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REVIEW

Ammonia as a possible element in an energy infrastructure: catalysts for ammonia decomposition

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The possible role of ammonia in a future energy infrastructure is discussed. The review is focused on the catalytic decomposition of ammonia as a key step. Other aspects, such as the catalytic removal of ammonia from gasification product gas or direct ammonia fuel cells, are highlighted as well. The more general question of the integration of ammonia in an infrastructure is also covered.

1. Introduction

There is widespread consensus that fossil fuel reserves, especially oil reserves, will be exhausted to a large extent in the course of the current century, possibly leading to shortages relatively soon. This causes a number of different problems: (i) since oil is one of the backbones in our energy supply structure, oil as a source of energy has to be replaced by an alternative energy source; (ii) it is also a key component in our energy infrastructure, providing the most important storage and transportation form of energy, and so also this function may need to be replaced; and (iii) due to its high energy density and easy storage, liquid hydrocarbons—and to some extent gaseous hydrocarbons in the form of methane or liquefied petroleum gas (LPG)—are today the only option for packing energy sufficiently well in cars to ascertain the driving ranges to which we are used to nowadays.

Several different options are being discussed for the replacement of hydrocarbons, both as the storage and transportation form of energy in our energy infrastructure as well as to provide the energy required for the propulsion of a car. The most prominent ones are probably hydrogen and methanol, also methane appears to be interesting. In some regions of the world, such as in Brazil, ethanol appears to be a viable choice as

transportation fuel. If lignocellulose could easily be depolymerised to fermentable sugars, ethanol might find more widespread use. Finally, synthetic hydrocarbons instead of fossil ones could gradually replace fossil energy carriers without changing the infrastructure. All of these options have their advantages and disadvantages, which are in more detail comparatively discussed in a recent publication.[1]

However, in addition to the possible infrastructure molecules mentioned above, several other compounds have been discussed. Among the more interesting ones is certainly ammonia.[2] There is well established production technology, liquefaction and transportation are relatively easy, and ammonia can be converted directly to other forms of energy, or it can be decomposed to produce exclusively hydrogen and nitrogen, so that it could function as a means for hydrogen storage. While it is not anticipated that ammonia will form the backbone of a future energy infrastructure, it could be an interesting storage compound for niche applications. The role of ammonia for hydrogen storage has been discussed some years ago by Klerke et al.[3] In that article, many aspects of the use of ammonia for this purpose are discussed. Here, we are focussing on two important issues, i.e. the decomposition reaction to release hydrogen from ammonia and the direct conversion to electricity in ammonia fuel cells. For more detailed information on infrastructural aspects of ammonia, the reader is referred to the review by Klerke et al., although some points will also be touched on in this contribution.

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Broader context

Ammonia decomposition is an important reaction in at least two different fields related to energy and environmental science: it can be used to provide CO_x-free hydrogen for fuel cells, and to remove ammonia from the reformate of internal gasification combined cycle (IGCC) power plants which might be widely deployed in the future as a CO_2-removal technology. The review is focussed on catalysts for ammonia decomposition, with an emphasis on hydrogen generation. While ammonia is not expected to form the backbone of a possible future energy infrastructure, it could find interesting niche application.

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2.   Ammonia infrastructure

Ammonia is gaseous at ambient temperature and pressure. Its boiling point at 1000 hPa (1 bar) is 240 K, resulting in a liquid with a density of 0.682 g cm^{-3} at 240 K; for liquefaction at 298 K a pressure of about 10 000 hPa (10 bar) is required (0.603 g cm^{-3}). Storing liquid ammonia is thus feasible in relatively inexpensive pressure or cryo-vessels. Disregarding the container weight, these values correspond to hydrogen storage densities of about 0.106 g cm^{-3} which meets the target of the US DOE for mobile applications (0.07 g cm^{-3} on the systems level as the ultimate full fleet target, current targets are lower[4]). However, due to the toxicity and the smell of ammonia, storage in cars in liquid or gaseous form would most probably not be acceptable. This does not seem to be an unsurmountable obstacle, though, since a number of solids exist, in which rather high amounts of ammonia can be safely stored. These are typically solid ammine complexes, of which many are known. To date, the most promising ones for ammonia storage are Mg(NH$_3$)$_6$Cl$_2$,[5] with a volumetric hydrogen storage capacity of 0.115 g cm^{-3} (9.19 wt%), and Ca(NH$_3$)$_8$Cl$_2$[6] with capacities of 0.116 g cm^{-3} and 9.78 wt%. For the magnesium compound, recently also a large scale/low cost synthetic pathway has been described.[7] These compounds have only moderate ammonia equilibrium pressures, 2.2 hPa (0.0022 bar) for the magnesium compound and 770 hPa (0.77 bar) for the calcium ammine, both at 300 K, and can thus relatively safely be handled. On the other hand, since PEM fuel cells operate at around 363 K, ammonia can be released at sufficient pressure by heat integration with the fuel cell. Ammonia desorption is facilitated by the formation of a pore system in the ammonia storage system.[6,8]

The production of ammonia by the Haber–Bosch process nowadays relies to a very large extent on steam reforming of natural gas for the production of hydrogen, followed by the ammonia synthesis reaction from hydrogen and nitrogen.[9] Ammonia synthesis is one of the most energy efficient processes implemented in industry. Specific energy consumptions of down to 27 GJ t^{-1}(NH$_3$) are quoted for ammonia synthesis for the most advanced processes, which, compared to a minimum energy requirement of 20.9 GJ t^{-1}(NH$_3$), corresponds to an energy efficiency for the overall process of 75%.[10] Most of the energy losses occur in turbines and compressors, the reaction stages (syngas production and the synthesis reaction) are associated with relatively small losses.[10] These losses actually compare favourably to the energy demands of hydrogen liquefaction (about 30%),[11] although one has to take into account an additional energy need for ammonia decomposition, see below. Ammonia production could alternatively be based on hydrogen generated from water electrolysis (the electricity coming from renewable sources). However, in this case, the overall efficiency is expected to decrease, since the electrolysis itself is quoted with an energy efficiency of only about 70–80%, depending on the process (the efficiency may be lower, if all balance of plant components and fluctuating electricity supply are taken into account).[12] This may come down with newer developments, such as gas phase or pressure electrolysis or novel electrocatalysts. Together with the energy losses in the other process steps, an overall efficiency not higher than about 60% can be expected for ammonia produced from renewable resources. However, this energy consumption during electrolysis holds for all hydrogen

storage technologies and is thus not a unique disadvantage of ammonia production from renewable electricity. For a sound comparison of different energy storage options a full life-cycle analysis would be required. This goes far beyond the scope of this contribution, the focus of which is the catalytic decomposition. Nevertheless, initial analysis and comparison with other storage options reveals that ammonia will probably only be a viable option for niche applications.[1]

Storage and transportation of ammonia are well developed at different scales.[10] It can be shipped in trucks, railroad cars, ships and pipelines. Storage is possible under pressure for smaller scale; large scale storage is mostly done in cryo-vessels, but also underground caverns are used for this purpose.[10] Adapting such infrastructure to even larger scale seems feasible; for small scale mobile applications, the solid state storage in metal ammines discussed above would probably be used.

