Electronic Supplementary Information

for

Fe-Zr-O catalyzed base-free aerobic oxidation of 5-HMF to 2,5-FDCA as a bio-based polyester monomer

Dongxia Yan[a,b,c], Jiayu Xin[b], Qiu Zhao[b], Kai Gao[b,c], Xingmei Lu[b,c], Gongying Wang*[a], and Suojiang Zhang*[b]

[a] *Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, 610041, P. R. China*

[b] *Beijing Key Laboratory of Ionic Liquids Clean Process, Key Laboratory of Green Process Engineering, State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190, P. R. China*

[c] *University of Chinese Academy of Sciences, Beijing 100049, P. R. China*

*Corresponding author: Gongying Wang, Professor, Ph.D., E-mail: gywang@cioc.ac.cn

*Corresponding author: Suojiang Zhang, Professor, Ph.D., E-mail: sjzhang@ipe.ac.cn, Tel./fax: +86-10-82627080

This Supporting Information contains 8 pages, including Table S1-S2, and Figure S1-S7.

The details for the catalyst characterization

The X-ray diffraction (XRD), Raman and X-ray photoelectron spectroscopy (XPS) were performed as reported previously.[1] Hydrogen temperature-programmed reduction (H_2-TPR) was measured using an Autochem II 2920 (Micromeritics, USA). A total of 50 mg of sample was loaded into a quartz reactor and pretreated using Ar flow (20 mL min^{-1}) at 200 °C for 2 h. Then the sample was cooled to 50 °C and subsequently the test was performed under a flow of 10% v/v H_2/Ar (20 mL min^{-1}) from room temperature to 850 °C (10 °C min^{-1}). The acid and base features of the catalysts were determined in an Autochem II 2920 (Micromeritics, USA) equipment by temperature-programmed desorption (TPD) of ammonia and carbon dioxide (NH_3 and CO_2-TPD), respectively. Previously, the samples were pretreated under He flow (20 mL min^{-1}) at 200 °C for 2 h. The samples were cooled to 50 °C and then exposed under a 10% NH_3/He mixture or 10% CO_2/He mixture stream (20 mL min^{-1}) for 1 h. Subsequently, the physically adsorbed NH_3 or CO_2 was removed by flowing He flow at 50 °C for 30min (20 mL min^{-1}). Thereafter, the NH_3-TPD or CO_2-TPD profile of the samples were recorded by increasing the temperature from 50 °C to 850 °C at a heating rate of 10 °C min^{-1} in flowing He (20 mL min^{-1}). A thermal conductivity detector (TCD) was used to continuously record the variation of ammonia and carbon dioxide concentration in the effluent helium stream.

TEM images were obtained with a JEOL 2010 transmission electron microscope operated at 200 kV. Previous to the observation, the samples were deposited on the TEM grids after ultrasonic dispersion in ethanol. SEM images were performed by using a SU800 Field-Emission Scanning Electron icroscope (Hitachi, Japan) operated at an acceleration voltage of 5kV. The metal compositions of the catalysts were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) (ICPE-9000, shimadzu) after digestion in acid (50 mg samples were dissolved with 10 ml of 36-38% HCl and 2ml of 40% HF) at 200 °C and then dilution with ultrapure water. The N_2 adsorption-desorption isotherms at 77 K were measured using a Sorptomatic 1900 apparatus (Carlo-Erba). Prior to measurement, all samples were outgassed at 160 °C under vacuum for 8 h. The specific surface area was calculated using the BET equation.

