

Supporting Information for

Accelerating Oxidation of 5-Hydroxymethylfurfural into

2,5-Furandicarboxylic Acid by High Entropy Alloy Catalyst

Design in Base-Free Condition

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1. Preparation of Catalysts

Materials. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sinopharm chemical)、 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sinopharm chemical)、 $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sinopharm chemical)、 $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Sinopharm chemical)、 $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Aladdin)、sodium borohydride (Aladdin)、methanol, ethanol (Tianjin Fuyu Chemical), 5-hydroxymethylfurfural, 2, 5-diformylfuran, 2-formyl-5-furanoic acid (Aladdin), 2,5-furandicarboxylic acid (J&K Scientific). deionized water, (18 M Ω cm)

Preparation of $\text{Fe}_1\text{Co}_{1.5}\text{Ni}_1\text{Cu}_{1.5}\text{Pt}_{1.5}/\text{C}$

In a typical HEA/C synthesis, 22.7 mg $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 32 mg $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 15 mg $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 38 mg $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 22.7 mg $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ were dissolved in 20 mL deionized water and ultrasound for 10 min, the obtained solution was named as A solution. In another flask, 50 mg sodium borohydride and 111 mg poly (vinyl alcohol) (PVP) were dissolved in 20 mL deionized water and stirred for 20 min, the obtained solution was named as B solution.

In HEA/C preparation, B solution was pumped into solution A at a rate of 2 mL/min under vigorous stirring. The mixed solution was further stirred for another 20 min after all B solution was added into A solution. Then 240 mg activate carbon (200 mesh) was added into the mixed solution and stirred for another 4 h. The solid material was separated centrifuged at 10000 r/min for 20 min, followed by washing with water and ethanol for twice, and dried in oven at 60 °C overnight. The obtained powder was grinded and transferred into a ceramic boat and placed it in a tube furnace. The sample was heated to 350 °C with a heating rate of 5 °C/min and kept at 350 °C for 2 h under flowing Ar/H_2 (95:5) gas and then cooled to room temperature naturally. The obtained sample was named as $\text{Fe}_1\text{Co}_{1.5}\text{Ni}_1\text{Cu}_{1.5}\text{Pt}_{1.5}/\text{C}$. The procedure for other elements ratio HEA/C catalyst is similar.

2. Catalytic performance test of catalysts

In a typical experiment, 20 mL H_2O containing 0.1 mol HMF was added into a 100 mL stainless steel autoclave with a Teflon vessel liner. 100 mg as-prepared

HEA/C catalyst was added into the reactor and 0.5 MPa oxygen was introduced into the reactor after the reactor was sealed. The reactant mixture was heated to desired temperature under vigorous stirring (800 rpm) and liquid samples were taken at pre-determined time interval and analyze as following method. In radical quenching experiment, 5 mmol HMF, 20 mL mixed methanol and water, 100 mg of catalyst were added into the reactor and 0.5 MPa oxygen was introduced into the reactor. The reactant mixture was heated at 120 °C for 6 h. In catalyst recycle tests, the catalyst was recovered by filtration and washed with 50 mL acetonitrile and water for three times and dried in oven at 105 °C overnight before next test.

HMF conversion and products yields were determined by high-performance liquid chromatography (HPLC, Aminex HPX-87H column from Bio-Rad Laboratories Co., Ltd., 0.5 mM H₂SO₄ aqueous solution as the eluent, 0.6 mL min⁻¹ flow rate, at 35 °C). The products were identified by comparison with known commercially pure samples. The HMF conversion, products yields were calculated as following equations:

$$\text{HMF conversion (mol. \%)} = \left(1 - \frac{n_{HMF}}{N_{HMF}}\right) \times 100\%$$

$$\text{Products Yield (mol.\%)} = \frac{n_p}{N_{HMF}} \times 100\%$$

Where: the n_{HMF} stands for HMF mole amount residues in reaction mixture;

the n_p stands for detected mole amount of products (it can be HMFCA, DFF, FFCA and FDCA) in reaction mixture;

the N_{HMF} stands for total HMF mole amount input the reactor in the beginning of reaction.

