

# Effect of Keggin polyoxometalate on Cu(II) speciation and its role in the assembly of $\text{Cu}_3(\text{BTC})_2$ metal organic framework

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HKUST-1 is one of the popular metal organic frameworks (MOF). The formation of this MOF is significantly accelerated by adding Keggin polyoxometalate anions to the synthesis solution. In this paper we investigated the chemistry behind this observation. Upon addition of Keggin type  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  heteropolyacid the speciation of Cu(II) cations in ethanol:H<sub>2</sub>O mixture drastically changes. Combining EPR and XANES measurements with accurate pH measurements and prediction of  $\text{Cu}^{2+}$  hydrolysis provides strong evidence for surface induced hydrolysis and consequent dimerisation of monomeric Cu species on Keggin ions in acidic conditions. This enables paddle wheel formation, hence explaining the instantaneous precipitation of  $\text{Cu}_3\text{BTC}_2$  at room temperature and the systematic encapsulation of Keggin ions in its pores.

## 1. Introduction

Heteropolyacids (HPAs) belong to the polyoxometalate compounds presenting intriguing structure<sup>1-4</sup>, excellent coordination capabilities<sup>5-9</sup> and strong catalytic activity. Heterogeneous catalytic applications of HPA have been almost exclusively based on insoluble HPA salts, (post-) synthetic modifications of MOFs<sup>10-15</sup> and zeolites<sup>16-18</sup>. One very elegant way to introduce HPA into MOFs is to exploit the ability of Keggin type HPA to serve as direct templates for the formation of porous HKUST-1 frameworks<sup>19-21</sup>. Within minutes after mixing an acidic ethanol/water based solution of Cu-decorated Keggin anions ( $\text{H}_{8-x}\text{XM}_{12}\text{O}_{40}$ ); X =  $\text{P}^{5+}/\text{Si}^{4+}$  and M =  $\text{W}^{6+}/\text{Mo}^{6+}$  with the organic linker 1,3,5-benzene-tricarboxylic-acid (BTC), micron-sized, highly crystalline  $\text{Cu}_3(\text{BTC})_2$  containing Keggin ions can be collected.

Direct structure templation is achieved by an agent with the ability to actively compile an assembly of building blocks into the desired arrangement. Though organic templation in all its variations is a well known approach for zeolite synthesis, reports on inorganic (HPA-based<sup>20</sup>) templation in metal organic frameworks are rare. A molecular-level understanding of the self-organization of  $\text{Cu}^{2+}$  species around the HPAs leading to the instant formation of a porous  $\text{Cu}_3\text{BTC}_2$  framework will allow to exploit their structure directing action, thereby enabling or facilitating the synthesis of new materials and applications.

## 2. Experimental

All the chemicals were obtained from Fluka except for 1,3,5-benzene-tri-carboxylic-acid (Acros organics) and absolute ethanol (VWR). Millipore water was used for all sample

preparations.

To elucidate the mechanism of the templating action of Keggin ions a set of standardized MOF synthesis solutions with  $[\text{Cu}]/[\text{PW}_{12}\text{O}_{40}]$  ratios varying between 1 and 100 were prepared. All solutions were based on a 0.1M  $\text{NaNO}_3$  in 50% vol ethanol in water. Each synthesis solution was prepared by addition 20 ml of a  $10^{-3}$  M  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  solution to the necessary amount of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  weighed in 50 ml centrifuge tubes. Upon complete dissolution of the Cu salt, 30 ml of  $1.259 \times 10^{-2}$  M 1,3,5- $\text{H}_3\text{BTC}$  solution was added. After thorough mixing the synthesis solutions were aged under quiescent conditions at RT for 5 to 270 days.