The details for the humins characterization

FT-IR spectrum of the humins was recorded from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} on a Thermo Nicolet 380 spectrometer by averaging 32 scans. Sample for FT-IR analysis was prepared by mixing the sample powder with KBr and compressing into thin slices. The morphology of the mixtures of catalyst and humins (SEM image) was observed using a SU800 Field-Emission Scanning Electron icroscope (Hitachi, Japan) operated at an acceleration voltage of 5kV. TGA analysis of the solid residue was implemented on a DTG-60H Simultaneous DTA-TG apparatus (Shimadzu, Japan) with 5 mg of sample by increasing the temperature from 30 °C to 800 °C at 10 °C min^{-1} under an air flow rate of 30 ml min^{-1}. GPC was performed on an Agilent PL-GPC 50 System equipped with three columns, which were PLgel 5 μm MIXED-C (300 x 7.5 mm), PLgel 5 μm MIXED-D (300 x 7.5 mm) and PLgel 5 μm Guard (50 x 7.5 mm). Polystyrene samples with different molecular weights were used to obtain a standard calibration curve. In a typical analysis, 4 mg product was dissolved in 2 mL tetrahydrofuran (THF), then filtered using PTFE 0.2 μm filter with a glass injector to avoid contamination from plastic parts, then added to a 1.5 mL autosample vial.

Table S1 The total number of acid sites and acid strength distribution for $Fe_xZr_{1-x}O_2$ samples, derived from NH_3-TPD.

Samples	Number of acid sites (mmol NH_3 g^{-1})			Total number (mmol NH_3 g^{-1})
	Weak acid	Medium acid	Strong acid	
Fe_2O_3	0.03	0.08	0.09	0.20
$Fe_{0.8}Zr_{0.2}O_2$	0.08	0.15	0.11	0.34
$Fe_{0.6}Zr_{0.4}O_2$	0.14	0.24	0.22	0.60
$Fe_{0.4}Zr_{0.6}O_2$	0.12	0.25	0.21	0.58
$Fe_{0.2}Zr_{0.8}O_2$	0.14	0.22	0.23	0.59
ZrO_2	0.13	0.15	0.15	0.43

Table S2 The total number of basic sites and base strength distribution for $Fe_xZr_{1-x}O_2$ samples, derived from CO_2-TPD.

Samples	Number of basic sites (mmol CO_2 g^{-1})			Total number (mmol CO_2 g^{-1})
	Weak base	Medium base	Strong base	
Fe_2O_3	0.07	0.15	0.20	0.42
$Fe_{0.8}Zr_{0.2}O_2$	0.16	0.35	0.40	0.91
$Fe_{0.6}Zr_{0.4}O_2$	0.29	0.81	0.36	1.46
$Fe_{0.4}Zr_{0.6}O_2$	0.25	0.34	0.38	0.97
$Fe_{0.2}Zr_{0.8}O_2$	0.23	0.32	0.41	0.96
ZrO_2	0.22	0.30	0.19	0.71

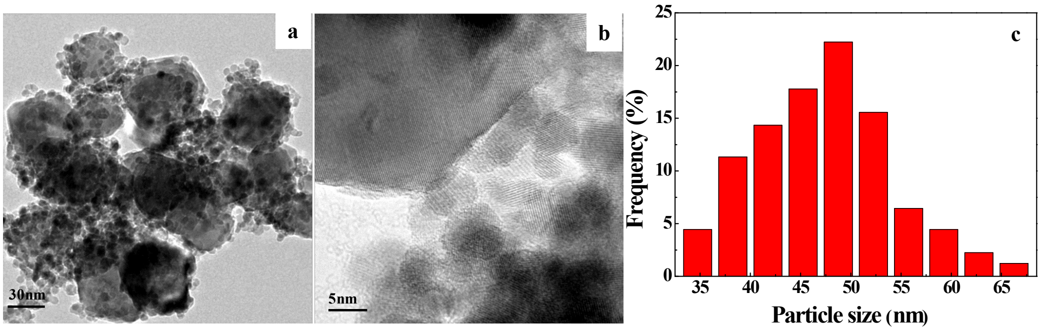

Fig. S1 TEM image and histogram showing the size distribution of $Fe_{0.8}Zr_{0.2}O_2$ samples (large particles).

