Supplementary Material

For

Off-line catalytic behavior in the preparation of FDCA from biomass and CO_2

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1. Experimental part

Manganese sulfate monohydrate ($MnSO_4·H_2O$), potassium permanganate ($KMnO_4$), cesium carbonate (Cs_2CO_3), iron(III) hydroxide, furfural, and furoic acid were purchased from MACKLIN and employed in catalyst synthesis.

1.1.1 Preparation of δ-MnO_2

δ-MnO_2 was synthesized hydrothermally by adding $KMnO_4$ (0.024 mol) and $MnSO_4.H_2O$ (0.004 mol) to deionized water (140 mL) under stirring for 30 min. The homogeneous solution was transferred to a 200 mL polytetrafluoroethylene-lined autoclave and maintained at 160 °C for 12 h. After cooling to room temperature, the precipitate was collected by filtration, washed thoroughly with deionized water, and dried at 80 °C for 12 h. The resulting material was designated as δ-MnO_2.

1.1.2 Preparation of FeFDCA

2 mmol of FDCA was mixed with 0.67 mmol of $Fe(OH)_3$, followed by the addition of 2 mL of deionized water. The mixture was magnetically stirred for 30 min. The completion of the acid-base reaction was determined by monitoring the pH value of the solution. Once the pH value stabilized at approximately 6, the resulting mixture was transferred to an oven and dried at 120 °C for 2 h to completely remove the residual water. The resulting powder was identified as FeFDCA.

1.2 Evaluation of the catalyst

1.2.1 Furfural oxidation to furfuryl acid

Catalyst evaluation was performed in a 100 mL batch autoclave reactor. In a standard procedure, furfural (50 mg), deionized water (10 mL), and catalyst (200 mg) were charged into the reactor. The system was purged with pure O_2 (5×) and pressurized to 1 MPa with O_2. Reactions were conducted at 100 °C for 1 h with continuous stirring (500 rpm). Parametric studies examining variable effects are detailed in subsequent sections. Following reaction completion, the reactor was rapidly cooled to ambient temperature. The product mixture was filtered through a 22 μm PTFE membrane syringe filter, diluted appropriately, and analyzed by high-performance liquid chromatography (HPLC) under these conditions: the column was a C_{18} column from Waters, the flow ratio was acetonitrile:water=1:1, the flow rate was 1 ml/min, the detection wavelength was 220 nm, and the column temperature was constant at 30 ° C. The reaction was carried out at a constant temperature of 30 ° C. The reaction was carried out at a constant temperature of 30 °C. The carbon equilibrium of the reaction was calculated by using the configured standard solution.

The formulae for furfural conversion, furfuryl acid selectivity, reaction rate and carbon balance of the furfural oxidation-to-acid reaction in this study were as follows:

$$\text{Conver.FF} = \frac{n_{\text{FF in}} - n_{\text{FFout}}(\text{by HPLC})}{n_{\text{FF in}}} \times 100\%$$

$$\text{Select.FA} = \frac{n_{\text{FA}}(\text{by HPLC})}{n_{\text{product}}(\text{by HPLC})} \times 100\%$$

$$\text{Reaction rate} = \frac{n_{\text{FF in}} \times \text{Conver.FF} \times \text{Select.FA}}{m_{\text{cat.}} \times t} \times 100\%$$

$$\text{Carbon balance} = \frac{n_{\text{FF out}} \times n_{\text{FA out}}}{n_{\text{FF in}}} \times 100\%$$

where Conver.$_{FF}$ denotes furfural conversion, Select.$_{FA}$ denotes furfuryl acid selectivity; n_{FF} in denotes the feed molar amount of furfural, n_{FF} out denotes the molar amount of furfural in the product detected by HPLC; n_{FA} denotes the molar amount of furfuryl acid in the product detected by HPLC, nproduct denotes the total molar amount of the product detected by HPLC; mcat. denotes the total mass of catalyst and t denotes the reaction time.

1.2.2 Evaluation of direct carboxylation performance of furoic acid/furoate with CO_2

A mixture of furoic acid (2 mmol) and hydroxide (1 mmol) in deionized water (2 mL) was magnetically stirred for 5 min. Cesium carbonate (Cs_2CO_3, 1.2 mmol) was subsequently added, followed by magnetic stirring for 15 min. The resulting mixture was dehydrated at 150°C for 2 h.The dried powder was transferred to a 100 mL batch reactor with magnetic stirring. The system was purged with CO_2 (5×), pressurized to 2 MPa, and heated to 230°C. The reaction proceeded for 12 h at 300 rpm.

