

Ammonium-substitution for successfully activating the bulk of Keggin acid salts in the 1-butanol dehydration

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Supporting information

In situ IR spectroscopy, H3PW:

On the spectra between 4000 and 2500 cm^{-1} (figure SI1), one observes bands between 2800 and 3000 cm^{-1} that correspond to stretching of CH_3 from 1-butanol in gas phase and adsorbed at the surface. Additionally between 3100 and 3600 cm^{-1} appear large bands that correspond to OH stretching of 1-butanol and of remaining water traces. We cannot see any new band in this case, so we have no formal evidence of 1-butanol entering the bulk.

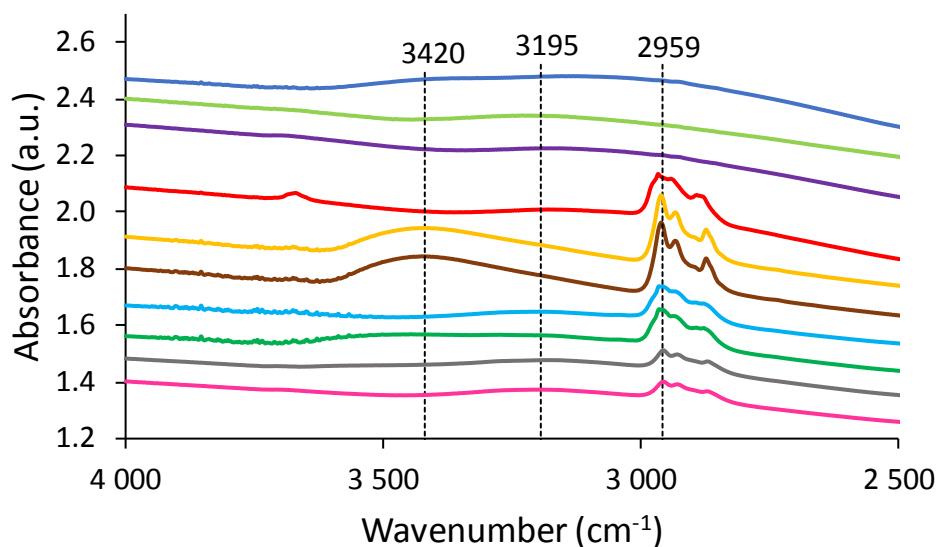


Figure S11 : Evolution of the IR spectrum of H3PW during the bulk activation procedure between 2500 and 4000 cm^{-1} : 1 Vacuum 21.5 °C, 2 Vacuum 320 °C, 3 Vacuum 114 °C, 4 BuOH 1.5 Torr 134 °C, 5 BuOH 1.5 Torr Room Temperature, 6 BuOH 1.5 Torr 19.8 °C, 7 BuOH 1.5 Torr 140 °C, 8 BuOH 1.5 Torr 32 °C, 9 Vacuum 25 °C, 10 Vacuum 113 °C

In situ Raman spectroscopy, (NH₄)₂.5PW:

In the case of (NH₄)₂.5PW, the thermal treatment does not lead to a visible modification of the position of the band $\text{W}=\text{O}_t$ (figure S12a to c). The 1-butanol exposure does not lead to any shift neither (figure S12d). The $\text{W}=\text{O}_t$ band in interaction with the remaining H^+ is probably too low and is hidden by the $\text{W}=\text{O}_t$ band in interaction with NH_4^+ that does not shift. Even if a small part of the $\text{W}=\text{O}_t$ band shifts due to H^+ dehydration, it is not observed on the spectrum.