3.   The ammonia decomposition as a key step

Catalytic ammonia decomposition is important in three different fields, each having different requirements with respect to the catalyst: a niche application is the facile production of a protective, reducing gas atmosphere composed of hydrogen and nitrogen. Such gases are used for the production of controlled atmospheres for heat treatment in the metallurgical industry.[13] Catalysts for these processes should be cheap and have sufficiently high activity. Typical systems are based on supported nickel.

A field where ammonia decomposition could become much more important in the future is clean-up of coal or biomass derived fuel gas.[14–17] In coal or biomass gasification, for instance for an internal gasification combined cycle (IGCC) power plant, a fuel gas is produced. Nitrogen compounds in the coal or the biomass (typically 0.5–2% of N) are to a large extent converted to ammonia in the gasification process, and removal of this ammonia (typical concentration levels of 0.5%) is advantageous, before the fuel gas is further processed. Decomposition would be the ideal reaction for this purpose, since it produces additional hydrogen for the fuel. Catalysts for this purpose need to be rugged, since the fuel gas may contain many possible catalyst poisons, depending on the place where the catalyst is located in the overall process. It is advantageous to place the decomposition catalyst directly following the gasifier to exploit the high gas temperature; however, here the gas still contains particulates, which can be highly detrimental to the catalyst.[15]

Finally, ammonia decomposition is interesting for the production of high purity hydrogen to feed PEM fuel cells, either on-site of the fuelling station or even directly on board of a car. Reforming of hydrocarbons always leads to CO impurities which are detrimental to the fuel cell catalysts, and catalytic ammonia decomposition instead of hydrocarbon reforming would circumvent this problem. This application places highest demands on the catalyst with respect to activity, since high temperatures are very unfavourable for on-board hydrogen generation in cars, and even for stationary decomposition units, for instance in hydrogen fuelling stations, a high temperature reactor would require additional energy. On the other hand, the catalyst system does not need to be as rugged as in coal
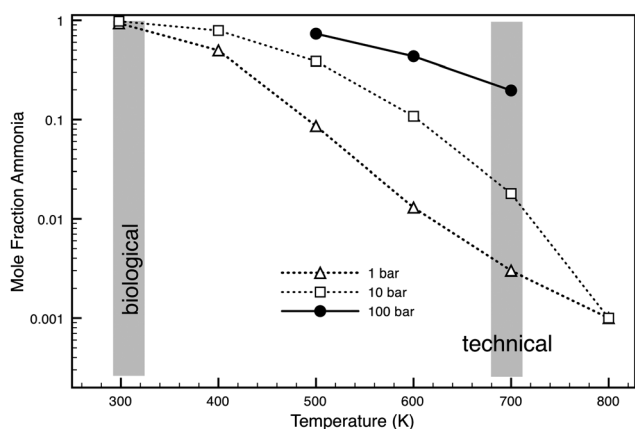
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Fig. 1 The ammonia synthesis equilibrium at three different pressures and stoichiometric compositions as a function of temperature (reprinted with permission from ref. 18).

gasification units, since the ammonia supplied for hydrogen generation would be rather pure.

If ammonia should be used as a hydrogen storage compound, the decomposition reaction which results in the formation of nitrogen and hydrogen is a key step. This reaction proceeds to a sufficiently large extent only, if carried out at elevated temperature due to thermodynamic limitations (Fig. 1, from ref. 18). For on-board hydrogen generation in cars, where no complex recycle of undecomposed ammonia appears feasible due to weight and space limitations, a decomposition of more than 99% seems necessary. Since the hydrogen needs to be supplied to the fuel cell at somewhat elevated pressure over atmospheric pressure, decomposition temperatures exceeding about 650 K are required for thermodynamic reasons alone. There is thus no need for catalysts to be active at lower temperature, at least for mobile applications.

In any case, some ammonia slip is to be expected for any ammonia decomposition system. Since ammonia would poison the anode catalyst and the acidic membrane of the fuel cell—in case a PEM fuel cell is used (ref. 19)—it would have to be removed before the feed gas enters the fuel cell. If the decomposition reaction is carried out in the fuelling station, the ammonia could be removed by different technologies, such as freezing it from the gas mixture or adsorption. On board of a car, this could probably best be achieved with an acidic adsorber, such as a resin or a zeolite, in an exchangeable cartridge. Resins have high adsorption capacities, because their acid site concentration goes up to around 5 meq g^{-1} while acidic zeolites, with Si/Al ratios at the lower end of the commercially available grades of about 5, only have acid site concentrations below 2 meq g^{-1}. Assuming a hydrogen requirement of 6 kg for a typical driving range and an ammonia slip of 1% (molar fraction), a total of about 20 kg of zeolitic adsorber or 8 kg of resin adsorber would be required. However, zeolites have the advantage that they could be regenerated thermally to recover gaseous ammonia, while this is more difficult for resins due to the limited thermal stability. Thus, on board regeneration of such an adsorber could be possible, since the ammonia decomposition reactor needs a temperature level of more than 600 K. This is also the typical temperature range at which ammonia is released from zeolites, and thus heat integration of such systems seems feasible.

4. Ammonia decomposition catalysts

The state of the art with respect to ammonia decomposition catalysts until about 2004 has been reviewed by Yin et al.[20] The more important catalysts studied, with a focus on the period after this first review had been published, will be discussed in the following sections. Due to the different conditions used in the various studies, it is often not easy to compare the performance of the different catalyst systems. To allow for comparison, it has been attempted for a number of different catalysts to convert rates from the information given in the different publications to a common unit, i.e. kg NH_3 kg_{cat}^{-1} h^{-1}; where at all possible, rates are given for a temperature of 773 K or extrapolated to this temperature. One should keep in mind, though, that rate information for identical concentrations and temperatures was not always available, and this is noted, if comparisons are made in the following. In some cases, the rate data had to be inferred from graphs in publications. The data should thus not be considered to be highly precise, but rather as indications of activity levels of different systems to facilitate comparison.

