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KN11

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Energy related materials: borohydrides

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Metal borohydrides attract a particular interest as potential hydrogen storage materials, capable to release hydrogen by thermolysis and hydrolysis. Recently, a significant progress was made in synthesis of bimetallic borohydrides, their characterization and in establishing composition-structure-property relations. The structure of these compounds can be rationalized in terms of different bonding schemes between metal atoms and the BH₄ groups, involving various degrees of iono-covalent interaction. Their hydrogen storage properties are not a simple average of the monometallic borohydrides, but depend mostly on the nature of the complex-forming cation. Indeed, the BH₄ group can be considered as a directional ligand which can form complexes with less electropositive metals. In some cases, inorganic frameworks similar to MOFs are obtained, e.g. interpenetrated and porous frameworks, the latter capable to absorb reversibly and selectively guest species. Metal borohydrides reveal rich coordination chemistry and their properties can be changed by chemical modification, for instance by means of so-called “anion substitution”, i.e. by using different ligands along with the BH₄ groups.

In-situ powder diffraction is the primary technique to characterize new phases, study their formation, decomposition, and to evaluate a reversibility of hydrogen desorption. Synthetic screening combined with a “decomposition-aided indexing” of the *in-situ* powder diffraction data, followed by a structure solution in direct space and an energy optimization by DFT methods becomes a standard approach to characterize new systems. Diffraction allows to find conditions for reversible dehydrogenation: different decomposition pathways are commonly detected in vacuum, in argon and under hydrogen back-pressure, while the reversibility strongly depends on the nature of decomposition products. Therefore, high throughput diffraction measurements under working conditions become a part of the characterization protocol of a new hydrogen storage system [1]. Naturally, structural information from diffraction methods is combined with data on dynamics from Raman/IR spectroscopies and spin-lattice relaxation NMR measurements [2], physico-chemical characterization by TGA, DSC, PCT etc (see for example Ref. 3).

A large work front is initiated on reactive hydride composites. These systems usually are mixtures of borohydrides, binary hydrides, amides, ammonia borane or metal amidoboranes, metal-coordinated ammonia and sometimes catalytic amounts of transition metal salts. These combinations allow to decrease further dehydrogenation temperatures, increase the useful hydrogen weight content, and suppress the undesirable release of borane and ammonia gases. Information on structure, bonding, properties and reactivity of the individual components, the experimental and analytical protocols to study the reaction composites as well as the use of theoretical methods [4] are the prerequisites for finding a suitable hydrogen storage material in these multicomponent systems.

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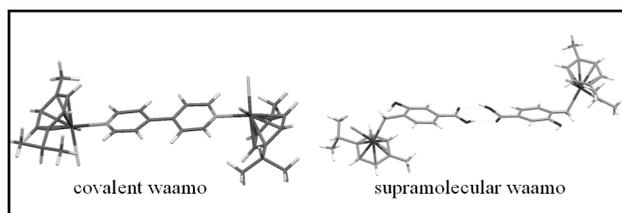
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Crystal engineering of flexible metallorganic networks

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During the past twenty years much effort has been devoted to design crystalline species capable of incorporating small molecules into the lattice through weak interactions, which might be broken at will, producing crystalline materials with host-guest properties [1]. These have been classified according to the behavior of the host framework when the guests are removed [2]: first-generation compounds have microporous frameworks that collapse on the removal of guest molecules, second-generation compounds exhibit a permanent porosity also in the absence of included guests, and third-generation compounds have flexible and dynamic frameworks, which rearrange reversibly in response to the presence of guests.

In this contribution the full toolkit of crystal engineering is used to rationalize the design of third generation porous metallo-organic materials with flexible dynamic frameworks, able to create pores on demand to accommodate small guest molecules [2]. The size and shape of the organic ligands are crucial in determining the inclusion propensity of these materials, and we focused on wheel-and-axle (*waa*) systems that are constituted by two bulky groups (wheels) connected by a rigid linear spacer (axle) [3]. In particular, trans-palladium wheel-and-axle complexes of carbinol ligands (*waad*) have shown suitable structural requisites to give host-guest properties, and display reversible vapor solvents uptake without loss of crystallinity [4]. This paradigm has evolved into the class of wheel-and-axle metal-organic systems (*waa-mo*) based on two ruthenium half-sandwich units (HSRu) playing as wheels, connected by a linear axle that may be covalent or supramolecular [6] (Figure). These compounds combine the inclusion properties of the wheel-and-axle molecular motif with the chemical properties of HSRu complexes, known as catalysts of a variety of important organic transformations, such as the enantioselective reduction of polar bonds under hydrogen transfer conditions. A careful design of both the HSRu unit and the ligands that constitute the molecular axle permits to finely tune the supramolecular properties of the crystalline frameworks. Based on the number of hydrogen bond donors and acceptors and on their nature materials exhibiting a range of inclusion propensities have been obtained, from stiff networks that do not include any guest to extremely dynamic materials that easily transform in the solid state to exchange guests by solid/vapour and solid/liquid processes.



