

Supporting Information

Convenient synthesis of $\text{Cu}_3(\text{BTC})_2$ encapsulated Keggin heteropolyacid nanomaterial for application in catalysis

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Experimental procedures

A solution was prepared by dissolving $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Sigma-Aldrich) (5.17 mmol, 1.215 g) and $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ (Fluka) (0.28 mmol, 0.8 g) in 10 ml of deionized water and $\text{H}_3\text{-BTC}$ (Acros) (2.77 mmol, 0.5825 g) in 13.3 ml of absolute ethanol (BDH) via vigorous stirring. The dilution was varied in order to vary the nucleation and growth kinetics of the nanocrystallites. The diluted solutions contained $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1.44 mmol, 0.349 g) and $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ (0.0082 mmol, 0.231 g) in 10 ml of deionised water and $\text{H}_3\text{-BTC}$ (0.856 mmol, 0.180 g) in 10 ml of absolute ethanol. The solution was frozen in liquid nitrogen, shortly after mixing the reagents. The solid materials were then dried under vacuum for 18 h. The collected products were washed through centrifugation and redispersion. The products were dried in an oven at 50 °C for 48 h. For comparison, $\text{HPW}/\text{Cu}_3(\text{BTC})_2$ crystals were also synthesised under hydrothermal conditions at 110 °C for 16 h in Teflon-lined stainless steel autoclaves. The as-synthesised materials were characterised by a scanning electron microscope (SEM, Philips XL-30 FEG equipped with a tungsten filament), powder X-ray diffractometer (XRD, STOE StadiP diffractometer in high-throughput transmission mode employing Cu K α 1 radiation), Attenuated Total Reflection-Infrared spectrometer (ATR-IR, Bruker Vertex 70 V equipped with a diamond golden gate ATR cell), solid-state MAS NMR spectrometer (Bruker AMX300, 7.0 T), thermogravimetric instrument (TGA, Q 500) and N_2 adsorption instrument (Micromeritics Tristar 3000). Esterification reactions were performed with acetic acid (1 mol) and 1-propanol (40 mol) in close vials inserted into a copper block. The reaction temperature was set at 60 °C and the content magnetically stirred. The weight of solid catalysts (as-synthesized $\text{HPA}/\text{Cu}_3(\text{BTC})_2$ nanocrystals, ultrastable Y (CBV 720) zeolite and conventional hydrothermally synthesised $\text{HPA}/\text{Cu}_3(\text{BTC})_2$) was 2.23 wt%. Aliquots of the reaction mixture were periodically withdrawn with a microsyringe at the intervals of 1, 3, 5 and 7 h throughout the reaction. Clear aliquots were obtained via centrifugation prior to gas chromatography analysis (GC, Chrompack 8760 WCOT Fused Silica capillary column, 30 m long). After the reaction, the catalyst was washed through a series of centrifugation and redispersion steps, and dried in an oven at 50 °C for subsequent recycling experiments.

