

Electronic Supporting Information

Direct use of the solid waste from oxytetracycline fermentation broth to construct Hf-containing catalysts for Meerwein-Ponndorf-Verley Reactions

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Feedstock

Ethyl levulinate (EL, 98%), γ -valerolactone (GVL, 98%), furfuraldehyde (FD, 99%), furfuryl alcohol (FA, 98%) were provided by J&K Scientific Ltd. Hafnium tetrachloride (HfCl_4 , 98+%) were obtained from Alfa. Isopropanol (iPrOH, 99.9%) was provided by Innochem. N, N-Dimethylformamide (DMF, >99.9%) were provided by Aladdin Industrial Corporation. Decane (AR) and other chemicals were obtained from Beijing Institute of Chemical Reagent. The oxytetracycline fermentation broth residue sample was obtained from Oxytetracycline Refining Workshop in Inner Mongolia Chifeng Pharmaceutical Co., Ltd., China. The fungus residue sample was crushed and ground to fine powder with the average sizes ca. 75-150 μm , followed by drying at 105 $^\circ\text{C}$ in air for 12 h.

Catalyst characterization

Scanning electron microscopy (SEM) measurements were performed using a Hitachi S-3400N scanning electron microscope operated at 20 kV with an energy dispersive spectrometer (EDS) apparatus. Fourier transform-infrared spectra (FTIR) were obtained using a PerkinElmer spectrometer. X-ray diffraction (XRD) was carried out via a Produce-Rigaku SmartLab 9 KW X-ray diffractometer with a Cu target configuration and a highly sensitive D/teX Ultra 250 inspection system at 20° per minute ranging from 5° to 90°. The tube voltage was 45 kW, and the current was 200 mA. The thermogravimetric (TG) analysis of Hf-GO was performed using a thermogravimetric analysis system (Diamond TG/DTA6300, PerkinElmer Instruments) under an N_2 atmosphere at the heating rate of 10 $^\circ\text{C min}^{-1}$. The surface

area

and

pore

diameters and pore volumes were determined via the nitrogen adsorption-desorption method using a NOVA 4200e analyzer (Quantachrome Co. Ltd). The XPS measurements were carried out via an ESCALAB 250Xi spectrometer (Thermo Fisher Scientific) at a pressure of $\sim 3 \times 10^{-9}$ mbar using Al K α as the excitation source ($h\nu=1486.6$ eV) and operating at 15 kV and 150 W, and C 1s orbital (284.8 eV) was used to correct the binding energy. Temperature-programmed desorption of carbon dioxide (CO₂-TPD) and ammonia (NH₃-TPD) were performed on MicrotracBELCAT II. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was conducted using an Agilent 720 system. Elemental analysis (EA) was performed using a Thermo Fisher Flash 2000 system. Analyze the acid type and content of the catalyst sample by using PE company's FT-IR Frontier type pyridine infrared spectrum (py-FTIR).

OFR demineralization methods

50 g of the example was weighed and put into a 1000 mL beaker, and 500 mL of an 18% hydrochloric acid solution was added according to a mass ratio of 1:10 (ROFR sample to hydrochloric acid), and the mixed slurry was mechanically stirred for 12 hours. Then the residue was filtered, and repeatedly washed with distilled water until it was pH neutral and no Cl^- could be detected by AgNO_3 solution. The demineralized OFR(DOFR) was dried at 105 °C in air for 24 h, and then the sample was crushed and ground to a fine powder with the average sizes ca. 75-150 μm .

Industrial analysis methods

Moisture: a certain amount of air-dried OFR sample was placed in a drying oven at 105-110°C, and was dried in an air stream until the quality was constant. Calculate the mass fraction of water based on the mass loss of bacterial residue.

Ash: The ash dish containing OFR was sent to a muffle furnace preheated to 810 °C and for ashing and burning to a constant quality. Take the percentage of the mass of the residue to the mass of the OFR as the ash content of the bacteria residue.

Volatiles: a certain amount of air-dried OFR was placed in a porcelain crucible with a lid, and was heated for 7 minutes at 900 °C in isolation from air. The reduced mass in the OFR minus the moisture content of the OFR was used as the volatile.

