SUPPLEMENTARY INFORMATION

Molecular Structure and Thermal Stability of Oxide-Supported Phosphotungstic Wells-Dawson Heteropolyacid

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X-ray Diffraction Analysis

The X-ray diffraction spectra of the bulk phosphotungstic heteropolyacid \( \text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}.x\text{H}_2\text{O} \), the oxide supports and the samples \( 11\text{aq WDTi}, 11\text{aq WDZr}, 12\text{aq WDAI} \) and \( 11\text{aq WDSi} \) (calcined at 573 K for 4 h) were performed at RT with a D5000 diffractometer (Siemens, Germany) with Ni filter, Cu K\( \alpha \) (\( \lambda = 1.540589 \) Å) radiation working at 40 kV and 20 mA. The diffraction patterns were obtained within 2\( \theta \) = 5° and 60° at a scan rate of 2° min\(^{-1}\) and steps of 0.1°. The following figure shows the X-ray spectra of the bulk HPA, the bare oxide supports and the supported HPA synthesized in aqueous media.

**Figure 1S.** X-Ray diffraction spectra of bulk phosphotungstic Wells-Dawson heteropolyacid \( \text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}.24\text{H}_2\text{O} \); bare oxide supports (\( \text{SiO}_2 \), \( \text{TiO}_2 \), \( \text{Al}_2\text{O}_3 \) and \( \text{ZrO}_2 \)) and oxide-supported HPA (\( 11\text{aq WDTi}, 11\text{aq WDSi}, 12\text{aq WDAI} \) and \( 11\text{aq WDZr} \))
Temperature Programmed Raman Spectra of Transition Metal Oxide Supports

Figure 2S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of bulk phosphotungstic Wells-Dawson heteropolyacid $H_6P_2W_{18}O_{62}\cdot xH_2O$

Figure 3S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of titanium dioxide $\text{TiO}_2$ anatase (Aeroxide® P-18 Evonik Ind., 46.8 ± 0.1 m$^2$/g)
Figure 4S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of zirconium dioxide ZrO$_2$ (fumed Evonik Ind., 31.5 ± 0.4 m$^2$/g)

Figure 5S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of alumina Al$_2$O$_3$ (Engelhard, 95.8 ± 0.2 m$^2$/g)
Figure 6S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of silica SiO$_2$ (Cab-O-Sil, 328.9 ± 0.8 m$^2$/g)

Temperature Programmed Raman Spectra of Oxide-supported Wells-Dawson Heteropolyacid Synthesized in Organic Media

Figure 7S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of 11org WDTi
**Figure 8S.** *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of 11org WDZr

**Figure 9S.** *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of 12org WDAI
**Temperature Programmed Infrared Spectra of Transition Metal Oxide Supports**

**Figure 10S.** In situ TP-IR spectra upon heating from R.T. towards 773 K of titanium dioxide TiO$_2$ anatase (Aeroxide® P-18 Evonik Ind., 46.8 ± 0.1 m$^2$/g).

**Figure 11S.** In situ TP-IR spectra upon heating from R.T. towards 773 K of zirconium dioxide ZrO$_2$ (fumed Evonik Ind., 31.5 ± 0.4 m$^2$/g).
**Figure 12S.** *In situ* TP-IR spectra upon heating from R.T. towards 773 K of alumina $\text{Al}_2\text{O}_3$ (Engelhard, 95.8 ± 0.2 m$^2$/g).

**Figure 13S.** *In situ* TP-IR spectra upon heating from R.T. towards 773 K of silica $\text{SiO}_2$ (Cab-O-Sil, 328.9 ± 0.8 m$^2$/g).
Evolution of the Raman Signals of the Wells-Dawson Heteropolyacid Dispersed Over TiO$_2$ at Various Loadings

**Figure 14S.** Evolution of the Raman signals of the Wells-Dawson heteropolyacid dispersed over TiO$_2$ at various loadings ranging from 1.7 towards 22.5 W$_{\text{atoms}}$/nm$^2$ in aqueous media and calcined *in situ* at 573 K. Open squares □ indicate Raman signals in the 999-1008 cm$^{-1}$ range and filled squares ■ indicate Raman signals in the 1018-1021 cm$^{-1}$ range.