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Catalytic Ammonia Decomposition in Molten Salt and Ionic Liquid Media

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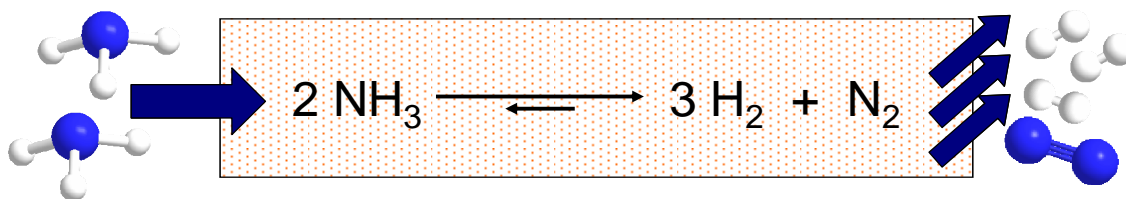
1 Introduction

The increasing daily consumption of energy per person in the industrialised countries like Europe or the U.S. along with the upcoming developing countries like China or India has triggered a deep reflection about the way to generate and store energy. The actual society way of life, indeed, is pushing the consumption of electrical energy higher and higher. Thus, to store and to provide the energy necessary to at least preserve the actual life standards is going to be one of the biggest challenges the mankind is going to face in the nearly future.

Hydrogen has emerged as viable medium as energy carrier as its high energy density. Thanks to well known fuel cell technologies or combustion applications and due to the easy availability of co-reactant oxygen, its usage in energy production is almost universally possible. However, the main problem for energy supplying systems based on hydrogen is its storage. In fact, a device like a common gas bottle reaches a storing capacity of 1,5 wt.-% for hydrogen (calculation made considering a 50 l steel tank weighting ca.95 kg charged at 200 bar hydrogen). On the other hand, storing hydrogen in liquid form will not solve the problem, requiring a huge amount of energy for the liquefaction, high pressure resisting tanks those will have, in addition, the known problem of loss over time by effusion, without considering the risk of handling hydrogen at high pressures. Other systems provide hydrogen through physically bound metal hydrides, which show good results for releasing velocity but have only limited storing capacities [1]. Therefore, alternative hydrogen storing systems with high capacities, low releasing temperatures and high purity of the released gas are needed. These systems use compounds with mostly chemically bound hydrogen like ammonia-borane [2,3]. The problem here is hidden in the difficult production and recycling process of these compounds. To overcome the various difficulties in this field a chemically storing system should be easy to produce and recycle. With its 17,6 wt.-% of hydrogen, ammonia is an interesting possibility. As a matter of fact, it is widely produced in big amounts and easy to liquefy at the relatively low pressure of 8 bar, leading to a capacity of 120 kgH₂/m³ [4]. The decomposition of ammonia occurs at temperature around 400 °C releasing hydrogen and nitrogen, which was taken from the air during production, as only side product [5,6]. This product gas mixture can in principle directly be used in a hydrogen fuel cell or combustion system.

Ionic Liquids and Molten Salt media are well known as electrolytes in batteries or heat transfer media in various applications [7]. Moreover, especially for Ionic Liquids, great interest has been devoted to these materials as solvents or co solvents in catalytic reactions [8]. Ionic Liquids are pure salts of melting points below 100°C [9]. Besides their low volatility and high thermal stability, compared to common organic solvents, Ionic Liquids dissolve

hydrogen and nitrogen in negligible amount whereas they show high solubilisation capability for ammonia [10]. Another property of these solvents is the stabilization effect on catalysts in chemical reactions. Our contribution deals with the idea to generate a catalytic reaction system consisting of a catalyst stabilized in Ionic Liquid or Molten Salt as solvent, being able to decompose ammonia to hydrogen and nitrogen. The underlying idea is that due to the high solubility of ammonia in such a media and the very low solubility of hydrogen and nitrogen, the ammonia decomposition equilibrium might be shifted towards the latter, so allowing the decrease of the reaction temperature but reaching same conversions.