Ammonia decomposition catalysts were originally investigated in order to understand the ammonia synthesis, although in the early days of catalysis, ammonia decomposition had been studied already for fundamental reasons as well.[21,22] In fact, ammonia decomposition is one of the very first catalytic reactions studied, and Thenard described an activity pattern of different metals for this reaction (Fe > Cu > Ag > Au > Pt),[23] at a time when not even the word "catalysis" existed for this phenomenon! If one looks at the pure metals, the decomposition activity follows a classical volcano shaped curve (Fig. 2, from ref. 10). On the x-axis in this graph, the enthalpy for dissociative nitrogen adsorption is plotted, which is the key step in ammonia synthesis, but also seems to be highly important in ammonia decomposition. Of the pure elements, ruthenium is clearly the most active one, and most
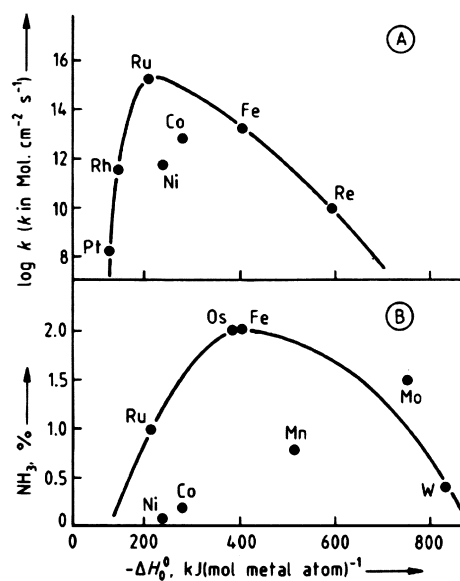

Fig. 2 (A) The rate constants of ammonia decomposition on metals as a function of $-\Delta H_0^0$ and (B) ammonia synthesis capacity of metals as a function of $-\Delta H_0^0$. (Mol. denotes molecule, mol denotes mole, reprinted with permission from ref. 10.)
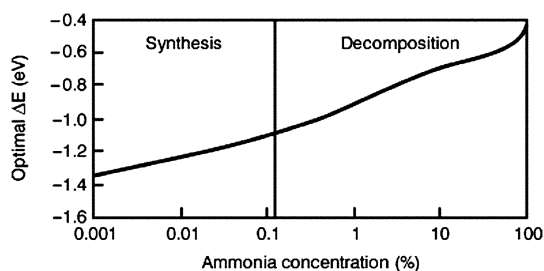
Fig. 3 Dissociative N_2 adsorption energy of optimal catalysts for ammonia synthesis/decomposition at 773 K, 1000 hPa (1 bar) and 3 : 1 H_2/N_2. Equilibrium corresponds to *ca.* 0.13% ammonia (reprinted with permission from ref. 26).

published data in the literature indeed rely on the use of ruthenium based catalysts. Similar volcano shaped curves can be obtained, if the nitrogen binding energy is used as the descriptor. This correlation was then used to predict the ammonia decomposition activity of bimetallic catalyst compositions based on single crystal systems.[24,25] Highly interesting catalysts were identified this way, with Fe on Pt(111) and Co on Pt(111) the most promising ones identified by the computational study. The high activity was verified experimentally, the single crystal materials showed decomposition activity already at 350 K. However, whether such results could be extrapolated to technical conditions remains to be seen, since the activity is dependent on the exact nature of the system. Fe and Co in the subsurface of the Pt(111) resulted in inactive catalysts, and it will be difficult to stabilize a defined system at the conditions above 650 K which would be required for ammonia decomposition under industrial conditions.

Based on the concept of microscopic reversibility, one would expect that the best ammonia synthesis catalyst is also the best ammonia decomposition catalyst. To a first approximation, this is certainly correct: ruthenium and iron based catalysts are suitable for both reactions. However, as Boisen *et al.*[26] have pointed out, the conditions for ammonia synthesis and ammonia decomposition are quite different. Calculations of the optimal energy for nitrogen dissociation in dependence of the ammonia concentration do not give a constant value, but different enthalpies for different concentrations (Fig. 3, from ref. 26). Nevertheless, the maximum rate is still found at nitrogen adsorption enthalpies close to those observed on ruthenium.

Mechanism

A number of mechanisms have been suggested for the decomposition of ammonia, many of which were based on measurements at conditions far away from the ones relevant for ammonia decomposition to generate pure hydrogen. Nevertheless, irrespective of the catalytic material, two possible rate limiting steps are discussed, cleavage of the first N–H bond to result in the formation of adsorbed NH_2 and H, or the recombination of adsorbed nitrogen atoms to result in desorption of N_2. For ruthenium a model with both steps being rate determining was proposed which accounted for the positive reaction order of about 0.75 for ammonia and the strongly negative order in hydrogen pressure.[27] A recent temporal analysis of products

(TAP) study revealed substantial differences for pure Ru- and Na-modified Ru catalysts. Nevertheless, for both systems, the recombination of the nitrogen atoms was assessed to be the slow step.[28] However, in studies on a NiPt/Al_2O_3 catalyst at higher pressures, it was reported that hydrogen did not have an inhibitory effect, and that the reaction could be described with a simple first order rate law in ammonia, suggesting the recombinative desorption of nitrogen as rate limiting. In most studies, which are compiled in ref. 20 and 27, desorption was identified as the key step. However, this seems to be to some extent dependent on the catalytic material studied and the exact conditions of the reaction. The last statement is corroborated by an extensive study aimed at elucidating the kinetically relevant steps in ammonia decomposition over ruthenium based catalysts.[29,30] Recently, very detailed kinetic models have been developed for specific catalysts, *i.e.* for nickel[31] and for Ru/γ-Al_2O_3.[32] These models incorporate all relevant steps, moreover, the importance of lateral interactions between adsorbates has been highlighted. In addition, new insight might come from computational investigations of this reaction which are able to reproduce measured reaction rates very well, as recently described.[33] Ganley *et al.*[34] concluded from their data on different catalysts that recombinative nitrogen desorption is rate limiting for Fe, Co and Ni as catalysts, while for Rh, Ir, Pd, Pt, and Cu the N–H bond scission is limiting. However, a density functional theory (DFT) study suggests for Fe_{55} clusters that the first hydrogen abstraction is the rate limiting step.[35] The question of the mechanistic pathway of the reaction is thus not conclusively answered. It appears that there is probably no simple and general answer to the question of a single rate limiting step, and that each system needs to be analyzed in detail.

Ruthenium-based catalysts

As stated above, ruthenium is the most active metal for ammonia decomposition. However, depending on the exact nature of the catalyst, the activity can differ strongly. One of the most comprehensive studies was published by Yin *et al.*[36] These
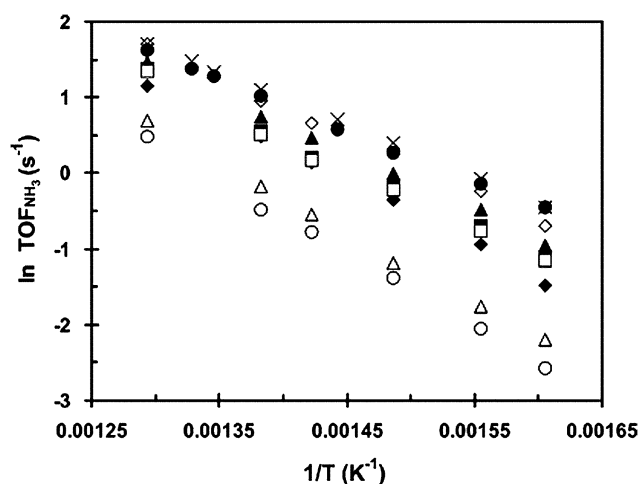

Fig. 4 Arrhenius plots of Ru catalysts on different supports ($\blacklozenge$, CNTs; $\diamondsuit$, MgO; $\blacktriangle$, TiO_2; $\triangle$, AC; $\blacksquare$, Al_2O_3; $\square$, ZrO_2; $\bigcirc$, ZrO_2-BD; $\bullet$, K/ZrO_2-BD; $\times$, K/CNTs). Reprinted with permission from ref. 36.

authors have compared—among other active metals—ruthenium supported on different support materials. While Ru supported on carbon nanotubes (CNTs) had the highest NH_3 decomposition activity, it did not have the highest activity based on the number of exposed metal atoms. In this case, Ru/MgO was superior to the CNT support. However, after doping with potassium, MgO and CNTs were almost similar with respect to the TOF (Fig. 4, from ref. 36). Productivities at 773 K for these catalysts range from about 10 kg NH_3 kg_{cat}^{-1} h^{-1} (on supports such as TiO_2, ZrO_2, or Al_2O_3) up to above 30 kg NH_3 kg_{cat}^{-1} h^{-1} (for K-doped CNTs).

