SUPPLEMENTARY INFORMATION

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

Silvana R. Matkovic[a] Sebastián E. Collins[b], Adrián L. Bonivardi[b], Miguel A. Bañares[c], Laura E. Briand[a],

[a] Centro de Investigación y Desarrollo en Ciencias Aplicadas –Dr Jorge J. Ronco CINDECA-CCT La Plata-CONICET. Calle 47 No 257, B1900AJK, La Plata, Buenos Aires, Argentina.

[b] Instituto de Desarrollo Tecnológico para la Industria Química (UNL-CONICET).Güemes 3450, S3000GLN, Santa Fe, Argentina.

[c] Catalytic Spectroscopy Laboratory, ICP-CSIC. Marie Curie 2, E-28049 Madrid, Spain.

X-ray Diffraction Analysis

The X-ray diffraction spectra of the bulk phosphotungstic heteropolyacid $H_6P_2W_{18}O_{62}.xH_2O$, the oxide supports and the samples 11aq WDTi, 11aq WDZr, 12aq WDAl and 11aq WDSi (calcined at 573 K for 4 h) were performed at RT with a D5000 diffractometer (Siemens, Germany) with Ni filter, Cu Kα (λ=1.540589 Å) radiation working at 40 kV and 20 mA. The diffraction patterns were obtained within 2θ= 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.

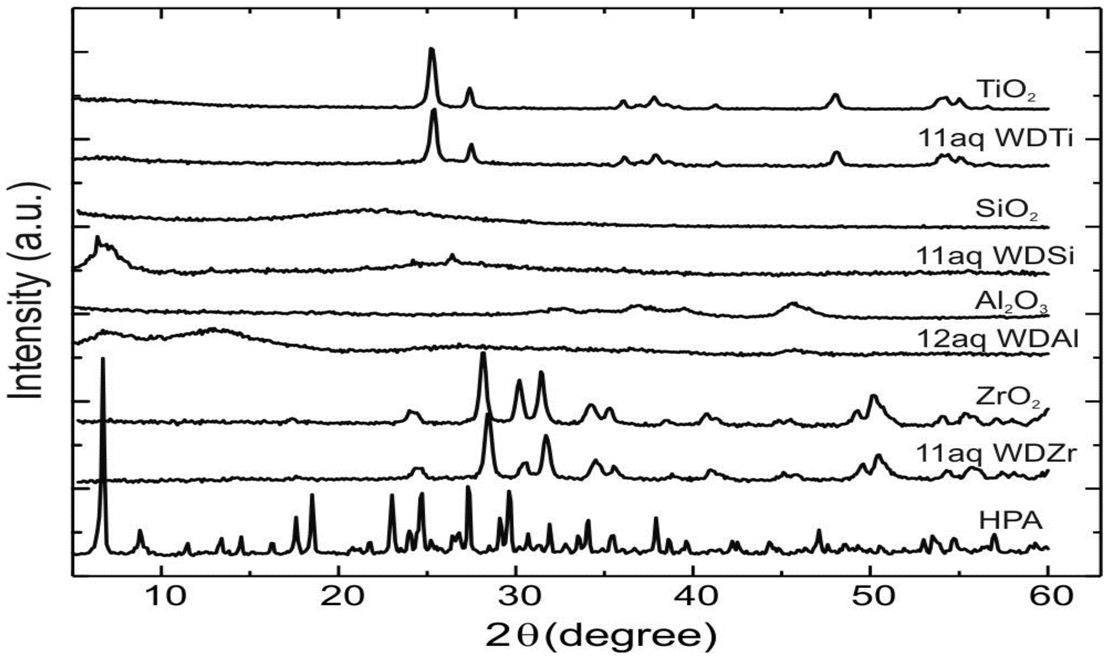

Figure 1S. X-Ray diffraction spectra of bulk phosphotungstic Wells-Dawson heteropolyacid $H_6P_2W_{18}O_{62}.24H_2O$; bare oxide supports ($SiO_2$, TiO_2, Al_2O_3 and ZrO_2) and oxide-supported HPA (11aq WDTi, 11aq WDSi, 12aq WDAl and 11aq WDZr)