For all systems several parameters, such as pH, Cu and W concentration, were recorded as function of time to allow evaluation of MOF formation. The pH of all systems was first measured after complete dissolution of the Cu salt, immediately after addition and homogenization with the  $\text{H}_3\text{BTC}$  solution and every time the system was sampled to determine Cu and W concentrations in the supernatant. Sample volumes were negligible compared to the total solution volume. Before sampling the synthesis solutions for Cu and W determination, the suspensions were centrifuged in a Heraeus Megafuge 3.0R centrifuge at 2500xg for 10 minutes to assure complete precipitation of the MOF crystals. Cu and W concentrations were determined both after respectively 5 and 270 days using AAS and ICP-OES measurements. EPR measurements were performed on a separate set of Cu/HPA solutions prepared in a 50% vol ethanol:H<sub>2</sub>O 0.1 M  $\text{NaNO}_3$  solution.

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### 2.1 Characterization

PXRD diffraction was performed on a Stadi P ( $\text{CuK}_\alpha$ ), STOE

& Cie GmbH. Software Win X POW, Search/Match module supporting ICDD PDF 2 was used to process the data.

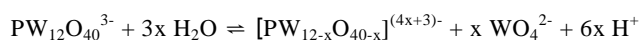
W L3 XANES data was recorded in transmission mode at 15 K on flash frozen solutions at the DUBBLE beamline, ESRF, Grenoble, France.

All EPR signals were recorded on a Bruker ESP 300E X-band EPR spectrometer at 295 K, using a 50 KHz magnetic field modulation and a microwave frequency of 9.592 GHz.

Special attention was given to pH determination. All measurements were performed with a Hamilton (Flushtrode) combination pH electrode, calibrated using aqueous pH buffers at pH 7 and 4. While it is known<sup>22</sup> combination pH electrodes measure accurate proton activities down to 10% water in water miscible organic solutions an extra contribution to the measured potential has to be expected, whenever the composition of solvent deviates from the equilibration medium. This was confirmed for Cu<sup>2+</sup> hydrolysis 0.1 M NaNO<sub>3</sub> in both water and 50% vol ethanol:H<sub>2</sub>O solutions.

### 3. Results and discussion

The formation of Cu<sub>3</sub>(BTC)<sub>2</sub> by templation with Keggin ions at room temperature (RT) emerges from a delicate equilibrium between various reactions competing for the available Cu<sup>2+</sup> ions involving water, BTC-molecules, and the PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> heteropolyanions. Essential for the assembly of the framework with HKUST-1 topology is the arrangement of dimeric copper centers in paddle wheels. Water and pH also play an important role: At low pH (pH <3) the speciation in aqueous copper solutions is dominated exclusively by solvated mononuclear hydrates<sup>23, 24</sup>, whereas insoluble Cu(OH)<sub>2</sub> is formed above pH 6. In the intermediate pH region around pH 5 an equilibrium exists between mononuclear [Cu(OH)<sub>x</sub>(OH<sub>2</sub>)<sub>y</sub>]<sub>2-x</sub> and dinuclear species such as [Cu<sub>2</sub>(OH)<sub>x</sub>(OH<sub>2</sub>)<sub>y</sub>]<sub>4-x</sub> (Fig. SI-1). Water-based non templated hydrothermal synthesis routes towards HKUST-1 occur in this pH range. There are indications that in suitable hydrothermal conditions BTC competes for dimeric hydrolysis species resulting in Cu<sub>2</sub>(OH)BTC(H<sub>2</sub>O)] or insoluble [Cu<sub>2</sub>BTC<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>], which precipitates into the final MOF framework<sup>25</sup>. Based on these observations it can be concluded especially the formation of dinuclear Cu-species which then are linked by BTC is the most critical step in the crystallisation. Furthermore, as the inclusion of non-lacunary Keggin ions is desired, the MOF synthesis has to occur at low pH and in partially organic solvents such as 50% vol ethanol:H<sub>2</sub>O, to avoid PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> hydrolysis according to reaction:



This process becomes significant at a pH above 3.5 and not only leads to lacunary Keggin ions<sup>26</sup> but can result in HPAs where tungsten partially is replaced by Cu<sup>27</sup> and also affects the pH. Too low pH on the other hand leads to increasing protonation of BTC (pK<sub>1</sub>=2.12, pK<sub>2</sub>=3.89, pK<sub>3</sub>=4.70)<sup>28</sup>. Therefore, pH 3 was chosen as optimum pH, where Keggin ions are still intact in ethanol:H<sub>2</sub>O medium and BTC is singly deprotonated.

