Supporting Information

Porous Hafnium Phosphonate: Novel Heterogeneous Catalyst for Conversion of Levulinic Acid and Esters into γ -Valerolactone

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Table S1. Physical properties of different catalysts.

Sample ^a	BET surface area (m ² g ⁻¹) ^b	Pore volume (cm ³ g ⁻¹) ^c	Pore diameter (nm) ^d
Hf-ATMP	222.6	0.25	16.7
HfO_2	6.74	0.07	
Hf-EDPA	206.8	0.39	13.9
Cr-ATMP	4.81	0.03	15.8
Zn-ATMP	31.71	0.13	47.3
Al-ATMP	62.54	0.36	41.4
Cu-ATMP	129.86	0.14	3.6

^aThe samples were degassed at 120 °C for 24 h. ^bSurface area based on multipoint BET method. ^cPore volume based on BJH method. ^dPore diameter based on BJH method.

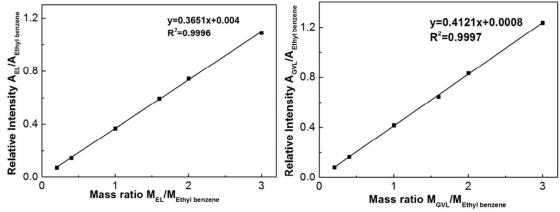


Figure S1. The calibration curves for GC using 0.05g ethylbenzene as the internal standard. (A=Peak area, M=Weight)

$$R = * - N \xrightarrow{CH_2 - PO_3} CH_2 - PO_3$$

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Scheme S1. The most plausible connectivity pattern between ATMP and Hf⁴⁺.

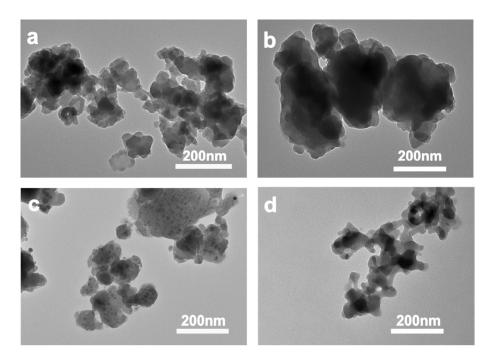
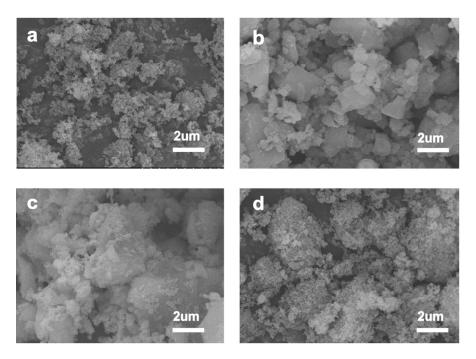


Figure S2. The TEM images of Al-ATMP (a), Cr-ATMP (b), Cu-ATMP (c), and Zn-ATMP (d).



 $\textbf{Figure S3.} \ \text{The SEM images of Al-ATMP (a), Cr-ATMP (b), Cu-ATMP (c), and Zn-ATMP (d).}$

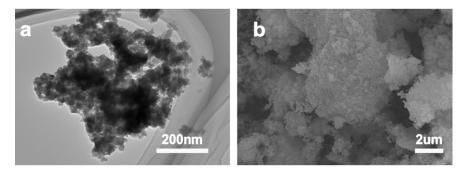


Figure S4. The TEM (a) and SEM (b) images of Hf-EDPA.

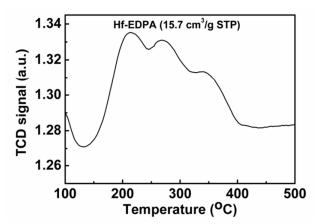


Figure S5. CO₂-TPD examination for Hf-EDPA.