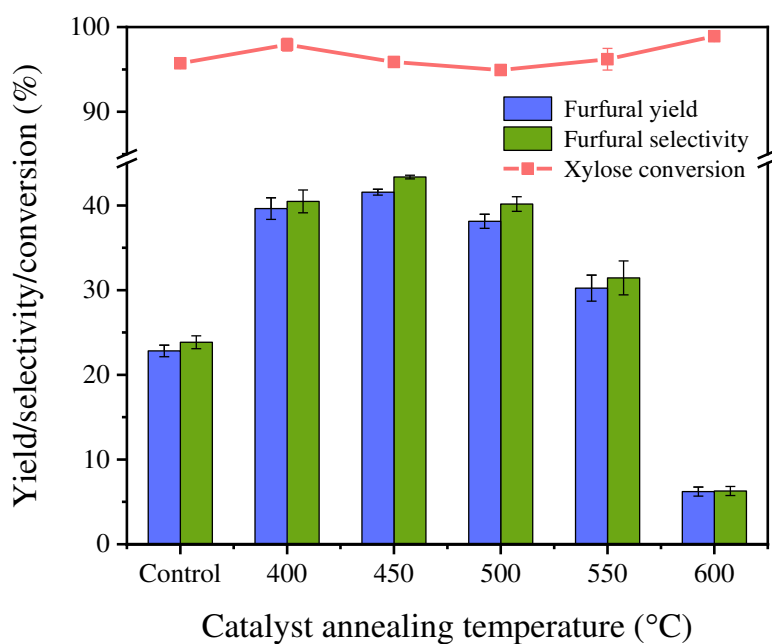
299 It is worth noting that similar reduction reactions can occur in the preparation of other  
300 carbon-supported metallic oxide catalyst. The changes of metal valence and volatilization  
301 of low boiling point metal compounds should be considered when performing catalytic  
302 reactions.

303

### 304 *3.3. Effect of MC-SnO<sub>x</sub> catalyst annealing temperature on catalytic conversion*

305 The catalytic effect on furfural production from xylose of MC-SnO<sub>x</sub> annealed at different  
306 temperatures was evaluated in the batch reactor at 170 °C with a reaction time of 30 min  
307 and summarized in Fig. 6. The addition of MC-SnO<sub>x</sub> catalysts annealed at 400 to 550 °C  
308 showed acceptable catalytic effect. When adding 0.15 g MC-SnO<sub>x</sub>-400 in the reaction, the  
309 highest furfural yield of 41.6% was reached, which corresponded to an increase of 18.8%

310 compared with the control group. MC-SnO<sub>x</sub>-400 and MC-SnO<sub>x</sub>-500 gave furfural yields of  
311 39.6% and 38.1% respectively. While annealing temperature was further increased above  
312 450 °C, the furfural yield went down. In the reaction with 0.15 g MC-SnO<sub>x</sub>-600, the furfural  
313 yield was only 6.2% and inferior to that of the control group, indicating its negative effect  
314 in the reaction. In these six reaction groups, xylose conversions were always higher than  
315 94.9%, which made furfural selectivity have similar trend with furfural yield. Formation  
316 of humins or other intermediates causes that the xylose cannot converted completely into  
317 furfural (Qing et al., 2017; Sweygers et al., 2020).



318 **Fig. 6.** Influence of annealing temperature (400 to 600 °C) of MC-SnO<sub>x</sub> catalyst on  
319 catalytic conversion. Batches were conducted at 170 °C for 30 min with 0.15 g MC-SnO<sub>x</sub>