Table S1 Industrial analysis (wt%) of ROFR and the DOFR

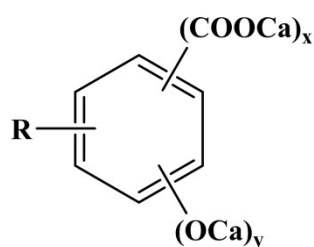
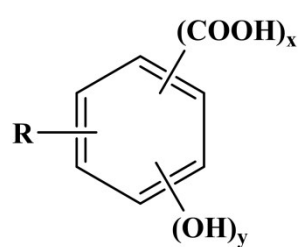
Sample	Moisture	Ash	Volatiles	Carbon
OFR	6.65±0.087	12.50±0.050	61.41±0.12	19.44±0.080
DOFR	7.14±0.10	2.73±0.067	64.53±0.056	25.60±0.085

Table S2 Inorganic elemental analysis (wt%) of ROFR and the DOFR

Sample	C	H	O	N	S	P	Total
OFR	40.48	4.12	22.80	8.20	0.37	0.35	76.32
DOFR	50.48	5.51	30.19	9.20	0.70	0.046	96.13

Table S3 Metallic element analysis (wt%) of ROFR and the DOFR

Sample	Ca	Zn	Fe	Na	Si	K	Al
OFR	4.28	0.89	0.77	0.12	0.034	0.033	0.024
DOFR	0.015	0.75	0.77	0.027	0.045	0.0029	0.0046

a**b****Figure S1.** Structural formula of OFR's acidic functional groups before and after demineralization, (a) ROFR, (b) DOFR, (R= OFR main structures).

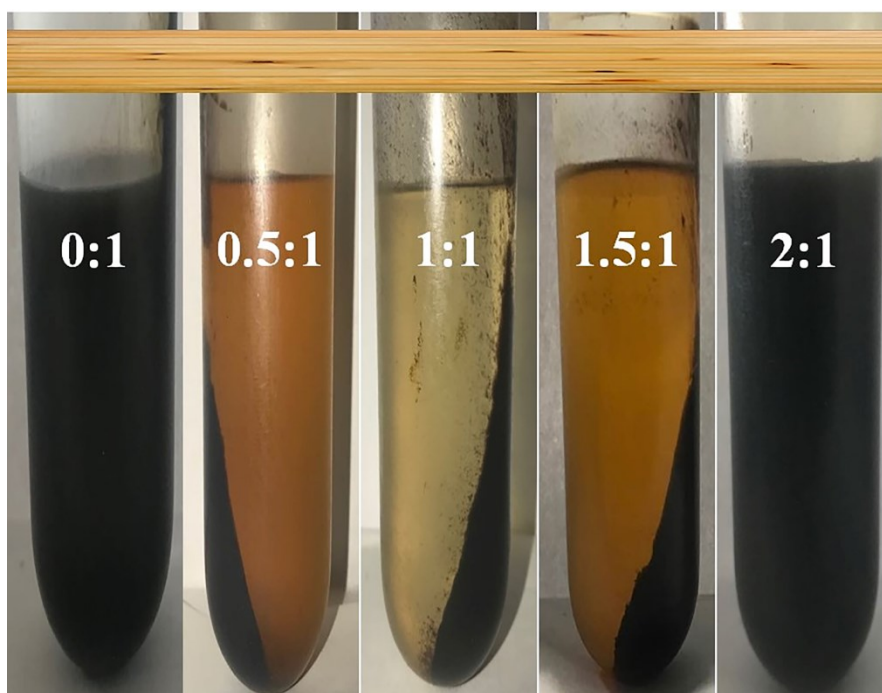


Figure S2. Optical images of DOFR solutions at different mass ratios of HfCl₄ to Hf-OFR catalyst.

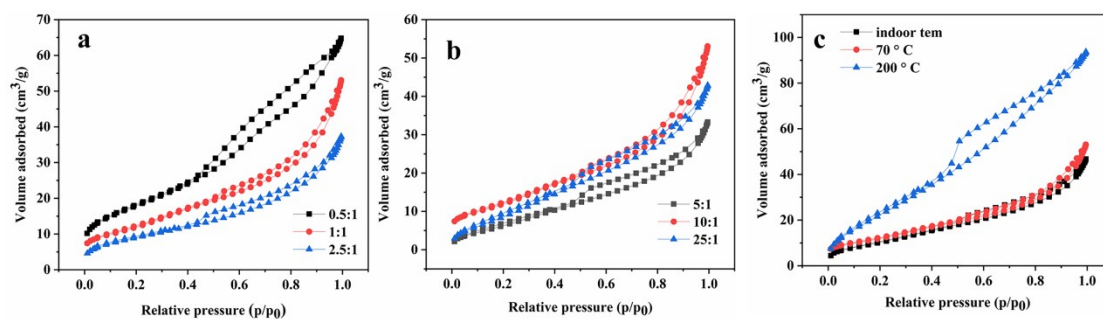


Figure S3. N₂ adsorption–desorption isotherm under different preparation conditions: (a) mass ratio of HfCl₄ to DOFR, (b) molar mass ratio of triethylamine to HfCl₄, (c) the aging temperature.

