Electronic Supporting Information

Construction of novel and efficient hafnium catalysts using naturally existing tannic acid for Meerwein-Ponndorf-Verley Reduction

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Product analysis

FD (furfuraldehyde), FA (furfuryl alcohol), and other liquid substrates conversion and products yield were quantitatively analysed by gas chromatography (GC, Techccomp 7900) with a FID (flame ionization detector) using decane as the GC internal standard. The products were identified by GC-MS (Agilent 7890B-7000D). The conversion of substrates (e.g., FD) and yields of products (e.g., FA) were calculated based on standard curves ($R^2 \geq 0.9994$) of corresponding commercial samples in five gradient concentrations along with a certain amount of internal standard (decane).[1, 2] Substrate conversion (Conv, %), product yield (Yield, %) and selectivity (Sel, %) were calculated using the following equations:

Conv (%) = [1-(mole of substrate after reaction) / (mole of initial substrate)]×100 %

Yield (%) = (mole of the obtained product) / (the theoretical mole of the product under total conversion of the initial substrate)×100 %

Sel (%) = (product yield) / (substrate conversion)×100 %

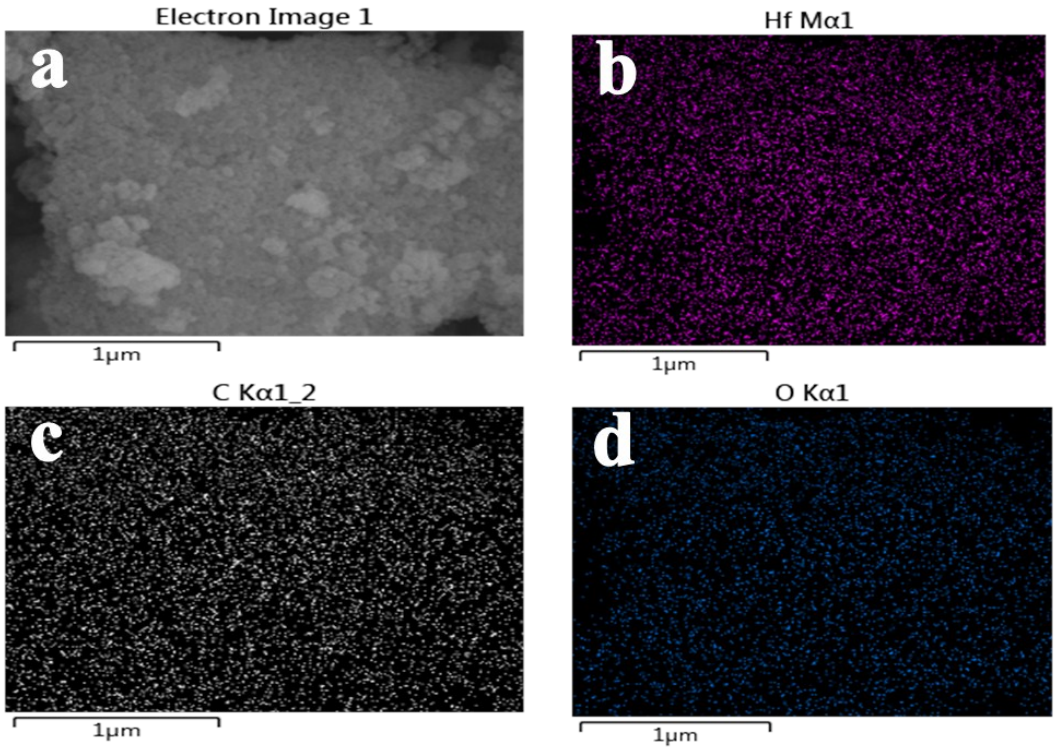
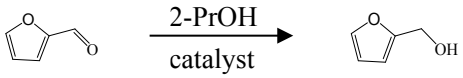


Figure S1 Element mapping images of Hf-TA: (a) scanning range of the EDS mapping, (b) Hf element, (c) C element, and (d) O element.