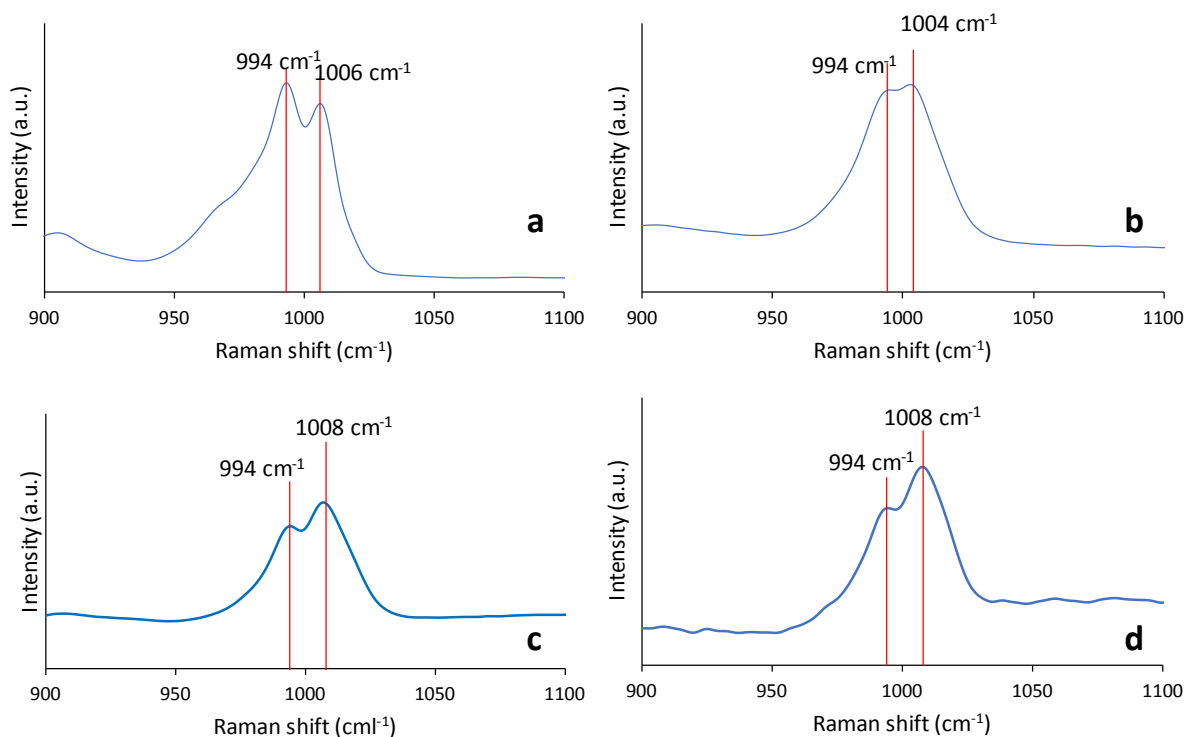


Figure S12 : Raman spectrums of $(\text{NH}_4)_2.5\text{PW}$ during the bulk activation procedure. **a** : at 25 °C under N_2 , **b** : at 320 °C under N_2 , **c** : back to 25 °C after thermal treatment under N_2 , **d** : at 25 °C after thermal treatment under 1% 1-butanol in N_2 .

1-Butanol conversion of H3PW with and without 1-butanol exposure:

Comparing the activity of the original HPA H3PW with and without 1-butanol exposure (figure SI3), it appears that the gain in 1-butanol conversion is not so important at each temperature explored, confirming what was observed during *in situ* characterizations, namely that the bulk activation does not take place properly for 1-butanol in the presence of H3PW.

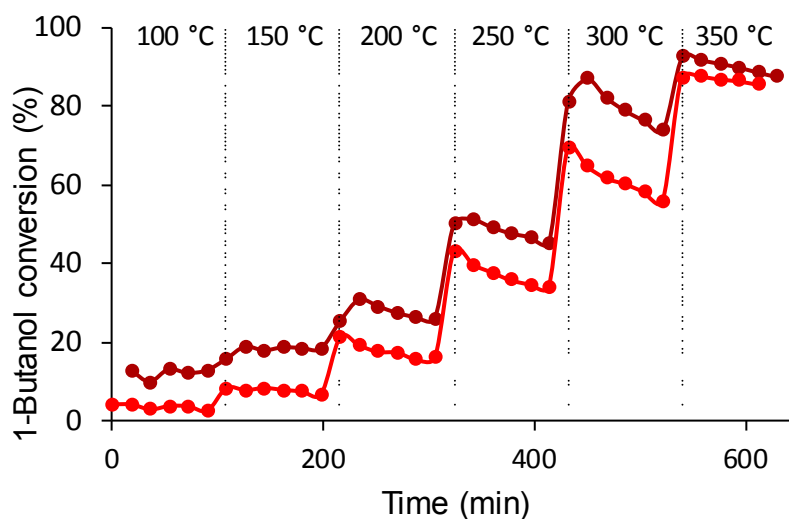


Figure SI3 : Catalytic activity of *H3PW* BuOH exposure compared to *H3PW* no exposure.

N₂ physisorption measurements :

All samples were analysed by N₂ physisorption to compare their specific surface area (figure SI4). All specific surface areas are below 2 m².g⁻¹, except for (NH₄)₂PW₁₂O₄₀ (S_{BET} = 16 m².g⁻¹) and for H₃PW₁₂O₄₀ (S_{BET} = 4 m².g⁻¹). An increase in specific surface area with x cannot explain the gain in activity.

