Supporting Information

Direct use of humic acid mixtures to construct efficient Zr-containing catalysts for Meerwein-Ponndorf-Verley reactions

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Table S1. Comparison of Zr-HAs^{C} catalyst with different catalysts in typical literatures.[a]

	Catalysts	H donor	Reaction conditions	C./%	Y./%	S./%	Refs.
1	Zr-HAs	IPA	70 °C,9 h, IPA	97.3	80.4	82.6	This work
2	Zr-HAs	IPA	50 °C，15 h, IPA	97.2	97.2	>99	This work
3	Zr-PhyA	IPA	100 °C，2 h, IPA	99.3	99.3	100.0	1
4	Zr-SBA-15	IPA	90 °C，6 h, IPA	65.0	45.0	69.2	2
5	ZrPN	IPA	100 °C，15h, IPA	93.0	90.0	96.8	3
6	γ-Fe_2O_3@HAP	IPA	180°C，3 h, IPA	96.2	91.7	95.3	4
7	Ni-Cu/Al_2O_3	IPA	200 °C，4h, IPA	95.4	95.4	100	5
8	MgO	IPA	170 °C, 5 h, IPA	100.0	74.0	74.0	6
9	Fe/NC	IPA	160 °C，15h, IPA	91.6	76.0	83.0	7
10	Ru/Uio-66	H_2	20 °C, H_2 0.5 MPa, 4h, H_2O	94.9	94.9	100	8
11	Ru(II) complex	H_2	85 °C，H_2 1 MPa, 2h, Ethanol	100.0	93.0	93.0	9
12	Pt(5 wt%)/Al_2O_3	H_2	25 °C, H_2 2 MPa, 8 h, in IPA	95.5	90.7	95.0	10
13	Pt/γ-Al_2O_3	H_2	50 °C，1 atm，7h, in methanol	80.0	79.2	99.0	11
14	5%Pt/TECN	H_2	100 °C， H_2 1 MPa, 5 h, H_2O	100.0	99.0	99.0	12
15	Au/TiO_2	CO/H_2O	90 °C，4 MPa CO	100.0	100.0	100.0	13
16	Fe(NiFe)O_4-SiO_2	H_2	90 °C, H_2 2MPa, 4h, Heptane	94.3	94.3	100.0	14
17	Co/SBA-15	H_2	150 °C，2MPa H_2,1.5h，	95.0	91.2	96.0	15
18	Capped Ni	H_2	110 °C, H_2, 3 MPa, 3 h, IPA	96.6	91.8	95.0	16
19	Ni-Sn/AlOH	H_2	180 °C，H_2 3 MPa, 1 h，IPA	98.0	94.0	95.9	17
20	5 wt%Ni/NDC	H_2	200 °C， H_2 1MPa,5h, IPA	96.0	91.2	95.0	18
21	CuNi/MgAlO	H_2	100 °C，H_2 4MPa, 4 h, IPA	99.0	98.0	99.0	19
22	CuO-Cr_2O_3	H_2	200 °C，H_2 6 Mpa, 3 h, Octane	75.0	64.5	86.0	20

[a] C., conversion of furfural; Y., Yield of FA; S., Selectivity of FA.

