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Mixed Salts for Ammonia Storage

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Ammonia, with a hydrogen content of 17.6 % by mass, can be converted to hydrogen and nitrogen by a catalytic process and is thus a high-capacity hydrogen storage medium. The use of metal halides for solid state ammonia storage offer the best qualities, among the different materials available on the market, for a large spectrum of applications, such as thermochemical heat pumps, ammonia separation, ammonia storage and delivery for fuel cells or selective catalytic reduction of NOx gasses. However, for further penetration on the market, searches for cheaper and more efficient materials are still needed and for their development, understandings of the basic mechanisms for NH3 desorption/adsorption and their relations with the crystal structures and structural changes must be acquired.

Strontium ammine, Sr(NH3)8Cl2 is already used by AMMINEX A/S, in solutions for selective catalytic reduction of NOx gasses in vehicle exhaust. However, the working storage capacity is lower than the theoretical one and controversy exists regarding the existence of the di-ammine phase. Furthermore, the full crystal structures for different degrees of ammonia loading remain unknown. Using ex-situ X-ray diffraction, we have recently identified Sr(NH3)2Cl2 and suggested structural models for the ammines with 1, 2 and 8 ammonia molecules but to further investigate the structural changes, and get the accurate hydrogen positions and conclude on the remaining open questions on that compound in situ powder neutron diffraction would be a must.

In collaboration with AMMINEX A/S, we are also investigating mixed salts as new media and are performing a DFT screening, starting with more than 20 different salts and have already identified new attractive mixed compounds. We have synthesized some of them, in form of solid solutions for example of SrBaCl2 and SrBaZnCl2 and recorded their excellent efficiencies for NH3 storage. However, we have no knowledge about their crystal structures and would like to investigate the correlations between the different ammonia binding energies, the crystal structures and structural changes.

Thus, we propose a series of in-situ neutron diffraction measurements studying the time-temperature-pressure dependence of the Sr-Ba-Zn chlorides ammines systems to start with. These in situ studies will be done using several different temperatures and partial pressures of ammonia. We have already studied the desorption/adsorption properties of these system and together with the neutron diffraction will be able to draw the different phase diagrams.

A specially designed gas tight vanadium container, (volume 3 cm^3) connected to a gaz manifold, using a SrCl2 storage unit will be used as ammonia source. Typically, a maximum of 2 bar of deuterated NH3 will be used within a temperature range from 100K to 400K. With typical taping density of 0.5 g.cm^-3 up to 1.5 g of sample will be used.

The powder diffractometer PUS is very well suited for this type of study, aiming at Rietveld analysis of the structural data acquired. Ideal for studying both fine structural details in the stable ammines phases and follow structural changes as a function of the partial pressure of ammonia.

The applicants have many years of experience with in situ diffraction and will use density functional theory (DFT) calculations combined with thermodynamic and crystal structure analysis to described the experimental results.