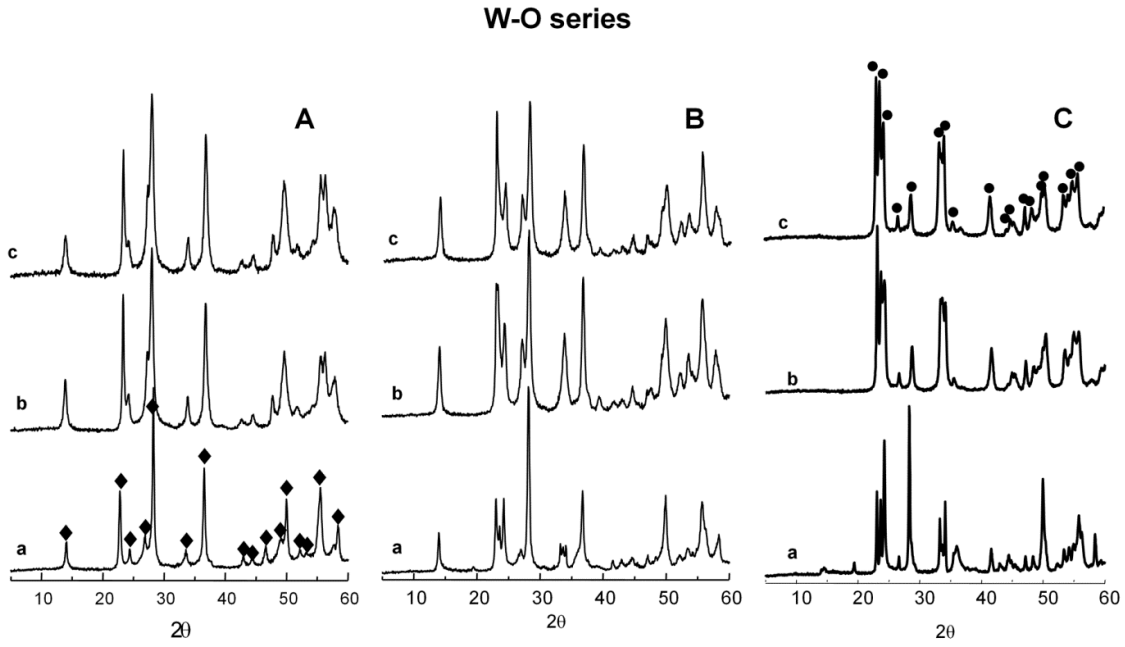

Figure S1. Powder XRD patters of W-O series: pristine samples (A), samples calcined at 450 ºC (B) and samples calcined at 600º C (C). On each series, (a), (b) and (c) refers to (Na)**W-O**, (NH_4)**W-O** and (Na/NH_4)**W-O** materials, respectively. Symbols: (♦) h-WO_3, (●) m-WO_3.