Table S1 CTH reaction of FD to produce FA catalyzed by various catalysts.[a]



Entry	Catalyst type	Conv. (%)	Yield. (%)	Sel. (%)
1	Hf-TA	97.2	96.2	98.9
2	Zr-TA	62.6	45.4	72.5
3	Al-TA	19.4	7.8	40.2
4	Cr-TA	14.7	4.1	27.9
5	Sn-TA	12.1	6.8	56.2
6	Fe-TA	4.9	4.3	87.7
7	Cu-TA	4.8	3.3	68.8
8	$HfCl_4$	60.3	3.6	5.9
9	HfO_2	20.0	4.0	20.0
10	$Hf(OH)_4$	4.0	1.0	25.0

[a] Typical reaction conditions were as follows except otherwise stated in the table: FD 1 mmol, 2-PrOH 5 mL, catalyst 200 mg, reaction temperature 70 ºC, reaction time 5 h

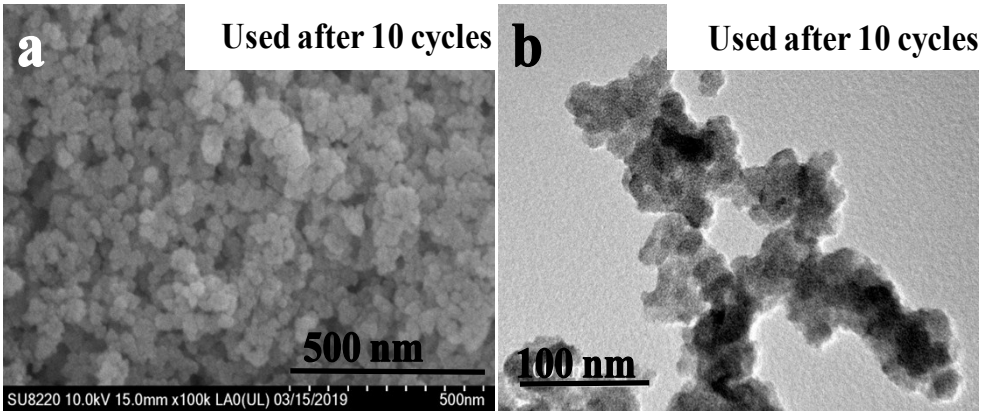


Figure S2 SEM image (a) and TEM image (b) of the recycled Hf-TA catalyst after 10 cycles.

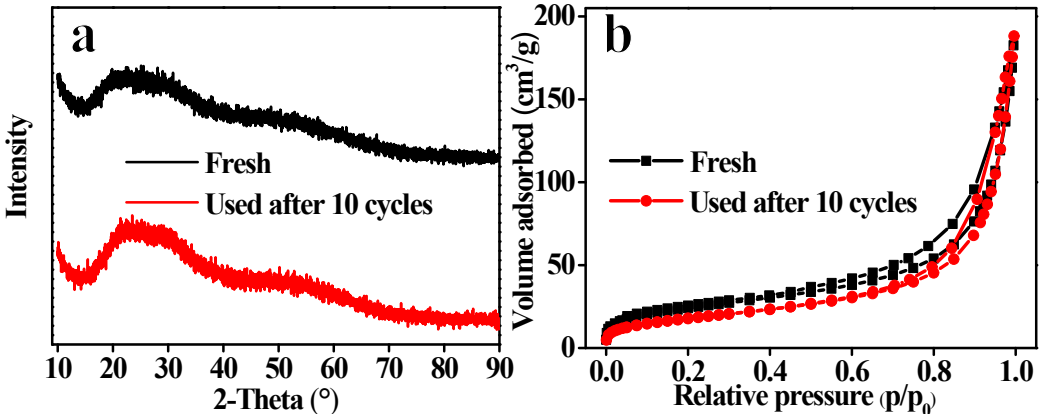


Figure S3 XRD patterns (a) and nitrogen adsorption desorption isotherms (b) of the fresh Hf-TA and recycled Hf-TA catalyst after 10 cycles.