Control experiment: Furoic acid was directly mixed with Cs_2CO_3 in deionized water (2 mL), stirred for 20 min, dried, and reacted under identical conditions.

The above reaction products were analyzed in the following two ways:

High Performance Liquid Chromatography (HPLC): the above obtained solid was dissolved in the mobile phase and filtered using a 0.2 μm PTFE filter membrane and then the above filtrate was analyzed by HPLC. The chromatographic detection conditions were as follows: the chromatographic column was a Waters C_{18} column, the mobile phase ratio was acetonitrile: water = 1:9, the flow rate was 1 ml/min, the detection wavelength was 254 nm, and the column temperature was constant at 40 °C. The chromatographic detection conditions were as follows.

The conversion of furoic acid in this study, the FDCA selectivity was calculated as follows:

$$\text{Conver.FA} = \frac{n_{\text{product}}(\text{by HPLC})}{n_{\text{product}}(\text{by HPLC}) + n_{\text{FA out}}(\text{by HPLC})} \times 100\%$$

$$\text{Select.FDCA} = \frac{n_{\text{FDCA}}(\text{by HPLC})}{n_{\text{product}}(\text{by HPLC})} \times 100\%$$

Where Conver.$_{\text{FA}}$ denotes the conversion of furoic acid, Select.$_{\text{FDCA}}$ denotes the selectivity of FDCA, nproduct (HPLC) denotes the total molar amount of the product detected by HPLC, n_{FA} out denotes the molar amount of unreacted furfural detected by HPLC, and n_{FDCA} denotes the molar amount of furandicarboxylic acid in the product detected by HPLC.

1.3 Catalyst characterization

XRD: The crystalline phase and growth direction of the samples were characterized using an X-ray diffraction (XRD) analyzer (PANalytical X'pert3) with Cu target, Kα(λ = 1.54056 Å), 40 kV tube voltage and 40 mA tube current as the parameters tested.

SEM: Scanning electron microscope (JSM-7001F) was utilized to observe the morphology of the samples.

Furfural-IR: Furfural-IR experiments were performed on a Nicolet iS10 infrared spectrometer. The catalyst was first purged under argon atmosphere at 80°C for 30 min and sample spectra were collected. The furfural was then bubbled with argon gas into the in situ cell until the catalyst was saturated with adsorption. After the catalyst is saturated with adsorption, argon gas is switched to remove the physically adsorbed furfural for 30 min, and finally oxygen or argon is switched to start the oxidation reaction for 30 min.

FA-DRIFTS: The in situ infrared experiments of furoate were carried out on a Nicolet iS10 infrared spectrometer with the following procedure: a mixture of appropriate amount of furoate and carbonate (mixing ratio of furoate: carbonate = 1:1.2, mixed and fully ground) was placed in a reaction cell, and the temperature was raised from room temperature to 120 °C at a rate of 10 °C/min in an Ar gas atmosphere, and held for 60 The water was removed in 60 min. The temperature was then raised from 120 °C to 230 °C, and the gas was switched from nitrogen to CO_2 to allow the carboxylation reaction to occur, and the time-dependent infrared spectral changes were recorded over a period of 30 min.

In order to clarify the reaction mechanism of carboxylation, the in situ IR of furfurylates was carried out in Ar gas atmosphere, and the specific experimental procedure was as follows. A mixture of appropriate amount of furoate and carbonate (mixing ratio of furoate: carbonate = 1:1.2, mixed and ground thoroughly) was placed in a reaction cell, and the temperature was increased from room temperature to 120 °C at a rate of 10 °C/min in Ar gas atmosphere, and kept for 60 min to remove water. The temperature was then raised from 120 °C to 230 °C in an Ar gas atmosphere to allow carboxylation to take place, and the time-dependent changes in the IR spectra were recorded over a period of 30 min.

2. The characterization results.

Fig. s1. SEM image of δ-MnO_2.

Fig. s2. XRD pattern of δ-MnO_2.

Fig. s3. Carboxylation properties of ferric furoate in different atmospheres.

Fig. s4. In situ ^{1}H NMR spectra of furoic acid (left) and iron furoate (right) dissolved in CD_3CN after the addition of D_2O.