2 Results and Discussion

At first, Ionic Liquids were investigated as solvent media. Therefore, the thermal stable Ionic Liquid [EMIM][NTf₂] (1,2-Dimethyl-3-ethylimidazolium Bis(trifluorosulfonyl)imide) with its favourable solubility performance was chosen. As catalyst, Ruthenium supported on MgO was suspended into the system. The results obtained in experiments at different temperature are shown in Figure 1.

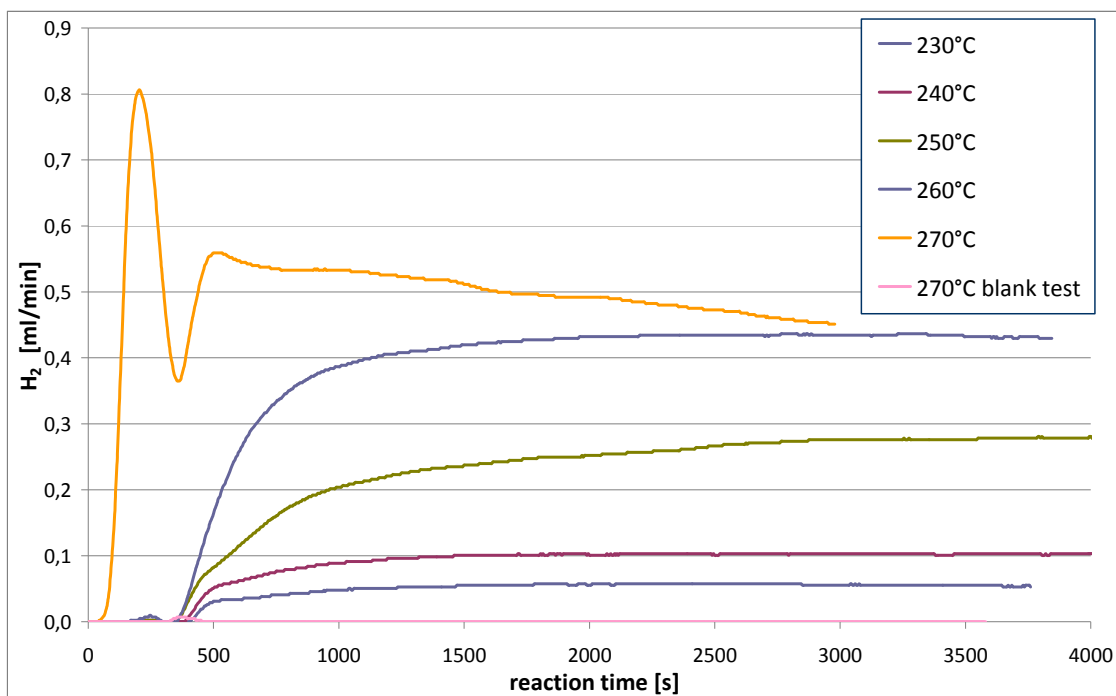


Figure 1: Hydrogen evolution during decomposition of ammonia at different temperatures in [EMIM][NTf₂] with Ru on MgO.

During the reaction, the conversion reaches a stable level, with the highest stable conversion got at 260 °C. In these conditions, the Ionic Liquid and the dispersed catalyst showed to be unaffected after the reaction was stopped. Conversely, at 270 °C, the ionic liquid decomposed as indicated by the decreasing profile of conversion vs. time, as well as by the tarry substance which form from the ionic liquid in the reactor. It could be concluded that the thermal limit for the actually known Ionic Liquids had been reached. As solvent with higher stability is necessary, molten Salts mixtures were examined for their possible application. To reach better catalyst dispersion, eutectic mixtures with low melting point were chosen. An eutectic salt mixture of K/Li/Cs Acetate was found a suitable candidate [11]. As catalyst in this reaction setup, RuCl_3 was used. The results of this experiment at different temperatures are shown in Figure 2.