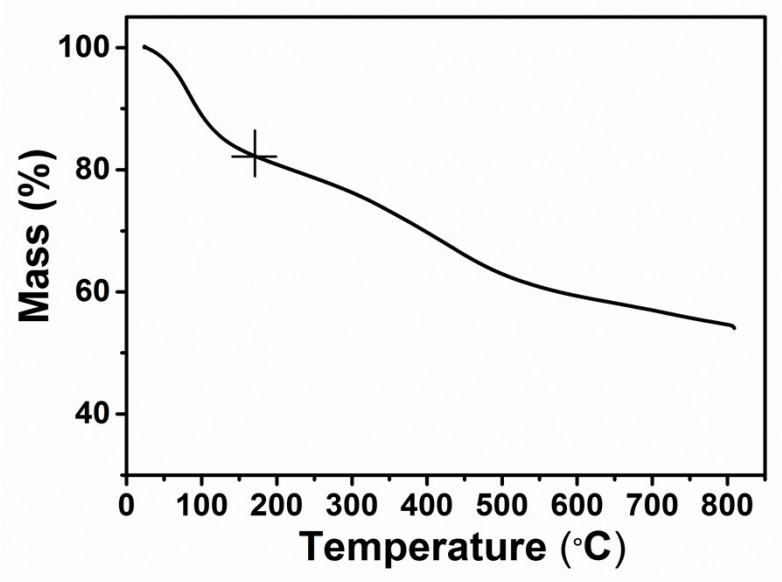

Figure S1. TG analysis of the Zr-HAs^{C} catalyst

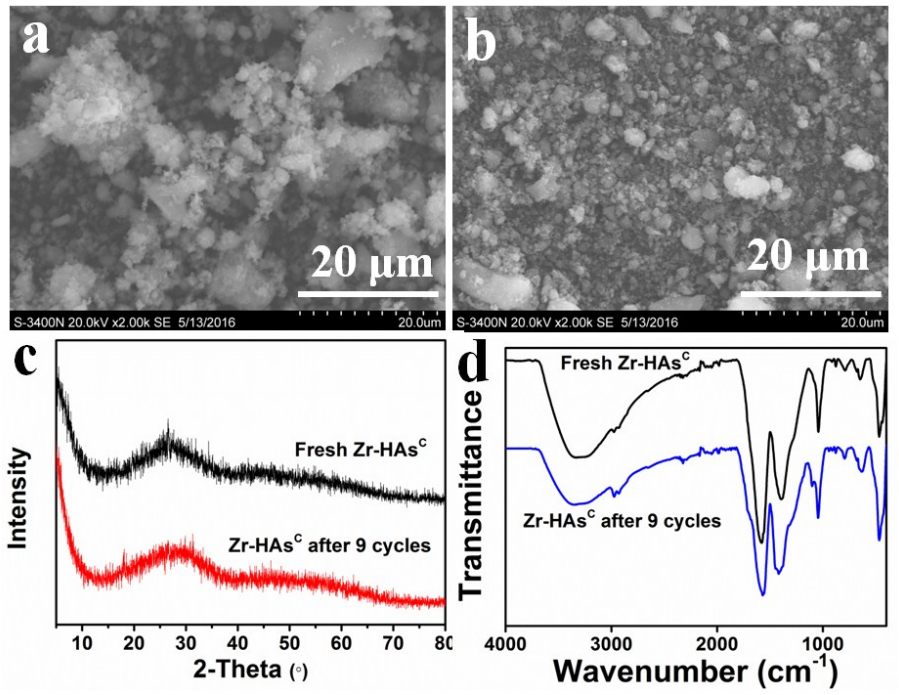

Figure S2. Comparison of the freshly prepared and recycled Zr-HAs^{C} catalysts after nine reuses. SEM of the fresh (a) and recycled Zr-HAs^{C} (b), XRD spectra (c), and FTIR patterns (d).

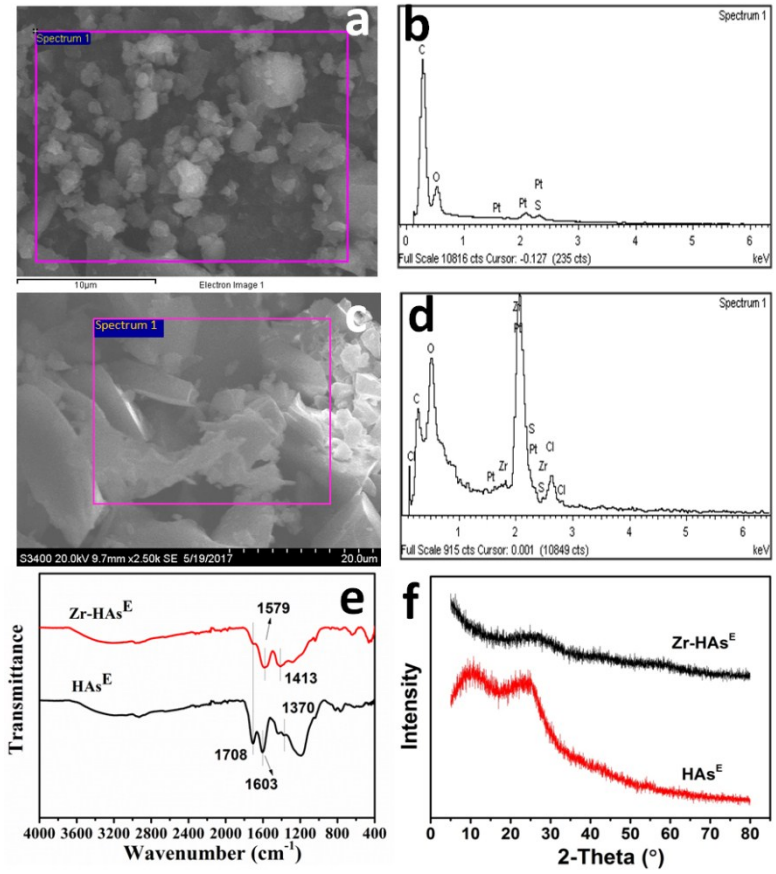

Figure S3. Characterization of the extracted HAs and corresponding Zr-HAs^{E} catalyst. SEM-EDS of the extracted HAs (a, b) and Zr-HAs^{E} catalyst (c, d), FTIR spectra (e) and XRD patterns (f).

In the IR spectra of Zr-HAs^{E}, the peak at 1708 cm^{-1} assigned to the C=O bond vibration in the carboxylic acid groups became much weaker compared to that of HAs^{E}, indicating that the carboxylic acid groups were converted into their metal salt form after interaction with Zr^{4+}.[21, 22] HAs^{E} and Zr-HAs^{E} also displayed the characteristic asymmetric (HAs^{E}, 1603 cm^{-1}; Zr-HAs^{E}, 1579 cm^{-1}) and symmetric vibrations (HAs^{E},1370 cm^{-1}; Zr-HAs^{E}, 1413 cm^{-1}) of carboxylate groups. Compared with the IR spectrum of HAs^{E}, the wavenumber difference of asymmetric and symmetric vibrations of carboxylate anions in Zr-HAs^{E} was narrowed from 233 cm^{-1} to 16 cm^{-1}, which indicated that carboxylate groups were coordinated to Zr^{4+} ions.[23, 24]

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