This was attributed to the conductive nature of the CNT-support which made electron transfer to the ruthenium easier. Overall, CNTs as support were found to give the highest conversion, since the dispersion of the ruthenium on this support was the best. Modification of the CNTs with nitrogen improved the catalytic activity further by a factor of about two[37,38] (but not above the activity of the K-doped CNT system). This increases the basicity of the support which also plays a major role for activity. This is also the reason why MgO is a highly suitable support material. Ruthenium particles in the size range of 2–7 nm, supported on base-treated ZrO_2, were also found to be highly effective catalysts for ammonia decomposition; in this study the basicity of the support was suggested to have the highest influence.[39] The high activity of MgO supported ruthenium particles and the beneficial effect of alkali doping were corroborated by Zhang who produced about 2 nm sized ruthenium particles on high surface area MgO.[40] Cs as promoter was found to be superior over potassium, connecting to earlier results by Wang et al.,[41] who described the order of the promoting effect as K > Na > Li > Ba > Ca, with Ce and La at intermediate levels of promoting activity. A similar promoting effect was also reported for the thermally very stable $MgAl_2O_4$ as support:[42] upon promotion with caesium and barium, the activity increased up to tenfold, with the effect of caesium being stronger than that of barium. A very active Ru catalyst was based on the very basic support Pr_6O_{11} after additional modification with Cs_2O. This system showed a productivity of more than 2 kg NH_3 kg_{cat}^{-1} h^{-1} at 673 K.

An interesting concept for the promotion of supported Ru catalysts for ammonia decomposition was recently suggested by Klerke et al.:[43] instead of using bulk titania as support and doping it with alkali metal compounds, they produced the defined nanoscale alkali titanate phases $Na_2Ti_3O_7$, $K_2Ti_6O_{13}$ and $Cs_2Ti_6O_{13}$ in which the corresponding alkali metal centers are atomically dispersed. Again the clear promoter effect Cs > K > Na was observed. However, these supports are not useful for technical applications, since they decompose at temperatures of about 750 K. An interesting effect of K-doping and the discovery of a novel catalyst were reported by Pyrz et al.[44] They found that in the presence of potassium a hollandite phase KRu_4O_8 was formed from a Ru/Al_2O_3 catalyst. This hollandite phase was reported to have high ammonia decomposition activity at temperatures as low as 300 °C—albeit only at 15% NH_3 content in the gas phase. However, the hollandite phase was found to be unstable under temperature cycling conditions and under reducing atmosphere at higher temperatures, resulting again in a more conventional supported metallic ruthenium on alumina catalyst.

Different carbon-based supports for ruthenium were investigated by Li et al.[45,46] Two main effects of the support were identified: (1) a semiquantitative correlation between the graphitization degree of the support and the catalytic activity was established, i.e. the catalysts with the highest degree of graphitization, as detected by Raman spectroscopy, had the highest TOF, which was attributed to easier electron transfer from conducting support materials and (2) an optimum ruthenium particle size of about 3–4 nm was suggested. The correlation of decomposition activity with the degree of graphitization of the same CNT support is also reported by Zheng et al.,[47] together with the finding that large ruthenium particles on the outside of the CNTs are more active than those smaller particles inside the tubes, which was tentatively ascribed to the fact that the CNT support offers different sites inside or outside the tubular channels for Ru nanoparticles, masking the possible beneficial effect of the enhanced electron density of CNTs with high graphitization degree. The authors attributed the decreasing activity of smaller ruthenium particles to more difficult recombinative nitrogen desorption from these particles.

Zheng et al.[48] observed a substantial decrease of the reaction rate for ruthenium particles with sizes below 2 nm, while average ruthenium particle sizes of 2.2 nm resulted in the most active Ru/Al_2O_3 catalysts. A similar optimum ruthenium particle size was described by Garcia-Garcia et al.[49] The high activity of particles in this size range was attributed to the presence of B_5 sites, which are most abundant for particle sizes in the range of 3–5 nm. Such B_5 sites consist of an arrangement of three ruthenium atoms in one layer and two further ruthenium atoms in the layer directly above this at a monoatomic step on a Ru(0001) terrace. They had been suggested earlier as crucial sites for many reactions and it had been inferred that a minimum size of about 2 nm was required to accommodate such sites.[50] However, this statement has to be modified to some extent, since it has recently been shown that the appearance of the B_5 sites does not solely depend on particle size, but also on particle shape.[51] While for hemispherical particles, the highest TOF was observed for particles with sizes between 1.8 and 3 nm, for flat elongated particles, the maximum occurred at a size of 7 nm. This study was supported by first principle simulations, and a kinetic model was constructed which allows correlation between activity and size/shape of the ruthenium particles. Highly relevant for ammonia decomposition is the fact that the B_5 sites are key for NO dissociation[52] and in ammonia synthesis for the dissociation of the nitrogen,[53,54] the reverse reaction of one of the suggested rate limiting steps in ammonia decomposition, and thus a strong influence of the presence of B_5 sites on ammonia decomposition may in fact be expected. There thus seems to be agreement that an optimum ruthenium based catalyst for ammonia decomposition should have ruthenium particle sizes of around 3 nm which are supported on a basic, conductive support. Chlorine compounds should be avoided in the catalyst synthesis, since the presence of chlorine in the final catalyst has been reported to reduce the activity.[39,41] When choosing a suitable support material, however, one should keep stability under reaction conditions in mind. Carbon based supports may undergo methanation at higher temperature in the presence of hydrogen and metallic catalysts, and this problem could be a severe obstacle for technical implementation of

ruthenium catalysts—or any other metal—on carbon supports for ammonia decomposition.

Supports obtained from waste materials, such as fly ash,[55,56] red mud (waste product of the Bayer process), or Halloysite, a cheap naturally occurring tubular alumosilicate,[57] have also been described in several publications.[55] However, the activities of the catalysts were lower than those reported for other supports in the literature, and considering the fact that the ruthenium is the most expensive component of the catalysts, one would try to optimize the support primarily for activity, not so much for cost. This makes it improbable that such waste product supports would be used in practical applications.