Fig. s5. (a) O_2-TPD profiles of δ-MnO_2, (b) Water signaling in the O_2-TPD process.

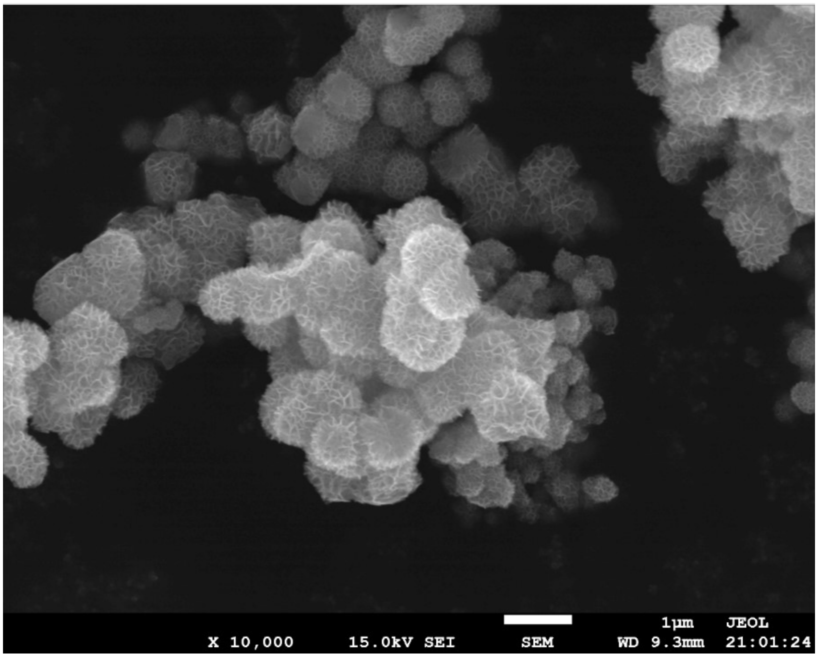

Fig. s1. SEM image of δ-MnO_2.

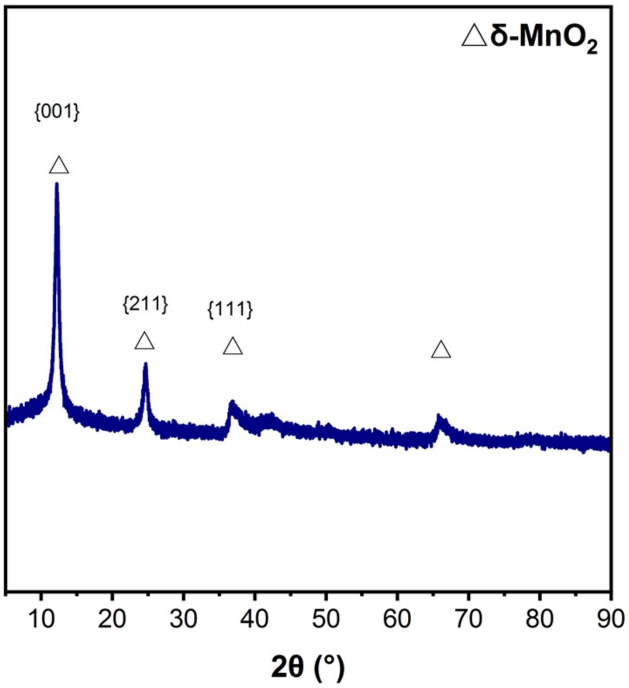

Fig. s2. XRD pattern of δ-MnO$_2$.

