

RUTHENIUM-BASED CATALYSTS AND AMMONIA CRACKING

Precious Metal Figures Prominently in the Energy Equation

By Santiago Casu, PhD

Heraeus is a leading global technology group headquartered in Hanau. The Heraeus Group is divided into twelve Global Business Units under the umbrella of Heraeus Holding GmbH. Heraeus Precious Metals, (HPM), is one of these Global Business Units and specializes in precious metal services and products. The product portfolio includes precious metal-based process and emission catalysts, which are used in the chemical industry and for the purification of motor and industrial exhaust gases. As a manufacturer of catalysts with a strong focus on precious metals, HPM is highly active in the development of new catalysts to support the emerging ammonia economy. This paper presents the most recent results obtained during a study performed on Ru-based catalysts for the ammonia cracking reaction.

'Ammonia is the basic raw material for all other nitrogen compounds.'

One of the major issues of our current energy supply is the huge negative environmental impact caused by our energy dependency on fossil fuels. A large share of global greenhouse gas emissions (GHG) result from the combustion of coal, oil and natural gas, mostly in the form of CO₂.

Alternatives to fossil fuels have been studied in the past decades and existing technologies have been greatly improved. Nevertheless, decarbonizing our industrial world to combat climate change probably represents the biggest challenge of our times and will require a radical change in our energy system, the so called "energy transition". In the context of this energy transition, renewable energy generated from solar, wind or hydropower plants, is becoming increasingly important, especially since a significant decrease in cost for these technologies has been recently observed. There is also a growing awareness that ensuring energy security from these intermittent low-carbon sources requires the identification of suitable energy carriers for long-term and sustainable energy storage.

The Hydrogen Economy

Hydrogen has been identified as a possible energy vector a long time ago and led to the introduction of the "hydrogen economy" concept back in the 1970s.¹ In this concept, the use of hydrogen is presented as a fundamental cornerstone of the energy transition by enabling the generation of clean and sustainable energy. The idea of using hydrogen as a low-carbon energy source is attractive, as, whether it is combusted to produce heat or used in a fuel cell to produce electricity, ideally the only byproduct is water.

Currently, most of the hydrogen is produced using the steam reforming process of fossil fuels (mainly natural gas). This well-established technology represents the most economically viable way of producing hydrogen on a large scale.² Alternative technologies like water electrolysis are also well known but have been suffering from major drawbacks in the past. The recent drastic decrease of the costs of electricity from renewable energies should enable the green hydrogen to compete with conventional sources of energies in the coming years.

While major progress has been made in the field, a fundamental technical challenge for the use of hydrogen resides in its storage and transport. Despite a high gravimetric storage density, hydrogen suffers from a relatively low volumetric storage density. Nowadays, the storage and transport of hydrogen requires hydrogen to be compressed or liquified, which is consuming a significant amount of energy. Approximately 12% of the energy content of hydrogen is used for compression to a pressure of 700 bar, whereas 20-30 % of the energy content is necessary for the cryogenic liquefaction to -253 °C. The alternative cryo-compression process, where hydrogen is cooled down until the pressure required for its compression is lowered to 350 bar is also energy consuming.³ Furthermore, evaporation/boil off occurs during cryogenic hydrogen liquefaction and transport of liquid hydrogen due to unavoidable heat insulation losses. To prevent the pressure in the tanks from rising too much due to boiling hydrogen, hydrogen gas must be vented via a pressure relief valve, which limits the effective range for hydrogen transport, since the tank is gradually emptied during transport. Thus, with the rise of the hydrogen economy, better tools for the storage and transport of hydrogen have been considered.^{4,5}

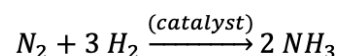
Metal hydrides have been studied in the past decades and allow to store hydrogen in a solid form, but these technologies are associated with high losses of energy for the synthesis and difficulties in the regeneration process of the materials. Liquid organic hydrogen carriers (LOHC) on the other hand enable the storage and transport of hydrogen in a liquid form. Mainly using dybenzyltoluene as a hydrogen vector, these technologies are currently only used at demonstration scale but seem to be of interest for the storage, transport, and release of energy on a large scale. Other compounds that are of interest for the storage of hydrogen are liquid fuels which can be easily transported over long

distances, stored for a long time and later decomposed to produce hydrogen when needed. Among these many liquid fuels, ammonia is considered to be particularly promising.