To unravel the exact mechanism of Keggin templated Cu<sub>3</sub>(BTC)<sub>2</sub> formation, analysis of the exact fate of Cu<sup>2+</sup> in the ethanolic synthesis mixtures upon addition of Keggin ions was necessary. According to the Minteq.v4 hydro-geological datababase Cu(NO<sub>3</sub>)<sub>2</sub> dissolves into predominantly Cu(H<sub>2</sub>O)<sub>x</sub><sup>2+</sup>, Cu(NO<sub>3</sub>)(H<sub>2</sub>O)<sub>x-1</sub><sup>+</sup> and Cu(OH)(H<sub>2</sub>O)<sub>x-1</sub><sup>+</sup> in aqueous conditions at the required low pH. To verify both the pH measurements in ethanol:H<sub>2</sub>O solutions and the prediction of Cu<sup>2+</sup> hydrolysis in both water and ethanol:H<sub>2</sub>O solutions, a comparison was made between the experimentally observed and modeled pH of Cu(NO<sub>3</sub>)<sub>2</sub> dissolved in 0.1 M NaNO<sub>3</sub> solutions. The observed curves closely match the theoretical prediction, which clearly proved 50% vol ethanol did not significantly affect the speciation. All modeled pH values reported below have been corrected for the offsets shown in Fig. 1.

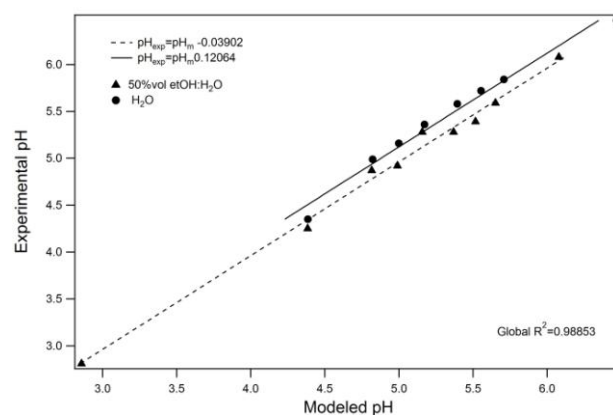


Figure 1. Correlation between experimentally measured and modeled pH for Cu<sup>2+</sup> hydrolysis in water and 50% vol ethanol:H<sub>2</sub>O solutions. Cu<sup>2+</sup> hydrolysis was modeled using phreeqc<sup>29</sup> in combination with the minteq.v4 database.

A previous study has shown a strong affinity between Cu<sup>2+</sup> and Keggin anions. Upon addition of the heteropolyacid solution to Cu(NO<sub>3</sub>)<sub>2</sub> in ethanol:H<sub>2</sub>O solutions, significant shifts in the <sup>31</sup>P NMR spectrum of PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> and in the NIR spectrum of Cu were observed<sup>20</sup>. While <sup>17</sup>O NMR<sup>20</sup> has shown at very low Cu concentrations Keggin ions interact with one single Cu<sup>2+</sup> ion via a terminal oxygen atom, at higher concentrations, necessary for framework formation, complexes with a currently unknown Cu nuclearity, state of hydration and structure had to be expected.

The interaction with Keggin ions significantly influences the Cu<sup>2+</sup> hydrolysis behavior as can be seen in Fig. 2 showing the measured and predicted pH of the Cu+HPA solutions versus Cu concentration. Predicted pH values were calculated using phreeqc<sup>29</sup> in combination with the Minteq.v4 database by replacing the HPA concentration in solution with a corresponding concentration of nitric acid.

