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Keywords: structural genomics, high-throughput, influenza

KN11

Acta Cryst. (2011) A**67,** C9

Energy related materials: borohydrides

Yaroslav Filinchuk,[a] [a]*Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Louvain-la-Neuve (Belgium).* E-mail: yaroslav.filinchuk@uclouvain.be

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 BH_4 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 BH_4 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 BH_4 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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Keywords: Hydride, Synchrotron, Chemistry

KN12

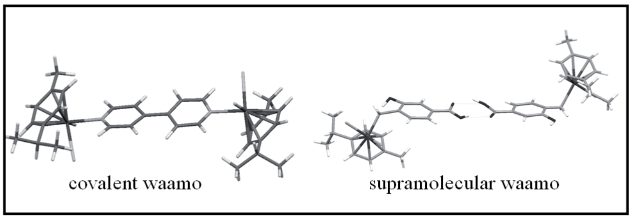
Acta Cryst. (2011) A**67,** C9-C10

Crystal engineering of flexible metallorganic networks

Alessia Bacchi, *Dipartimento di Chimica GIAF, University of Parma, Parma (Italy).* E-mail: alessia.bacchi@unipr.it

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 (*waamo*) 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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