Ammonia as a Hydrogen Carrier

With a volumetric energy density, that is about 1.5 times higher than that of liquid hydrogen, and a low liquefaction pressure, ammonia presents many advantages over other hydrogen carriers, can be stored and transported relatively easily and requires relatively low quantities of energy.⁶ Due to its already great importance, for example in the fertilizer industry, a transport infrastructure is already in place.

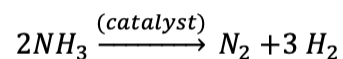
Currently, ammonia is produced almost exclusively via the Haber-Bosch process, which has been technically established for over a hundred years. This process is based on the catalytic reaction of hydrogen and nitrogen.



The reaction takes place at temperatures between 400-600 °C and pressures around 150-300 bar. Industrial catalysts are mostly based on iron and are promoted with various oxides such as aluminium oxide or calcium oxide. In the 1990s, a variation of the Haber-Bosch process was developed and commercialized, the so-called Kellogg Advanced Ammonia Process. Instead of an iron catalyst, this process uses a ruthenium-based catalyst that has a much higher catalytic activity.⁷ The increased activity of the Ru catalyst allows to reduce the operating pressure down to about 90 bar. As a result of the lower pressure, fewer synthesis gas compressors are needed to reach the operating pressure. In addition, the wall thicknesses of the reactor can be reduced, thus reducing the design and material requirements, resulting in high energy and cost savings. However, the industrial use of the Kellogg Advanced Ammonia Process has been limited in the past by the high material cost of ruthenium, which has increased fourfold in the 2000s due to new applications in the electronics industry.⁸

Ammonia is the basic raw material for all other nitrogen compounds and is the second most widely produced chemical worldwide with over 200 Mt/y, most of it being then further processed into fertilizers. The production is expected to increase two or threefold in the coming 20 to 30 years. The production of ammonia via the Haber-Bosch process is one of the largest energy consumers and greenhouse gas (GHG) emitters process in the world and is responsible for about 1.2 % of the global CO₂ emissions.⁹ The reason for these very high CO₂-emissions is the almost exclusive use of fossil fuels to produce H₂ and N₂, which are needed for the ammonia synthesis. The last century was characterized by the abundance of fossil energy sources, so that only these were used for hydrogen production. In the context of the energy transition, there are signs of a paradigm shift, so that more attention should be paid to climate-friendly hydrogen production. Several projects are currently running to achieve the decarbonization of the ammonia production and concepts like "blue ammonia" (associated with carbon capture technologies) or "green ammonia" (where hydrogen is produced via water-electrolysis that is powered by alternative energy) have been introduced.

Following ammonia synthesis, the ammonia can either be stored or transported. At the point of demand, ammonia can either be used in its pure form or split into hydrogen. The hydrogen in the ammonia molecule can be released via the decomposition or cracking. Ammonia cracking is the reverse reaction of ammonia synthesis, in which ammonia is split into its basic components with or without the aid of a catalyst as shown in the following equation.



Since ammonia cracking is an endothermic reaction, it is favored at high temperatures. Moreover, an increase in volume takes place during the reaction, therefore the reaction is favored at low pressures and for this reason a lot of studies have been performed at relatively low pressure. The effect of pressure has also recently been investigated, considering that the hydrogen that is produced will have to be compressed for downstream applications. Some studies evaluated the catalytic activity of various catalysts between 1 and 10 bar, and some tests were also carried out up to 40 bar.^{9,10} The presence of a catalyst allows to reduce the temperature necessary to decompose ammonia. From a process point of view, it is advantageous to keep the required temperature as low as possible to reduce the energy demand for heat generation.

Lots of different elements have been studied in the past for the decomposition of ammonia. Initially, Fe and Ru were considered for the reaction as these elements are also well known to catalyze the synthesis of ammonia. After that, other elements like Cu, Co, Ni, Ir, Pt, Pd, Rh or combinations such as Co-Mo, Ni-Mo, Ni-Co, Ni-Pt, Ni-Pd were also studied.¹¹⁻¹³ Currently, Ni-based catalysts supported on alumina are the commercially available catalysts used in industry for ammonia cracking. They combine a high thermal stability and good mechanical properties but only show catalytic activity at relatively high temperatures. In contrast to this, Ru was found to be the most active element for the decomposition of ammonia. It shows high catalytic activity at relatively low temperatures and has been extensively studied in the past few years. Di Carlo et al. tested Ru supported on alumina at various pressures and Ru supported on carbon carriers have also been widely considered.^{14,15} However, Ru is part of the platinum group metals (PGM) and therefore quite an expensive material. Platinum group metals are very rare elements in the Earth's crust, with their annual production amounting to around 400 tons

– several orders of magnitude lower than many common metals. Platinum group metals mining is a capital, energy, and work-intensive process. In contrast to platinum and palladium - the most important metals in the platinum group metals mix - ruthenium, rhodium as well as iridium and osmium are just mined as co-products, resulting in an even lower availability.

