

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 (MOFs). The formation of this MOF is significantly accelerated by adding Keggin polyoxometalate anions to the synthesis solution. In this paper the chemistry behind this observation was investigated. Upon addition of Keggin type $\text{H}_3\text{PW}_{12}\text{O}_{40}$ heteropolyacid the speciation of Cu^{2+} cations in ethanol : H_2O mixture drastically changes. Combining EPR and XANES measurements with accurate pH measurements and prediction of Cu^{2+} hydrolysis provides strong evidence for surface induced hydrolysis and consequent dimerisation of monomeric Cu^{2+} 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,^{1–4} excellent coordination capabilities^{5–9} and strong catalytic activity. Heterogeneous catalytic applications of HPA have been almost exclusively based on insoluble HPA salts, (post-) synthetic modifications of MOFs^{10–17} and zeolites.^{18–20} 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.^{21–23} Within minutes after mixing an acidic ethanol/water based solution of Cu-decorated Keggin anions ($\text{H}_{8-x}\text{XM}_{12}\text{O}_{40}$), $\text{X} = \text{P}^{5+}/\text{Si}^{4+}$ and $\text{M} = \text{W}^{6+}/\text{Mo}^{6+}$, with the organic linker 1,3,5-benzene-tri-carboxylic-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-based²²) templation in metal–organic frameworks are rare. A molecular-level understanding of the self-organization of Cu^{2+} species around the HPAs leading to the instant formation of a porous $\text{Cu}_3(\text{BTC})_2$ framework will allow

exploitation of 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 0.1 M NaNO_3 in 50% vol ethanol in water. Each synthesis solution was prepared by adding 30 ml of a 10^{-3} M $\text{H}_3\text{PW}_{12}\text{O}_{40}$ solution to the necessary amount of Cu (NO_3)₂·3 H_2O weighed in 50 ml centrifuge tubes. Upon complete dissolution of the Cu^{2+} salt, 20 ml of 1.259×10^{-2} M 1,3,5- H_3BTC 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^{2+} and W concentrations, were recorded as a function of time to allow evaluation of MOF formation. The pH of all systems was first measured after complete dissolution of the Cu^{2+} salt, immediately after addition and homogenization with the H_3BTC solution and every time the system was sampled to determine Cu^{2+} and W concentrations in the supernatant. Sample volumes were negligible compared to the total solution volume. Before sampling the synthesis solutions for Cu^{2+} and W determination, the suspensions were centrifuged in a Heraeus Megafuge 3.0R centrifuge at $2500 \times g$ for 10 minutes to assure complete precipitation of the MOF crystals. Cu^{2+} and W concentrations were determined both after respectively 5 and 270 days using

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AAS and ICP-OES measurements. EPR measurements were performed on a separate set of Cu/HPA solutions prepared in a 50% vol ethanol : H₂O, 0.1 M NaNO₃ solution.

2.1. Characterization

PXRD diffraction was performed on a Stadi P (CuK_α1), STOE & Cie GmbH. Software Win X POW, Search/Match module supporting ICDD PDF 2 was used to process the data.

W L3 XANES data were recorded in transmission mode at 15 K on flash frozen solutions at the DUBBLE beamline, ESRF, Grenoble, France.³⁶

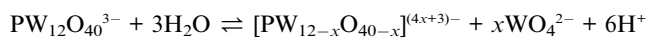
All EPR signals were recorded on a Bruker ESP 300E X-band EPR spectrometer at 295 K, using a 50 kHz magnetic field modulation and a microwave frequency of 9.592 GHz.

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 known²⁴ 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 Cu²⁺ hydrolysis, 0.1 M NaNO₃ in both water and 50% vol ethanol : H₂O solutions.

3. Results and discussion

The formation of Cu₃(BTC)₂ by templation with Keggin ions at room temperature (RT) emerges from a delicate equilibrium between various reactions competing for the available Cu²⁺ ions involving water, BTC-molecules, and the PW₁₂O₄₀³⁻ 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,^{25,26} whereas insoluble Cu(OH)₂ is formed above pH 6. In the intermediate pH region around pH 5 an equilibrium exists between mononuclear [Cu(OH)_x(OH₂)_y]^{2-x} and dinuclear species such as [Cu₂(OH)_x(OH₂)_y]^{4-x} (Fig. S1†). 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 [Cu₂(OH)BTC(H₂O)] or insoluble [Cu₂BTC₃(H₂O)₃], which precipitates into the final MOF.²⁷ Based on these observations it can be concluded that 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 : H₂O, to avoid PW₁₂O₄₀³⁻ hydrolysis according to reaction:



This process becomes significant at a pH above 3.5 and not only leads to lacunary Keggin ions²⁸ but can result in HPAs

where tungsten partially is replaced by Cu.²⁹ Too low pH on the other hand leads to increasing protonation of BTC (pK₁ = 2.12, pK₂ = 3.89, pK₃ = 4.70).³⁰ Therefore, pH 3 was chosen as the optimum pH, where Keggin ions are still intact in ethanol : H₂O medium and BTC is singly deprotonated.

To unravel the exact mechanism of Keggin templated Cu₃(BTC)₂ formation, analysis of the exact fate of Cu²⁺ in the ethanolic synthesis mixtures upon addition of Keggin ions was necessary. According to the Minteq.v4 hydro-geological database Cu(NO₃)₂ dissolves into predominantly Cu(H₂O)_x²⁺, Cu(NO₃)(H₂O)_{x-1}⁺ and Cu(OH)(H₂O)_{x-1}⁺ in aqueous conditions at the required low pH. To verify both the pH measurements in ethanol : H₂O solutions and the prediction of Cu²⁺ hydrolysis in both water and ethanol : H₂O solutions, a comparison was made between the experimentally observed and modeled pH of Cu(NO₃)₂ dissolved in 0.1 M NaNO₃ 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.

A previous study has shown a strong affinity between Cu²⁺ and Keggin anions. Upon addition of the heteropolyacid solution to Cu(NO₃)₂ in ethanol : H₂O solutions, significant shifts in the ³¹P NMR spectrum of PW₁₂O₄₀³⁻ and in the NIR spectrum of Cu were observed.²² While ¹⁷O NMR²² has shown at very low Cu concentrations Keggin ions interact with one single Cu²⁺ 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 Cu²⁺ hydrolysis behavior as can be seen in Fig. 2 showing the measured and predicted pH of the Cu + HPA solutions *versus* Cu²⁺ concentration. Predicted pH values were calculated using phreeqc³¹ in combination with the Minteq.v4 database by replacing the HPA concentration in solution with a corresponding concentration of nitric acid.

According to the tabulated equilibrium constants the pH values should slightly increase with increasing Cu²⁺ concentration. The measured values, however, significantly decrease. Since

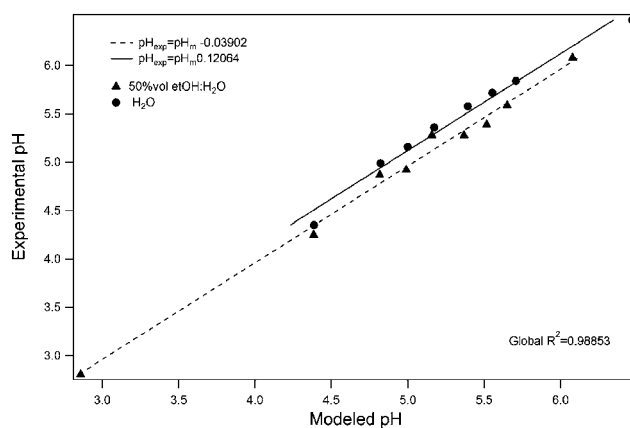


Fig. 1 Correlation between experimentally measured and modeled pH for Cu²⁺ hydrolysis in water and 50% vol ethanol : H₂O solutions. Cu²⁺ hydrolysis was modeled using phreeqc³¹ in combination with the minteq.v4 database.

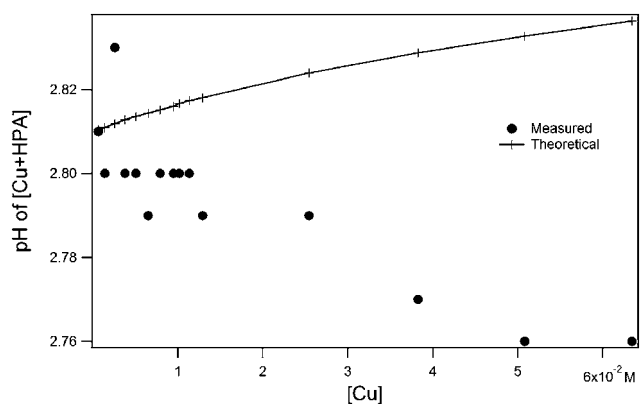


Fig. 2 Plot showing the theoretical³¹ and measured pH values of a series of Cu^{2+} + HPA solutions vs. the total concentration of Cu in solution. In HPA free Cu^{2+} solutions at pH 3 (no hydrolysis, Fig. S1†) the major effect of an increasing [Cu] is an increase in ionic strength hence a decrease in proton activity (pH).