Table S2 Surface area, volume and Hf content of different catalysts.

Catalyst	S_{BET} (m^2/ g) [a]	V_{pore} (cm^3/ g) [b]	D_{mean} (nm)[c]	P_{size} (nm)[d]	ICP_{Hf} (%) [e]
Fresh Hf-TA	87.8	0.2	12.9	68.4	35.3
Reused Hf-TA[f]	66.0	0.2	17.6	90.9	34.5

[a] S_{BET}: BET surface area was obtained from N_2 adsorption isotherm. [b] V_{pore}: Volume of pores. [c] D_{mean}: Adsorption average pore diameter. [d] P_{size}: Average particle size. [e] ICP_{Hf}: ICP-OES detected hafnium content. [f] Hf-TA: Used Hf-TA after 10 cycles.

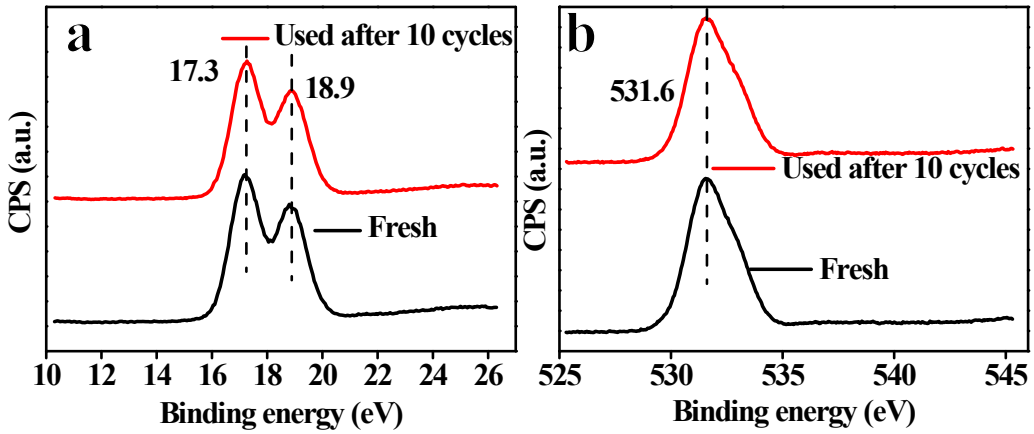


Figure S4 XPS spectra of Hf 4f (a) and O1s (b) in the fresh Hf-TA and recycled Hf-TA catalyst after 10 cycles.

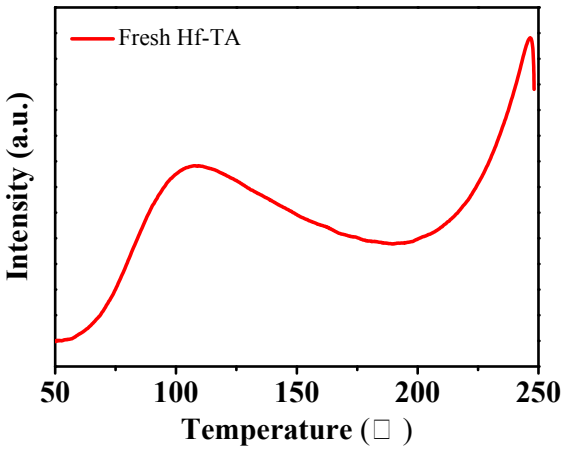


Figure S5 NH_3-TPD spectra of Hf-TA. Due to the decomposition temperature of the as-prepared catalyst was about 250 ℃, the test could conduct under the temperature lower than 250 ℃.

References

1. H. Li, T. Yang and Z. Fang, *Applied Catalysis B: Environmental*, 2018, **227**, 79-89.
2. W. Wu, Y. Li, H. Li, W. Zhao and S. Yang, *Catalysts*, 2018, **8**, 264-278.