Nevertheless, related to the twelve green chemistry principles, two of them title the use of catalysis (as selective as possible) as well as the general design for energy efficiency within the processes. Therefore, Ruthenium could play a very important role for the ammonia economy and especially for the ammonia cracking process. In comparison to a Ni-based catalyst, the process temperature during cracking can be drastically reduced using Ru as an active material, leading to a much lower energy consumption in total. The higher price and lower availability of Ru compared to Ni can be ignored if the Ru was to be recycled after the end of the catalyst's lifetime. As a side effect of this, recycled Ru has a much lower CO₂ footprint compared to the primary material.

Experimental

Catalyst Preparation

All the Ru catalysts tested in the context of the present work were prepared by means of a specifically designed incipient wetness impregnation using an aqueous solution of an Ru salt and high specific surface area alumina spheres as the carrier. The water uptake of the alumina carrier was measured, and the concentration of the precious metal base impregnation solution was then adjusted to reach the targeted precious metal loading. After impregnation, the obtained catalysts were dried, calcined and reduced. A series of Ru catalysts supported on alumina spheres with increasing Ru loading was prepared. The Ru loading is denoted in the sample name. For example, Ru (0.5)/Al₂O₃ indicates that the concentration of the impregnation solution was adjusted to reach a Ru weight loading of 0.5 % on the final catalyst. Moreover, the addition of promoters such as K, Na, Li, Ce, Ba can greatly enhance the activity of Ru based catalysts and the addition of such elements has been widely studied.^{16,17} In the present work we also investigated the effect of two promoters hereafter referred to as A and B on the Ru catalyst loaded with 1.5% Ru. These promoters were also incorporated in the final catalyst by an incipient wetness impregnation method, followed by a drying step. The promoted catalysts are denoted Ru(1.5)/Al₂O₃-A(x:1), with x:1 representing the molar ratio between the promoter and the precious metal. .

Catalyst Characterization

Characterization of the catalysts consisted in the determination of the precious metal content via inductively coupled plasma analysis (ICP) and transmission electron microscopy (TEM).

ICP analysis were performed using a Thermo Scientific iCAP 7000 Series. TEM investigations were conducted using a FEI Talos 20-200 transmission microscope at 200kV. The measurements were performed in TEM mode and in scanning transmission electron microscopy (STEM) mode using Bright Field (BF) imaging and a high angle annular dark field (HAADF) detector. Energy-dispersive x-ray spectroscopy (EDX) was used to detect differences in local chemical composition. The analysis of the TEM pictures allows to determine the particle size distribution of the Ru nanoparticles on the alumina carrier.

Catalyst Testing

The prepared catalysts were tested in a fixed bed test bench in cooperation with the "Institut für Nichtklassische Chemie" (INC) in Leipzig, Germany. A simplified scheme of the test setup is presented in **Figure 1**. The reactor consists of a quartz glass tube that is heated with an oven. Prior to the reaction, the catalyst is installed in the reactor under the inert material (silicon carbide, SiC) and activated under hydrogen at 550 °C for 3 h. After this in-situ pre-activation, the volume flow of the feed is adjusted via the two mass flow controllers, namely an OMEGA FMA 2617A for the nitrogen flow and a Brooks GF040 for the ammonia. The volume flow and the catalyst bed volume were adjusted to achieve a space velocity of 3000 h⁻¹ for all the tested catalysts. The pressure in the reactor is set via a Brooks 5866 pressure regulator at the reactor outlet. The results presented in this paper were obtained at atmospheric pressure. The test setup could, however, be used to perform the ammonia cracking reaction at up to 5 bar. The influence of pressure on the catalytic activity could thus be investigated.

