

MS36-O2 The Emergence of Medicinal MechanochemistryTomislav Frišćić¹

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This presentation will highlight how the overlap of previously unrelated areas of solid-state mechanochemical synthesis,^[1] *i.e.* screening for API solid forms, organic synthesis by milling, and mechanochemical screening for molecular recognition, enables the emergence of a new research discipline in which different aspects of pharmaceutical and medicinal chemistry are addressed through solid-state reactivity, rather than the conventional solution-based routes. This nascent area of *medicinal mechanochemistry*^[2] is likely to have a strong impact on future pharmaceutical and medicinal chemistry, by offering not only access to materials and reactivity that are sometimes difficult or even impossible to access from solution, but also by providing a general answer to the demands of pharmaceutical industry for cleaner, safer and efficient synthetic solutions.^[3,4]

[1] James *et al.* *Chem. Soc. Rev.* **2012**, *41*, 413.[2] Tan, Loots, Frišćić, *Chem. Commun.* **2016**, *52*, DOI:10.1039/C6CC02015A[3] Bonnamour, Métro, Martinez, Lamaty, *Green Chem.* **2013**, *15*, 1116.[4] Tan *et al.* *Chem. Commun.* **2014**, *50*, 5248.

Keywords: Solid-state reactions, pharmaceutical materials, drugs, mechanochemistry

MS36-O3 Last advances in *in situ* monitoring of mechanochemical reactions by X-ray diffractionVorakmsy Ban¹, Nikolay Tumanov², Yolanda Sadikin³, Yaroslav Filinchuk², Radovan Černý³, Nicola Casati¹

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The *in situ* characterization of materials is a widespread technique as it gives an accurate description of the sample in a particular state without disturbing the system and adding supplemental parameters/errors in the measurement. It allows to describe and understand phenomena during a process but it also plays a key role to the development of new materials. The renewed interest of mechanochemistry as an eco-friendly synthetic route has inspired creative methodologies to probe reactions.

One of the last methodologies was developed by Frišćić *et al.* and for the first time the progress of milling reactions was monitored by synchrotron X-ray diffraction [1]. Recently, they were able to detect and unveil a new topology intermediate during the mechanochemical synthesis of the metal-organic framework ZIF-8 [2]. Nevertheless, such setup has limitations: it is only adapted for high-energy synchrotron X-rays providing diffraction patterns in a squeezed Q-range with strongly overlapping Bragg peaks and does not yield high quality data. With the aim of improving such situation, we developed a completely different setup yielding higher resolution powder diffraction data and providing continuously a representative part of the bulk for probing [3,4]. The particular geometry of the ball mill designed at Materials Science beamline (SLS, Switzerland) shows a significant improvement of diffraction data quality (Fig.1): new intermediates were precisely identified during ball milling syntheses and crystal structures might be solved from it. Moreover with this novel design, it will be easier and more efficient to couple it with other analytical techniques *e.g.* infra-red/Raman spectroscopies [5] or laser diffraction analysis. Such setup will be available to users at the MS beamline.

[1] T. Frišćić *et al.* *Nat Chem*, 2013, *5*, 66-73[2] A. D. Katsenis *et al.* *Nat Chem*, 2015, *6*, 1-8

[3] N. Casati, V. Ban, M. Lange, Patent EP15197992

[4] V. Ban, N. Tumanov, Y. Sadikin, Y. Filinchuk, R. Černý, N. Casati manuscript in preparation

[5] L. Batzdorf *et al.* *Angew. Chem. Int. Ed.*, 2015, *54*, 1799-1802

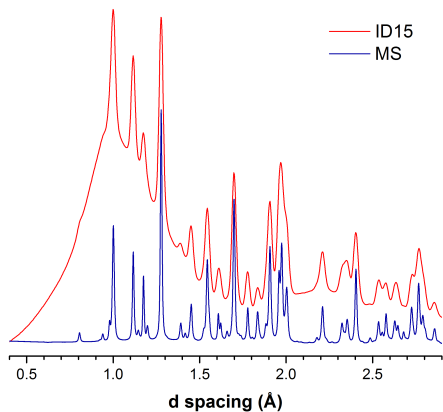


Figure 1. Comparison of data collected with the shaker mill at ID15 and our ball mill setup at MS beamline

Keywords: Mechanochemistry, in situ technique

MS36-O4 Hindered reduction of NiO on Al containing carriers studied by *in situ*

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Steam reforming of natural gas using Ni-based catalysts is an important process in production of synthesis gas and hydrogen. Activation of the catalyst is carried out by reducing NiO to Ni in a mixture of steam and hydrogen (or hydrocarbons) from as low as 450°C. Full reduction and stability are vital for optimal performance and lifetime of the catalyst system. A detailed understanding of the reduction process is therefore of great importance in relation to plant operation.

To better understand this process, reduction behavior of NiO supported on industrial-like steam reforming carriers was studied under wet reduction conditions (1% H₂ + 3% H₂O, in He) using *in situ* X-ray diffraction (XRD), temperature programmed reduction (TPR) and scanning transmission electron microscopy (STEM) mapping.

It is found that the interaction of NiO with the support greatly influences the reduction behavior. When free MgO is in the carrier, it will react with Ni²⁺ during impregnation and calcination to form a Ni_{1-x}Mg_xO solid solution, which results in increasingly high reduction temperatures with increased Mg content.

Increased reduction temperatures are also observed when the calcination temperature during preparation is increased. In this case, the higher reduction temperatures are caused by migration of Al-species from the support to the surface of the NiO particles during calcination.

Calcination at 850°C results in NiO particles completely covered by Al-species, forming a thin (<3nm) protective surface spinel, resulting in reduction temperatures above 700°C. Based on the observed data, it is proposed that Al-species are mobile during calcination already at 450°C. Formation of the protective surface spinel seems to be a general feature for Al-containing carriers as similar reduction behavior is observed on both MgAl₂O₄, calcium aluminate, and α -Al₂O₃ carriers.[1]

[1] Lundegaard, L. F., Tiruvalam, R. R., Tyrsted, C., Carlsson, A., Morales-Cano, F., and Ovesen, C. V. *Catalysis Today*, 2015, available online, article in press. (doi:10.1016/j.cattod.2015.08.055)