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Generation of Nanopores during Desorption of NH_3 from $Mg(NH_3)_6Cl_2$

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Metal ammine complexes have been known for more than a century,[1] but they still turn out to have new and interesting properties. Recently, they have, for example, been considered for separation of NH_3 from low-pressure ammonia plants[2] and as sorption systems for refrigeration.[3,4] The latest suggestion is to use them as solid hydrogen storage materials.[5] Metal ammine complexes, such as $Mg(NH_3)_6Cl_2$, can store 9.1% hydrogen in the form of NH_3, which is relatively high compared to most solid hydrogen storage materials currently studied.[6,7] Hydrogen can be obtained by combining the metal ammines with an NH_3 decomposition catalyst.[8−10]

One particularly interesting property of the $Mg(NH_3)_6Cl_2$ material is that it can be compacted into shaped objects essentially without any void.[5] Thus, very high volumetric storage capacities similar to that of liquid ammonia can be achieved, and still the desorption process is facile. Here, we investigate the reason for this behavior. By a combination of decomposition rate and pore size distribution measurements and density functional theory (DFT) calculations, we provide new insight into the decomposition process. In particular, we show that during decomposition of $Mg(NH_3)_6Cl_2$ an extended system of nanosized pores develops. This system of channels facilitates the transport of desorbed NH_3 away from the interior of large volumes of compacted storage material.

The temperature-programmed desorption (TPD) of NH_3 from $Mg(NH_3)_6Cl_2$ powder has already been reported.[5] Desorption takes place in three stages. The first desorption peak involves four molecules of NH_3, and the last two peaks each correspond to one molecule of NH_3. Here, we have conducted eight consecutive desorption and readsorption experiments. From these, it is clear that the absorption and desorption of NH_3 is reversible, in agreement with previous findings.[2−4] In all runs, the integrated ammonia content was 5.85 ± 0.15. X-ray powder diffraction (XRPD) showed only pure $Mg(NH_3)_6Cl_2$ and $MgCl_2$ before and after decomposition. During the first four runs, it is noteworthy that the first desorption peak moves toward slightly lower temperatures and broadens. From the X-ray diffraction patterns that show a successively increasing line width, it is clear that this can be attributed to the relative large crystals (>150 nm) of $MgCl_2$ used in the first experiment gradually transforming into smaller and smaller crystals. Already in the second experiment, a crystal size of about 14 nm is estimated by the Scherrer equation. From the fourth to the eighth absorption and desorption, there is essentially no change in the TPD trace. Thus, the exact position of the desorption peak depends on the partial pressure of ammonia, the temperature ramp, and the crystal size. To gain a more complete understanding of the decomposition process, a series of DFT calculations were performed. The starting point was $Mg(NH_3)_6Cl_2$, which crystallizes with the same structure as K_2PtCl_6.[11,12] The structure and lattice parameters were well reproduced in the calculations. In Figure 1, the calculated NH_3 binding energies are shown. They show interestingly that the first two NH_3 to desorb are bound by almost the same energy and stronger than the next two. This immediately explains the almost simultaneous desorption of four coordinated NH_3 molecules. The first two ammonia molecules will desorb at almost the same temperature, after that, the next two must follow immediately. The binding energy is higher for the fifth and highest for the sixth NH_3 molecule, corresponding to the last two molecules of NH_3 being desorbed during the temperature ramp. For the last two structures, we find another crystal structure to be more favorable than the K_2PtCl_6 structure, namely, the one which is also found experimentally for $x = 2$ by Leineweber et al.[13] In the present analysis, this structural change is not included since it is not clear that the system has time to rearrange during the TPD experiment. The average bonding enthalpy of the first four NH_3 molecules is calculated to be 44.5 kJ/mol. This should be compared to the measured value of the bonding enthalpy of 55.7 kJ/mol.[2,3]

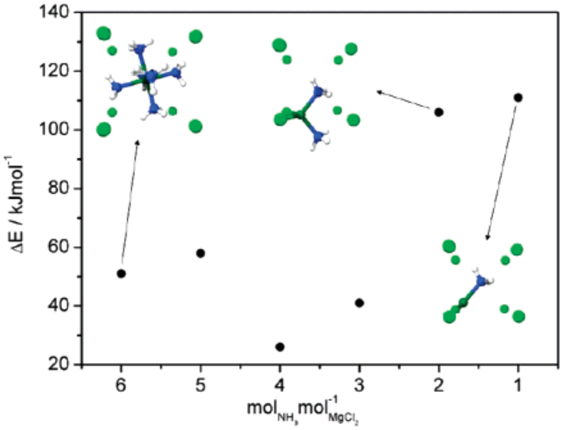

Figure 1. Structures of selected $Mg(NH_3)_xCl_2$ ($x = 6, 3, 1$) and calculated energies of coordinated NH_3 relative to gas-phase ammonia. Black dots are calculated by DFT from the K_2PtCl_6 structure reported by Hwang et al.[12]