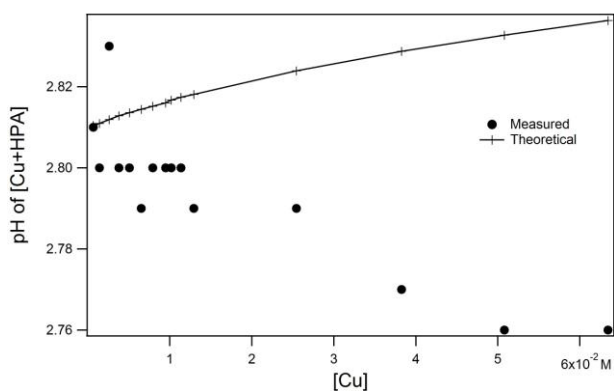


Figure 2: Plot showing the theoretical<sup>29</sup> and measured pH values of a series of  $\text{Cu}^{2+}$ -HPA solutions vs the total concentration of Cu in solution.

5 According to the tabulated equilibrium constants the pH values should slightly increase with increasing  $\text{Cu}^{2+}$  concentration. The measured values, however, significantly decrease. Since all solutions were prepared in ethanol: $\text{H}_2\text{O}$  this increased proton activity was not caused by heteropolyacid hydrolysis as was confirmed by XANES (vide infra). Therefore, the  $\text{Cu}^{2+}$ -HPA interaction, changed the hydrolysis behaviour of Cu in solution, affecting the pH. The most probable explanation is HPA induced Cu-dimerisation of HPA adsorbed  $\text{Cu}^{2+}$  ions. This is supported by the observation  
 10 of successive silencing of the Cu EPR signal (Fig. 3) in presence of Keggin ions, which points at the formation of antiferromagnetically coupled dimeric  $\text{Cu}^{2+}$  centers. Related surface hydrolysis behaviour and its associated silencing of the Cu EPR signal has been observed upon changing the water  
 15 content of  $\text{Cu}^{2+}$  loaded hectorite, a clay material offering extended interfaces<sup>30</sup>.

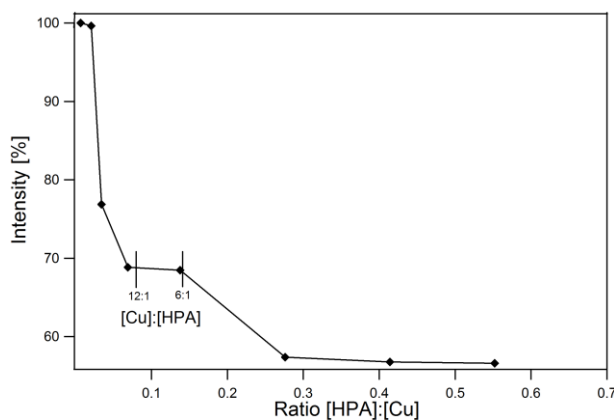


Figure 3: Plot of the X-band Cu ESR signal intensity as a function of Cu ratio for a series of solution at constant [Cu] and pH.

25 To undisputably verify the stability of the  $\text{PW}_{12}\text{O}_{40}^{3-}$  ions in ethanol: $\text{H}_2\text{O}$  upon interaction with  $\text{Cu}^{2+}$  ions, W-L3 XANES spectra were recorded for a HPA solutions with and without copper (Cu/HPA ratios of 0 and 16). Except for a small, but  
 30 significant variation in the whiteline intensity, the XANES fingerprints (Fig. 4) were identical. This proved the speciation of W in these solutions was unchanged and hence excluded

$\text{PW}_{12}\text{O}_{40}^{3-}$  hydrolysis<sup>31, 32</sup>. Small variations in the whiteline intensity can be caused by a change of the unoccupied density of states (DOS)<sup>33</sup>. A slight decrease of the ligand-metal charge transfer (LMCT) between O-W upon interaction of  $\text{Cu}^{2+}$  with the oxygens of the HPA ions, readily explains the observed increase in whiteline intensity. This interpretation is in full accordance with the shift of the P resonance in NMR as it  
 40 implied lowered electron density, hence less shielding of the nucleus than in absence of  $\text{Cu}^{2+}$ .