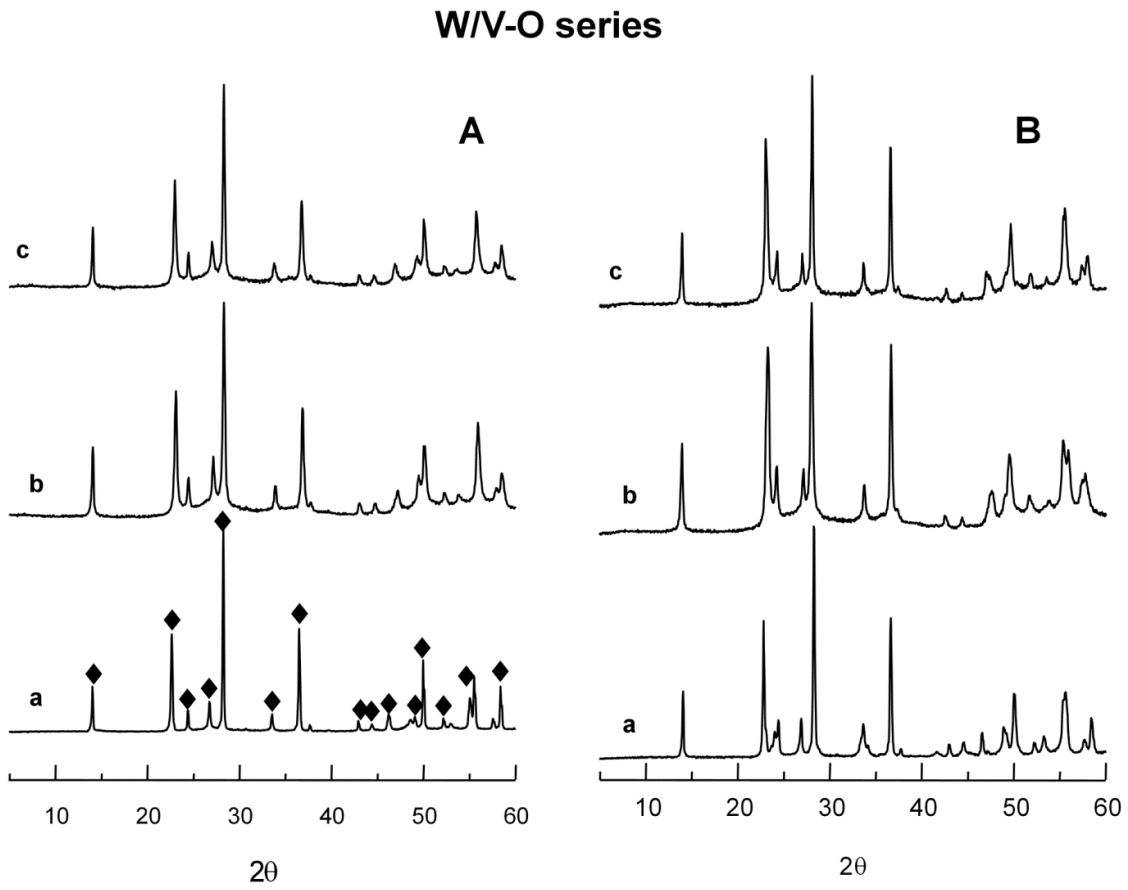

Figure S2. Powder XRD patters of W/V-O series: pristine samples (A) and samples calcined at 600º C (B). On each series, (a), (b) and (c) refers to (Na)**W/V-O**, (NH_4)**W/V-O** and (Na/NH_4)**W/V-O** materials, respectively. Symbol: (♦) h-WO_3.

