MS36-P7 Spontaneity of heterogeneous (solid/gas) chemical reactions: Theoretical study of dimensionality changes induced by ammonia in zinc phosphates

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Previous researches in our group [1] shown that two-dimensional zinc phosphate $NH_4Zn_2(PO_4)(HPO_4)$ (1), via ammonia vapor interaction at room temperature, transforms to a one dimensional novel compound $NH_4Zn(NH_3)PO_4$ (2). By ammonia desorption (in air at room temperature) 2 transforms to NH_4ZnPO_4 (3) . The structures of three compounds include extra-framework ammonium cations to the 4-fold coordinated zinc (ZnO_4 tetrahedra for 1 and 3, and ZnO_3N tetrahedra for 2 and phosphorus (PO_4 tetrahedra) with bi-, mono- or three-dimensional linkages, respectively for 1, 2 or 3. To our knowledge, the process described here constitutes the first example of dimensionality change in the solid phase promoted by a solid–gas interaction at room temperature in metal phosphates. The thermodynamics of the transformation between these three compounds can shown why this reactions have been played. In order to obtain the theoretical values of Δ_rG^0, the corresponding values of Δ_rH^0, and Δ_rS^0,have been calculated. For the enthaply calculation, the suite *Quantum Espresso* [2] was used, applying DFT metolodgy with plane waves and pseudopotentials. For the entropy, only the gas contribution was calculated (ideal crystal approximation), and the software *Gaussian 03* [3] was used for this computation, applying also DFT metodology, but, in this case, with the hybrid functional B3LYP and the 6,31-G(d,p) basis. The theoretical methodology was tested by studying the formation of the crystalline chlorides of the two first groups of periodic table, and some transition metals. The test results are in agreement with the experimental data available for Δ_rG^0, and allow us to validate the method.

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Keywords: DFT, Theoretical calculations, zinc phosphates, dimensionality changes, thermodynamics, heterogeneous reactions

MS36-P8 Synthesis of New Functional, Catalytic Materials by Thermal Decomposition of Ag(I)/Yb(III) Bimetallic Coordination Networks

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Bimetallic coordination networks facilitate the preorganization of the two cations in three-dimensional space. The nanoscale, predefined distribution of the different metal cations is used to design new catalytic materials. Thermal decomposition of those bimetallic networks, *e.g.* removal of the organic linker, results in a bimetallic metal/metal oxide compound. Those decomposition compounds have been analysed by X-ray powder diffraction, SEM-SEI, SEM-BSE, EDX and XRF.

In previous works, a non-commercial acetylacetone derivative has been used successfully as an organic linker [*Dalton Trans*. **2012**, *41*, 4664–4673]. The decomposition compound containing silver and ytterbium oxide exhibited catalytic activity towards the decomposition reaction of nitrous oxide, N_2O, at 500 °C (commercially-available catalyst: 600 °C). The aims of the new project were to optimize the catalyst system by using cheaper, commercially-available ligands, such as EDTA (see scheme), and try to decrease the reaction temperature.

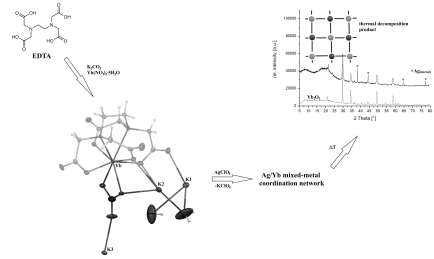

Figure 1. Schematic illustration of the synthesis path starting from ethylenediaminetetraacetic acid going to Ag nanoparticles and Yb_2O_3.

Keywords: Mixed-metal polymers, MOF, Catalysis, N2O decomposition, Ag nanoparticles, X-ray powder diffraction, Single-Crystal XRD, Rare-earth metal