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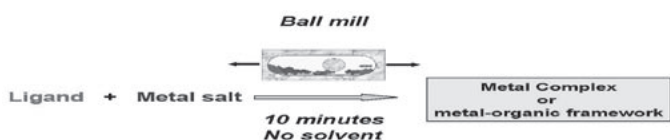
Mechanochemical solvent-free synthesis of metal-organic frameworks

Stuart L James

Queen's University Belfast, Chemistry and Chemical Engineering, David Keir Building Stranmillis Road, Belfast, Northern Ireland, BT9 5AG, UK, E-mail : s.james@qub.ac.uk

Simply grinding together metal salts and organic bridging ligands, in the absence of solvent in a shaker mill can provide crystalline, microporous metal-organic frameworks in only a few minutes and in quantitative yield[1]. Systematic studies of this unusual type of synthesis will be presented, including microscopy, structural templation by guests and by-products, the formation of interpenetrated structures, structures based on mixed-ligands, and the sorption characteristics of the resulting products.

[1] Solvent-free synthesis of a microporous metal-organic framework, A. Pichon, A. Lazuen-Garay and S.L. James *CrystEngComm* 2006, 8, 211.



Keywords: reactivity, mechanochemistry, metal-organic complexes

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Application of the pair-distribution-function method to *in-situ* studies in catalysis

Peter J Chupas

Argonne National Laboratory, X-ray Science Division, 9700 South Cass Ave. Building 433, Argonne, IL, 60439, USA, E-mail : chupas@anl.gov

Recent advances in PDF measurements combining 2-dimensional area detectors and high-energy (>60 keV) X-rays have dramatically decreased measurement times for high resolution PDF (Pair-Distribution-Function) measurements to times as fast as 30 milliseconds. This time-resolution has opened up the possibility of time-resolved and *in-situ* measurements. Specifically this talk will cover the application of time-resolved PDF measurements to investigate the mechanism and kinetics of formation of catalytic nano-particles. Recent work investigating the formation of highly-dispersed supported metal nano-particles with time-resolved PDF will be discussed. Pivotal to the development of catalytic materials with controlled reactivity, is the understanding of the fundamental mechanisms that drive the formation of catalytic nano-particles. A key step towards this goal is the ability to discriminate between the separate processes including the initial reaction of the precursors and the subsequent nano-particle sintering. Here we use time-resolved PDF methods to monitor the structural evolution and kinetics associated with the formation of Pt(0) nano-particles from Pt(4+). Differential-PDF (d-PDF) methods are applied, which allow the atom-atom correlations involving Pt to be separated from those of the support material (TiO₂), to probe the structure of the nano-particles directly. The application of d-PDF methods to the study the structure of the complexes that molecules form when bound to catalysts will also be discussed.

Keywords: catalysis, pair-distribution-function, *in-situ* structural studies

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***In situ* studies on hydrogen/ammonia storage materials**

Kenny Stahl, Rasmus Z Sorensen, Claus H Christensen

Technical University of Denmark, Department of Chemistry, Building 207, Lyngby, N/A, DK-2800, Denmark, E-mail : kenny@kemi.dtu.dk

Mg(NH₃)₆Cl₂ is a new promising hydrogen storage material. It already fulfils the U.S. DOE goals for 2015 in terms of gravimetric and volumetric hydrogen density, and energy density. On mild heating this material releases four to six NH₃ that can be used directly in some fuel cells or in deNO_x-processes. Alternatively, NH₃ can be decomposed into N₂ and H₂ prior to use in standard fuel cells. For the present study Mg(NH₃)₆Cl₂ was sealed in quartz capillaries and studied *in situ* with X-ray synchrotron powder diffraction under varying temperature at beamline I711, MAXlab, Lund, Sweden. The experiments showed that under autogenous pressure, Mg(NH₃)₆Cl₂ loses four NH₃ before melting at 600 K. Repeated temperature cycling between 323 and 453 K demonstrated that the process is essentially reversible, but some Mg(NH₃)₂Cl₂ is retained at 323 K under transformation to a low-temperature phase. Below approximately 300 K it reverts completely to Mg(NH₃)₆Cl₂. Analogous studies of related materials Ni(NH₃)₆Cl₂ and Cu(NH₃)₅SO₄ showed different deamination sequences: Ni(NH₃)₆Cl₂ transforms to Ni(NH₃)₂Cl₂ at 450 K, to Ni(NH₃)Cl₂ at 575 K, and to pure nickel metal at 700 K. Returning to room temperature the sample reverts to a mixture of Ni(NH₃)_xCl₂-phases. Cu(NH₃)₅SO₄ showed transformations to Cu(NH₃)₄SO₄ at 373 K, to Cu(NH₃)₂SO₄ at 450 K, and to Cu(NH₃)SO₄ at 550 K. Repeated cycling between 323 and 523 K showed complete reversibility between Cu(NH₃)₅SO₄ and Cu(NH₃)₂SO₄. The experimental results, crystal structures and structure relationships will be presented and discussed.

Keywords: *in situ* powder diffraction, energy storage materials, structural relationships

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***In situ* synchrotron powder X-ray diffraction studies of catalytic materials**

Poul Norby

University of Oslo, Department of Chemistry and Centre for Materials Research and Nanotechnology, P.O. Box 1033, Oslo, Oslo, 0315, Norway, E-mail : poul.norby@kjemi.uio.no

Development of *in situ* powder diffraction methods has made a significant impact in materials science. Particularly utilization of synchrotron X-ray radiation has greatly improved the ability to investigate materials under operative or realistic working conditions or during synthesis. Information extracted from diffraction experiments may contribute to the understanding of catalytic processes and the

