Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

One-pot transformation of furfural into γ-valerolactone catalyzed by hierarchical Hf-Al-USY zeolite with balanced Lewis and Brønsted acid sites

Bo Tang, Shuang Li, Wei-Chao Song, Yan Li, En-Cui Yang*

Tianjin Key Laboratory of Structure and Performance for Functional Molecules, College of Chemistry, Tianjin Normal University, Tianjin 300387, People's Republic of China

*Corresponding author

E-mail address: encui_yang@163.com

Initial reaction rate: In the present study, the initial reaction rate k_i for the target reaction was defined as moles of formed product divided by gram of catalyst per reaction time (conversion not exceeding 30%), as shown below.

For the reduction of FA to FOL, k_1 ($molh^{-1}g^{-1}$) = $\frac{moles\ of\ FOL\ formed}{amount\ of\ catalyst\ \times\ reaction\ time}$

For FOL conversion to IPL, k_2 ($molh^{-1}g^{-1}$) =

$$\frac{moles\ of\ IPL\ formed}{amount\ of\ catalyst\ \times\ reaction\ time}$$

For IPL lactonization to GVL, k_3 ($molh^{-1}g^{-1}$) = $\frac{moles\ of\ GVL\ formed}{amount\ of\ catalyst\ \times\ reaction\ time}$

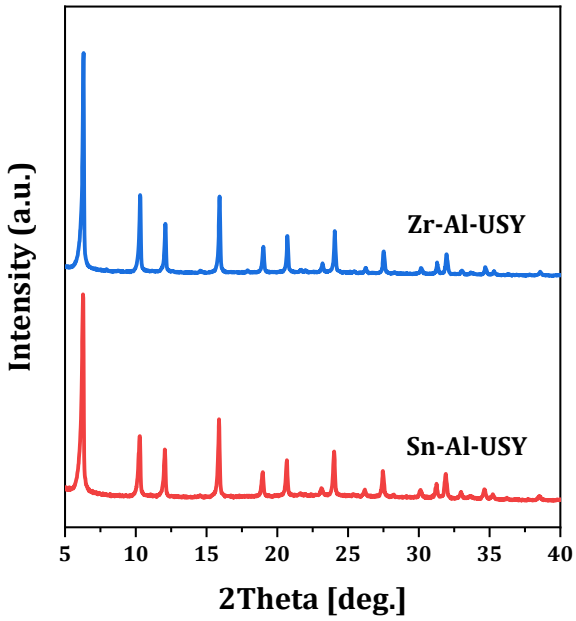

Fig. S1 XRD patterns of Sn-Al-USY and Zr-Al-USY.

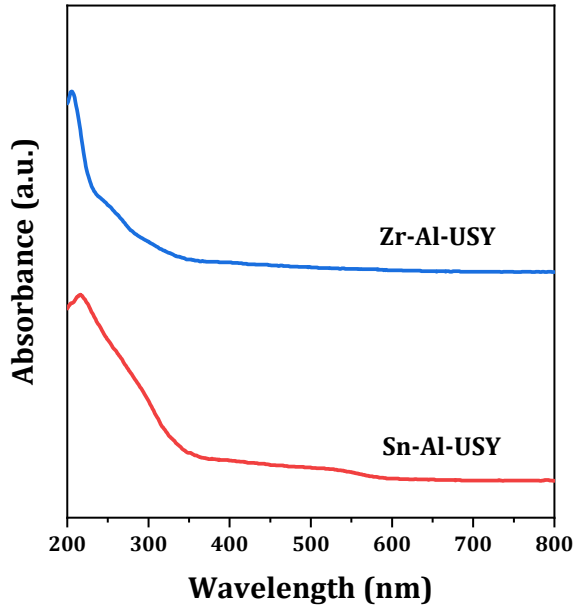

Fig. S2 UV-vis spectra of Sn-Al-USY and Zr-Al-USY.