all solutions were prepared in ethanol : H_2O this increased proton activity was not caused by heteropolyacid hydrolysis as was confirmed by XANES (*vide infra*). Therefore, the Cu^{2+} -HPA interaction changed the hydrolysis behaviour of Cu^{2+} in solution, hence affecting the pH. The most probable explanation is HPA induced dimerisation of Cu^{2+} ions adsorbed on HPA. This is supported by the observation of successive silencing of the Cu^{2+} EPR signal (Fig. 3) in the presence of Keggin ions, which points at the formation of antiferromagnetically coupled dimeric Cu^{2+} centers. Related surface hydrolysis behaviour and its associated silencing of the Cu^{2+} EPR signal has been observed upon changing the water content of Cu^{2+} loaded hectorite, a clay material offering extended interfaces.³²

To indisputably verify the stability of the $\text{PW}_{12}\text{O}_{40}^{3-}$ ions in ethanol : H_2O mixtures upon interaction with Cu^{2+} ions, W-L3 XANES spectra were recorded for HPA solutions with and without copper (Cu/HPA ratios of 0 and 16). Except for a small, but significant variation in the white line 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.^{33,34} Small variations in the white line intensity can be caused by a change in the unoccupied density of

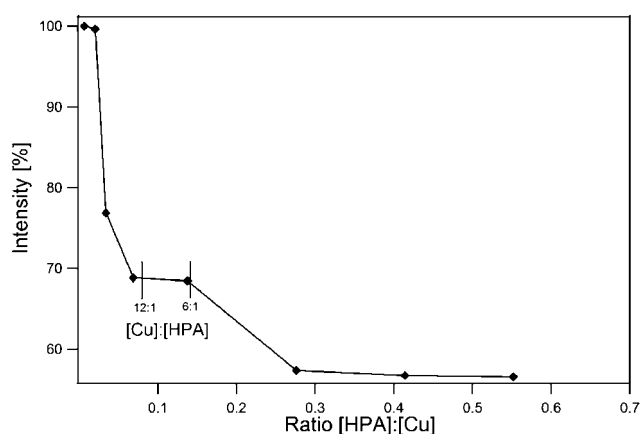


Fig. 3 Plot of the X-band Cu ESR signal intensity as a function of Cu ratio for a series of solutions at constant [Cu] and pH.

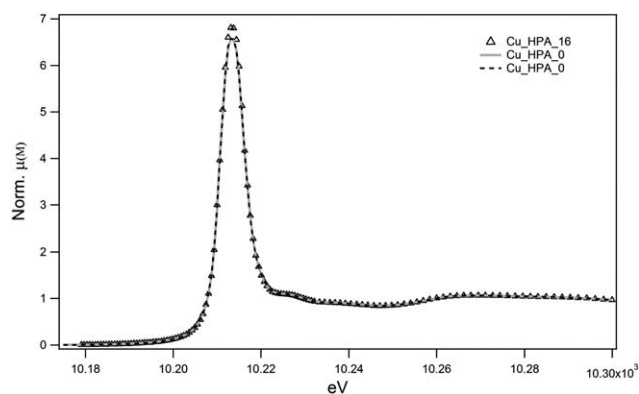


Fig. 4 Except for the white line intensity, W L3 XANES spectra showing identical fingerprints for HPA and Cu/HPA solutions thereby indicating that no W speciation changes occur. Several scans of Cu^{2+} free solutions show identical white line intensities hence proving the absence of normalization errors.

states (DOS).³⁵ A slight decrease in the ligand–metal charge transfer (LMCT) between O–W upon interaction of Cu^{2+} with the oxygens of the HPA ions readily explains the observed increase in the white line intensity. This interpretation is in full accordance with the shift of the P resonance²² in NMR as it implied lowered electron density, hence less shielding of the nucleus than in the absence of Cu^{2+} .

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 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 parameters refined for the recovered solid phases (Cu/HPA ratio >12) did not reveal any difference between the solid phases (Fig. 5).