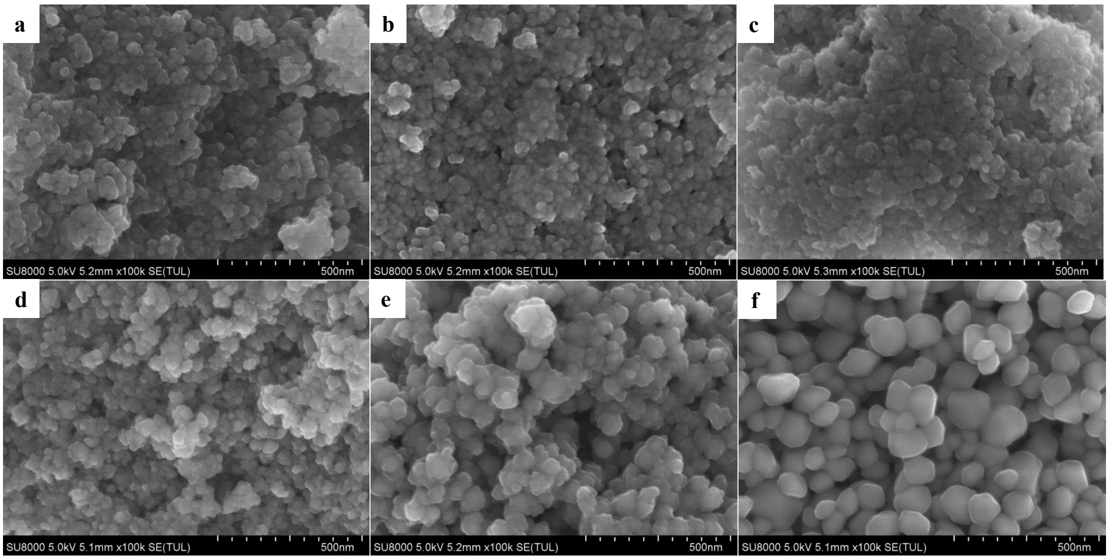

Fig. S2 SEM images of $Fe_xZr_{1-x}O_2$ samples for (a) ZrO_2, (b) $Fe_{0.2}Zr_{0.8}O_2$, (c) $Fe_{0.4}Zr_{0.6}O_2$, (d) $Fe_{0.6}Zr_{0.4}O_2$, (e) $Fe_{0.8}Zr_{0.2}O_2$, and (f) Fe_2O_3.

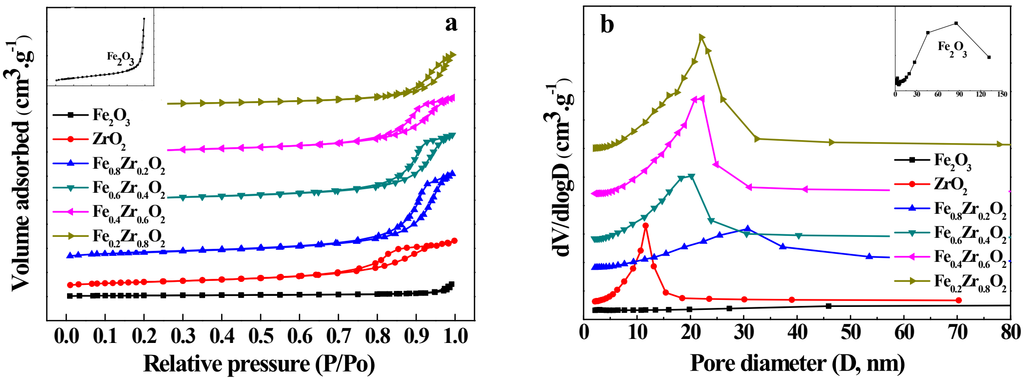

Fig. S3 Nitrogen adsorption-desorption isotherms at 77 K (a) and pore size distribution curves (b) of $Fe_xZr_{1-x}O_2$ samples.

Fig. S4 The insoluble humins formed after the aerobic oxidation of 5-HMF. Reaction conditions: HMF (0.1 mmol), catalyst (0.01 g), [Bmim]Cl (1 g), O_2 (2 MPa), 160 °C, 24 h.