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Bacterial pathogenesis and peptidoglycan degradation machines

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The bacterial cell wall is comprised of cross-linked strands of peptidoglycan (PG), which encase the entire cytoplasm. A healthy cell wall is critical for survival of bacteria and serves as a docking station for bacterial surface proteins, some of them representing key players in adhesion, colonisation and virulence. Therefore cell wall remodeling is critical in host-pathogen interactions, cell division, virulence, PG recycling and antibiotics resistance. Choline-binding proteins (Cbp) are pneumococcal surface proteins that have received considerable attention because of their versatility, and their sophisticated role in the interaction with host proteins. The three-dimensional structure of Pce (70 KDa), in complex with the reaction product and choline analogs has been solved [1]. We have showed that Pce hydrolyses PAF, a potent lipidic first messenger of inflammatory processes. Besides, the structural analysis indicated that Pce selectively remodels the bacterial surface impairing the ability of host proteins to efficiently bind the bacteria, and would provide a mechanism for pneumococci escaping attack by the host defense system [1].

CbpF (38 KDa) has been solved [2] demonstrating that CbpF inhibit the activity of autolysin LytC and providing the first example of a regulatory system to tune the activity of an autolysin. LytC is involved in the virulence mechanism of fratricide. Pneumococci that are competent for natural genetic transformation kill and lyse non-competent sister cells or members of related species that are present in the same environment. This phenomenon has been termed fratricide. We have reported the functional characterization of the key effector of pneumococcal fratricide CbpD [3] and the crystal structure of LytC in a ternary complex with choline and a PG fragment [4] that explain the activation of LytC by CbpD in fratricide and provide the first structural insights into the critical and central function that LytC plays in pneumococcal virulence.

During homeostasis, including growth, cell wall is simultaneously biosynthesized and degraded. Lytic transglycosylases (LTs) initiate the degradative events on cell wall. The products of LTs are internalized to the cytoplasm, and hydrolysed by glucosaminidase NagZ and amidase AmpD. The reaction products of AmpD play roles in both PG recycling events and in an induction event that leads to the expression of β -lactamase, a key β -lactam antibiotic resistance enzyme. Despite the 3D structure for AmpD enzyme was known by NMR techniques, we have performed crystal structure determination of some LTs and AmpD. Unexpectedly we have observed that AmpD undergoes an activation mechanism from an inactive form (that determined by NMR) to an active form we solved. Changes produced in the activation process are among the largest structural rearrangements ever reported for a single domain protein.

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Coherence in crystallography for imaging materials and biology

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In crystallography, we consider nanometre-sized crystals to be a new frontier of opportunity to tailor physical properties using ‘size’ as a control variable. This general view of crystallography “beyond the unit cell” opens a wide field of opportunity for methods development. However, when we think about nanostructures, we must reconsider the standard bulk concepts of lattices and crystal defects. Changes here provide nanomaterials with new and exciting properties. This lecture is about coherence-based methods for the determination of crystal structures using coherence. One example is micron-sized ZnO crystals, attached by bonding to a SiO₂ substrate, which showed internal strain arising from accidental damage during manipulation. Use of more than one Bragg peak from the same crystal allows components of the full strain tensor to be mapped inside the crystal.

These new crystallographic methods have a fundamental need for beam coherence, so benefit directly from 3rd generation synchrotron sources. The coherence leads to interference fringes in the diffraction patterns of sufficiently small crystals. When the fringes are measured using a fine-pixel detector the data can be oversampled beyond their Nyquist/Shannon frequency. To invert the diffraction, we then solve the crystallographic ‘phase problem’ using a support-constrained HIO algorithm. This leads to quantitative three-dimensional maps of the density of the crystal with a real-space phase, which is interpreted as the deformation of a crystal from its equilibrium lattice spacing.

We have also used the methods to examine twin domain structures within crystals as well as real-space phase domains due to ordering. In biology, we have investigated collagenous tissue, which shows an analogous phase domain structure. For extended objects such as these, we are applying the principles of ‘ptychography’, in which the crystallographic phase information emerges from overlaps between coherent diffraction patterns.

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Structure-Property Relationships of Inclusion Compounds

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Multicomponent crystals based on the encapsulation of guest molecules by suitable hosts may exhibit a number of interesting properties and structural phenomena. For example, guest-templated