MS19-O5 Templation effects and novel ZIF structures by solid state synthesis

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In the last decade zeolitic imidazolate frameworks (ZIFs), a subclass of metaloorganic frameworks (MOFs), have been rising in popularity due to their diverse topologies, good thermal and chemical stability, and large pore volumes, which could enable their use for gas-storage, separation of gases, and catalysis.[1] However, traditional solution synthesis methods are very energy demanding, they use large quantities of organic solvents and rather expensive inorganic nitrates as starting material, and, above all, are often irreproducible and hard to control, giving mixtures of different ZIF frameworks in often low yields. Mechanochemical alternatives have been proposed, including neat grinding[2], ion and liquid assisted grinding (ILAG)[3], and most recently, accelerated aging[4].

We explored several different methods for solid state ZIF synthesis, including neat and liquid-assisted grinding, slurrying, as well as a modified accelerated aging procedure, giving rise to novel ZIF structures. We also show that we can direct the outcome of ZIF syntheses to frameworks containing a specific structural motif by employing an organic template using several different synthetic methods.

[1] Park, K.S.; Ni, Z.; Côté, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H.H.; O'Keeffe, M.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 10186–10191.

[2] Tanaka, S.; Kida, K.; Nagaoka, T.; Otaa, T.; Miyake, Y.; *Chem. Commun.,* **2013**, *49*, 7884-7886.

[3] Beldon, P. J.; Fabian, L.; Stein, R. S.; Thirumurugan, A.; Cheetham, A. K.; Friščić, T. *Angew. Chem. Int. Ed.* **2010**, *46*, 9640–9643

[4] Cliffe, M. J.; Mottillo, C.; Stein, R. S.; Bučar, D.-K.; Friščić, T. *Chem. Sci.,* **2012**, *3*, 2495.

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MS20-O1 High-pressure high-temperature synthesis of new covalent metals

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In the last two decades, the advent of modern in-situ high-pressure x-ray diffraction techniques has markedly developed our knowledge of exotic structure patterns. The alteration of atomic configurations opens perspectives to substantially manipulate the electronic properties of solids. The increased number of neighbors in the atomic coordination sphere may give rise to an enlarged band dispersion and evenually metallization. Particularly in covalent framework assemblies, the combination of directed bonding with a significant density of states at the Fermi level creates the promising situation of covalent metals. This unique blend of properties has proven to be beneficial for phonon-mediated superconductivity.

This way, high-pressure studies have supplemented the map of high-temperature superconductors as much as they stimulated profound studies of the underlying principles. A straightforward method to access the useful effects of compression at ambient pressure is provided by synthesizing metastable compounds at extreme conditions. Recent preparation results and physical propeties of selected binary compounds comprising covalent framework patterns will be discussed.

References

A. Wosylus, Yu. Prots, U. Burkhardt, W. Schnelle, U. Schwarz, STAM 8, 383 (2007). K. Meier, R. Cardoso-Gil, W. Schnelle, H. Rosner, U. Burkhardt, U. Schwarz, ZAAC 636, 1466 (2010). K. Meier, L. Vasylechko, R. Cardoso-Gil, U. Burkhardt, W. Schnelle, M. Schmidt, Yu. Grin, U. Schwarz, ZAAC 636, 1695 (2010). A. Wosylus, K. Meier, Yu. Prots, W. Schnelle, H. Rosner, U. Schwarz, Yu. Grin, Angew. Chemie Int. Ed. 49, 9002 (2010). W. Schnelle, A. Ormeci, A. Wosylus, K. Meier, Yu. Grin, U. Schwarz, Inorg. Chem. 51, 5509 (2012). K. Meier, A. Wosylus, R. Cardoso-Gil, U. Burkhardt, C. Curfs, M. Hanfland, Yu. Grin, U. Schwarz, ZAAC 638, 1446 (2012). U. Schwarz, A. Wosylus, H.