Temperature Programmed Raman Spectra of Transition Metal Oxide Supports

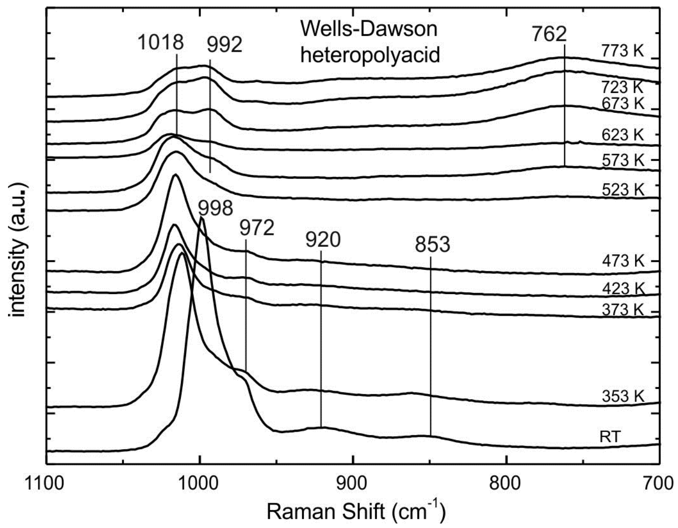

Figure 2S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of bulk phosphotungstic Wells-Dawson heteropolyacid $H_6P_2W_{18}O_{62}.xH_2O$

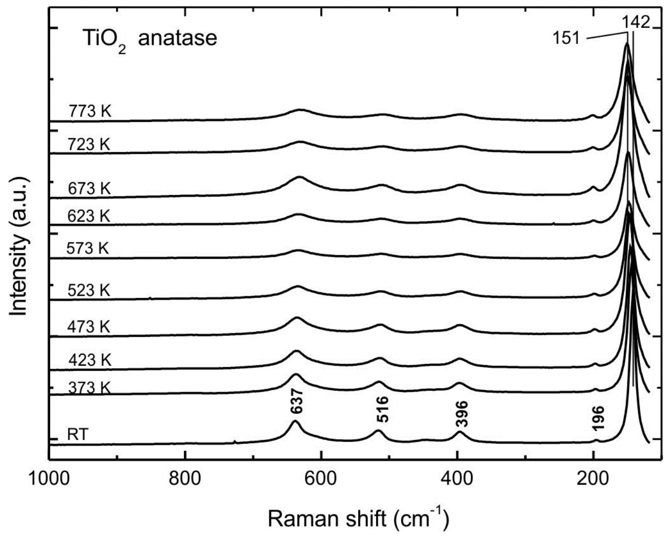

Figure 3S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of titanium dioxide TiO_2 anatase (Aeroxide® P-18 Evonik Ind., 46.8 ± 0.1 m^2/g)

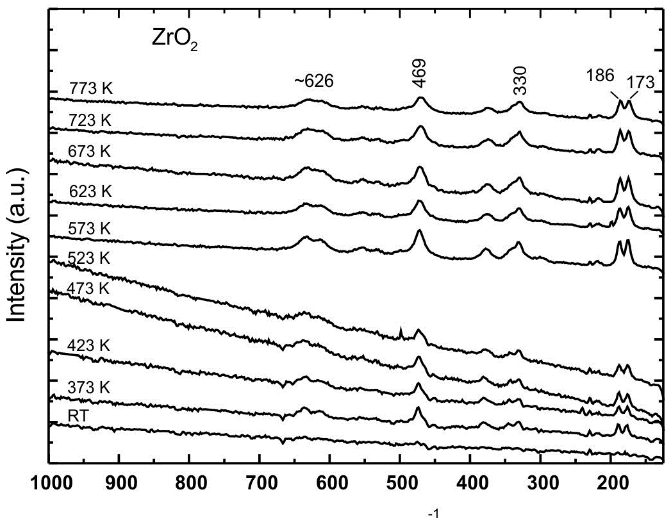

Figure 4S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of zirconium dioxide ZrO_2 (fumed Evonik Ind., 31.5 ± 0.4 m^2/g)

