Chapter 5: Discussion

Hydrogen is an ideal clean energy carrier for both at mobile and stationary applications, due to its high (theoretical storage capacity, 7.6 wt%, low cost and lightweight. However, wide spread commercial applications are impeded by its high desorption temperature (between 300-400'C), and a relatively slow absorption/desorption kinetics. Particularly the desorption kinetics has not been well studied before. Not much experimental effort has been devoted to the key issues of H_3BNH_3. A clear understanding of the important factors that influence the hydrogen storage properties is highly desirable, and so is the material structural evolution associated with the factors.

The main objective of this study was set:

1) To determine the effect of milling on particle size, microstructure, lattice parameter, phase composition and hydrogen desorption of the powder mixture.
2) To evaluate experimentally the effect of selected chemical addition on hydrogen desorption of milled mixture
3) To improve the hydrogen storage properties of H_3BNH_3, including desorption kinetics, activation and thermodynamic stability.

The overall aim is to develop new H_3BNH_3-based hydrogen storage material with high hydrogen capacity and rapid kinetics for hydrogen application. One point that I would Like to make at this point is that nobody have tried ball milling on H3BNH3, so it is difficult to compare results with other.

5.1 As received H_3BNH_3

To establish the basics to understand the system, scanning mass spectrometry of as received sample was done, to know the basic products that are coming out of the sample during thermal processing. Coupled Mass spectrometry with TG/DSC was used, the graphs are plotter in Fig. 4.1.1 and 4.1.2. When comparing these results with the results of wolf et al. they are a bit different from fig. 2.5.3.6. This is explainable since we have reported the release of 2amu = hydrogen, 14amu = Nitrogen, 16amu = NH_2 -, 17amu = NH_3, 18amu = H_2O but they have taken spectra from 21amu-90amu. This means they cannot report any thing on the region from 1amu-20amu. We have also reported release of 28 amu, 32amu, 36amu, and 44amu, 32 amu.

Fig. 4.1.2 is at ramping temperature from 60°C-450°C. Here it is clear that at ramping there are two major reactions one at 105^{o}C and the other at 160°C. Hydrogen is evolved in these two reactions but hydrogen intensity that is released is higher in the first reaction and is low in the second reaction. But the weight loss of the reaction is 40% that means that there is a lot of by products that came out as well which can be seen in the fig. 4.1.2. When comparing both fig 4.1.1 and fig. 4.1.2 it becomes clear that the intensity might have increased or decreased otherwise the evolved masses are around the same, except 30 amu. 30 amu is evolved in ramping test, it is evolved because the heating rate is not slow like isothermal test, so it is evolved, and it is of very low intensity as well as for a small duration from 80-200’ C.

5.2 Effect of Milling on H_3BNH_3

The as received powder has a lamellar and flake like structure figs. 4.2.1.2 after milling, the structure changes to wire like, further milling to 1 hour, their is no flake like structure left in the material figs. 4.2.1.3 – 4.2.1.8. The milling has a limitation as well since the melting point of H_3BNH_3 is 105°C and after two hours milling the powder become welded and it don't remain a powder rather it become welded lava, for this reason powder is milled in 15 minutes duration and than given a break. Milling reduces the size of peaks, after 1 hour milling the peaks are quite small, which is not easily explainable, but either the particle is no longer crystalline. This might be due to the particle size and morphology change that is obvious from figure 4.2.1.2 and 4.2.1.8.

For 15minutes milled sample the weight loss is 8%, the DSC curve shows that the exothermic reaction starts at 50°C, which is in comparison with the hydrogen release as well. On the hydrogen desorbtion curve, there is a little amount of hydrogen evolved at around 70°C, which is different from other results obtained. This peak correspond to the heat flow peak at 20 minute so there is a reaction at this point which can be investigated in detail latter with a heating rate of 0.1-0.5'C/minute.

The graph for sample milled for 30 minutes shows a weight loss of 16%, which can be compared with other graphs where the normal weight loss is around 8-9% Fig. 4.2.3.2. This graph is smooth and it is different from other graphs. This might be because the powder polymerises, so during testing its polymerisation has an effect on the weight loss. Another Test would be done for this sample. If there is a weight loss of 16 % it

should have an effect on hydrogen evolved but the hydrogen evolved curve is same as the other milled results.

5.3 Effect of Ti addition

Titanium has quite a different effect on the surface, it makes the particles round and the more titanium the more particles are round. In the specimen where 1% titanium is added there are some wire and flake like structures (fig 4.3.1.3) but in the sample where 6% Ti is added there is no wire like structure (fig. 4.3.1.8).

Titanium addition reduces the peak height, as the trend can be seen in the fig.4.3.2.2. The peak height is reduced as well as the peaks are sharp and the width is narrow which means that crystallite size is reduced. This phenomenon can be explained when comparing microstructures, since the particles are round and small in size. Also there are peaks for Ti which means no new compound is formed.

The weight loss graph fig. 4.3.3.1 also shows improvement and for 3-6% Ti added sample has a weight loss of 9.8%. This can be by products, but when comparing this with the hydrogen evolved curves fig. 4.3.3.2 it shows that there is more hydrogen evolved for 6% Ti added specimen. Considering that 9% of weight is of titanium, so there was a reduced amount of hydrogen in the sample. Figure 4.3.3.2 hydrogen dsorption peak at 38 minutes which is misleading, it might be because of a delay in the simultaneous calculation, the correct time can be compared with as received scanning results fig.4.1.1 which shows that the peak is at 50 minutes.