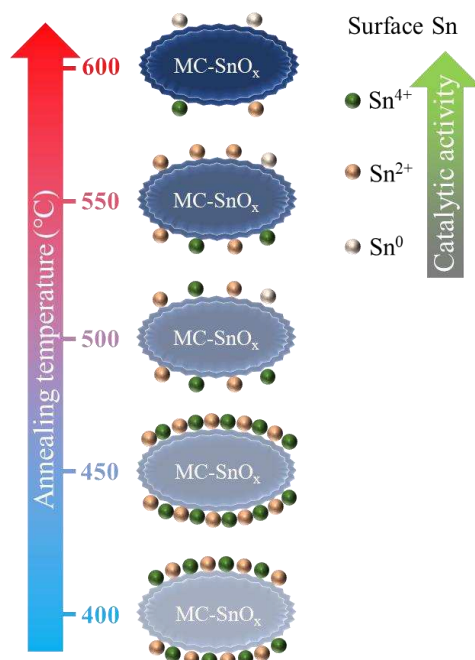
320 catalyst (Control group contained no MC-SnO<sub>x</sub> catalyst.) in 1:1 (v/v) 20 g/L xylose  
321 aqueous phase/2-MTHF phase.

322

323 As the results showed in [Fig. 5](#) and [Fig. 6](#), trends of acid site concentration characterized  
324 by NH<sub>3</sub>-TPD and catalytic effect represented by furfural yield are very similar. Thus, the  
325 catalytic effect difference can be ascribed to the different intensity of acid site  
326 concentration. MC-SnO<sub>x</sub> catalysts with higher acid site concentration have better catalytic  
327 capability in the conversion of xylose to furfural, consistent with previous reports  
328 ([Chatterjee et al., 2019](#); [Lin et al., 2017](#)). Combining with the results of EDS Sn element  
329 content and XPS Sn distribution, it was indicated that MC-SnO<sub>x</sub>-400 and MC-SnO<sub>x</sub>-450  
330 had similar Sn species distribution, but extra surface Sn content can lead to a higher acid  
331 concentration and catalytic effect for MC-SnO<sub>x</sub>-450. MC-SnO<sub>x</sub>-500 and MC-SnO<sub>x</sub>-550  
332 showed little difference in surface Sn content. However, MC-SnO<sub>x</sub>-500 had both more Sn<sup>4+</sup>  
333 species and better catalytic effects, which demonstrate the higher catalytic activity of Sn<sup>4+</sup>.  
334 Further increasing annealing temperature induced the greatest amount of Sn<sup>0</sup> species and  
335 the lowest catalytic effect of MC-SnO<sub>x</sub>-600. These results probably indicate a catalytic  
336 activity order of Sn<sup>4+</sup> > Sn<sup>2+</sup> > Sn<sup>0</sup> in the reaction of xylose to furfural. To conclude, the  
337 difference in both Sn content and Sn species distribution influences the acid site abundance



338 and finally causes the variation of catalytic effect. Fig. 7 shows the probable Sn  
339 transformation in MC-SnO<sub>x</sub> catalysts.



340 **Fig. 7.** Transformation schematic diagram of MC-SnO<sub>x</sub> catalysts.

341

342 Morphology and microstructure changes further explain the catalytic effect variation.

343 XRD results (see Fig. 4) prove the formation of metallic Sn in MC-SnO<sub>x</sub> annealed higher

344 than 500 °C. At the same time, crystallite dimension of both SnO<sub>2</sub> and Sn grew larger with

345 the increase of annealing temperature (see Table S1). The growth of crystallite dimension

346 means that the distribution of Sn species becomes concentrated, which can diminish the

347 effective contact area of the catalysts.