Samples H₃PW₁₂O₄₀ and (NH₄)₂HPW₁₂O₄₀ were also analysed by N₂ physisorption after thermal treatment at 320 °C and 1-butanol exposure at 25 °C, to verify that these steps could not modify the texture of the catalysts and increase the specific surface area. The S_{BET} of both samples were very low (< 1 m².g⁻¹). These measurements erase all doubts concerning the influence of specific surface area on an increase in the activity.

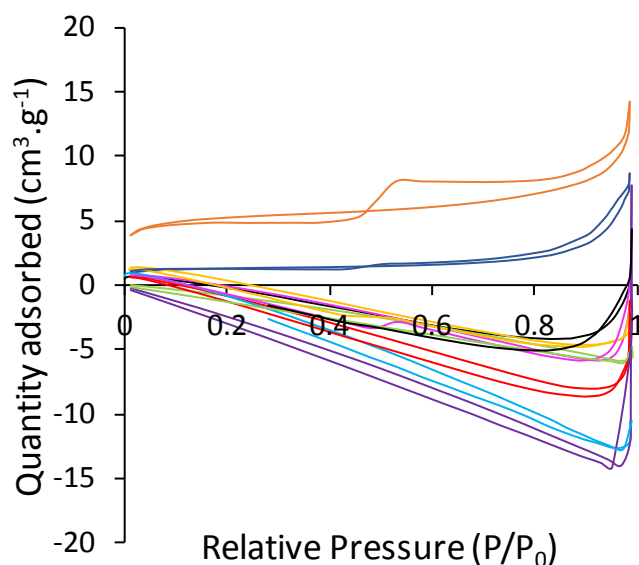


Figure S14 : Quantity of N_2 adsorbed as a function of relative pressure, after degassing at $150\text{ }^\circ\text{C}$ under vacuum for 10 hours, for samples $(NH_4)_{0.5}H_{2.5}PW_{12}O_{40}$, $(NH_4)H_2PW_{12}O_{40}$, $(NH_4)_{1.5}H_{1.5}PW_{12}O_{40}$, $(NH_4)_2HPW_{12}O_{40}$, $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40}$, $(NH_4)_3PW_{12}O_{40}$, $H_3PW_{12}O_{40}$, $(NH_4)_2HPW_{12}O_{40}$ exp BuOH, and $H_3PW_{12}O_{40}$ exp BuOH.

Selectivities:

For all catalysts, at low temperature, the dibutylether is favoured, and when increasing the temperature, butenes are more and more favoured (figure S15). Concerning $(NH_4)_{2.5}PW_{12}O_{40}$ BuOH exposure, the shift of selectivities from dibutylether to butenes takes place at a higher temperature than for the samples with other values of x. It can be due to the weaker acidity of this catalyst (as revealed by the NH_3 -TPD), so the inversion of selectivities would need a higher temperature to compensate the weak acidity. Concerning all other catalysts, the profiles of selectivities in function of the temperature are similar and the major difference is the high selectivity around 95 % toward dibutylether for $(NH_4)_2HPW_{12}O_{40}$ BuOH exposure at low temperature compared to a value around 70 % for $H_3PW_{12}O_{40}$ BuOH exposure and $(NH_4)_2HPW_{12}O_{40}$ no exposure. The bulk activation through 1-Butanol exposure

helps increasing the selectivity towards dibutylether at low temperature and dibutylether is still present at higher temperature (300-350 °C) where only butenes are present for other catalysts.