5.4 Effect of $TiCl_3$ addition

The microstructure of 1% $TiCl_3$ added specimen is quite porous which is obvious from figs. 4.4.1.2 and 4.4.1.3, which shows a cage of porous structure. The structure of 3% $TiCl_3$ added specimen like welded and melting and particles agglomerated fig.4.4.1.5. This might be because $TiCl_3$ is spontaneously flame able in air, the amount of $TiCl_3$ is quite high that is 13.4 wt%. Also under microscope with a voltage of 10KV localized on a specific area means it might have released some heat. This is a possibility since charging of the particles can be seen, that's why we focus on a particle and then move the beam a bit and take picture.

Due to coupled effect of milling as well as $TiCl_3$ addition, it has reduced the height of peaks as well as width fig. 4.4.2.2. Comparing the results with 30 minutes milled samples XRD pattern it become obvious that $TiCl_3$ also have an effect on the H_3BNH_3 peak. This effect is due to the weight of $TiCl_3$ or it also have some structural change it is not clear. Comparing the SEM results it becomes clear that there is a phase change as well, which is obvious in fig. 4.4.1.2 and 4.2.1.6. $TiCl_3$ addition of 3-mol% show very good kinetics and the weight loss starting at 35min as well as hydrogen absorption at 35min, which is about 10min faster and it starts directly when the sample temperature becomes 90°C.

5.5 Effect of MgH_2 addition

Magnesium Hydride (MgH_2) sample was pre-milled for 20hr before its addition in H_3BNH_3. This is because coxia et al. results have shown an improvement in hydrogen absorption kinetics for 20hr-milled specimen.

In the ratio of 1:1, the particles are homogeneous as in fig 4.5.1.3 & fig.4.5.1.4. There is no flake-like structure, which is obvious in 1:2 ratio of 1hour milled; the flake-like structure is because of the H_3BNH_3 in abundance. In the samples where the H_3BNH_3:MgH_2 is in the ratio of 10:1 (figs 4.5.1.7 – 4.5.1.9), the flake-like structure is in abundance and there are a little patches of granules in between. A conclusion can be made that milling breaks the flakes and convert them to granules. The milling overall effect is quite unclear dot mapping results can make them clear and understandable what exactly these structures are.

The peak height is decreased with the increase of amount of MgH_2 the height become lower as well as increases in the height of MgH_2. As there is very low peaks for weight ratio of 1:1 specimen milled for 1 hour this phenomena can be compared with SEM fig. 4.5.1.3 where the particles are all round shaped.

At Isothermal temperature the weight loss for 1:1 was 2.5 wt% fig. 4.5.3.1, but for 1:2 sample fig. 4.5.3.2 it was only 0.6. The weight loss for 10:1 samples was 8wt%, which is around the same for as received specimen. The low amount of weight loss for the samples that contain high amount of MgH_2 is due to the large amount of MgH_2 that reduces the kinetics at isothermal temperature.

Ramping tests from 60-430'C were done to see the effect of MgH_2 on H_3BNH_3, as well as H_3BNH_3 on MgH_2 since 20 hour milled MgH_2 desorbs hydrogen at 380°C. The results show that for samples with the ratio of 1:1 the weight loss is only 3.5% fig. 4.5.3.5, which is quite different than expected. When comparing the effect of H_3BNH_3 on MgH_2 it shows that the kinetics is reduced and that they make a very stable compound. There is very high quantity of hydrogen but still at 430°C it is not released in high quantity. If H_3BNH_3 is in its original form it must have a weight loss at least of 17% since H_3BNH_3 is present in 50-wt%.

Chapter 6: Conclusions & Future Work

Conclusions

From our extensive work on H_3BNH_3 we can conclude some basic points that would help us as well as others to have a better understanding of the system.

- Milling makes particle size small and wire like, so the powder has more surface area. But this effect is not obvious in the TG/DSc analysis.
- Milling reduces crystal structure, and crystalline phase.
- Titanium makes the particles round and the more titanium the more particles are round.
- Titanium addition improves kinetics as 3-6% Ti added sample has a weight loss of 9.8%.
- $TiCl_3$ addition makes powder porous.
- 3-mol% $TiCl_3$ addition show very good kinetics and the weight loss starting at 35min as well as hydrogen absorption at 35min, which is about 10min faster and it starts directly when the sample temperature becomes 90°C.
- MgH_2 addition breaks the flakes and converts them to granules.
- MgH_2 reduces the kinetics of H_3BNH_3. Also H_3BNH_3 reduces the kinetics of MgH_2.

Future Work

When you want to get the answer of a question, you might not find the answer, but one thing that you would find is other unanswered question. Research on a small area of concern opens up large areas of questions. The following may be considered to be done in order to strengthen and further verify the scope of the current project.

- Isothermal tests at different temperatures can be performed to understand the kinetics in a better way.
- Tests can be carried out for lower change in temperature (< 1^{o}C).
- TG/FTIR studies can be performed to understand the reaction products.
- Larger quantities of Titanium Chloride may be added to see the effect of titanium chloride.
- Dot mapping can be performed to know the exact phases that are present.
- Modelling can be done to understand the phenomena of the thermal processing.
- Milling for short time as well as with small intervals can explain the effect of milling in detail.
- One thing where I my self cannot really think of is processing, I don't know but I think that different processes can be used to make the system running, one thing is for sure there is 20% hydrogen.

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