Ruthenium based catalysts are presently the most promising system for ammonia decomposition to generate CO_x free hydrogen. Lines of development include the search for stable systems and still higher activity at low temperatures of about 650 K. But as active as ruthenium catalysts are, it is a rather expensive metal at around 5000 \$ kg^{-1}, and thus alternative catalysts would be attractive both for large scale application and in applications where more rugged catalysts are needed, such as in gasification processes.

Iron-based catalysts

Ruthenium is a highly active metal for ammonia synthesis, and so is iron, which still forms the backbone of most catalysts in ammonia plants. Thus, it comes to no surprise that also iron based catalysts have been intensively studied, albeit more for the ammonia decomposition in hot gas from coal gasification than for the supply of CO_x-free hydrogen, since overall the activity of iron based catalysts is appreciably lower than that of ruthenium. In comparative studies, TOFs lower by more than two orders of magnitude[58,59] have been reported.

Iron forms stable nitrides,[18] and ammonia treatment at elevated temperatures is in fact used for nitridation of iron. Mostly temperatures above 773 K are needed for this reaction,[60] but for nitridation of nanocrystalline surfaces temperatures as low as 573 K have been reported.[61] Thus, under conditions of ammonia decomposition, the catalysts may be in different states, depending on the gas phase composition and temperature. One may expect the presence of iron nitrides as active species, if the reaction is carried out in pure ammonia. On the other hand, iron, iron oxides, oxynitrides, or carbides, depending on the exact conditions, may be present, if the catalysts are used for the ammonia removal from coal gasification product gas, in which, in addition to low concentrations of ammonia, oxygen and carbon containing molecules are present as well. Thus the discussion of these two application fields has to be separated. Since the focus of this article is on the use of ammonia as an element of an energy infrastructure, the removal of ammonia from gasification product gas is of limited interest only and catalysts for this purpose will therefore only briefly be touched. Such catalysts typically have to be cheap, and often natural iron ores are used as precursors.[62] A goethite-rich limonite has been identified as a suitable catalyst precursor, after such materials had been found active in the decomposition of 2000 ppm NH_3 in helium at 773 K.[63] This catalyst is reduced to α-iron in hydrogen, but after exposure to pure syngas is converted predominantly to Fe_3C. Similar results had previously been obtained with FeOOH

supported on brown coal.[64] However, in the presence of water or carbon dioxide, as found in gasification product gas, the iron is retained in its metallic state which appears to be the most active for ammonia decomposition under these conditions.[65] At 1023–1223 K, which are typical temperatures in ICGG plants, conversions exceed 90% at 2000 ppm NH_3 concentration at a space velocity of 45 000 h^{-1}. Especially important in this target application is the fact that this catalyst system also seems to be sulfur tolerant.[66] More complex catalyst systems, i.e. Fe/Ni on activated carbon, have also been studied under the conditions of gas cleanup.[67] However, the performance does not seem to be better than for the cheap systems discussed above. This system also reaches 90% conversion at 1023 K under the same conditions.

For ammonia decomposition under the conditions of hydrogen generation (pure ammonia, partial pressure of ammonia close to atmospheric) only a few studies have been reported, several of which were rather targeted at understanding the ammonia synthesis catalyst than at developing a catalyst for providing clean hydrogen. Kowalczyk et al.[68] have studied the decomposition of ammonia over doubly and triply promoted ammonia synthesis catalysts. A strong increase in the rate was found for ammonia concentrations exceeding 20% at atmospheric pressure, which was attributed to the successive formation of iron nitride phases with higher catalytic activity. However, recently ammonia decomposition over iron and Fe_4N has been studied and the nitride was found to be less active.[69,70]

For the iron based catalyst, rates at 673 K of 0.6 kg NH_3 kg$_{cat}^{-1}$ h^{-1} were reported for the highest ammonia concentration of 80%,[68] which, extrapolated to 773 K, comes close to the activities of ruthenium-based catalysts, even considering the uncertainties associated with such an extrapolation. However, one has to keep in mind that the ruthenium-based systems are supported, with 1–5% of the active phase present in the catalyst, while the iron based catalysts are bulk systems. Rates observed over an industrial iron catalyst for ammonia synthesis at an ammonia concentration of 6% and atmospheric pressure at
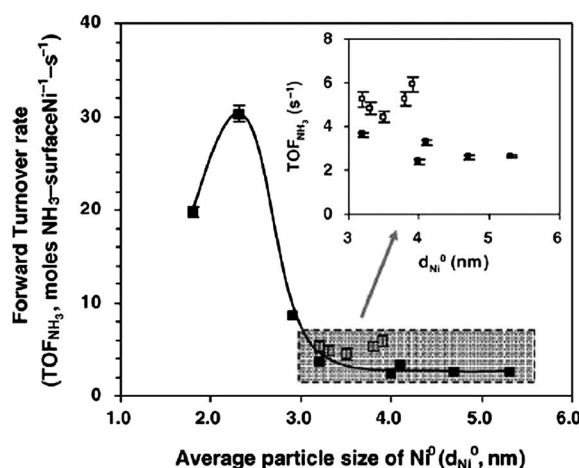

Fig. 5 Effect of Ni^0 particle size on the forward NH_3 turnover rate (TOF$_{NH3}$) for NH_3 decomposition. Solids: Ni/Al$_2$O$_3$; hollows: Ni/La–Al$_2$O$_3$. Conditions: 5.0 mg catalyst, d_p = 100–150 μm, dilution ratio = 1 : 100, total space velocity = 6 000 000 ml g$_{cat}^{-1}$ h^{-1}, 150 hPa (0.15 bar) NH_3, balance He (reprinted with permission from ref. 82).

700 K were in the same range as those reported by Kowalczyk, taking into account the somewhat higher temperature (0.05 kg NH_3 kg_{cat}^{-1} h^{-1} at 673 K, estimated from Fig. 2 in ref. 68, *versus* 0.12 kg NH_3 kg_{cat}^{-1} h^{-1} at 700 K, estimated from Fig. 5 in ref. 71). In the study of Kowalczyk, also a cobalt-based catalyst was investigated which had an activity higher by a factor of 2–3 than the iron-based system, while in the synthesis reaction the iron based catalyst was more active, confirming again the statement that the optimal synthesis catalyst is not necessarily the optimal decomposition catalyst.[26]

Fe/CNT samples were also studied in this reaction for the decomposition of pure ammonia at atmospheric pressure.[72] However, the iron used here was the residual catalyst in commercial CNTs for their synthesis. The iron was unpromoted, and amounted to about 2.3 wt% of the sample. These catalysts were expected to be less active, and only showed rates of approximately 2.8 kg NH_3 kg_{cat}^{-1} h^{-1}, at the higher temperature of 973 K. Under reaction conditions, also in this case iron nitride phases were dominant. Iron catalysts supported on CNTs may suffer from deactivation due to the strong interaction of iron with carbon at high temperature. This was prevented by additionally supporting Fe/CNT samples on mica which resulted in the formation of smaller, well separated iron particles. The samples showed appreciable activity of approximately 2.3 kg NH_3 kg_{cat}^{-1} h^{-1} at 773 K.