After activation, the catalyst is heated up to the reaction temperature under a nitrogen flow (100 mL/min). After a 10 min tempering phase, the gas mixture is passed over the catalyst and the analysis process is started. Gas samples are taken from the gas phase at the reactor outlet using a gas-tight syringe and the nitrogen-hydrogen ratio is determined by gas chromatography (GC) using a Chrompack GC CP 9001 equipment. By integrating the corresponding peaks, the ammonia conversion is determined. Alternatively, in steady-state operation (at constant conversion), the outlet gas leaving the reactor is fed for 30 or 60 min into a water scrubber that was charged with

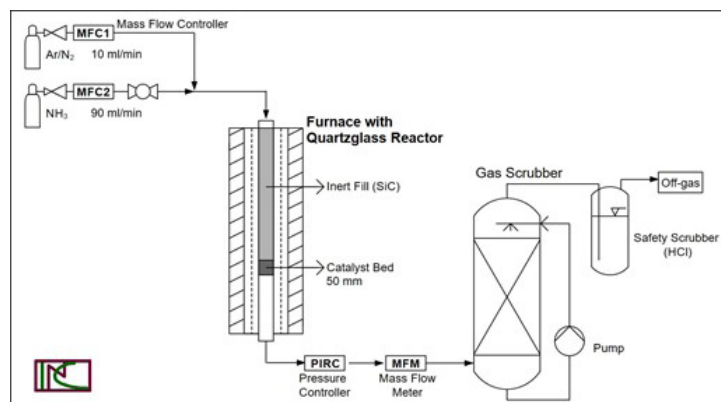


Figure 1: Test setup for the decomposition of ammonia at INC, Leipzig.

a well-defined amount of ultrapure water. Here, the educt ammonia is completely washed out. The concentration of ammonia in the wash water was determined by ion chromatography using a DIONEX ICS 1100 ion chromatography system. The gas chromatography analysis provides accurate results at lower NH₃ conversion whereas the ion chromatographic analysis facilitates an accurate determination of higher ammonia conversion rates.

Results and Discussion

TEM Characterization

Figure 2 compares the particles size distribution for the four catalysts with increasing Ru loading. Among the four materials, the catalyst loaded with 0.5% Ru shows a slightly larger particle size compared to the other catalytic systems with a relatively broad distribution and an average particle size of 7.8 nm. The catalysts impregnated with 1% Ru and 2% Ru both show a very similar particle size distribution with an average particle size of about 7 nm. Finally, the smallest particle size was observed for the catalyst impregnated with 1.5% Ru. For this material, the Ru is slightly better dispersed on the alumina surface and the particle size distribution is centered on 6 nm.

Although it has been extensively studied by various research groups, the effect of the Ru particle size remains questionable and no real consensus seems to emerge about the optimum Ru particle size for the ammonia cracking reaction. For Ru supported on carbon nanotubes, some studies suggest that the optimum size is between 3-7 nm whereas some DFT studies predicted an optimum Ru particle size of 2-3 nm.^{18,19} Lee et al. investigated the effect of Ru particle size by calcining Ru/SiO₂ catalyst at various temperatures.²⁰ They observed the superior catalytic activity of the samples calcined at higher temperatures (300 °C, 500 °C and 700 °C) compared to the sample calcined at 100 °C and concluded that the 6 nm-sized Ru particles perform better than the smaller 2 nm-sized particles. Finally, Karim et al. found that ammonia decomposition on Ru/Al₂O₃ is highly structure sensitive and observed an increase of the turnover frequencies with increasing particle size up to 7 nm.²¹ They also observed that the number of active sites strongly depends on the particle size and shape.

Catalytic Performance for Ammonia Decomposition

The ammonia conversion as a function of the reaction temperature for the catalysts with increasing Ru loading is presented in **Figure 3**. Among the four tested catalysts, Ru(0.5)/Al₂O₃ shows the lowest ammonia conversion at all temperatures. Due to its relatively low PGM loading and lower Ru dispersion this catalyst clearly shows the lowest catalytic activity for the ammonia cracking. Ru(1)/Al₂O₃ and Ru(2)/Al₂O₃ both shows similar ammonia conversion at 400 °C and 500 °C. At the higher temperature of 550 °C, Ru(1)/Al₂O₃, despite a lower Ru loading, shows superior catalytic activity compared to the 2% loaded catalytic system. Both catalysts have similar particle size distributions according to the TEM analysis but the Ru(2)/Al₂O₃ catalyst has more bigger agglomerated particles in the 10-20 nm range as can be seen in the particle size distribution in **Figure 2**. This broader particle size distribution might explain the lower catalytic activity observed during the tests. Finally, Ru(1.5)/Al₂O₃ shows the highest ammonia conversion at every temperature. This catalyst has a relatively high Ru loading and the best Ru dispersion according to the TEM analysis. With a particle size of about 6 nm, it is close to the optimum particle size described in the literature for Ru/Al₂O₃ catalytic systems.