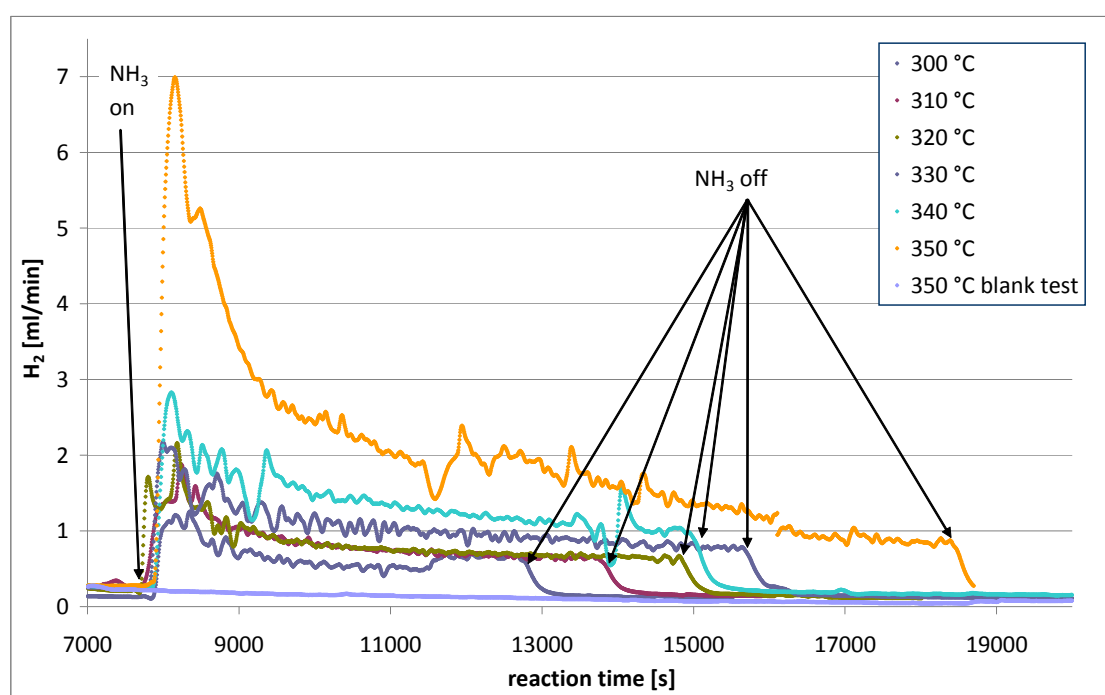


Figure 2: Evolution during decomposition of ammonia at different temperatures K/Li/Cs Acetate with Ru Cl_3 .

As expected, the decomposition rate of ammonia is higher at increased temperatures. However, the conversion is decreasing over the time indicating a catalyst deactivation. This reasonably occurred due to agglomeration. In fact, it is reasonable to assume that the Ru salt formed Ru nano-particles in the reaction conditions, which are the active species. These particles agglomerated during the reaction leading to less active metal centres. Highest conversions were achieved at 350 °C with a hydrogen production rate of about 7 ml/min which corresponded to a yield of 23 % of the ammonia feed introduced into the system.

3 Conclusion

In summary, the feasibility of the decomposition of ammonia to hydrogen and nitrogen in a reaction system comprising Ionic Liquids or Molten Salts as solvent media has been proven.

The hydrogen output rates of about 0,5 ml/min at stable level in the Ionic Liquid system is relatively low. However, the maximal reachable reaction rate in this experiment was limited by the thermal stability of the solvent media. Thus, the use of higher thermally stable Eutectic Molten Salt mixtures like K/Li/Cs Acetate allowed overcoming this problem. This second reaction system shows higher conversion and the highest hydrogen production rate of 7 ml/min, 14times bigger than in the former series of experiments. Moreover, although the rapid deactivation of the catalyst, a stable hydrogen production rate of 1 ml/min, more than double as in the experiment with the Ionic Liquid solvent, was obtained.

The results obtained are quite promising and this work gives insights into new approaches for known reactions leading to innovative ways of hydrogen supply and with this an improving support for energy. The catalyst deactivation and the improvement of overall conversion are currently under investigation.

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