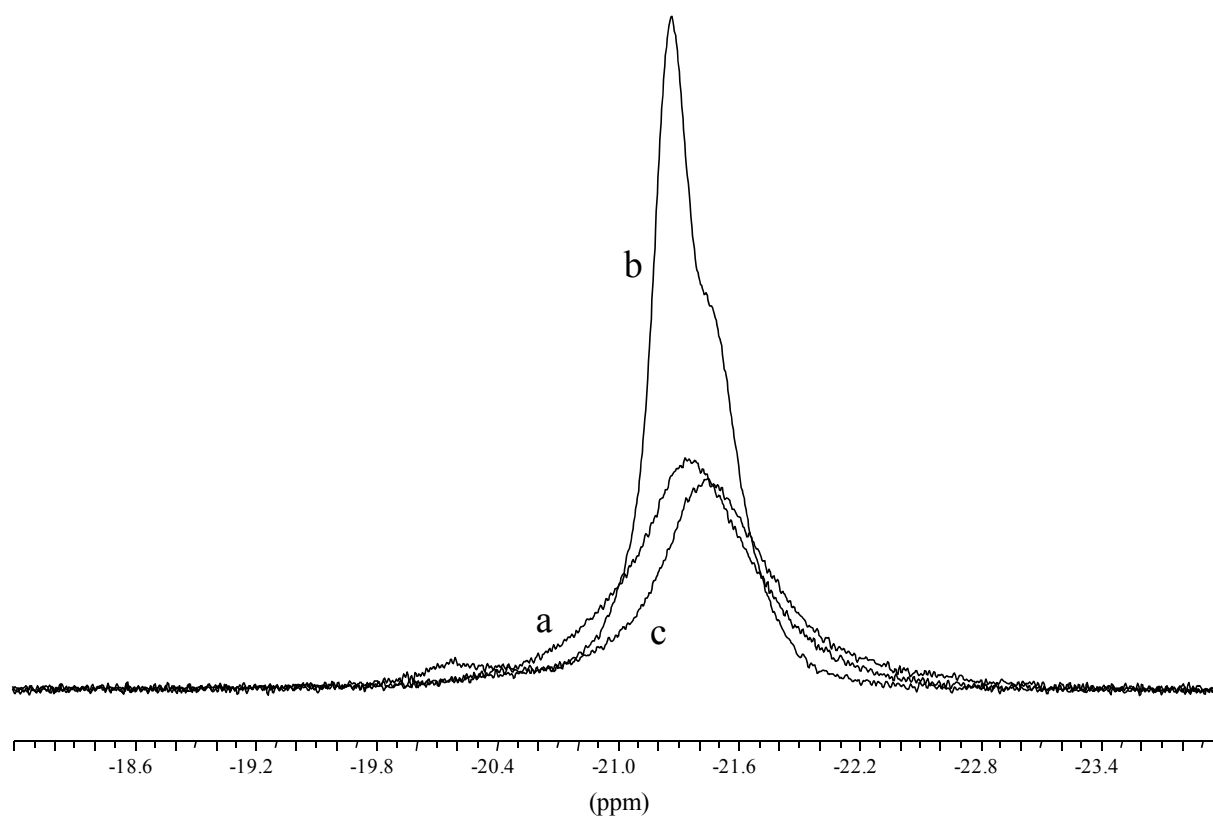


Figure S1. ^{31}P solid-state MAS NMR spectra of HPW/ $\text{Cu}_3(\text{BTC})_2$ prepared from (a) hydrothermal synthesis, (b) room temperature synthesis for 16 h and (c) room temperature synthesis with quenching of concentrated solution 1 minute after mixing reactants.

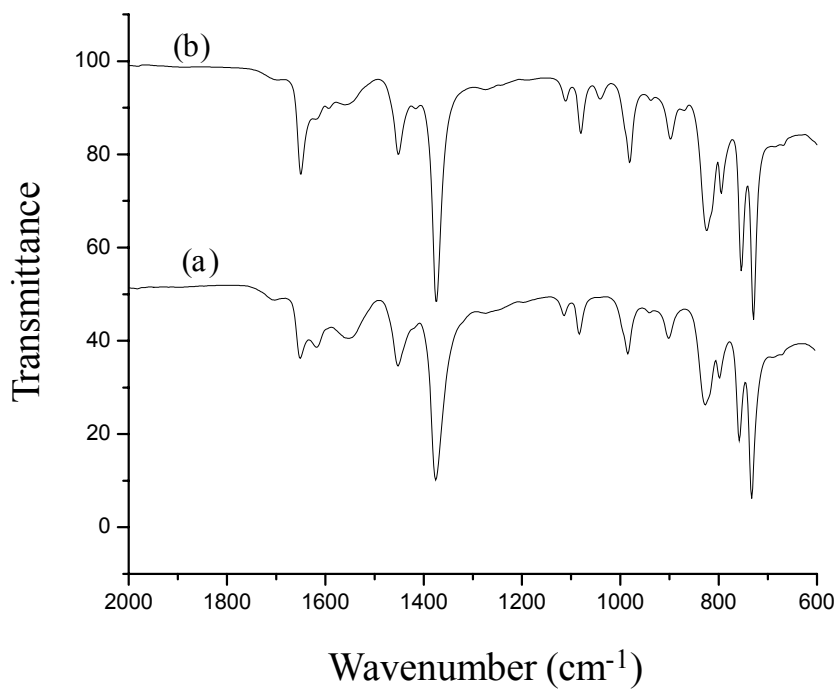


Figure S2. ATR-IR spectra of HPW/Cu₃(BTC)₂ prepared from (a) hydrothermal synthesis and (b) room temperature synthesis with quenching of concentrated solution 1 minute after mixing reactants.