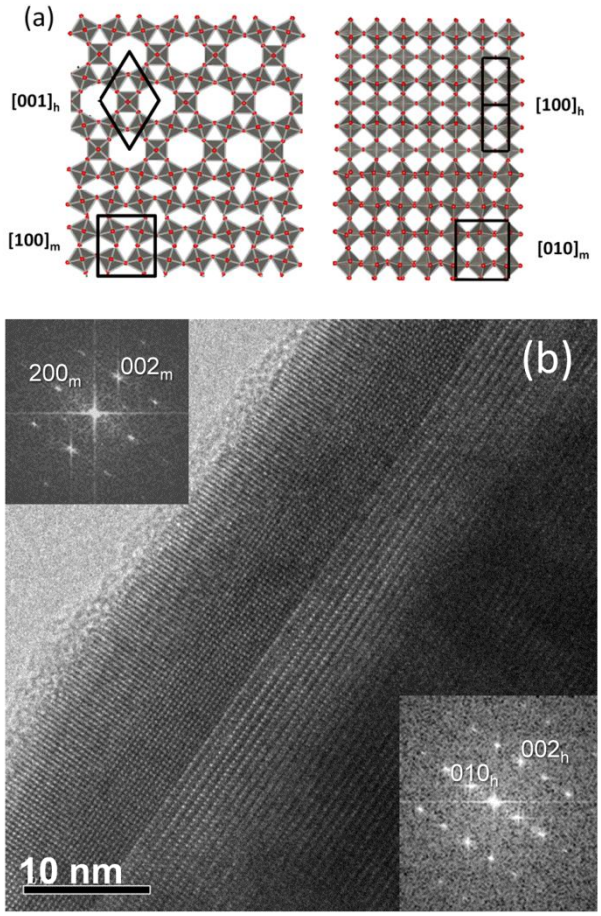

Figure S3. (a) Schematic representation illustrating the intergrowth of *h*-WO_3 and *m*-WO_3 in two different projections. (b) High resolution electron micrograph of a crystal in the $[100]_h$ projection. The change of contrast in the crystal edge corresponds to the transformation to *m*-WO_3 in the [010] projection. Similarity between $d_{001}$for the two structures provide a good basis for the intergrowth of both polymorphs. The corresponding Fourier Transforms of each area have been included to illustrate the origin of the different diffraction effects.

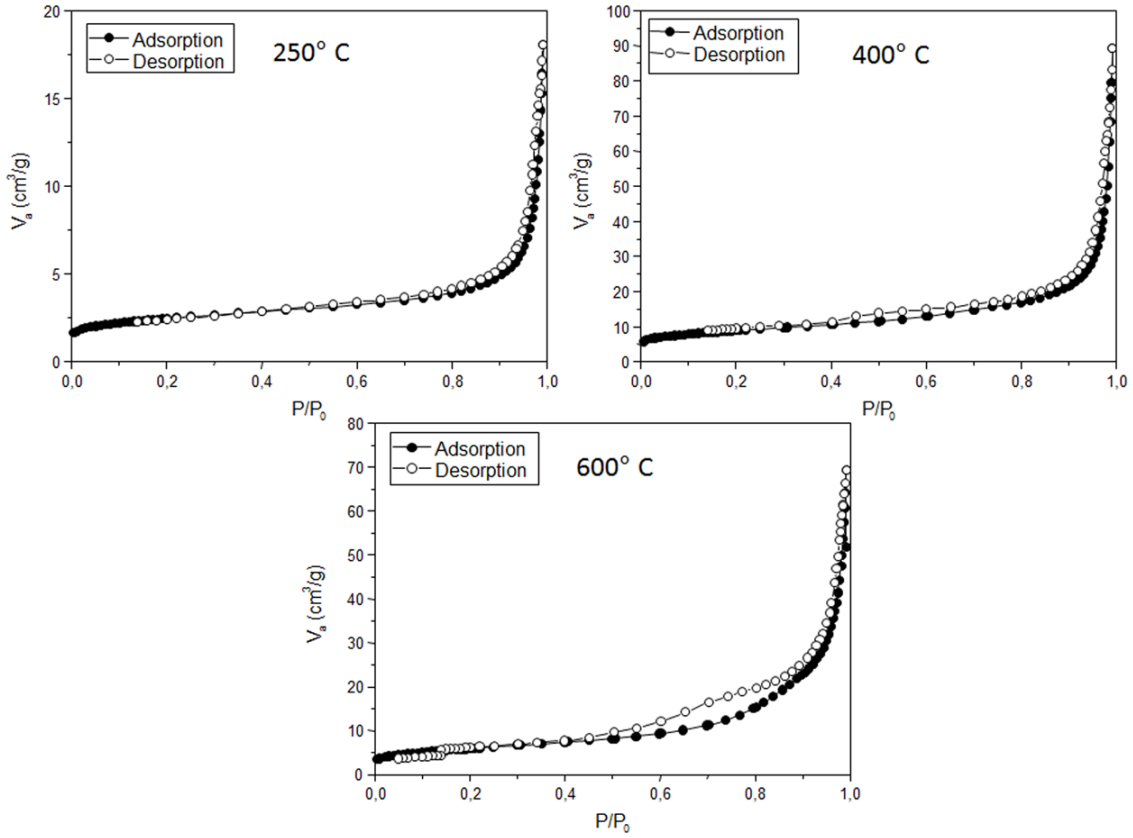

Figure S4. Nitrogen (N_2) adsorption–desorption isotherms of (NH_4^+)**W/V-O** heated at (a) 250 ºC, (b) 400 ºC and (c) 600 ºC.

