Oral Contributions

[MS37] The role of crystallography in chemical reactivity/kinetics/catalysis

Co-Chairs: Simone Techert (DE), Marijana Dakovic (HR)

[MS37-01] Solid-state Reactions by Milling and Aging: Diversity of Reactions and Opportunities for Reaction Monitoring

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The exhaustion of natural resources and growth of industrial production have made the development of new, efficient and "green" methodologies for chemical synthesis and materials processing a central task of modern chemists and materials scientists. Over the past decade, such developments have brought heterogeneous transformations of organic and molecular solids into the focus of modern synthetic chemistry. Our research group is using solid-state reactions to develop general methodologies for solvent-free and low-energy synthesis and this presentation will illustrate two directions of this research effort. One is the development and mechanistic studies of chemical reactions induced by mechanical force. Such mechanochemical reactions,[1] conducted by milling or grinding, have recently been applied for the clean and efficient syntheses of metal-organic materials (porous frameworks, metallodrugs) by direct transformation of oxides and sulfides at room temperature. This presentation will also highlight the recently developed and currently the only methodology for real-time and in situ monitoring of mechanochemical milling reaction using hard synchrotron X-rays. [2] Another area of our research which will be illustrated is the development of a conceptually novel methodology for chemical, low-energy and solvent-free synthesis, named "accelerated aging". Accelerated aging is inspired by normally slow processes of geological biomineralization (mineral weathering). We demonstrate that mineral weathering reactions can be readily mimicked, as well as accelerated in the laboratory for the mild, solvent-free synthesis of microporous materials in multi-gram scale. [3] In contrast to mechanochemical or solution-based methodologies, accelerated aging aims to synthesize materials from the simplest precursors through catalyzed, diffusion-controlled reactivity which minimizes the input of solvent and energy. Whereas aging reactivity offers itself readily to mechanistic studies using conventional powder X-ray diffraction techniques, it also allows us the use of less conventional techniques for reaction monitoring, such as solid-state fluorescence emission spectroscopy, recently employed for real-time and in situ observation of transformations of solid forms of the pharmaceutical indomethacin. [4]

[1] Friščić, T. (2012) Chem. Soc. Rev., 41, 34933510. Friščić, T., Halasz, I., Beldon, P. J., Belenguer, M., Adams, F., Kimber, S. A. J., Honkimäki, V. & Dinnebier, R. E., (2013) Nature Chem., 5, 66-73.
Cliffe, M. J., Mottillo, C., Stein, R. S., Bučar, D.& Friščić, T. (2012) Chem. Sci., 3, 2495-2500.

[4] Frenette, M., Cosa, G. & Friščić, T. (2013) CrystEngComm, 15, 5100-5106.

Keywords: mechanochemistry, solvent-free reactions, mechanisms