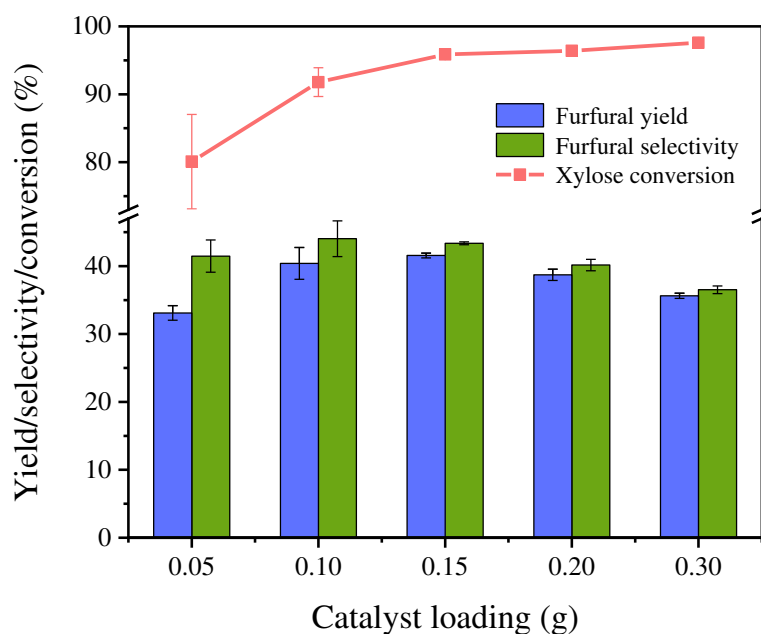
348

349

350 *3.4. Effect of MC-SnO<sub>x</sub> catalyst loading on catalytic conversion*

351 To analyze the impact of catalyst loading on the reaction of xylose to furfural, different  
352 catalyst amounts (0.05 g, 0.1 g, 0.15 g, 0.2 g and 0.3 g) of MC-SnO<sub>x</sub>-450 catalyst were  
353 selected for reactions at 170 °C for 30 min. Fig. 8 showed that catalyst loading influenced  
354 the furfural yield, selectivity and xylose conversion. When adding 0.15 g of MC-SnO<sub>x</sub>-450  
355 catalyst, the reaction reached a highest furfural yield of 41.6% at a catalyst loading of 0.15  
356 g. However, a further increase of catalyst loading above 0.15 g did not lead to a higher  
357 furfural yield. At the same time, the xylose conversion was improved gradually with  
358 increasing catalyst loading. Trends were recognized in furfural selectivity, whereby  
359 batches with more than 0.1 g catalyst were observed to increase xylose conversion.  
360 However, furfural yields were in growth in low catalyst loading and decreased in higher  
361 catalyst loading.

362 Excess catalyst loading may cause more side reactions, hence a decreased furfural yield  
363 and an increased xylose conversion simultaneously. Humins by-products may formed by  
364 the reaction between furfural and other intermediates in the presence of excess catalyst  
365 (Sweygers et al., 2020; Zhang et al., 2017). As seen in Fig. 8, the furfural yield using 0.15  
366 g catalyst loading was only slightly higher than that using 0.1 g catalyst. Thus, a catalyst  
367 loading of 0.1 g was chosen in the following sections.



368 **Fig. 8.** Influence of MC-SnO<sub>x</sub>-450 catalyst loading on catalytic conversion. Batches were  
369 conducted at 170 °C for 30 min with 0.05-0.3 g MC-SnO<sub>x</sub>-450 catalyst in 1:1 (v/v) 20  
370 g/L xylose aqueous phase/2-MTHF phase.

371

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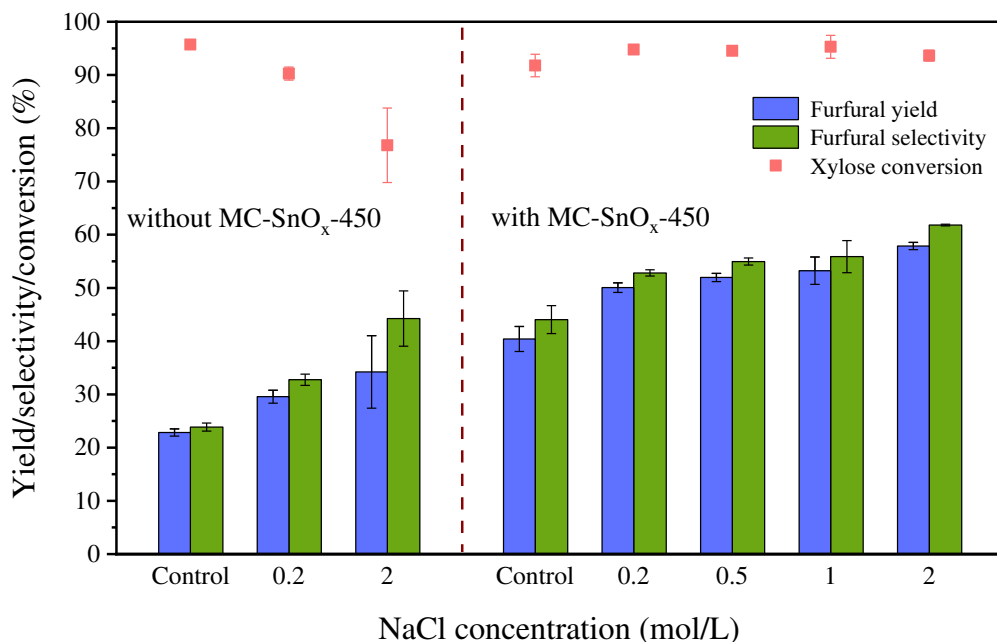
### 373 3.5. Synergistic effect of MC-SnO<sub>x</sub> and NaCl catalyst