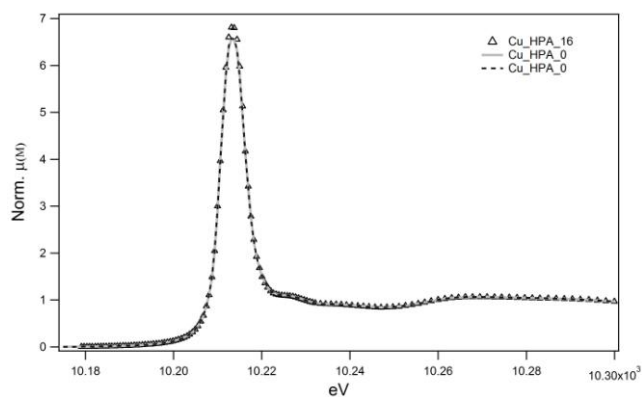


Figure 4: XANES spectra showing identical fingerprints for HPA and  
 45 Cu/HPA solutions indicating that no W speciation changes occur.

Upon mixing the HPA-MOF synthesis solutions, the systems with a Cu/HPA ratio above 40 exhibited MOF precipitation within minutes. After 5 days, all systems containing a  
 50 Cu/HPA ratio > 10, showed MOF formation to an extent proportional to the Cu/HPA ratio. 270 days of static, RT equilibration allowed for MOF formation in all systems except for those containing the 1 and 2 Cu/HPA ratios. Careful comparison of the XRD patterns and unit cell  
 55 parameters refined for the recovered solid phases (Cu/HPA ratio > 12) did not reveal any difference between the solid phases (Fig. 5).

CuBTC does not form at room temperature in 50% vol ethanol: $\text{H}_2\text{O}$  due to the failure to form of paddle wheels.  
 60 Hence, its formation in presence of Keggin provided further evidence for the dimerisation of Cu on  $\text{PW}_{12}\text{O}_{40}^{3-}$ .

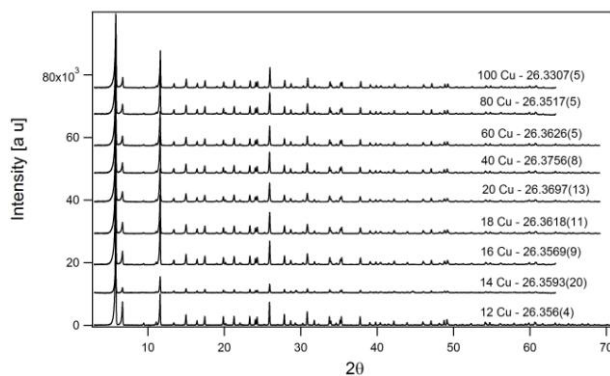


Figure 5: PXRD patterns of the MOF with Cu/HPA ratio > 12 showing the  
 65 formation of a uniform phase in the system.

## Conclusions

Extensive knowledge of the formation mechanism of HPA incorporated CuBTC-type MOF at room temperature is key to obtain stable, highly porous frameworks. The interaction of HPA with Cu cations forming different Cu<sup>2+</sup> hydrolysis species as well as its effect on pH of the system are clearly demonstrated by pH and XANES measurements and successful MOF synthesis at room temperature.

In aqueous and 50% vol ethanol:H<sub>2</sub>O solutions hydrolysis and dimerisation of dissolved Cu<sup>2+</sup> ions only becomes significant at pH 6 and above. In Keggin containing solution, surface enhanced hydrolysis and dimerisation of Cu<sup>2+</sup> upon interaction with PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> was indisputably demonstrated to occur at pH 2.8. This observation not only is important in the context of material synthesis but can also be exploited to actively change the speciation of Cu and possibly also other transition metal ions for other applications.

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† Electronic Supplementary Information (ESI) available: [Fig. SI-1. Predicted Cu speciation as a function of pH]. See DOI: 10.1039/b000000x/

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35