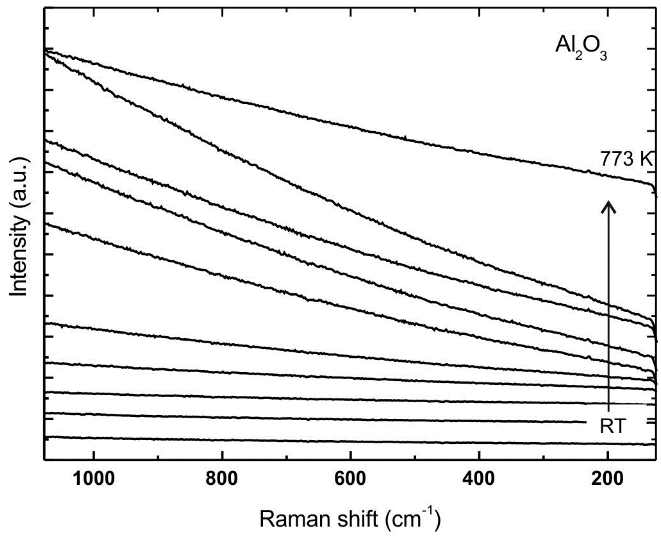

Figure 5S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of alumina Al_2O_3 (Engelhard, 95.8 ± 0.2 m^2/g)

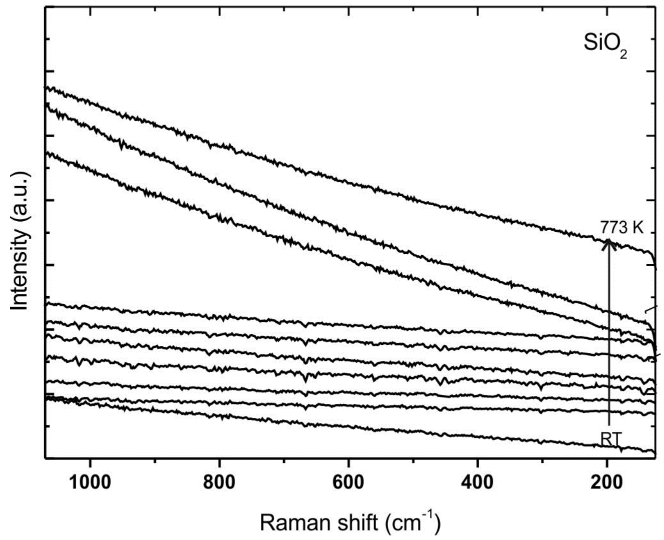

Figure 6S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of silica SiO_2 (Cab-O-Sil, 328.9 ± 0.8 m^2/g)