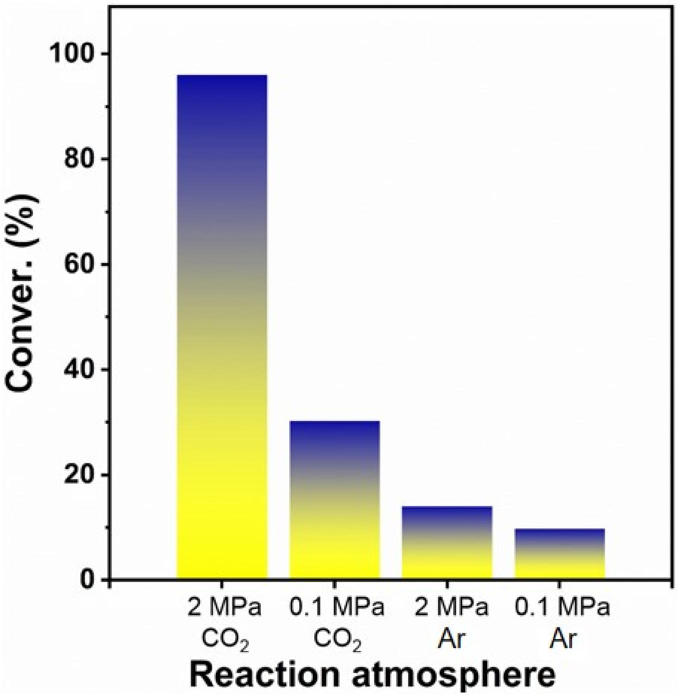

Fig. s3. Carboxylation properties of ferric furoate in different atmospheres.

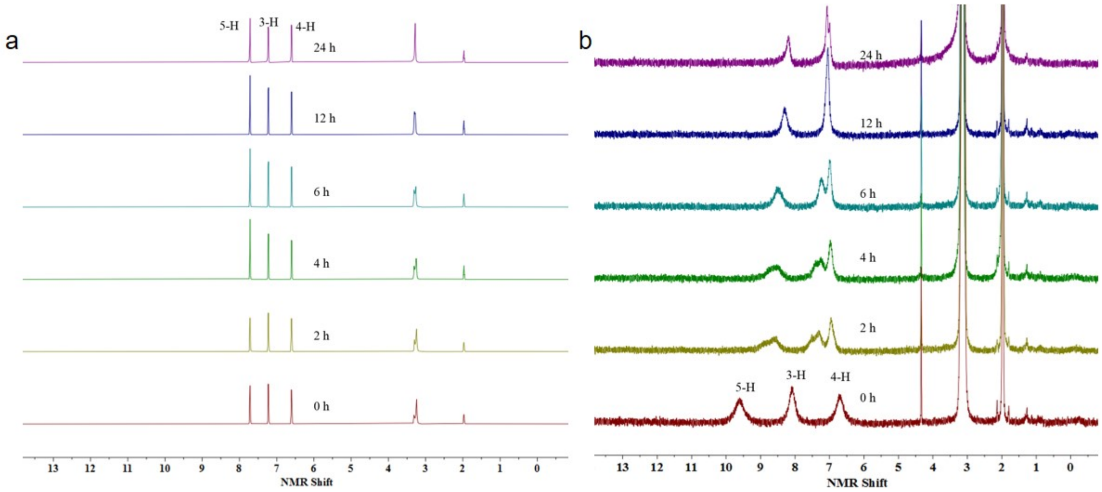

Fig. s4. In situ ^{1}H NMR spectra of furoic acid (left) and iron furoate (right) dissolved in CD_3CN after the addition of D_2O.

In-situ liquid-state NMR spectroscopy unambiguously demonstrates that the introduction of Fe facilitates the deprotonation of the 5-H on the furan ring, thereby promoting the insertion of CO_2 and consequently favoring the formation of 2,5-furandicarboxylic acid (FDCA).

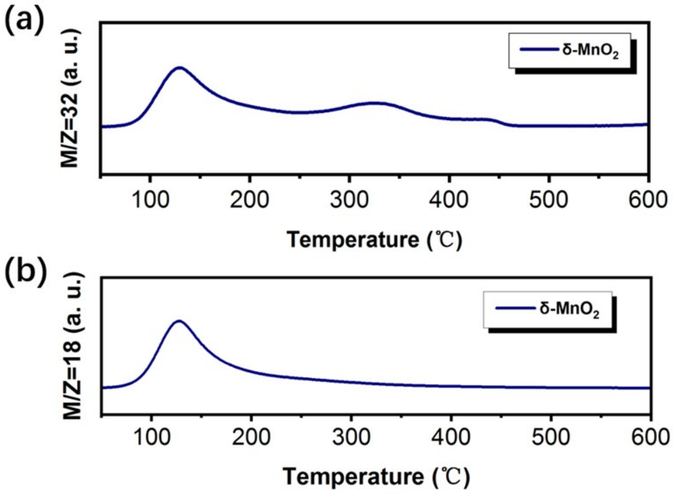

Fig. s5. (a) O_2-TPD profiles of δ-MnO_2, (b) Water signaling in the O_2-TPD process.