Elucidating and exploiting the chemistry of Keggin heteropolyacids in the methanol-to-DME conversion: enabling the bulk reaction thanks to *operando* Raman

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Supplementary Information

Thermogravimetric and thermodifferential profiles (under air, 10 °C/min) of $H_3PW_{12}O_{40}.xH_2O$ *(Sigma-Aldrich) after 1 night under vacuum (<5000 Pa) at room temperature.*

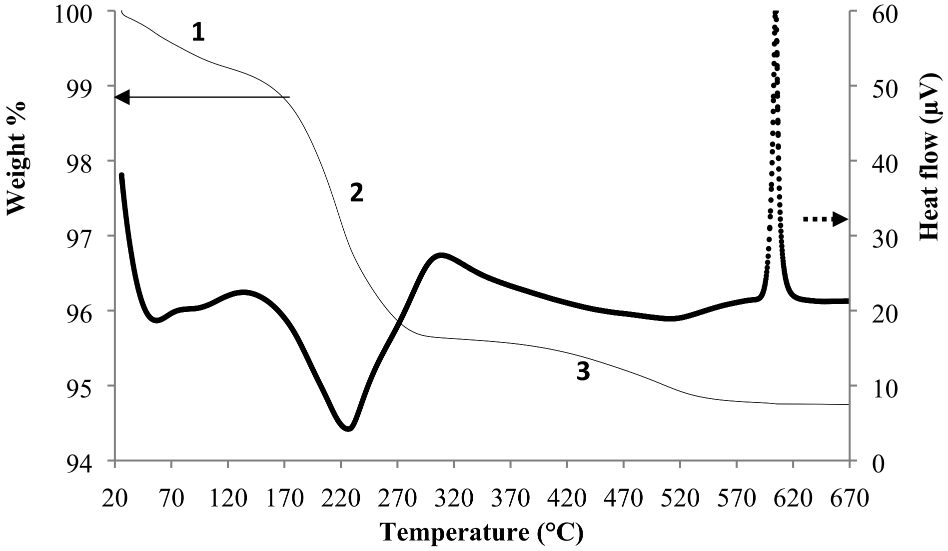

Fig. S1. Thermogravimetric (full line) and thermodifferential (dotted line) profiles (under air, 10 °C/min) of $H_3PW_{12}O_{40}.xH_2O$ (Sigma-Aldrich) after 1 night under vacuum (<5000 Pa) at room temperature.

These profiles allow:

1) **Determining the number of moles of crystallisation water per mole of $H_3PW_{12}O_{40}$ Keggin units.**

The powder contains 0.7% of physisorbed water (weight loss 1 on the thermogravimetric profile) and 3.7% of crystallisation water (weight loss 2 on the thermogravimetric profile).

If MM = molar mass [g/mol] and n = number of moles, the number of crystallisation water molecules per Keggin unit (x) in $H_3PW_{12}O_{40}.xH_2O$ is determined as follows:

MM of $H_3PW_{12}O_{40}.xH_2O$ = MM of $H_3PW_{12}O_{40}$ + n of crystallisation H_2O*MM H_2O + n of physisorbed H_2O*MM H_2O

= 2880.05 + x*18 + y*18 = 2880.05 + 0.037*MM of $H_3PW_{12}O_{40}.xH_2O$ + 0.007*MM of $H_3PW_{12}O_{40}.xH_2O$

= 2880.05 / (1 – 0.037 – 0.007) = 3012.6 g/mol.

x = (0.037*3012.6) / 18 = 6.2 mol of crystallisation water per mol of $H_3PW_{12}O_{40}$ Keggin units.

This value of x has been rounded to 6.

2) **Determining the temperature at which $H_3PW_{12}O_{40}$ has to be pre-treated in order to completely remove its crystallisation water but without losing its acidic protons.**

320 °C has been chosen as the pre-treatment temperature. Indeed, at 320 °C, weight loss 2 on the thermogravimetric profile (related to the loss of crystallisation water) is complete while weight loss 3 (related to the loss of the acidic protons in the form of water) has not yet started. On the thermodifferential profile, the endothermic peak related to weight loss 2 is also complete at 320 °C.

Thermogravimetric and thermodifferential profiles (under air, 10 °C/min) of $H_4SiW_{12}O_{40}.xH_2O$ (Sigma-Aldrich) after 1 night under vacuum (<5000 Pa) at room temperature.