Zhang *et al.* showed that adding cobalt to iron can significantly improve the stability of the catalyst in ammonia decomposition. In addition, a higher reaction rate (6.8 kg NH_3 kg_{cat}^{-1} h^{-1} at 823 K) was obtained on such alloyed Fe–Co nanoparticles.[73] Nanotubes containing cobalt alone[72] (the cobalt was left in the tubes from the synthesis) had an activity of 0.3 kg NH_3 kg_{cat}^{-1} h^{-1}. Iron based catalysts on carbon supports can have high activity though; an iron catalyst on CMK-3 as support reached rates of about 34 kg NH_3 kg_{cat}^{-1} h^{-1} at a temperature of 873 K which is among the highest activity reported for an iron based system.[74]

Summarizing the findings for iron-based catalysts, their activities normalized to the content of the active metal are about two orders of magnitude lower than those of the highly active ruthenium based systems, although normalized to catalyst weight, this activity difference is substantially reduced. Nevertheless, it appears improbable that iron based systems could substitute the expensive ruthenium in decomposition catalysts for the supply of pure hydrogen. Iron catalysts are, however, interesting for treatment of gasification product gas in order to reduce NO_x emissions in IGCC power plants.

Nickel-based catalysts

The catalysts for the supply of controlled reducing atmosphere are based on nickel as active component; nickel has also been used as a catalyst in devices for hydrogen production, especially in microstructured reactors, due to its substantially lower costs compared to ruthenium and the higher activity compared to iron. Ganley *et al.*[34] gave an order of activity (as TOF) Ru > Ni > Rh > Co > Ir > Fe, but one should note that the dispersion of these catalysts was extremely different, from 65% for 0.5% Rh/Al_2O_3 down to 0.9 for 1% Ni/Al_2O_3. In the comparative study of Yin *et al.*,[36] a somewhat changed activity order Ru > Rh > Ni > Pd $\approx$ Pt > Fe was given. At 773 K, the rate over 5% Ru/CNT was

about 19 kg NH_3 kg_{cat}^{-1} h^{-1} and that over 5% Ni/CNT about 2 kg NH_3 kg_{cat}^{-1} h^{-1}. However, for nickel, carbon nanotubes may not be the best support. Higher loaded catalysts[75] (10% Ni/SiO_2 or 65% Ni/SiO_2/Al_2O_3) gave rates of 2.2 kg NH_3 kg_{cat}^{-1} h^{-1} and 4.6 kg NH_3 kg_{cat}^{-1} h^{-1}. In addition, the activity can be improved by several means. Ir (total fraction 0.7%) was found to lead to an increase in activity by about 40% over an undoped 10% Ni/Al_2O_3 catalyst (rate 0.01 kg NH_3 kg_{cat}^{-1} h^{-1} at 723 K and 5.9% NH_3 in He at atmospheric pressure). However, even if one extrapolates this rate to 50 K higher temperatures and pure ammonia, the activity of this catalyst probably still falls short of the more active ones described above. More effective is higher dispersion of the nickel by using an ordered mesoporous support, such as SBA-15 (13 kg NH_3 kg_{cat}^{-1} h^{-1} at 773 K)[76] or the addition of CeO_2 to the Ni/Al_2O_3 catalyst (16.4 kg NH_3 kg_{cat}^{-1} h^{-1}).[77] The beneficial effect of the ceria was attributed to a number of factors, including facilitated nitrogen recombination, stabilization of nickel particles and increase of pore sizes. Such a ceria promoted Ni/Al_2O_3 catalyst has also been used in a miniaturized ammonia cracker to supply the hydrogen feed for a fuel cell.[78] Promotion of the Ni/SBA-15 catalysts with ceria also improved the activity, but only slightly to 14.8 kg NH_3 kg_{cat}^{-1} h^{-1}.[79]

The reaction of ammonia over nickel seems to be a strongly structure dependent reaction. Already in the 1980s was the difference in dissociation activity for ammonia of the Ni(110)[80] surface and the Ni(111)[81] surface observed. Fully in line with these surface science studies, Zhang *et al.*[82] reported a strong dependence of activity on nickel particle size in the case of Ni/Al_2O_3 catalysts (Fig. 5, from ref. 82). Note that the absolute numbers for the TOF appear to be too high, since the space velocities, catalyst amounts and reactor dimensions given in the paper do not seem to be consistent. However, since all samples were analyzed under the same conditions, the shape of the curve in the figure should not be affected by this.

Nickel therefore does appear to be a promising catalyst system. Due to its cost advantage over ruthenium and its still relatively high activity for ammonia decomposition, it could be a good alternative for supplying pure hydrogen.

Transition metal carbides and nitrides

Since the discovery in the 1970s that molybdenum nitride behaved rather similar to platinum with respect to its catalytic properties,[83] this finding has been extended to a number of other transition metal carbides and nitrides and other reactions.[84–86] The selection of transition metal nitrides and carbides as possible catalysts for ammonia decomposition is thus relatively obvious, especially, if one considers that under reaction conditions of ammonia decomposition nitrides may form anyway (for this reason, iron nitrides have already been discussed above).[69,70,72,87]

The most often studied systems for ammonia decomposition in recent years are tungsten carbides[88–91] and molybdenum nitrides,[92,93] which had already been described earlier, see the review cited above.[20] On such catalysts, ammonia was decomposed both under conditions of gasification product gas cleanup and decomposition to produce pure hydrogen. Tungsten carbide (α-WC) decomposed ammonia at a rate of 0.12 kg NH_3 kg_{cat}^{-1} h^{-1} at 773 K,[91] however, at a gas phase concentration of only 0.4% at atmospheric pressure which would be typical for

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gasification product gas treatment. Application in such gases is not possible at temperatures around 800 K, though, since the presence of CO and especially hydrogen led to the complete loss of activity, probably due to the removal of the carbon from the surface which is necessary to adjust the electronic structure.[89] At higher temperatures of 973 K, no activity loss was observed upon addition of hydrogen to the inlet stream, the reason for this different behaviour at different temperatures remained unresolved.[90] In these studies, tungstated zirconia had been evaluated as well, and the activity was found to be rather similar to the one observed over WC. The tungsten carbide used in the studies discussed above suffered from low surface area on the order of 1 m^2 g^{-1}. This problem was solved by using a mesostructured WC with a surface area of 138 m^2 g^{-1}.[88] Activities over such catalysts at an ammonia concentration of 2% and at atmospheric pressure can be calculated to be around 1 kg NH_3 kg_{cat}^{-1} h^{-1} at 773 K. However, even for the high surface area WC, judging from the activity and comparing this system to the rather cheap iron or nickel based catalysts discussed above, tungsten based catalysts appear to be inferior. For the decomposition of ammonia for hydrogen generation, the activities appear to be much too low in any case.