3. Catalyst characterizations

For the prepared catalyst, the powdered samples with grinding enough were used for the structure characterization. X-ray diffractometer (XRD) was produced by Bruker company in Germany, using Cu K α radiation at 40 kV and 40 mA with a scanning speed (2θ) of 20 °/min. X-ray photoelectron spectroscopy (XPS)

measurements were performed by a K-alpha XPS spectrometer using monochromatic Al K α radiation generated from an electron beam operated at 15 kV and 32.3 W. Samples were collected under ultra-high vacuum (at 10⁻⁷ mbar) and room temperature at a pass energy of 50 eV to avoid sample charging. In order to compensate for the charging effect, all binding energies were referenced to the C 1s of 284.8 eV. The peak fitting was carried out by the Advantage (Thermo Scientific) software package. The material morphologies and microstructures were characterized by High resolution field emission transmission electron microscope (TEM) conducting on a JEM-2100F microscope operated at 1000 kV. High-resolution TEM images (HRTEM) and electron energy dispersive spectroscopy (EDS) mapping were taken on the same microscope.

4. Estimated reaction rates for the aerobic oxidation of HMF in each steps

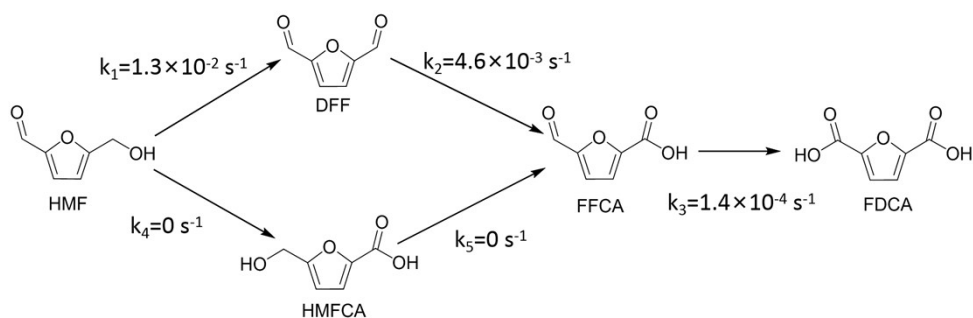


Figure S1. reaction pathway for HMF oxidation to FDCA, and estimated reaction rates for the aerobic oxidation of HMF in each steps