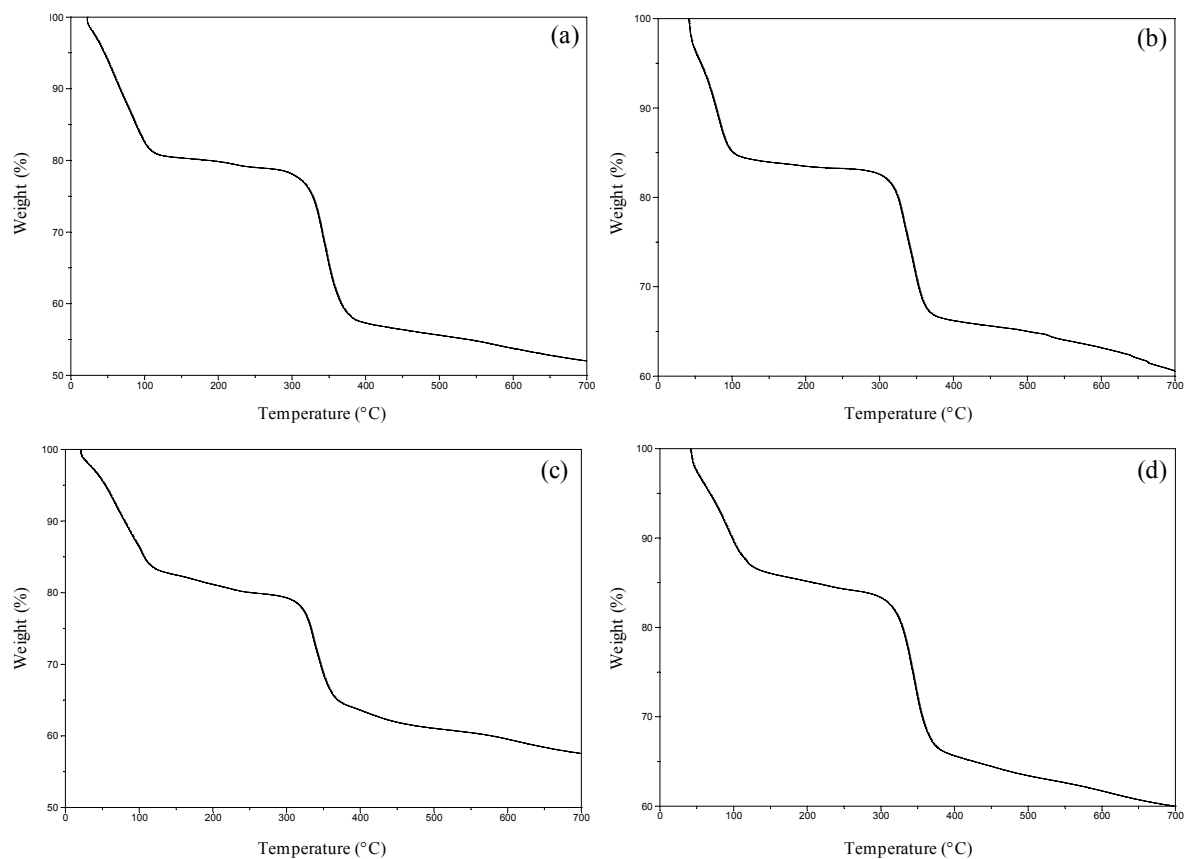


Figure S3. The thermogravimetric analysis curves of HPW/Cu₃(BTC)₂ prepared from (a) hydrothermal synthesis, (b) room temperature synthesis for 16 h, room temperature synthesis with quenching of (c) concentrated and (d) diluted solutions 1 minute after mixing reactants.