374 To study the catalytic effect of the MC-SnO<sub>x</sub> catalyst in the presence of NaCl, amount  
375 of 0.2 mol/L, 0.5 mol/L, 1 mol/L and 2 mol/L NaCl were added into the aqueous solution,  
376 and the reactions were conducted at 170 °C for 30 min with or without 0.1 g MC-SnO<sub>x</sub>-  
377 450 catalyst in each batch. The highest furfural yield of 57.9% was achieved when adding  
378 2 mol/L NaCl and 0.1 g MC-SnO<sub>x</sub>-450 catalyst in the reaction (Fig. 9). For batches adding  
379 both MC-SnO<sub>x</sub>-450 catalyst and NaCl, furfural yield and furfural selectivity rose gradually  
380 with the increase of NaCl from 0 to 2 mol/L, which is in accordance with literature results  
381 (Delbecq et al., 2018; Le Guenic et al., 2016).

382 Another two groups of experiments were done without addition of the MC-SnO<sub>x</sub>-450  
383 catalyst. Adding more NaCl can improve the furfural selectivity as shown in Fig. 9. While  
384 comparing two groups of data of adding 0.2 mol/L NaCl with MC-SnO<sub>x</sub>-450 catalyst and  
385 without MC-SnO<sub>x</sub>-450 catalyst and adding 2 mol/L NaCl with MC-SnO<sub>x</sub>-450 catalyst and  
386 without MC-SnO<sub>x</sub>-450 catalyst, it can be found that 0.1g MC-SnO<sub>x</sub>-450 catalyst  
387 contributed to the furfural yield by 20.4% and 23.7%, respectively. These results were a  
388 little higher than those batches only with 0.1 g MC-SnO<sub>x</sub>-450 catalyst (furfural yield  
389 contribution of 17.6% showed in Fig. 8), which can be ascribed to the improvement of  
390 salting out effect (Román-Leshkov et al., 2007; Sweygers et al., 2021). It proved that MC-

391 SnO<sub>x</sub> catalyst and NaCl have a synergistic catalytic effect in conversion from xylose to  
392 furfural.

393 However, contribution of furfural yield by adding more NaCl from 0.2 mol/L to 2 mol/L  
394 was only 7.7% and 0.2 mol/L NaCl itself improved furfural yield by 9.7%, which means  
395 that it is not economical to multiple NaCl concentration by 10 times. These results prove  
396 low concentration of NaCl to be effective and economical in conversion of xylose into  
397 furfural. In addition, the intense concentration of chlorine salt can cause severe corrosion  
398 of reactors and refractory wastewater pollution containing high concentration of salt. To  
399 balance the furfural yield and other factors, a NaCl concentration of 0.2 mol/L was selected  
400 to complete next part's experiments. At the same time, since seawater contains about 0.5  
401 mol/L NaCl, these results indicate the potential of applying seawater ([Mao et al., 2013](#)) or  
402 wastewater containing NaCl as a low cost reaction solvent and NaCl catalyst source in  
403 conversion of xylose to furfural.