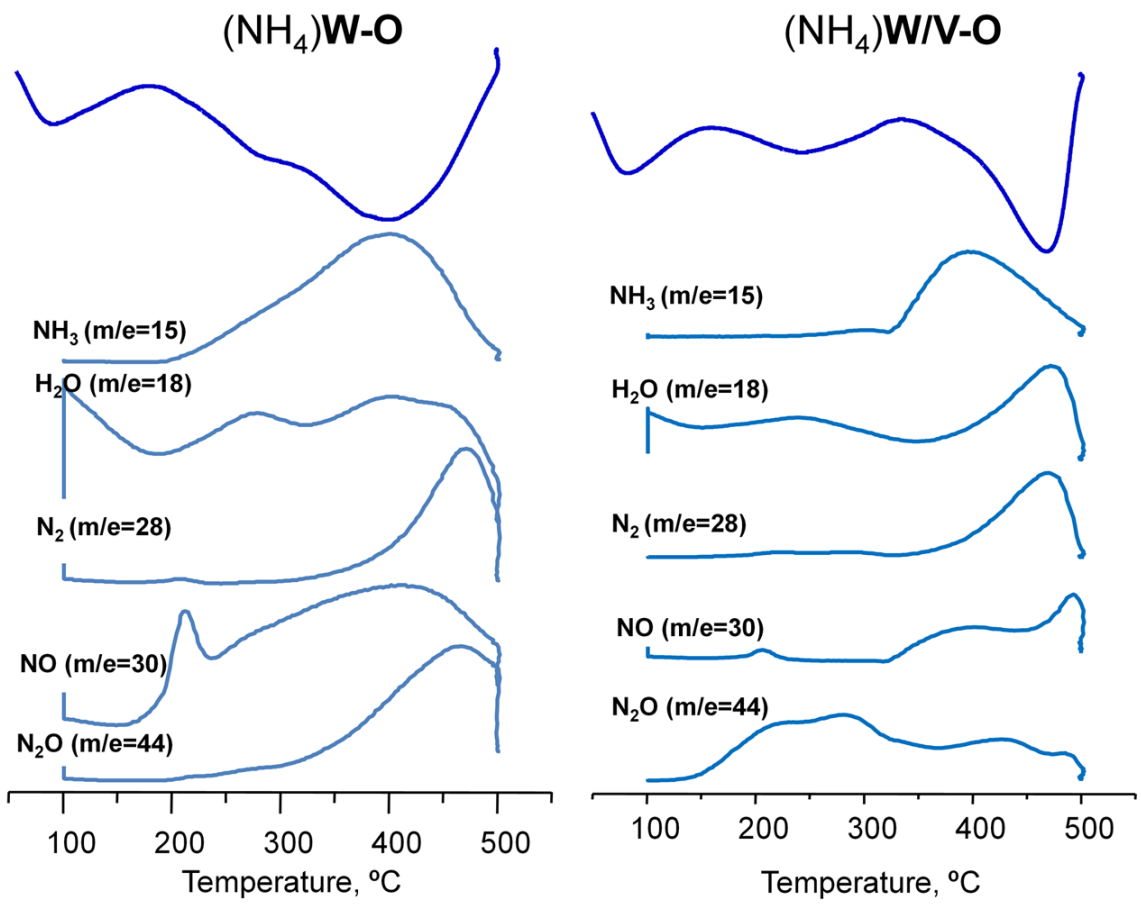

Figure S5. Simultaneous DTA/MS curves of (NH_4)**W-O** and (NH_4)**W/V-O** measured in 5% O_2/He.