## Keggin $H_3PW_{12}O_{40}$ pore blockage by coke can be reversible in the gas phase methanol-to-DME reaction

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## **Supplementary Information**

• Full *in situ* Raman spectra of HPW12 (having already been exposed to methanol at 50 °C) before (dotted line) and after (full line) heating from 50 to 350 °C under pure nitrogen.



Figure S1. Full *in situ* Raman spectra of HPW12 (having already been exposed to methanol at 50 °C) before (dotted line) and after (full line) heating from 50 to 350 °C under pure nitrogen.

• Thermogravimetric and thermodifferential profiles of pre-heated (Figure S2) and pre-coked (Figure S3) HPW12.



Figure S2. Thermogravimetric (full line) and thermodifferential (dotted line) profiles of HPW12 pre-heated at 350 °C.

For 1 g of HPW12 pre-heated at 350 °C introduced:

- Weight loss corresponding to protonic water = 98.68% \* 1 97.92% \* 1 = 0.0076 g
- Weight of anhydrous H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> = 98.68% \* 1 = 0.9868 g

 $\rightarrow$  Percentage of protonic water within anhydrous H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> = (0.0076/0.9868) \* 100 = 0.77%



Figure S3. Thermogravimetric (full line) and thermodifferential (dotted line) profiles of HPW12 pre-coked at 350 °C.

For 1 g of HPW12 pre-coked at 350 °C introduced:

- Weight loss corresponding to protonic water and coke = 98.97% \* 1 97.89% \* 1 = 0.0108 g
- Weight of anhydrous coked H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> = 98.97% \* 1 = 0.9897 g
- Weight of anhydrous  $H_3PW_{12}O_{40} = (0.9897 0.0108) / (1 0.77\%) = 0.9865 g$
- Weight of protonic water = **0.77%** \* 0.9865 = 0.0076 g
- Weight of coke = 0.0108 0.0076 = 0.0032 g

## $\rightarrow$ Percentage of coke within HPW12 pre-coked at 350 °C = (0.0032 / 1) \* 100 = 0.32%

## • NH<sub>3</sub>-TPD profiles.