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

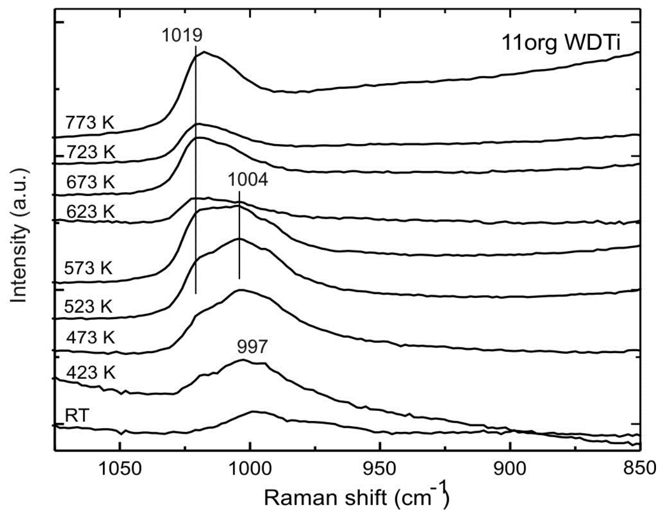

Figure 7S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of 11org WDTi

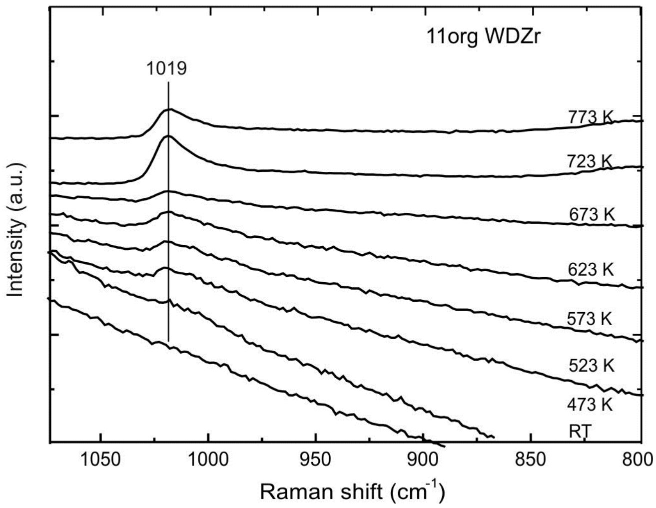

Figure 8S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of 11org WDZr

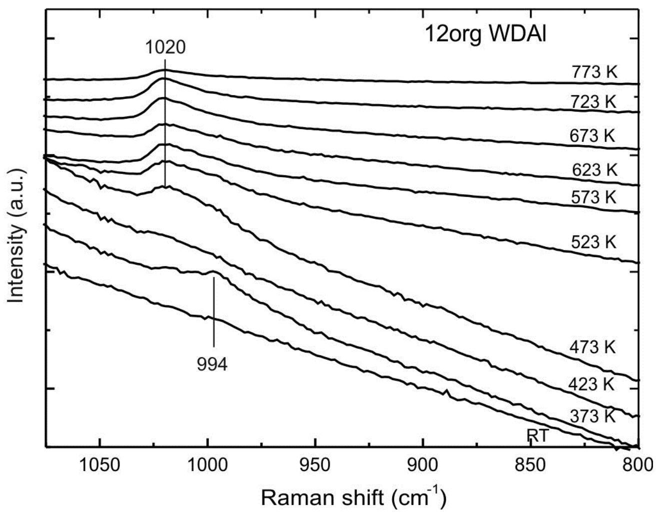

Figure 9S. *In situ* TP-Raman spectra upon heating from R.T. towards 773 K of 12org WDAl

Temperature Programmed Infrared Spectra of Transition Metal Oxide Supports

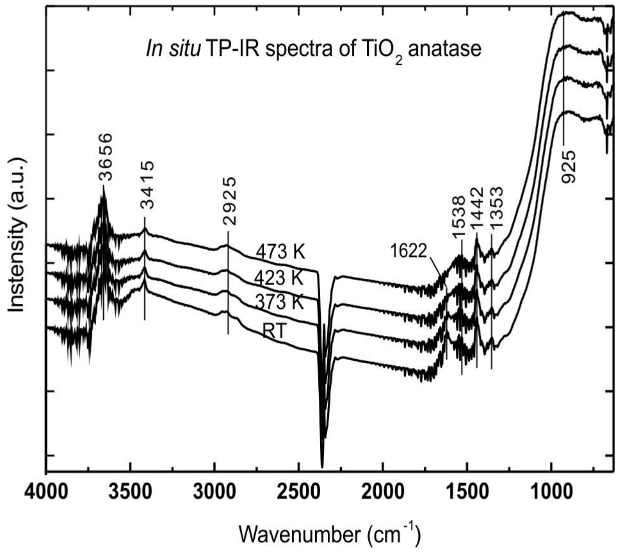

Figure 10S. *In situ* TP-IR spectra upon heating from R.T. towards 773 K of titanium dioxide TiO_2 anatase (Aeroxide® P-18 Evonik Ind., 46.8 ± 0.1 m^2/g).

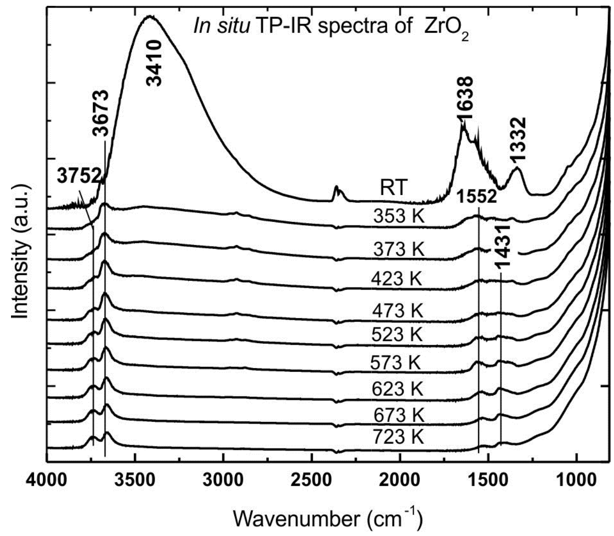

Figure 11S. *In situ* TP-IR spectra upon heating from R.T. towards 773 K of zirconium dioxide ZrO_2 (fumed Evonik Ind., 31.5 ± 0.4 m^2/g).

