## **Supporting Information**

## Superior acidic catalytic activity and stability of Fe-doped HTaWO<sub>6</sub> nanotubes

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**Figure S1.** (a) SEM image of TaW-Bulk, (b) TEM image of TaW-H, SEM images of (c) TaW-H and (d) TaW-Fe nanotubes, (e) SEM and (f) TEM images of TaW-SO<sub>3</sub>H nanotubes.



**Figure S2.** (a) SEM image, (b) EDS spectrum of TaW-Fe nanotubes and (c) their corresponding SEM elemental mapping.



Figure S3. XRD patterns of TaW-SO<sub>3</sub>H nanotubes calcined at different temperatures.



Figure S4. TGA curves of TaW-Bulk precursor, TaW-H, TaW-SO<sub>3</sub>H, and TaW-Fe nanotubes.



Figure S5. TEM images of (a) TaW-H-400 and (b) TaW-SO<sub>3</sub>H-400 nanotubes.



**Figure S6.** TEM images of (a) TaW-Fe-400, (b) TaW-Fe-500, (c) TaW-Fe-600, and (d) TaW-Fe-700 nanotubes; (e) SEM image, (f) EDS spectrum, and (g) corresponding elemental mapping of TaW-Fe-500 nanotubes.



**Figure S7.** TEM image of (a) TaW-Fe-500 nanotubes, (b) EDS spectrum, and (c) corresponding elemental mapping showing the distribution of Ta, W, and Fe elements in TaW-Fe-500 after impregnation in HCl (1.0 M) for 4h.



**Figure S8.** (a) FTIR spectra and (b) XRD patterns of TaW-Fe-500 nanotubes before/after reaction and calcined at 500 °C. In Figure S9a, The emerging absorption bands around 1500–1000 cm<sup>-1</sup> in recycled nanotubes can be assigned to the vibrations of benzene ring and ether linkage in anisole and products. In Figure S9b, the interlayer distance of TaW-Fe-500 nanotubes increased from 1.06 nm to 1.16 nm after reaction, demonstrating the intercalation of some anisole and products into the nanotubes after reaction. The annealing of recycled nanotubes at 500 °C led to the disappearance of the vibrations of organic species and shrinkage of interlayer distance to 1.06 nm, suggesting that the absorbed or intercalated organic species were removed.



**Figure S9.** (a) SEM image, (b) EDS spectrum, and (c) corresponding elemental mapping showing the distribution of Ta, W, and Fe atoms in TaW-Fe-500 after five cycles of recycling.



**Figure S10.** Esterification of acetic acid with ethanol catalyzed by TaW-Bulk, non-Fe- and Fe- containing nanotubes.



**Figure S11.** (a) NH<sub>3</sub>-TPD curves of TaW-Bulk, TaW-Bulk-500, TaW-SO<sub>3</sub>H, and TaW-SO<sub>3</sub>H-500. (b) NH<sub>3</sub>-TPD curves of TaW-Fe nanotubes calcined at different temperatures.