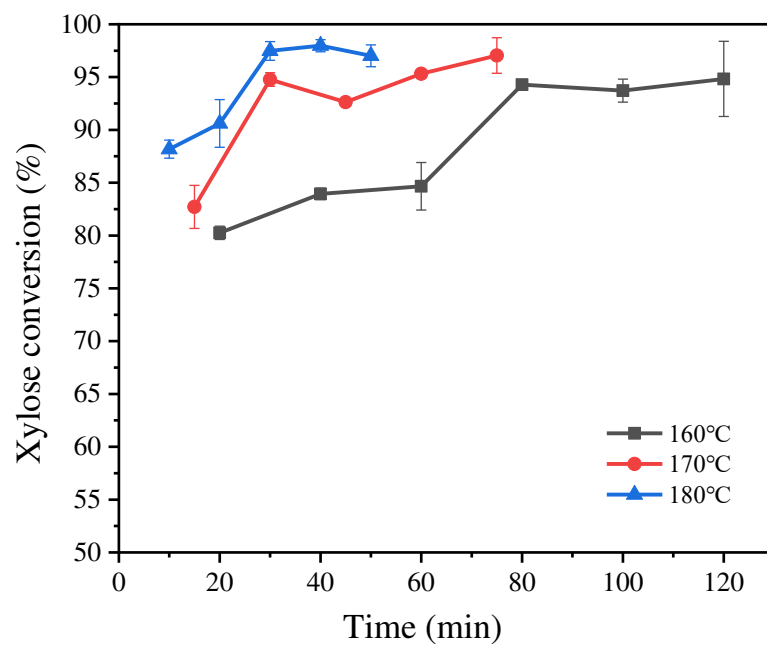
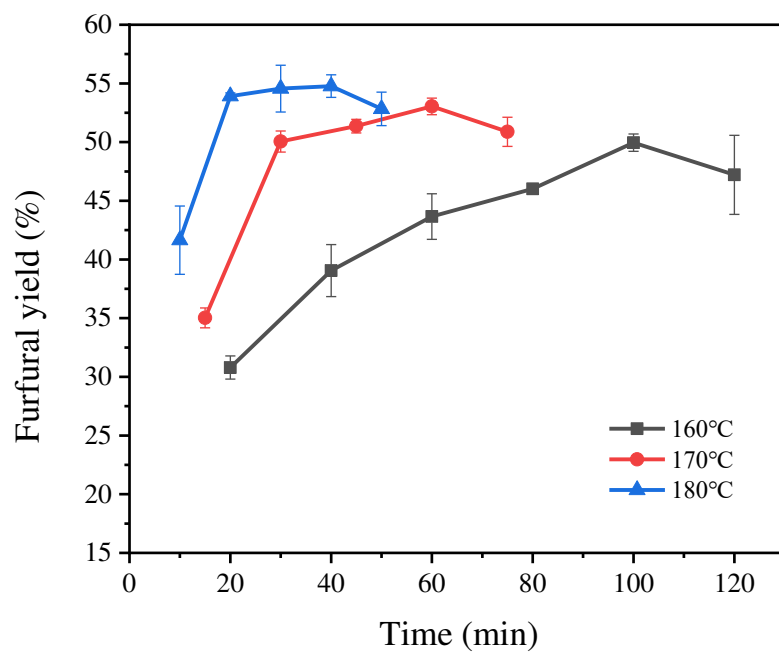
404 **Fig. 9.** Catalytic effect of NaCl in the system and synergistic effect between MC-SnO<sub>x</sub> and  
 405 NaCl. 0 mol/L (control groups), 0.2 mol/L, 0.5 mol/L, 1 mol/L and 2 mol/L NaCl were  
 406 added into 1:1 (v/v) 20 g/L xylose aqueous phase/2-MTHF phase and reacted at 170 °C for  
 407 30 min. Groups in right half contained 0.1 g MC-SnO<sub>x</sub>-450 catalysts.