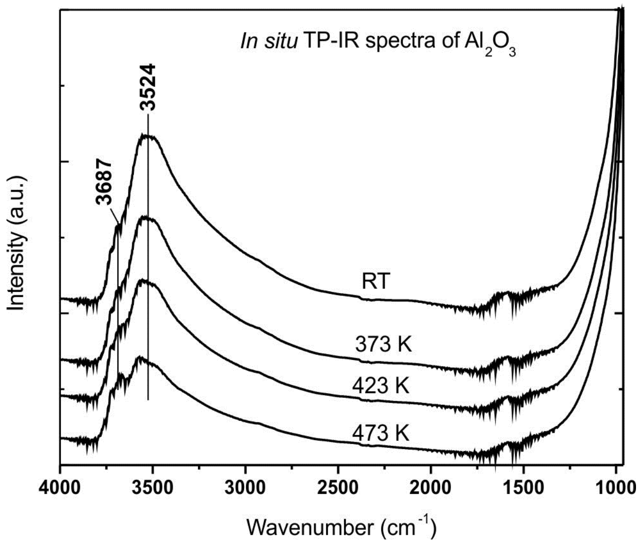

Figure 12S. *In situ* TP-IR spectra upon heating from R.T. towards 773 K of alumina Al_2O_3 (Engelhard, 95.8 ± 0.2 m^2/g).

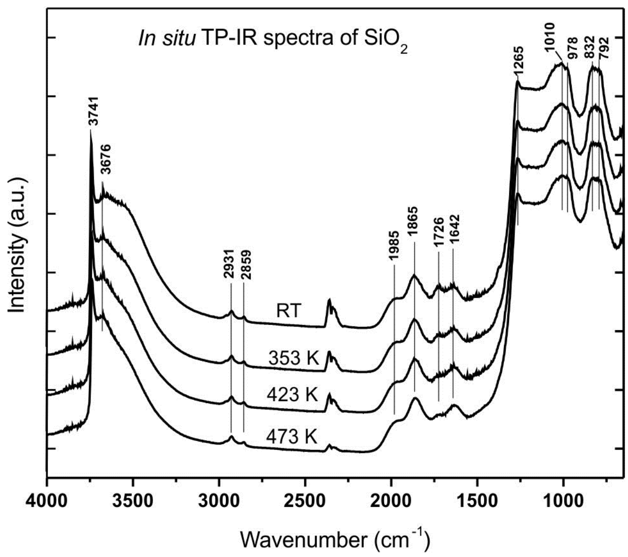

Figure 13S. *In situ* TP-IR spectra upon heating from R.T. towards 773 K of silica SiO_2 (Cab-O-Sil, 328.9 ± 0.8 m^2/g).

Evolution of the Raman Signals of the Wells-Dawson Heteropolyacid Dispersed Over TiO_2 at Various Loadings

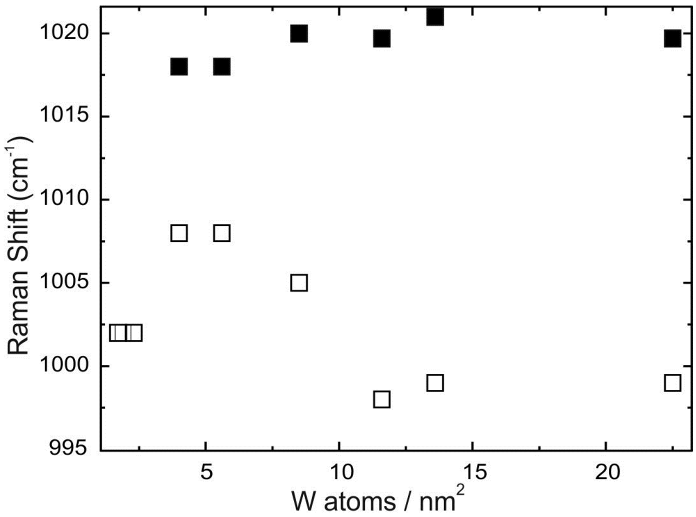

Figure 14S. Evolution of the Raman signals of the Wells-Dawson heteropolyacid dispersed over TiO_2 at various loadings ranging from 1.7 towards 22.5 W_{atoms}/nm^2 in aqueous media and calcined *in situ* at 573 K. Open squares □ indicate Raman signals in the 999-1008 cm^{-1} range and filled squares ■ indicate Raman signals in the 1018-1021 cm^{-1} range