We now turn to the question of why decomposition kinetics similar to that of a fine powder is observed from completely compact samples of $Mg(NH_3)_6Cl_2$ with a size of 1−2 cm^3. To study this, we have measured the pore size distribution during decomposition, as shown in Figure 2. During the desorption process, an extended nanopore system develops. The average pore diameters increase from initially 2−4 nm to roughly 20 nm.

In Figure 3, we compare the measured pore volumes to a model based on the DFT calculations. In constructing the model, we have used the fact that the calculations show that each crystal in the

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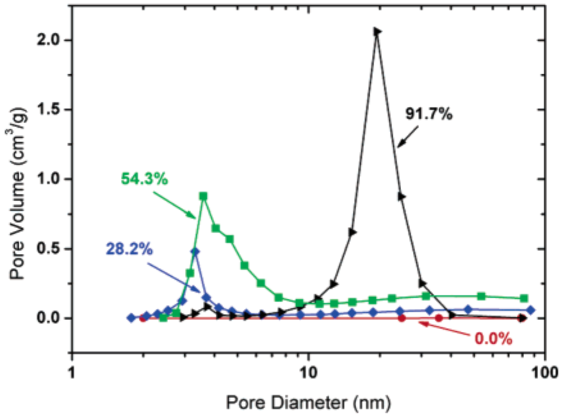

Figure 2. Pore size distributions from samples of compacted $Mg(NH_3)_xCl_2$ with varying amounts of ammonia desorbed.

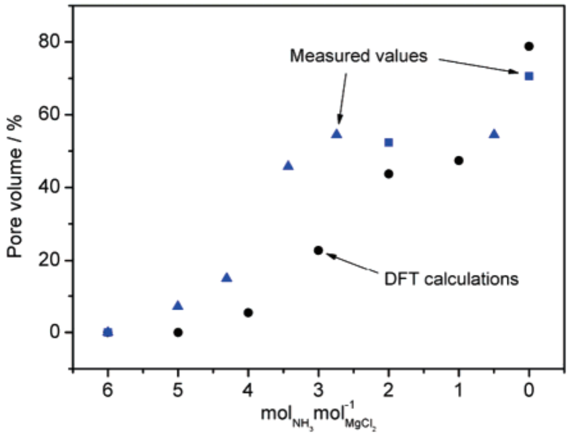

Figure 3. Pore volume as a percentage of the original volume obtained by different techniques. Blue triangles are measured by nitrogen adsorption, and blue squares are calculated from crystal structures reported in the literature.[11−13] Black dots are calculated by DFT from the K_2PtCl_6 structure reported by Hwang et al.[12]

material can release ammonia by a change in lattice constant and slight internal rearrangements within each unit cell. We can therefore assume that each crystallite in the polycrystalline material shrinks uniformly during decomposition. As illustrated in Figure 4, this leads directly to the development of a pore system.

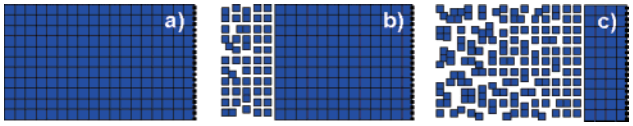

Figure 4. Two-dimensional schematic representation of the evolution of the pore system in the initially dense metal ammine structure. From a−c, a desorption front is moving toward the center, leaving behind a pore system of shrunken interconnected crystals.

This behavior of $Mg(NH_3)_6Cl_2$ is quite different from that of many other gas−solid processes involving solid-state diffusion of one component, which often lead to slow absorption and desorption kinetics.[14] Since this limitation does not exist for the metal ammine salts, they offer new possibilities in hydrogen storage. Thus, the generation of nanopores during desorption of NH_3 from $Mg(NH_3)_6Cl_2$ is necessary for achieving, at the same time, high volumetric storage capacities and acceptable desorption kinetics.

The metal ammine complexes have the complication as a hydrogen storage material that they need to be integrated with an ammonia decomposition catalyst in order to produce hydrogen. Today, this is a well-understood reaction, not least due to the detailed insight into catalytic ammonia synthesis,[15] but it still has the potential to be significantly improved.[16]

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Supporting Information Available: Experimental and computational details, pore volumes and surface areas, calculated structures of $Mg(NH_3)_xCl_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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