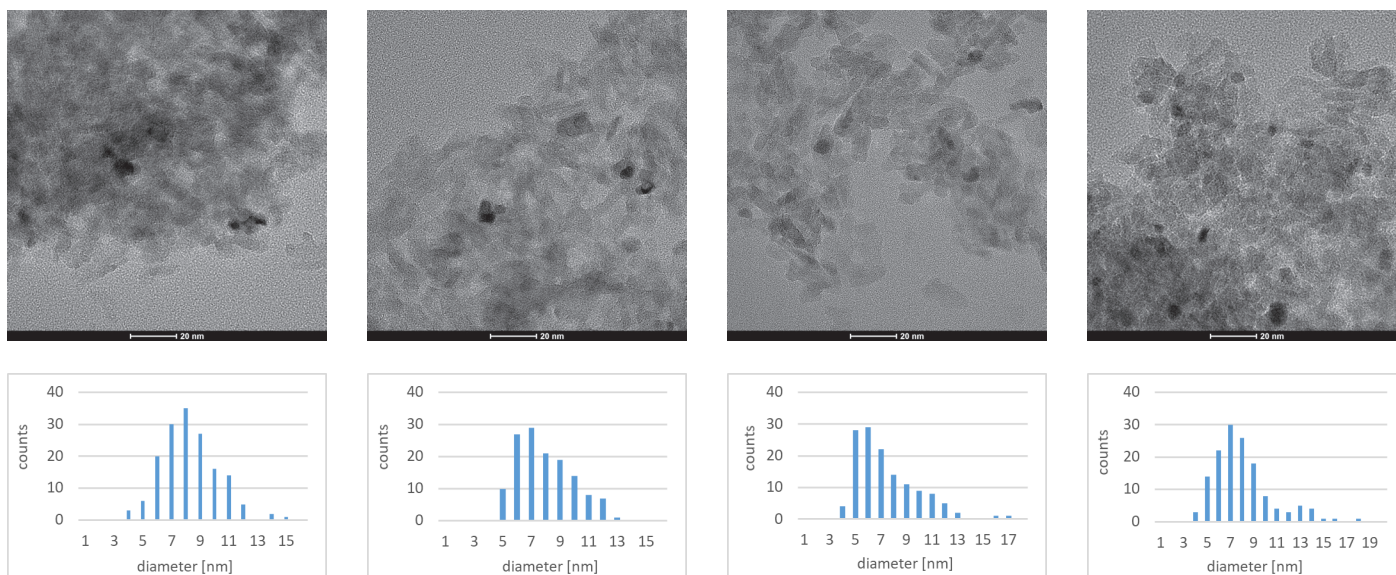


Figure 2: TEM images and particle size distribution of Ru for (A) Ru(0.5)/Al₂O₃, (B) Ru(1)/Al₂O₃, (C) Ru(1.5)/Al₂O₃ and (D) Ru(2)/Al₂O₃

As the 1.5% loading appears to be the optimum Ru loading for our catalytic system, this loading was selected to prepare further samples and study the effect of promoters on the catalytic activity. **Figure 4** presents the ammonia conversion as a function of the temperature for the catalysts promoted with promoters A and B at increasing promoter/Ru ratios. At 550 °C, the conversion of all catalysts are close to 100%. At 500 °C, some differences can be observed. The addition of promoter B at a high ratio of 5:1 has a minor positive influence on the ammonia conversion whereas the addition of smaller quantities (ratios 1:1 and 3:1) has no effect or even a negative effect on the catalytic activity. In comparison to this, the addition of promoter A at ratios of 3:1 and 5:1 increases the conversion of ammonia compared to the unpromoted catalyst. A more prominent trend is observed at 400 °C. Both catalysts prepared with promoter A (at 3:1 and 5:1 ratios) show an ammonia conversion increase of 10% compared to Ru(1.5)/Al₂O₃. The addition of promoter B at a ratio of 5:1 also leads to a noticeable increase of the catalytic activity at 400 °C. The addition of smaller quantities of promoter A and B tends to have no influence or a slightly negative impact on the ammonia conversion. Both elements A and B were selected for their electron donating properties. The increase in activity can be explained by the theory developed by Dahl et al.²² which states that the catalytic activity of Ru is improved by electron donation from the promoter to the carrier material, which enables charge balancing of the intermediary steps of ammonia cracking.

