Hydrolytic hydrogenation of cellulose with hydrotreated cesium salts of heteropoly acids and Ru/C – Supporting information

1. FTIR characterisation of native heteropoly acids and non-stoechiometric cesium salts of heteropoly acids calcined at different temperatures.

Representative IR spectra are presented for the commercial HPAs and for the Cs analogues, *viz*. CsSiW (Figure S1) and CsPW (Figure S2) calcined at various temperatures.

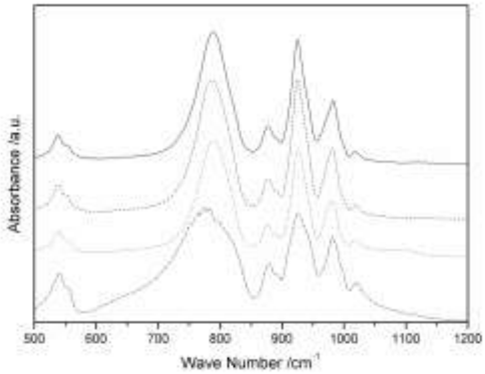

Fig. S1 FTIR spectra from lower to upper: $H_4SiW_{12}O_{40}.xH_2O$, $Cs_{3.5}H_{0.5}SiW_{12}O_{40}.xH_2O$ as prepared, $Cs_{3.5}H_{0.5}SiW_{12}O_{40}.xH_2O$ 300°C and $Cs_{3.5}H_{0.5}SiW_{12}O_{40}.xH_2O$ 600°C.

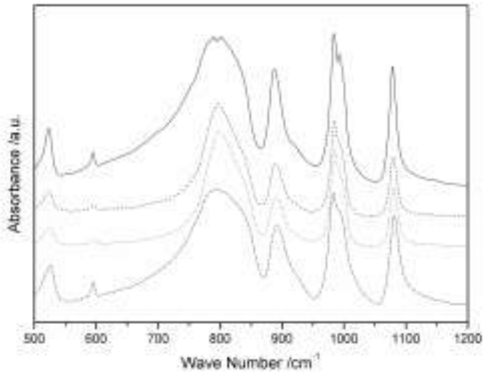

Fig. S2 FTIR spectra from lower to upper: H_3PW, CsPW as prepared, CsPW 300°C and CsPW 600°C.

The band at 982 cm^{-1} in figure S1 is assigned to the stretch vibration of the terminal W=O bond in the CsSiW samples. Presence of Cs^+ causes a slight broadening of the band and a shoulder at 999 cm^{-1} in accordance with literature. The W-O-W bridging bond, connecting two W_3O_{13} trimers in the Keggin anion, gives rise to a vibration at 884 cm^{-1}. The shoulder at 892 cm^{-1} is slightly more pronounced in the Cs containing HPAs, because of the interaction between the polyanion and the Cs-cation.[1] In the spectra of CsPW (figure S2), the vibration band at 1081 cm^{-1} represents the P-O stretch vibration, while the absorptions at 888 and 793 cm^{-1} are assigned to the W-O-W stretch vibration of WO_6 octahedrons that share a vertex or an edge, respectively. The band at 595 cm^{-1} is related to the bending vibration of the O-P-O bond. Finally, the bonds at 985 and 994 cm^{-1} are assigned to the W=O stretch. It is split into these two bands due to interactions with the Cs cation.[2] This splittting becomes slightly more resolved at higher calcination temperatures, probably due to the loss of water from the structure. Thus, inspection of the IR spectra shows no major changes of the characteristic Keggin vibrations for CsSiW or CsPW owing to the high calcination temperature.

See main text for XRD diffractograms of H3PW and CsPW calcined at different temperatures.

FTIR and XRD characterisation of CsSiW and CsPW before and after hydrothermal treatment

Figures S3 and S4 show the FTIR spectra of CsSiW600 and CsPW600 respectively, before and after hydrothermal treatment. For both materials, no significant changes can be observed in the spectra. In all spectra, the characteristic Keggin bands are intact, showing the stability of the polyanions towards the hydrothermal treatment.

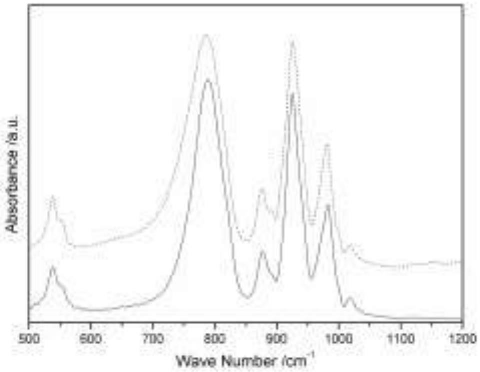

Fig. S3 FTIR spectra of $Cs_{3.5}H_{0.5}SiW_{12}O_{40}.xH_2O$ 600°C before (lower) and after hydrotreatment (upper).

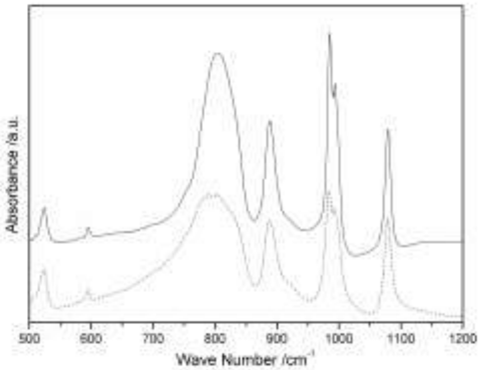

Fig. S4 FTIR spectra of $Cs_{2.5}H_{0.5}PW_{12}O_{40}.xH_2O$ 600°C before (lower) and after hydrotreatment (upper).

Finally, figure S5 shows the XRD diffractograms for CsPW600 before and after hydrothermal treatment. It can be seen that the treatment does not induce any changes in the anatase crystal phase, though it seems that it does cause a slight increase in particle dimensions and/or crystallinity.

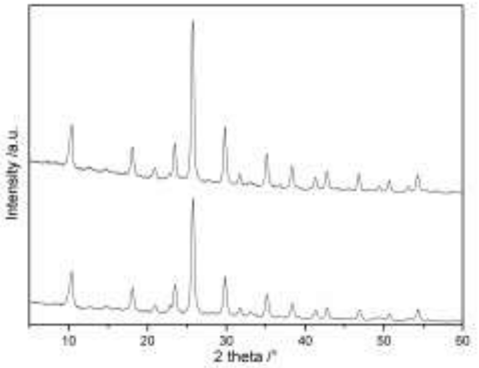

Fig. S5 XRD patterns of CsPW 600°C (lower) and HT CsPW 600°C (upper), showing the influence of hydrotreatment

References

1 L.R. Pizzio and M.N. Blanco, *Microporous Mesoporous Mater.*, 2007, **103**, 40-47.
2 L.R. Pizzio and M.N. Blanco, *Appl. Catal.*, *A*, 2003, **255**, 265-277.