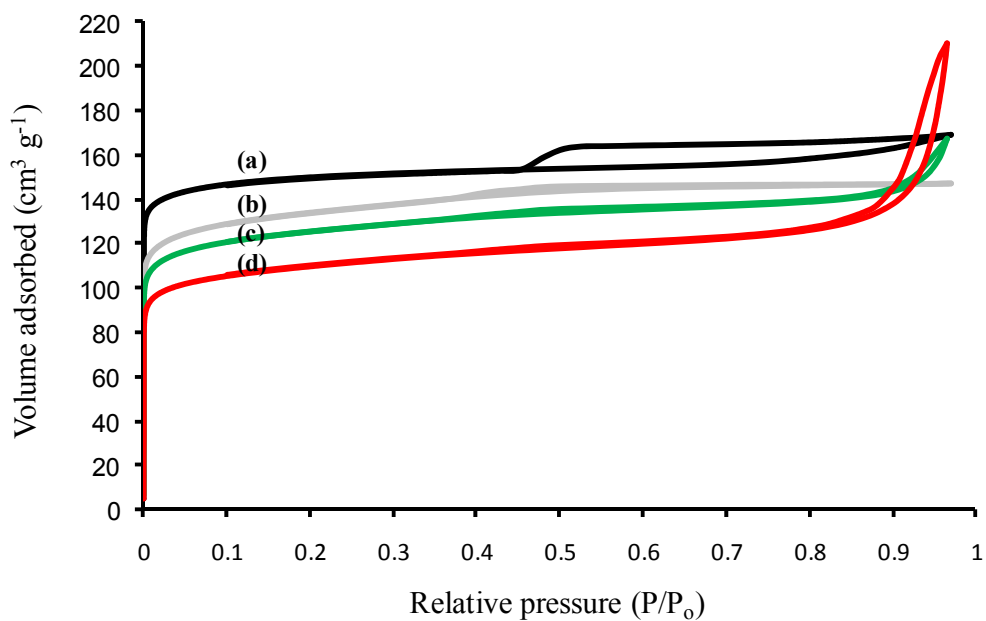


Figure S4. N₂ adsorption-desorption isotherms of HPW/Cu₃(BTC)₂ prepared from (a) hydrothermal synthesis, (b) room temperature synthesis for 16 h, room temperature synthesis with quenching of (c) concentrated and (d) diluted solutions 1 minute after mixing reactants.

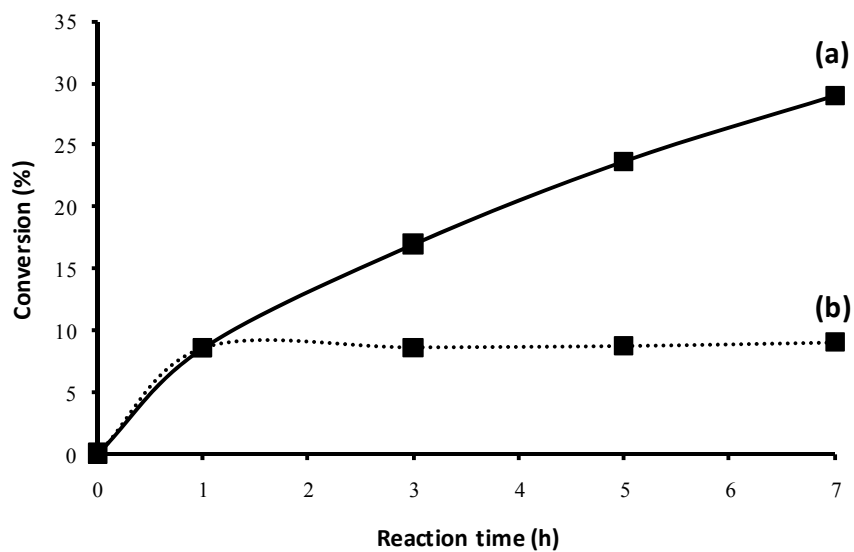


Figure S5. Esterification reaction of acetic acid with 1-propanol at 60 °C. Conversion of acetic acid catalysed by (a) 65 nm-sized HPW/Cu₃(BTC)₂ and (b) after removal of the solid catalyst by centrifugation after 1 h.

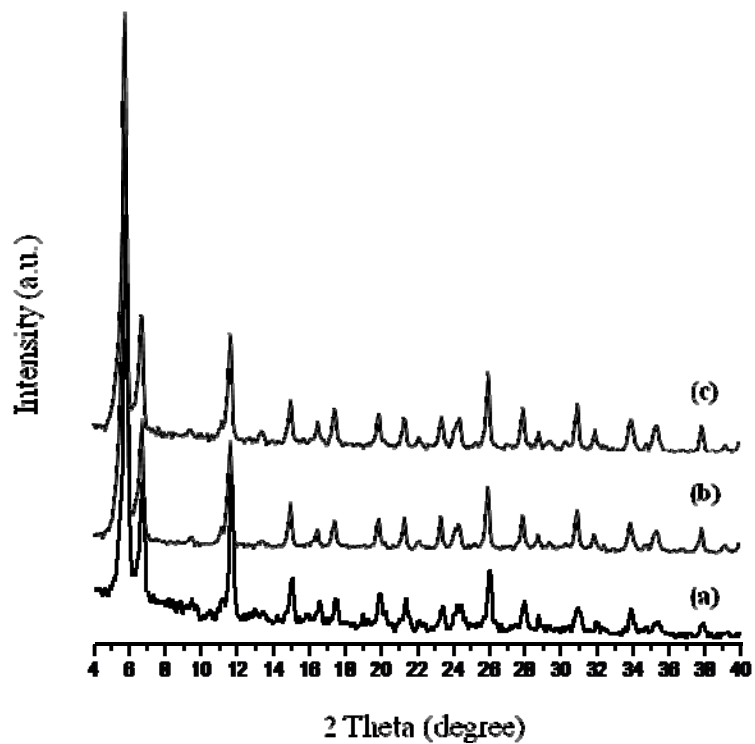


Figure S6. XRD patterns of (a) as-synthesised 65 nm-sized HPW/Cu₃(BTC)₂, (b) after the first catalytic test and (c) after the second catalytic test.