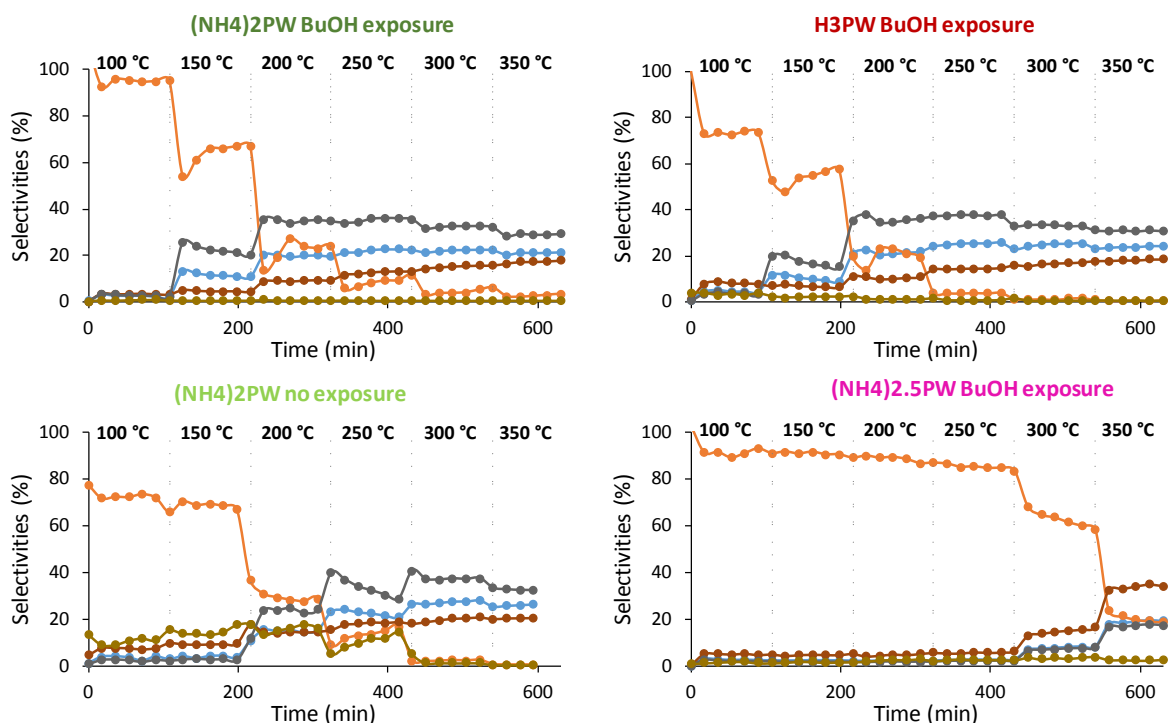


Figure S15 : Selectivities for *dibutylether*, *1-butene*, *trans-2-butene*, *cis-2-butene* and *isobutene*, for the catalysts $(\text{NH}_4)_2\text{PW}$ BuOH exposure, $(\text{NH}_4)_2\text{PW}$ no exposure, $(\text{NH}_4)_2.5\text{PW}$ BuOH exposure and H3PW BuOH exposure.

Carbon balance:

Figure S16 shows that the carbon balance decreases progressively when the temperature increases, suggesting that there is some coke formation occurring more and more in such conditions. The carbon balance of ammonium-salts is the same as or higher than for the H3PW catalyst, meaning that there is no additional coke formation related to the presence of ammonium species. It is important to notice that catalysts exposed to 1-butanol have a lower carbon balance than without 1-butanol exposure. The same phenomenon was reported during methanol dehydration after bulk activation of HPA [ref 30 of

the main paper]. There is more coke deposition related to higher activity after bulk activation, but the presence of numerous protons progressively reachable in the bulk tends to limit the deactivation and the loss of catalytic activity along the time.

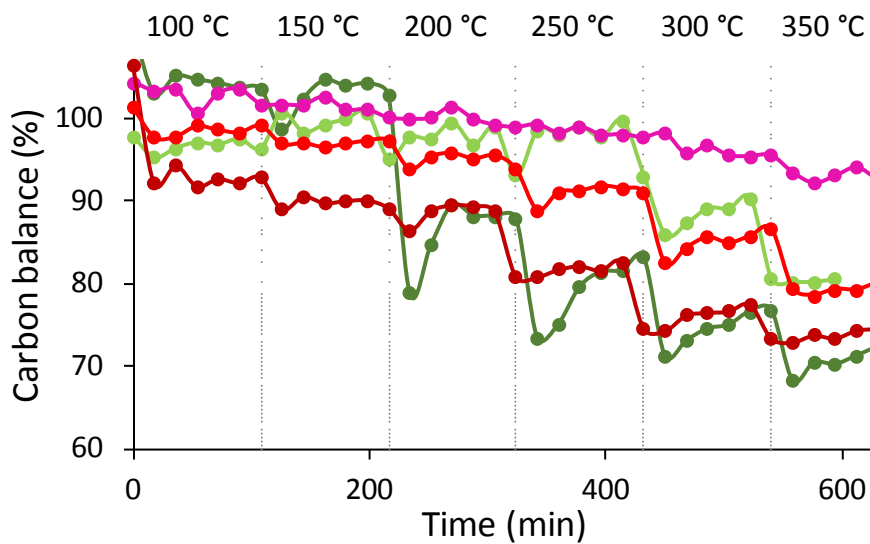


Figure S16 : Carbon balance for $(\text{NH}_4)_2\text{PW}$ BuOH exposure, $(\text{NH}_4)_2\text{PW}$ no exposure, $(\text{NH}_4)_2.5\text{PW}$ BuOH exposure, H3PW BuOH exposure and H3PW no exposure.