$\text{Cu}_3(\text{BTC})_2$ does not form at room temperature (pH 3) in 50% vol ethanol : H_2O due to the failure to form paddle wheels. Hence, its formation in the presence of Keggin provided further evidence for the dimerisation of Cu^{2+} on $\text{PW}_{12}\text{O}_{40}^{3-}$.

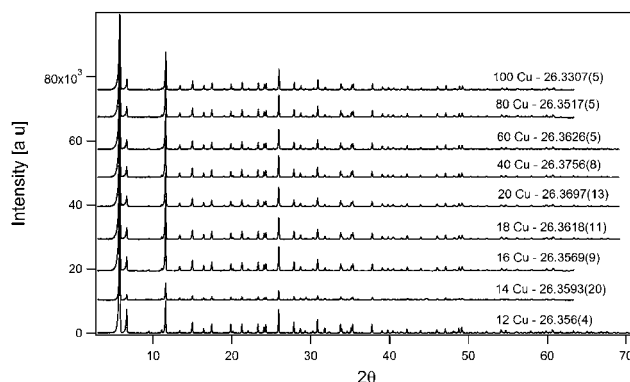


Fig. 5 PXRD patterns of the MOF with a Cu/HPA ratio >12 showing the formation of a uniform phase in the system.

Conclusions

Extensive knowledge on the formation mechanism of HPA incorporated $\text{Cu}_3(\text{BTC})_2$ -type MOF at room temperature is key to obtain stable, highly porous frameworks. The interaction of HPA with Cu^{2+} cations forming different Cu^{2+} hydrolysis species as well as its effect on pH of the system are clearly demonstrated by pH and XANES measurements in combination with successful MOF synthesis at room temperature.

In aqueous and 50% vol ethanol : H_2O solutions hydrolysis and dimerisation of dissolved Cu^{2+} ions only becomes significant at pH 6 and above. In Keggin containing solution, surface enhanced hydrolysis and dimerisation of Cu^{2+} upon interaction with $\text{PW}_{12}\text{O}_{40}^{3-}$ 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^{2+} and possibly also other transition metal ions.

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References

- 1 K. Fukaya and T. Yamase, *Angew. Chem., Int. Ed.*, 2003, **42**, 654–658.
- 2 D.-L. Long, E. Burkholder and L. Cronin, *Chem. Soc. Rev.*, 2007, **36**, 105–121.
- 3 C. P. Pradeep, D.-L. Long, C. Streb and L. Cronin, *J. Am. Chem. Soc.*, 2008, **130**, 14946–14947.
- 4 M. Zimmermann, N. Belai, R. J. Butcher, M. T. Pope, E. V. Chubarova, M. H. Dickman and U. Körtz, *Inorg. Chem.*, 2007, **46**, 1737–1740.
- 5 T. M. Anderson, W. A. Neiwert, M. L. Kirk, P. M. B. Piccoli, A. J. Schultz, T. F. Koetzle, D. G. Musaev, K. Morokuma, R. Cao and C. L. Hill, *Science*, 2004, **306**, 2074–2077.
- 6 R. Cao, T. M. Anderson, D. A. Hillesheim, P. Kögerler, K. I. Hardcastle and C. L. Hill, *Angew. Chem., Int. Ed.*, 2008, **47**, 9380–9382.
- 7 G. Hou, L. Bi, B. Li and L. Wu, *Inorg. Chem.*, 2009, **48**, 6474–6483.
- 8 S.-T. Zheng, J. Zhang, J. M. Clemente-Juan, D.-Q. Yuan and G.-Y. Yang, *Angew. Chem., Int. Ed.*, 2009, **48**, 7176–7179.