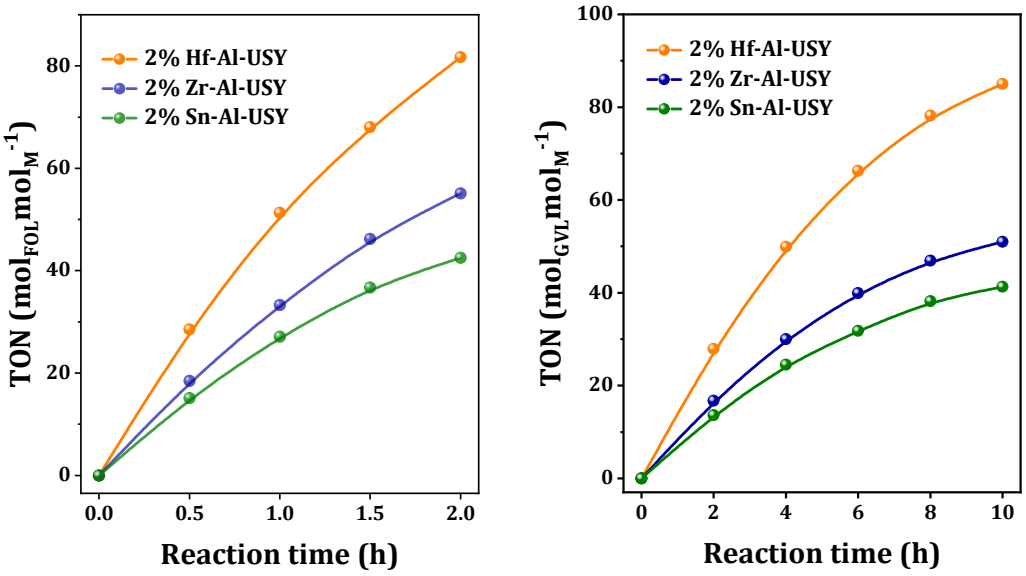

Fig. S3 Time-dependent conversion of FA (left chart) and LA (right chart) over 2% Hf-Al-USY, 2% Zr-Al-USY and 2% Sn-Al-USY zeolites. Reaction conditions: 1 mmol substrate, 5 mL solvent, 100 mg catalyst, 1.0 MPa N2; 373 K for FA conversion and 423 K for LA conversion, respectively.

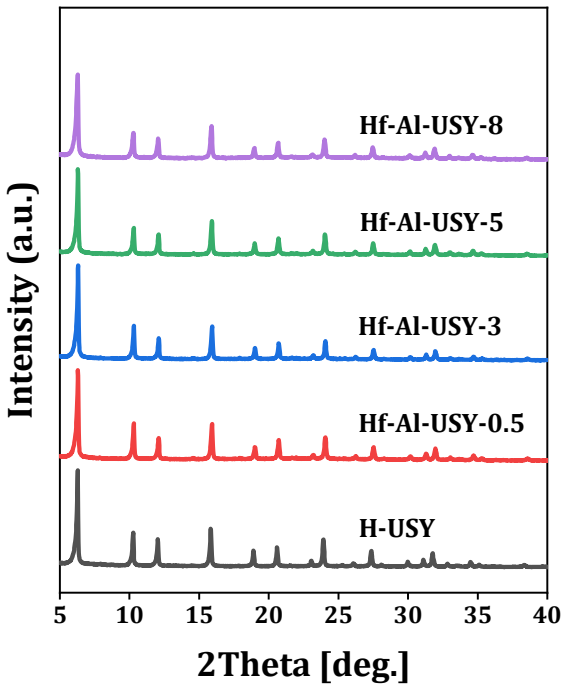

Fig. S4 XRD patterns of Hf-Al-USY zeolites prepared from different acid treatment time.

All the samples exhibited identical diffraction peaks with comparable intensity, indicating the framework integrity of USY framework during the post-synthesis procedures. Such a result can be explained by the fact that calcination of parent H-USY at a high temperature, i.e. 1073 K, can effectively improve its framework stability against destruction when treating with nitric acid aqueous solution.

Table S1 Physicochemical properties of zeolite samples under study.

Sample	Surface area (m^2 g^{-1})			Pore volume (cm^3 g^{-1})		
	S_{BET}	S_{micro}[a]	S_{meso}	V_{total}	V_{micro}[b]	V_{meso}
H-USY	835	740	95	0.40	0.29	0.11
DeAl-USY	985	772	213	0.54	0.30	0.24
Hf-Al-USY-0.5[c]	928	758	170	0.49	0.29	0.20
Hf-Al-USY-1[c]	975	769	206	0.53	0.30	0.23
Hf-Al-USY-3[c]	941	723	218	0.54	0.29	0.25
Hf-Al-USY-5[c]	935	715	220	0.56	0.28	0.28
Hf-Al-USY-8[c]	948	703	245	0.56	0.26	0.30
Sn-Al-USY	979	769	210	0.52	0.29	0.23
Zr-Al-USY	982	775	207	0.53	0.29	0.24

Hf-Al-USY-R[d]	763	628	135	0.45	0.27	0.18

[a] The specific surface area was obtained by the BET method. [b] Calculated from the *t*-plot (t = [13.99/(0.034-log(p/p_0))]^0.5) at a relative pressure p/p_0 of 0.55-0.8. [c] Parent H-USY was treated with nitric acid solution at 358 K for n h (n = 0.5, 1, 3, 5, 8).[d] Hf-Al-USY-R indicated reused Hf-Al-USY sample.