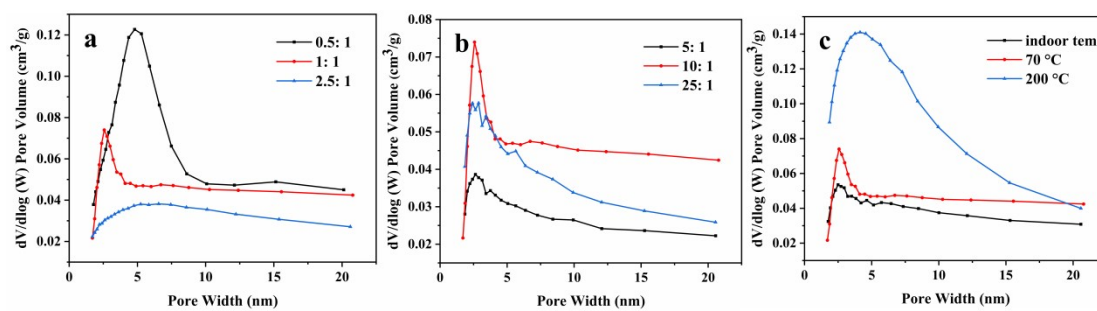


Figure S4. Pore structure analysis under different preparation conditions. (a) mass ratio of HfCl₄ to DOFR, (b) molar mass ratio of triethylamine to HfCl₄, (c) the aging temperature. (under the BJH desorption method).

Table S4. Compare the microstructure and hafnium content of Hf-OFR catalyst under different preparation conditions

Sample	S_{BET}	V_{pore}	D_{mea}	Hf
	(m²/g)^a	(cm³/g)^b	(nm)^c	(wt%)^d
Hf-OFR-0.5:1 ^e	64.50	0.100	5.17	11.7
Hf-OFR-1:1	43.80	0.083	6.20	27.3
Hf-OFR-2.5:1	32.84	0.056	6.10	30.6
Tri-Hf-5:1 ^f	25.74	0.049	5.37	24.5
Tri-Hf-25:1	35.53	0.061	5.26	17.4
Aging tem 25 °C	39.30	0.070	5.62	26.8
Aging tem 200 °C	90.70	0.134	4.43	29.0

^a S_{BET}:Brunauer-Emmett-Teller (BET) specific surface area.

^b BJH Desorption cumulative volume of pores.

^c BJH Desorption average pore width (4V/A).

^d Measurements by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

^e Mass ratio of HfCl₄ to OFR.

^f Molar mass ratio of triethylamine to HfCl₄.

Table S5 Contents of Lewis and Brønsted acid sites of the OFR and the Hf-OFR

	Lewis ($\mu\text{mol/g}$) ^a	Brønsted ($\mu\text{mol/g}$) ^b	Lewis ($\mu\text{mol/g}$) ^c	Brønsted ($\mu\text{mol/g}$) ^d
OFR	49.52	8.56	10.86	2.13
Hf-OFR	52.30	10.90	14.50	6.05

The data in this table were the average values of two times of tests.

^{a b} Lewis and Brønsted acidic sites at 150 ° C desorption temperature using pyridine infrared.

^{c d} Lewis and Brønsted acidic sites at 250 ° C desorption temperature using pyridine infrared.

Table S6 Hf content, specific surface area and the pore volume of the Hf-OFR catalyst before and after recycling

	ICP _{Hf} (wt%) ^a	S _{BET} (m ² /g) ^b	V _{pore} (cm ³ /g) ^c	D _{mean} (nm) ^d
Hf-OFR	27.3	43.8	0.083	6.20
Hf-OFR ^e	24.2	33.0	0.056	6.16

The data in this table were the average values of two times of tests.

^a ICP_{Hf}: ICP-OES detected hafnium content.

^b S_{BET}: BET surface area was obtained from N₂ adsorption isotherm.

^c V_{pore}: BJH Desorption cumulative volume of pores.

^d D_{mean}: BJH Desorption average pore width (4V/A).

^e Hf-OFR: Used Hf-OFR after 5 cycles.

Table S7 Contents of acid-base sites and C content of the Hf-OFR catalyst before and after recycling

	Basicity (mmol/g) ^a	Acidity (mmol/g) ^b	Lewis (μ mol/g) ^c	Brønsted (μ mol/g) ^d	Lewis (μ mol/g) ^e	Brønsted (μ mol/g) ^f	C wt% ^g
Hf-OFR	1.60	1.90	52.3	10.9	14.5	6.0	30.93
Hf-OFR ^h	1.43	1.44	53.7	8.8	16.2	3.0	33.96

The data in this table were the average values of two times of tests.

^{a b} Basicity and acidity of the catalysts were determined by CO₂- and NH₃-TPD, respectively, with a programmed temperature: heating from 50 to 300 °C at a rate of 10 °C/min and the number of sites is the cumulative total acid calculated from the peak area.

^{c d} Lewis and Brønsted acidic sites at 150 °C desorption temperature using pyridine infrared.

^{e f} Lewis and Brønsted acidic sites at 250 °C desorption temperature using pyridine infrared.

^g Elemental analysis of carbon content.

^h Hf-OFR: Used Hf-OFR after 5 cycles.