

Oral Contributions

[MS46-05] Gas-solid reactions in non-porous crystalline materials studied by in-situ XRPD

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The design and applications of molecule-based crystalline materials affects research and commercial activities ranging from pharmaceuticals, to energy and transport applications such as gas storage, catalysis and the design of sensors, and materials for entrapment and separation. Synthesis of molecular crystalline materials by mechanochemical means has begun a renaissance in recent years. It provides a synthetic route that either avoids the need for solvent. Uptake of gases by porous solids is well established, but nonporous molecular solids have also been shown to take up gases. A series of reactions between non-porous molecular crystals of coordination compounds trans-[CuX₂(n-Xpy)₂] (n=3, 4; X=Cl, Br) and anhydrous HX gas (X=Cl, Br) to produce crystalline salts (n-XpyH)₂[CuX₄] (n = 3, 4; X = Cl, Br) has been studied using in situ XRPD.¹⁻³ The reactions involve cleavage of Cu–N bonds and the formation of Cu–X (X = Cl, Br) bonds and N–H bonds within the crystals; crystallinity of the solids is maintained. The chemical transformations are reversible and result in desorption of gaseous hydrogen halides. The relative rates of the reactions is found to be governed by the strength of non-covalent interactions formed in the metallate salt crystals, specifically N–HCl hydrogen bonds are stronger than N–HBr hydrogen bonds and result in faster release of HCl gas than HBr gas and correspondingly slower uptake in the reverse process. The solid-gas reactions have been followed by in situ X-ray powder diffraction at beamline ID31 (ESRF) using a specially designed apparatus and extensive structural analysis.

[1] G. Mínguez et. al. *J. Am. Chem. Soc.* **2006**, 128, 9584. [2] G. Mínguez et. al. *Angew.* **2010**, 48, 8892. [3] I. Vitorica et.al. *CrystEngComm.* **2011**, 13, 3189.