Molybdenum nitrides form easily at high temperatures from oxides in reducing atmosphere containing nitrogen compounds, and thus molybdenum nitride (γ-Mo_2N) was already studied for decomposition of pure ammonia at atmospheric pressure in the early 1990s.[94,95] The materials had surface areas of up to 150 m^2 g^{-1} (after nitridation in H_2/N_2 mixtures). It is difficult to compare the rates in the units used throughout this paper, since the density of the Mo_2N bed was not reported and thus space velocities could not precisely be converted, but from the available data, one can estimate it to be 1.3 kg NH_3 kg_{cat}^{-1} h^{-1} at 773 K and under the assumption of a bed density of 5 g ml^{-1}. This activity is substantially lower than that of ruthenium based systems and in the same range as for nickel based systems. It was later attempted to improve the activity of molybdenum nitride based catalysts by dispersing it on SBA-15, but the productivity of the resulting samples was also only about 2 kg NH_3 kg_{cat}^{-1} h^{-1}, even at a temperature higher by 90 K.[92,93] We have studied comparatively a number of different nitrides and carbides.[96,97] Mo_2N was the most active system among the nitrides and carbides tested (tungsten carbides and nitrides, iron carbide, molybdenum nitride and carbide, iron-tungsten nitride), with an activity of approximately 2 kg NH_3 kg_{cat}^{-1} h^{-1} at 773 K. Interestingly, the carbides were found to remain stable at least as bulk phases under reaction conditions and were not converted to the nitrides.

Since nitrides are overall a class of materials which have not been extensively studied for ammonia decomposition, their activity might still have substantial potential for improvement. However, they are not as active as ruthenium-based systems and the cost advantage over ruthenium based catalysts is not very high. Molybdenum prices are on the order of 30 € kg^{-1} although the price fluctuated strongly over the last five years. While this is about two orders of magnitude lower than the ruthenium price, ruthenium is used in supported form at loadings in the percent range, while molybdenum nitride is used as bulk material. The catalyst costs are thus in the same range for both systems.

Miscellaneous catalysts

The cobalt containing systems have already been discussed in connection with the iron systems.[72,73] Several other systems have been claimed for ammonia decomposition in the patent literature. Zirconium oxynitride has been described as a catalyst which has, after having been heated under reaction temperature to temperatures exceeding 823 K, similar activities as iron based catalysts.[98] Heating to 823 K appears to be necessary for the demixing of the initial β'' phase to the more nitrogen-rich β' oxynitride phase, with increased nitrogen mobility, and monoclinic zirconia. The kinetics of ammonia decomposition could be described by a model, and the reason for the lower activity compared to other catalysts was attributed to the difficulty for recombination and desorption of the nitrogen atoms.[99] Chromium oxide (Cr_2O_3) was recently studied as a catalyst for ammonia decomposition.[100] However, this system was not particularly active, and reached activities around 20 kg NH_3 kg_{cat}^{-1} h^{-1} only at a temperature of 873 K. Soda and Sugiyama have claimed a number of Mn-Ce-Al-oxide catalysts[101] and Mn-containing silicates, aluminosilicate and zeolites[102] as catalysts for removal of ammonia from waste gases. Room temperature ammonia decomposition was observed over perovskites under ball milling conditions.[103] However, this paper leaves many questions open, since most of the ammonia, or its decomposition products, is trapped in the catalyst and is only released after heating at 900 °C. Thermodynamics would not favour decomposition at room temperature.

5. Stabilization of the catalysts by encapsulation

As stated before, ammonia decomposition is a high temperature reaction: for the production of clean hydrogen, at least 650 K is required for sufficiently high conversion, and in the treatment of coal or biomass gasification product gas, hot-gas cleanup directly after the gasifier is preferred. In both applications, the catalysts thus need to be stable against sintering, also at long times on stream. This can be achieved by encapsulation of the active phase in a porous shell with higher thermal stability. Research on such core–shell structures has exponentially grown over the last few years, after initial work in the 1990s of groups such as those of Liz-Marzan et al.[104] or Caruso et al.,[105] to name only a few. In 2006 we had described the strong effect of such encapsulation in hollow shells on the thermal stability of gold colloids,[106] and over the last few years, a number of studies has appeared in which related principles were employed for the stabilization of catalysts for ammonia decomposition against thermal degradation. Such encapsulation is more important for ruthenium-based catalysts, since here high dispersion is crucial due to the high price of ruthenium, but also other types of catalysts benefit from such stabilization strategies.

Lorenzut et al.[107] prepared ruthenium nanoparticles embedded in a porous lanthanum oxide/zirconia matrix. The synthesis relies on a general protocol which is often followed. First, the nanoparticles are prepared and stabilized by a protecting ligand shell, then, in a subsequent step, the nanoparticles are encapsulated in the matrix by inducing growth of the shell on the particles. These embedded ruthenium particles were substantially more resistant against sintering than those in a reference catalyst prepared by

incipient wetness impregnation, and the catalytic performance came close to that of the best ruthenium based catalysts reported in the literature, with a productivity of around 20 kg NH$_3$ kg$_{cat}^{-1}$ h^{-1}. The group of Au[108] has embedded Ru-particles synthesized by a modified polyol route, or by RuO$_2$ precipitation in the presence of cetyltrimethylammonium bromide[109,110] (RuO$_2$ is converted to metal under reaction conditions) in silica shells by a sonication assisted Stöber process. This process renders the silica shell rather porous, which is otherwise unusual for the Stöber process. Such catalysts had activities which were comparable to the one observed for the Ru@La$_x$Z$_{ry}$O$_2$ (the @ symbolizes "encapsulated by") discussed above, however, the silica embedded particles had only been exposed to 923 K instead of 1073 K. An interpretation of the high activity is given in an enrichment of reactant molecules in the shells; however, as to why such an enrichment, which is in contrast to the laws governing mass transfer in porous catalysts, should occur, is not discussed. Enhanced adsorption in micropores could be one explanation, but the pores between the core and shell are too large for this. Capillary condensation of the reagent would be another explanation, but for this the temperatures are too high. The reason for an enhanced activity of encapsulated catalysts in ammonia decomposition is thus as yet unresolved.

In addition to ruthenium, also a number of other active materials has been embedded in different types of shell materials in order to stabilize them against sintering, the most often studied system being iron-based catalysts. Feyen et al.[111] have embedded α-Fe$_2$O$_3$ nanoparticles, stabilized with polyvinylpyrrolidone, in silica by a modified Stöber process.

Porosity was induced by addition of cetyltrimethylammonium bromide during the silica coating process. A reference catalyst was prepared by leaching the iron oxide cores from the core–shell materials and then adding the same amount of naked iron oxide to the empty silica shells. Initially, both catalysts had a productivity of around 2 kg NH$_3$ kg$_{cat}^{-1}$ h^{-1} at 773 K which is rather high for iron based systems. However, while the encapsulated

catalyst showed stable performance at 1023 K, the reference catalyst lost activity due to the loss of surface area by sintering (Fig. 6).