5. Aerobic oxidation of HMF into FDCA at different temperature

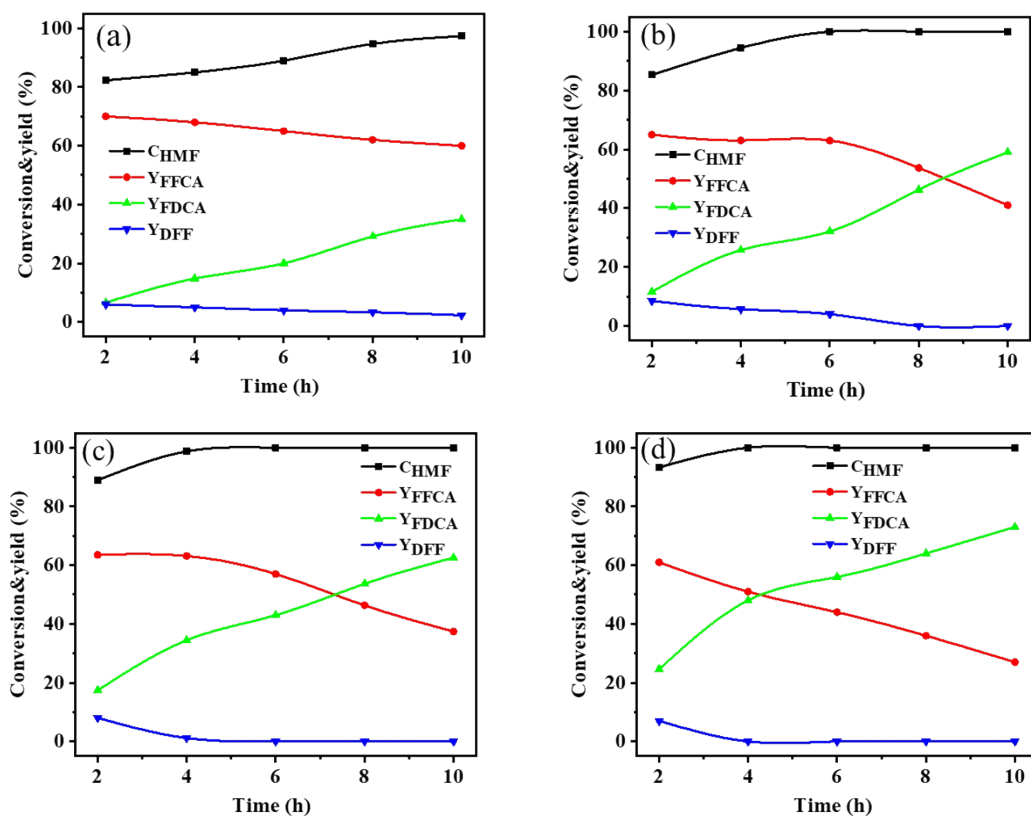


Figure S2. Effect of reaction temperature on aerobic oxidation of HMF into FDCA,

(a) 80 °C; (b) 90 °C; (c) 100 °C; (d) 110 °C; HMF 0.1 mol; H₂O, 20 mL;

Catalyst, 100 mg; O₂ pressure, 0.5 MPa

6. Catalyst recycling tests in aerobic oxidation of HMF into FDCA under base-free condition

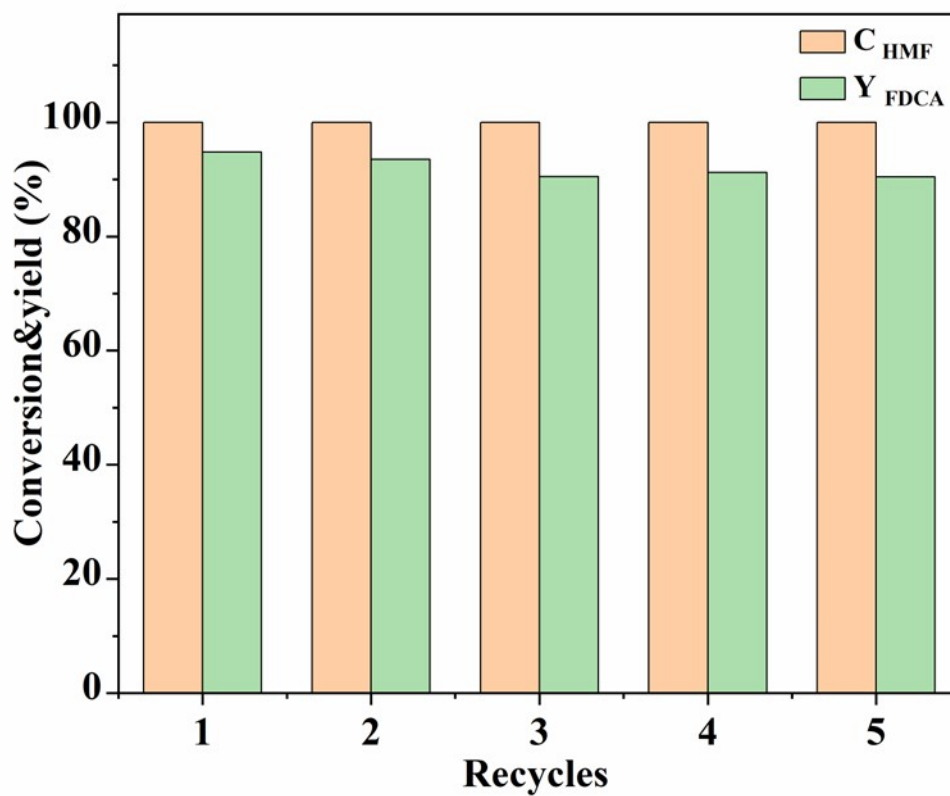


Figure S3. Recycling tests of HEA/C. Reaction conditions: HMF 0.1 mol; H₂O, 20 mL; Catalyst, 100 mg; O₂ pressure, 0.5 MPa; Reaction temperature, 120 °C; Reaction time, 6 h.