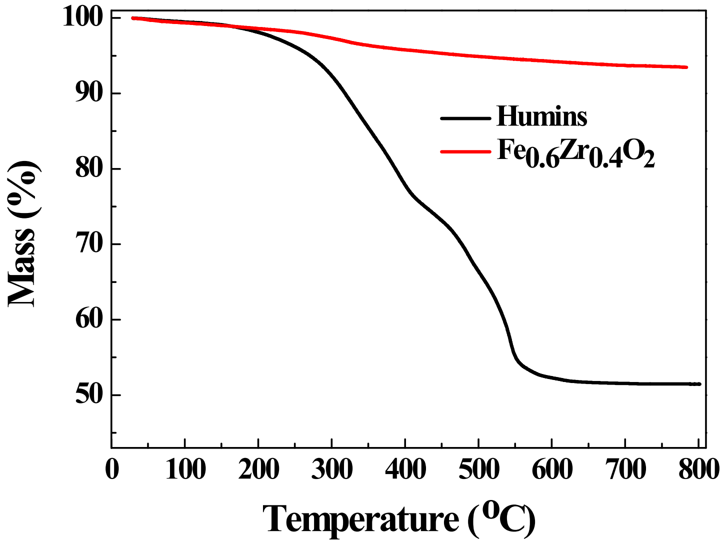

Fig. S5 TG curves of $Fe_{0.6}Zr_{0.4}O_2$ catalyst and solid residues (contained insoluble humins and catalyst) after the aerobic oxidation of 5-HMF. Reaction conditions: HMF (0.1 mmol), catalyst (0.01 g), [Bmim]Cl (1 g), O_2 (2 MPa), 160 °C, 24 h, successive reused for five times.

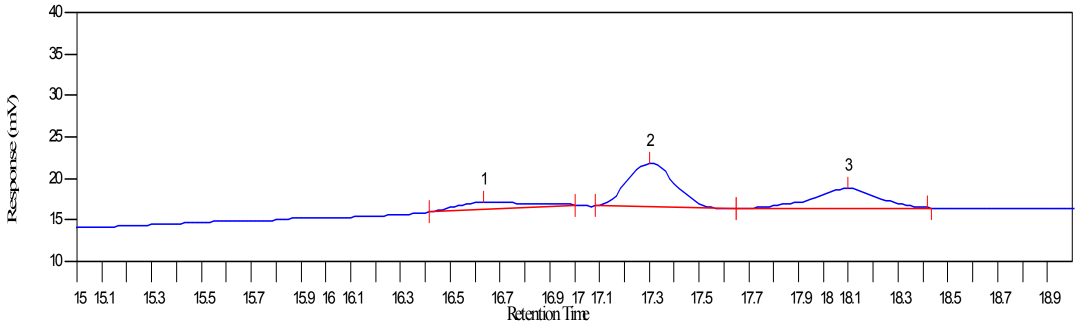

Fig. S6 Average molecular weight distributions of humins after the aerobic oxidation of 5-HMF (Mw determined by GPC relative to polystyrenes standards). Reaction conditions: HMF (0.1 mmol), catalyst (0.01 g), [Bmim]Cl (1 g), O_2 (2 MPa), 160 °C, 24 h.

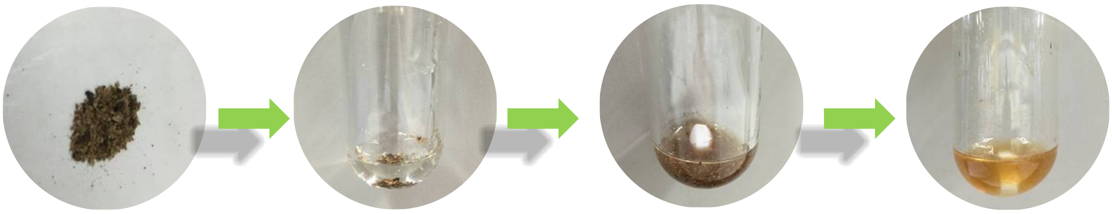

Fig. S7 The dissolution of humins generated after the aerobic oxidation of 5-HMF in [Bmim]Cl ILs. Reaction conditions: HMF (0.1 mmol), catalyst (0.01 g), [Bmim]Cl (1 g), O_2 (2 MPa), 160 °C, 24 h. Dissolution conditions: 160 ℃, 30 min.

Reference

(1) Yan, D. X.; Xin, J. Y.; Shi, C. Y.; Lu, X. M.; Ni, L. L.; Wang, G. Y.; Zhang, S. J. Base-free conversion of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid in ionic liquids. *Chem. Eng. J.* **2017,** *323*, 473-482.