408

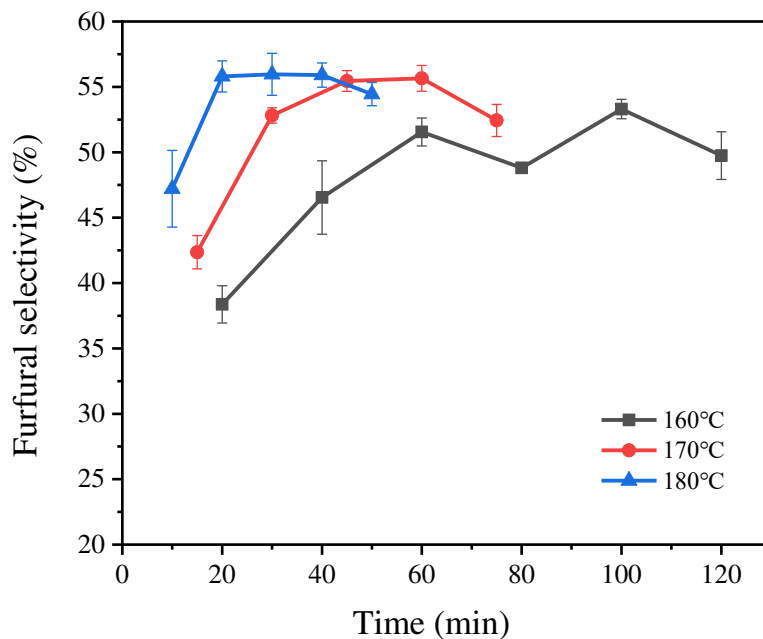
### 409 3.6. Effect of reaction temperature and time on catalytic conversion

410 In Fig. 10, the influence of reaction temperature and time was investigated (160–180 °C  
 411 and 10–120 min). Each batch contains 0.2 mol/L NaCl in aqueous phase and 0.1 g MC-  
 412 SnO<sub>x</sub>-450 catalyst. The highest furfural yield of 54.8% was reached at 180 °C for 40 min.  
 413 However, the batches at 180 °C for 20 and 30 min had a very close furfural yield at 53.9%  
 414 and 54.6%, which suggested that the reaction at 180 °C for 20 min is suitable for furfural

415 production. For all reaction temperature, furfural yield reached peak at certain reaction time  
416 (40 min for 180 °C, 60 min for 170 °C and 100 min for 160 °C). As shown in [Fig. 10](#), low  
417 reaction temperature reaction needs more time to reach the highest furfural yield. At the  
418 same time, the highest furfural yields were 50.0%, 53.0% and 54.8% for reaction at 160 °C,  
419 170 °C and 180 °C, which proves reaction at 180 °C can achieve better furfural yield than  
420 that at 160 °C and 170 °C in a shorter time. Higher temperature of 180 °C can accelerate  
421 the reaction greatly comparing to the lower temperature of 170 °C and 160 °C, which save  
422 time and possibly energy for reaction batches. A similar pattern was found for xylose  
423 conversion. With the increase of reaction temperature, the furfural yields first increased  
424 then decreased after reacting for more than 40 min at 180 °C, as excess reaction time can  
425 cause furfural degradation and limits furfural yield. Similar phenomena were observed for  
426 batches at 160 °C and 170 °C.







428 **Fig. 10.** Influence of reaction temperature and time on catalytic conversion. Batches were  
 429 conducted at 160–180 °C for 10–120 min with 0.1 g MC-SnO<sub>x</sub>-450 catalyst in 1:1 (v/v) 20  
 430 g/L xylose and 0.2 mol/L NaCl aqueous phase/2-MTHF phase.