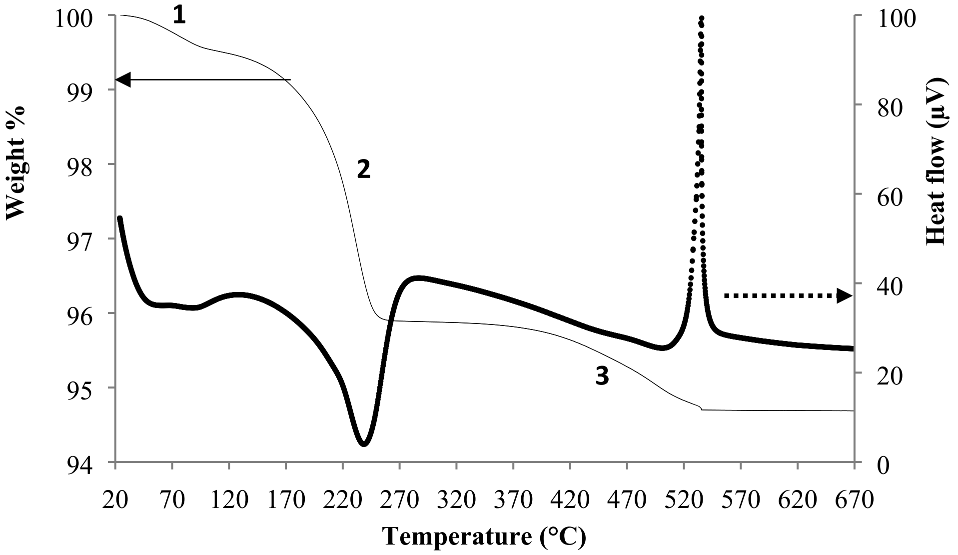

Fig. S2. Thermogravimetric (full line) and thermodifferential (dotted line) profiles (under air, 10 °C/min) of $H_4SiW_{12}O_{40}.xH_2O$ (Sigma-Aldrich) after 1 night under vacuum (<5000 Pa) at room temperature.

These profiles allow:

1) **Determining the number of moles of crystallisation water per mole of $H_4SiW_{12}O_{40}$ Keggin units.**

The powder contains 0.4% of physisorbed water (weight loss 1 on the thermogravimetric profile) and 3.6% of crystallisation water (weight loss 2 on the thermogravimetric profile).

If MM = molar mass [g/mol] and n = number of moles, the number of crystallisation water molecules per Keggin unit (x) in $H_4SiW_{12}O_{40}.xH_2O$ is determined as follows:

MM of $H_4SiW_{12}O_{40}.xH_2O$ = MM of $H_4SiW_{12}O_{40}$ + n of crystallisation H_2O*MM H_2O + n of physisorbed H_2O*MM H_2O

= 2878.17 + x*18 + y*18 = 2878.17 + 0.036*MM of $H_4SiW_{12}O_{40}.xH_2O$ + 0.004*MM of $H_4SiW_{12}O_{40}.xH_2O$

= 2878.17 / (1 – 0.036 – 0.004) = 2998.1 g/mol.

x = (0.036*2998.1) / 18 = 6 mol of crystallisation water per mol of $H_4SiW_{12}O_{40}$ Keggin units.

2) Determining the temperature at which $H_4SiW_{12}O_{40}$ has to be pre-treated in order to completely remove its crystallisation water but without losing its acidic protons.

300 °C has been chosen as the pre-treatment temperature. Indeed, at 300 °C, weight loss 2 on the thermogravimetric profile (related to the loss of crystallisation water) is complete while weight loss 3 (related to the loss of the acidic protons in the form of water) has not yet started. On the thermodifferential profile, the endothermic peak related to weight loss 2 is also complete at 300 °C.

Raman spectra as a function of time in the region from 2500 to 4000 cm^{-1} of HPW12.nH$_2$O (with 3<n<6) at 150 °C upon exposure to a flow of methanol (10 vol.% in nitrogen).

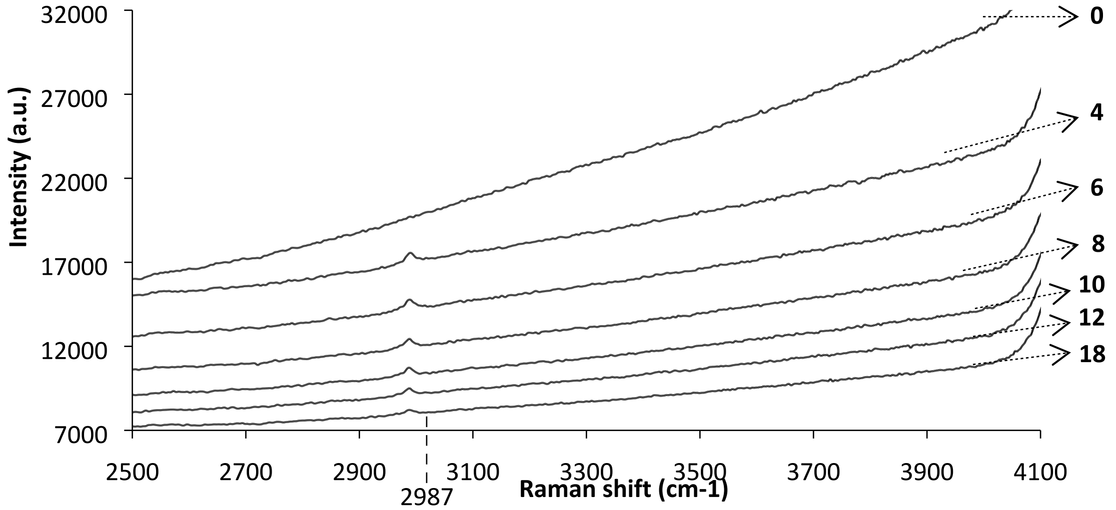

Fig. S3. Raman spectra of HPW12.nH$_2$O (with 3<n<6) at 150 °C upon exposure to a flow of methanol (10 vol.% in nitrogen) in the region from 2500 to 4000 cm^{-1} characteristic of C-H and O-H stretches.

A peak at 2987 cm^{-1} attributed to the symmetric methyl stretch[21] appears as soon as HPW12 gets exposed to methanol, reflecting the latter's adsorption onto the catalyst (not possible to distinguish between surface adsorption and adsorption within the bulk).