The group of Au[112,113] has performed a similar study, albeit with aging at lower temperature. They had compared the effect of a microporous and a mesoporous silica shell and found the catalysts with the mesoporous shell to perform somewhat better, which was attributed to improved accessibility of the iron-based core material. In these studies, they also included nickel[109,110] and cobalt[108] as active materials. These behaved rather similarly—with the nickel catalysts being slightly more active—compared to the iron catalysts, and since these elements are more expensive, they are overall inferior to iron.

Finally, encapsulation of iron-based catalyst particles was also found to be possible in the pore system of CMK-5.[114] Iron oxide particles were selectively synthesized in the inner voids of the carbon tubes forming the CMK-5 structure. This restricted their growth and anchored them effectively in the pore system. This effect was improved, if the silica was in fact not leached, as in the normal synthesis of CMK-5, but left in place. The interaction between the iron oxide particles and the silica through defects in the carbon wall improves the anchoring of the iron oxide in the pore system. Activities of the catalysts were high for the iron-based system, but fall about a factor of four short of the activities observed for the nanoparticles encapsulated in silica shells which were discussed above.

6. The direct ammonia fuel cell

An interesting application of ammonia decomposition catalysts is found on the anode side of the direct ammonia fuel cell ("internal reforming"). There are some reports in the literature that ammonia can directly be fed to a fuel cell, after earlier studies had rather focussed on the potential-assisted ammonia synthesis reaction or decomposition.[115–117] Construction of such direct ammonia fuel cells requires a high temperature proton conducting material as the solid electrolyte, a catalyst for ammonia decomposition and electron transfer at the anode side, and a catalyst for oxygen reduction on the cathode. High temperature proton conducting materials are available and are typically based on the perovskite structure, which is also the prevalent one for oxide ion conductors. Other proton conducting materials are known as well.[118] BaCeO$_3$ based materials, doped with various additives,[119] are presently the most promising class of membrane materials and have been used in several setups.[120–124] In addition, some systems were also based on other electrolytes, such as molten alkali hydroxide,[125] ytterbium-doped SrCeO$_3$,[126] or stabilized zirconias.[127]

Since presently the solid state electrolyte seems to be the performance limiting factor, research mostly concentrates on this aspect of direct ammonia fuel cells. In these investigations at temperatures typically between 800 and 1000 K (except for the molten hydroxide cell which was operated between 473 and 723 K), nickel-containing anodes are used, in line with the high activity of nickel based catalysts for ammonia decomposition in the gas phase. In the studies of the group from Ottawa, platinum, applied as ink, was selected as an electrode material.[120–122]

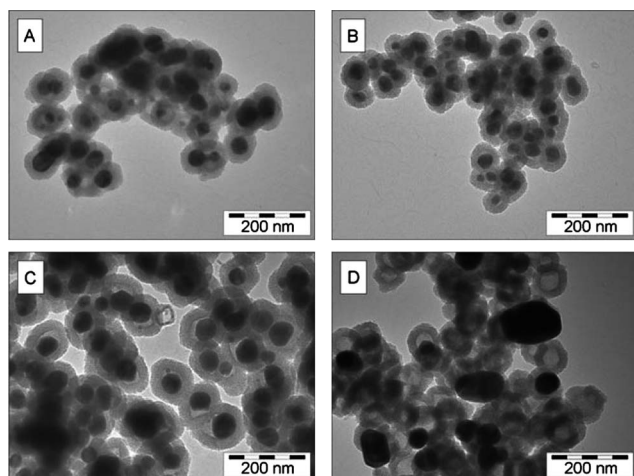In some studies, the effect of the catalyst on the performance of the fuel cell has also been investigated. Fournier et al.[127]

Fig. 6 α-Fe$_2$O$_3$@SiO$_2$ of 35 nm, 50 nm and 75 nm (A–C) after catalytic tests up to 1073 K, and reference catalyst α-Fe$_2$O$_3$ (50 nm) deposited on hollow SiO$_2$ after the same treatment (D). Sintering of the iron-phase in the non-encapsulated catalyst can clearly be seen. Reproduced with permission from ref. 111.

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compared the performance of nickel, platinum and silver based anode catalysts and found nickel to be far superior to the other systems investigated at a temperature of 773 K, both with respect to ammonia conversion reached and I–V characteristics of the cell. Ruthenium catalysts have also been used in combination with a solid proton conductor, but here the effect of the potential on the rate of ammonia decomposition was studied instead of the performance of the system as a fuel cell.[126] A comparison of electrocatalysts for ammonia oxidation to N_2 and H^+ was recently published.[128] However, since these experiments were carried out in the liquid phase at room temperature, the results can most probably not be transferred to the conditions of an ammonia fuel cell.

This discussion shows that the influence of the anode catalyst on the performance of ammonia fuel cells is not very well studied. Since ammonia as a fuel could have advantages over other fuels in high temperature fuel cells,[129] improvements in the catalysts, together with that in the solid electrolyte, seem to be of interest in order to further explore the potential of this technology. We are currently investigating the potential which different catalysts have in this application and as a first step have studied the interaction of catalysts with the electrolyte material. Initial results indicate that the decomposition activity of the catalyst does not change, if combined with the electrolyte material, but that it is rather enhanced.[130]

While encapsulation of the active phase introduces another element of complexity in the synthesis of ammonia decomposition catalysts, due to the high temperatures encountered in this reaction also in ammonia fuel cells, this may in fact be a rather useful strategy in order to reach long lifetimes of such fuel cell systems.

7. Conclusions

Ammonia has not been in the center of attention in discussions about future energy carriers, and presently there are more obvious choices than ammonia. Nevertheless, ammonia has several interesting features, such as a high energy density, a well established synthesis, and a high hydrogen content, so that its potential should be further explored. At least in niche segments, ammonia could find applications.

Ammonia decomposition catalysts are key elements of a possible ammonia infrastructure. In addition, such catalysts are important for product gas purification in IGCC power plants. Many lessons for ammonia decomposition can be learned from ammonia synthesis, but due to the deviations in conditions between synthesis and decomposition processes, some differences exist. Clearly the most active catalysts for ammonia decomposition are based on ruthenium. However, due to its high price, cheaper catalyst materials, such as iron, could make alternative systems attractive, even if the activity does not reach the level of the ruthenium systems. Some catalysts, such as molybdenum nitrides, are less active, but they have not yet been studied in much detail, and thus there might still be potential for improvement.

Ammonia decomposition catalysts are also interesting components in direct ammonia fuel cells. In addition to the requirements of high activity and stability, the catalysts have to be compatible with the solid state proton conducting membranes. So far, efforts on catalyst development for direct ammonia fuel cells were limited, since the proton conducting membranes are perceived as the crucial component. However, matched catalyst–membrane combinations could improve the performance of the systems.

Irrespective of whether ammonia is decomposed to hydrogen and nitrogen prior to feeding the hydrogen to a PEM fuel cell or directly fed into an ammonia fuel cell: new developments in the catalytic decomposition of ammonia or in the realization of high efficiency ammonia fuel cells could increase the potential of ammonia as an energy carrier, at least in special applications.

Acknowledgements

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