431

### 432 3.7. Reusability of MC-SnO<sub>x</sub> catalyst in the system

433 The reusability is critical to catalyst's application in the industrial production process.

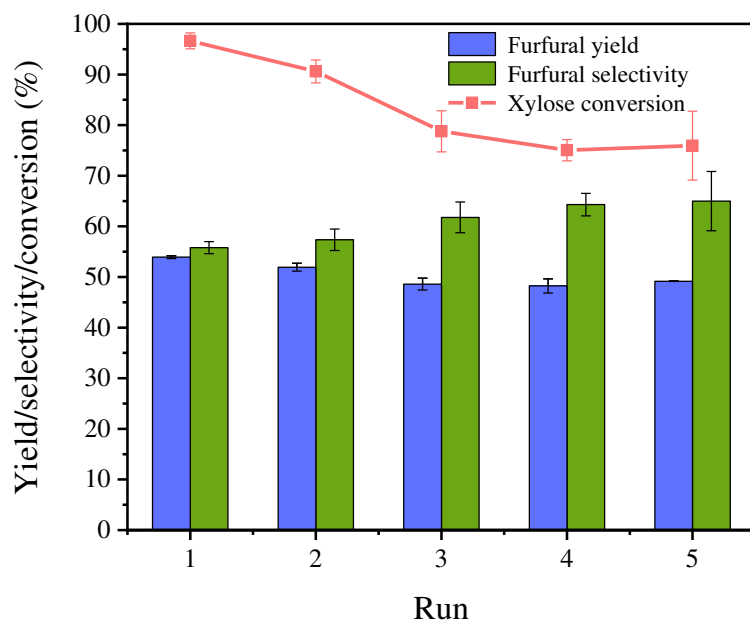
434 Fig. 11 showed results of MC-SnO<sub>x</sub> catalyst's reusability in 5 times' recycle. The MC-

435 SnO<sub>x</sub>-450 catalyst was separated and washed by pure water and ethanol for several times

436 to remove residues after each batch. The results demonstrate that MC-SnO<sub>x</sub>-450 catalyst

437 has a good reusability. The furfural yield went down from first run's 53.9% to third run's

438 48.6%, which caused only 9.8% total catalytic performance decrease (calculated by  
439 furfural production). After 3 times' run, furfural yield maintained stable and kept higher  
440 than 48.2%, which proves that MC-SnO<sub>x</sub> catalyst can maintain a stable catalytic  
441 performance in the following run. Xylose conversion rate also first decreased from first run  
442 to third run and then kept stable. Comparing with other catalysts such as sulfonated carbon  
443 based catalysts ([Deng et al., 2016](#)), SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> MMT ([Qing et al., 2017](#)), Sn-MMT ([Li et](#)  
444 [al., 2015](#)) and SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CFA ([Gong et al., 2019](#)), MC-SnO<sub>x</sub> catalyst showed prior  
445 reusability without regeneration. The trend that catalytic performance decreased slightly  
446 from first run to third run and maintained stable in the following run indicates promising  
447 application potential of MC-SnO<sub>x</sub> catalyst.



448 **Fig. 11.** Reusability of MC-SnO<sub>x</sub>-450 catalyst for conversion xylose into furfural. Batches  
 449 were conducted at 180 °C for 20 min with 0.1 g MC-SnO<sub>x</sub>-450 catalyst in 1:1 (v/v) 20 g/L  
 450 xylose and 0.2 mol/L NaCl aqueous phase/2-MTHF phase.

451

#### 452 **4. Conclusions**

453 We produced a novel MC-SnO<sub>x</sub> catalyst without acid treatment process to convert xylose  
 454 into furfural. In the preparation process, annealing temperature impacted most on catalytic  
 455 performance because higher temperature can cause decrease of surface Sn content and  
 456 promote reduction reaction, volatilization and aggregation of Sn species, which finally  
 457 influenced acid site concentration of catalysts and limited furfural yield. The best annealing  
 458 temperature was 450 °C. A reasonable furfural yield of 53.9% was achieved using the

459 conditions of 0.1g MC-SnO<sub>x</sub>-450 in 20 g/L xylose aqueous phase with 0.2 mol/L NaCl in  
460 the reaction at 180 °C for 20 min representing a balance between catalytic performance,  
461 cost, equipment safety and environmental concerns. The synergistic catalytic effect was  
462 found between MC-SnO<sub>x</sub> and NaCl and effectivity of low concentration of NaCl indicate  
463 the potential of applying seawater or wastewater containing NaCl as a low-cost reaction  
464 solvent and NaCl catalyst source in conversion of xylose to furfural. In addition, MC-SnO<sub>x</sub>  
465 catalyst displayed a good reusability. These results guide the further development of  
466 carbon-supported tin oxide catalysts in furfural production.

467

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473

#### 474 **Appendix A. Supplementary data**

475 E-supplementary data of this work can be found in online version of the paper.

476

477

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