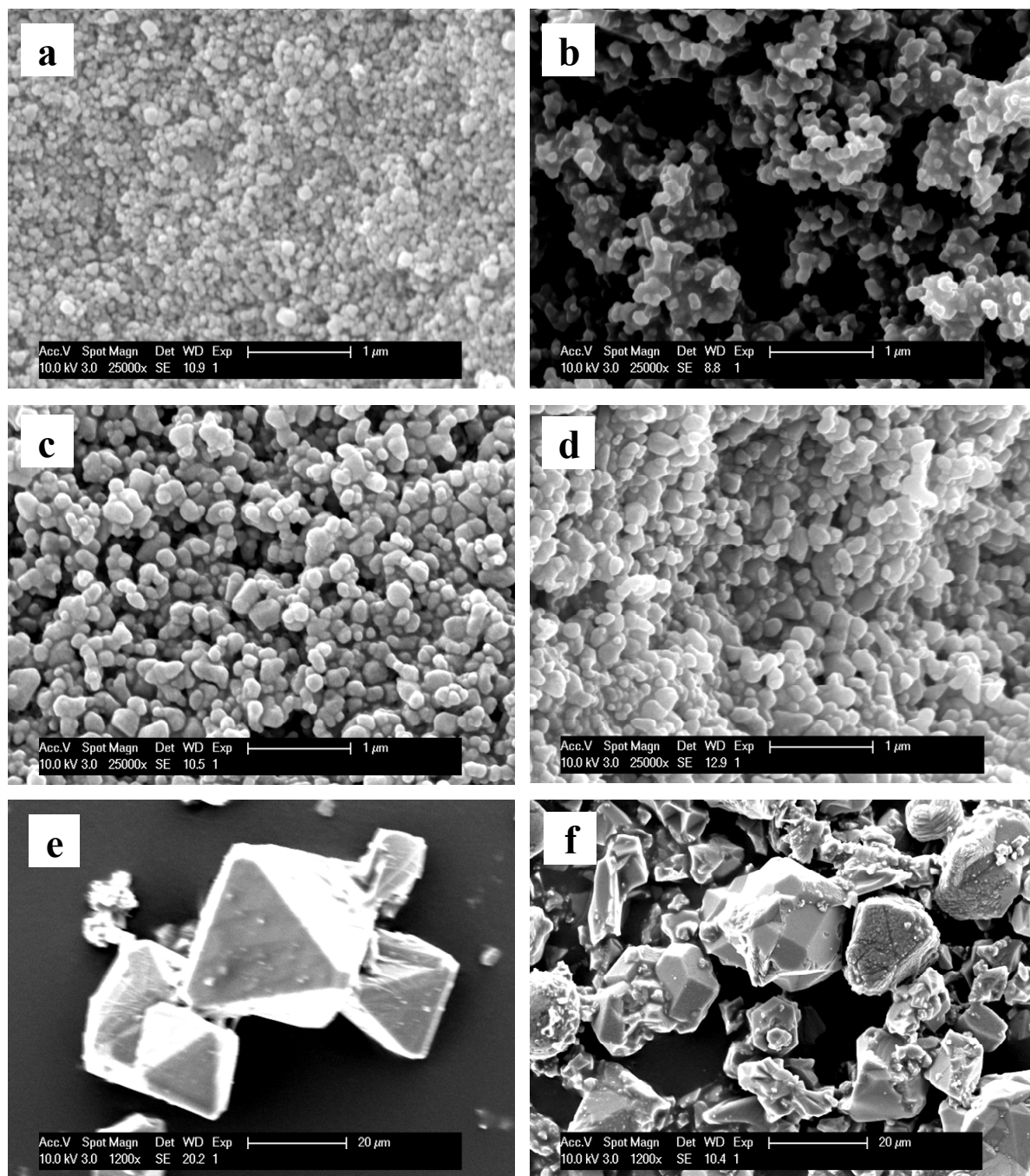


Figure S7. SEM images of (a) as-synthesised 65 nm-sized HPW/Cu₃(BTC)₂, (b) after first catalytic testing (molar ratio of acetic acid to 1-propanol = 1:40); 65 nm-sized HPW/Cu₃(BTC)₂ after (c) first and (d) second catalytic testing with increased acetic acid concentration (molar ratio of acetic acid to 1-propanol = 1:2), (e) hydrothermally as-synthesised HPW/Cu₃(BTC)₂ and (f) after first catalytic testing performed at higher acetic acid concentration (molar ratio of acetic acid to 1-propanol = 1:2).