- 9 S.-T. Zheng, J. Zhang and G.-Y. Yang, *Angew. Chem., Int. Ed.*, 2008, **47**, 3909–3913.
- 10 J. W. Han and C. L. Hill, *J. Am. Chem. Soc.*, 2007, **129**, 15094.
- 11 N. V. Maksimchuk, M. N. Timofeeva, M. S. Melgunov, A. N. Shmakov, Y. A. Chesalov, D. N. Dytsev, V. P. Fedin and O. A. Kholdeeva, *J. Catal.*, 2008, **257**, 315–323.
- 12 C.-Y. Sun, S.-X. Liu, D.-D. Liang, K.-Z. Shao, Y.-H. Ren and Z.-M. Su, *J. Am. Chem. Soc.*, 2009, **131**, 1883–1888.
- 13 D. J. Tranchemontagne, J. L. Mendoza-Cortes, M. O’Keeffe and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1257–1283.
- 14 K. K. Tanabe and S. M. Cohen, *Inorg. Chem.*, 2010, **49**, 6766–6774.
- 15 K. K. Tanabe, Z. Q. Wang and S. M. Cohen, *J. Am. Chem. Soc.*, 2008, **130**, 8508–8517.
- 16 J. Juan-Alcañiz, E. V. Ramos-Fernandez, U. Lafont, J. Gascon and F. Kapteijn, *J. Catal.*, 2009, **269**, 229–241.
- 17 Y. Zhang, V. Degirmenci, C. Li and E. J. M. Hensen, *ChemSusChem*, 2010, **3**, 59–64.
- 18 R. E. Boyett, A. P. Stevens, M. G. Ford and P. A. Cox, *Zeolites*, 1998, **17**, 508–512.
- 19 X. S. Zhao, F. Su, Q. Yan, W. Guo, X. Y. Bao, L. Lv and Z. Zhou, *J. Mater. Chem.*, 2006, **16**, 637–648.
- 20 H. Jin, Q. Wu, P. Zhang and W. Pang, *Solid State Sci.*, 2005, **7**, 333–337.
- 21 S. S. Chui, *Science*, 1999, **283**, 1148–1150.
- 22 S. R. Bajpe, C. E. A. Kirschhock, A. Aerts, E. Breynaert, G. Absillis, T. N. Parac-Vogt, L. Giebeler and J. A. Martens, *Chem.–Eur. J.*, 2010, **16**, 3926–3932.
- 23 L. H. Wee, S. R. Bajpe, N. Janssens, I. Hermans, K. Houthoofd, C. E. A. Kirschhock and J. A. Martens, *Chem. Commun.*, 2009, **46**, 8186–8188.
- 24 A. L. Bacarella, E. Grunwald, H. P. Marshall and E. L. Purlee, *J. Phys. Chem.*, 1958, **62**, 856–857.
- 25 J. Chaboy, A. Muñoz-Páez, P. J. Merkling and E. S. Marcos, *J. Phys. Chem.*, 2006, **110**, 64509.
- 26 P. Frank, M. Benfatto, R. K. Szilagy, P. D’Angelo, S. Della Longa and K. O. Hodgson, *Inorg. Chem.*, 2005, **44**, 1922–1933.
- 27 M. Schlesinger, S. Schulze, M. Hietschold and M. Mehring, *Microporous Mesoporous Mater.*, 2010, **132**, 121–127.
- 28 Z. Zhu and R. Tain, *Can. J. Chem.*, 2003, **81**, 1044–1050.
- 29 P. Mialane, A. Dolbecq, J. Marrot, E. Rivière and F. Sécheresse, *Chemistry (Weinheim an der Bergstrasse, Germany)*, 2005, **11**, 1771–1778.
- 30 J. I. Kroschwitz, *Kirk-Othmer Concise Encyclopedia of Chemical Technology*, John Wiley & Sons, Hoboken, N.J., 2003.
- 31 The Cu speciation in solution was modeled using PHREEQC, in combination with the minteq.v4 database; precipitation was disabled during the modeling because of the slow kinetics. <http://www.geo.vu.nl/users/posv/phreeqc/index.html> (PHREEQC for Windows, version 2.16.03 built using PREEQC 2.17.01).
- 32 M. B. McBride, *Clays Clay Miner.*, 1982, **30**, 200–206.
- 33 E. Breynaert, C. Bruggeman and A. Maes, *Environ. Sci. Technol.*, 2008, **42**, 3595–3601.
- 34 E. Breynaert, C. E. A. Kirschhock and A. Maes, *Dalton Trans.*, 2009, 9398–9401.
- 35 D. C. Koningsberger, J. T. Miller and K. L. Bonneviot and S. Kaliaguine, in *Studies in Surface Science and Catalysis*, Elsevier, 1995, pp. 125–131.
- 36 S. Nikitenko, A. M. Beale, A. M. J. van der Eerden, S. D. M. Jacques, O. Leynaud, M. G. O’Brien, D. Detollenaere, R. Kaptein, B. M. Weckhuysen and W. Bras, Implementation of a combined SAXS/WAXS/QuEXAFS set-up for time-resolved in situ experiments, *Journal of Synchrotron Radiation*, 2008, **15**, 632–640.