Conclusion

The decarbonization of our economy remains one of the biggest challenges of our times. In the context of the energy transition, renewable hydrogen energy technologies are becoming more and more relevant. However, hydrogen transportation suffers of major drawbacks and new carrier systems have been developed to ensure a safe, cheap and efficient distribution of this critical resource. Thanks to many advantages such as high energy density, ease of manufacture and transport, and long-term storage ability, ammonia is considered a promising hydrogen carrier. After transportation via ammonia, the hydrogen can be generated on-site and on-demand using the ammonia decomposition reaction. This reaction has been widely studied and the development of highly active and stable catalysts for this reaction is of uttermost interest. Ruthenium has been found to be the most active metal for the ammonia cracking reaction. In the present work, various Ru/Al₂O₃ catalysts were prepared, characterized and tested to study the effect of Ru loading and the impact of the addition of two different promoters. Based on our proprietary impregnation method, the optimal Ru loading was found to be at 1.5 %. For this loading the Ru nanoparticles have a diameter of about 6 nm, very close to the optimal size according to the literature. The addition of two electron donating promoters resulted in an improved activity of our Ru/Al₂O₃ catalytic system and an increase of 10% in ammonia conversion was observed at 400 °C. Ruthenium is part of the precious metal group and the Ru based catalysts are therefore more expensive than the conventional Ni based materials used currently for ammonia decomposition. However, because of its much higher activity, we believe Ru will play an important role in the future of ammonia decomposition.

As shown in this work, Heraeus Precious Metals can offer high-performance Ru-based catalysts for ammonia decomposition. In addition, the catalyst systems developed can be tailored to specific customer requirements and processes. In combination with precious metal recycling, which is a core competency at Heraeus, it is possible to recover the Ruthenium from the spent catalyst, which can then be reprocessed and used to produce new catalysts. This so-called precious metal loop plays a fundamental role both from a sustainability and economical point of view and helps to improve the cost-competitiveness of PGM based catalysts.

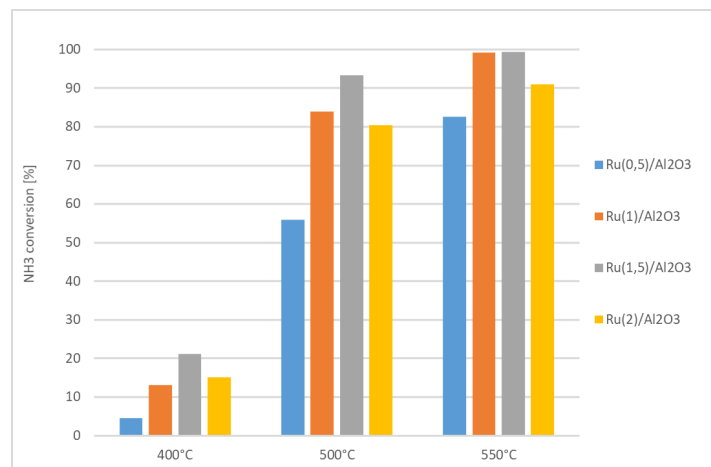


Figure 3: Ammonia conversion as a function of the temperature for the Ru/Al₂O₃ catalyst series.

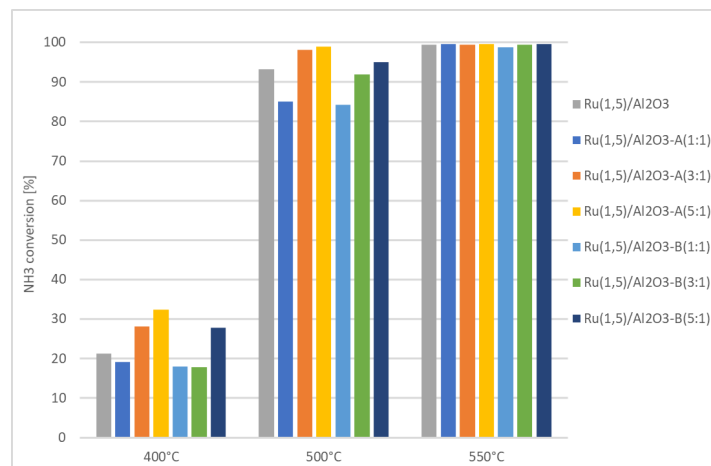


Figure 4: Ammonia conversion as a function of the temperature for the promoted catalysts

About the Author



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