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Ammonia decomposition over ruthenium catalysts

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Disclaimer

This BSc thesis has been carried out during the COVID-19 global pandemic (spring-summer 2020). In order to comply with all the learning goals specified for the BSc final project in Chemical Engineering at the University of Groningen, (some of) the results presented in this thesis were not experimentally obtained but provided by the main supervisor based on previous unpublished data and personal experience, or obtained from published literature. The source of data has also been specified explicitly or referenced wherever they appear in this text.

Abstract

This theoretical thesis provides a general overview on the research performed in the field of heterogeneous catalysis and different catalyst systems for the decomposition of ammonia. Furthermore, a possible research was proposed on the connection of catalytic activity and acidity of supports in ammonia decomposition. A commercially available family of supports with different alumina/silica compositions was suggested to be employed. Ru would be added to the supports by homogeneous deposition precipitation method, using ruthenium(III) chloride hydrate precursor. The prepared catalysts will be tested for ammonia decomposition in a fixed bed reactor and shall be characterized by an array of characterization techniques, such as transmission electron microscopy (TEM), nitrogen physisorption, X-ray diffraction (XRD), ammonia temperature programmed desorption (NH₃-TPD) and inductively coupled plasma (ICP).

Keywords: ammonia decomposition, heterogeneous catalysis, ruthenium, alumina and silica.

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1. Introduction

One of the greatest challenge in the 21st century that the scientific community faces is global warming and the resulting climate change.¹ A significant increase has been recorded in the atmospheric levels of greenhouse gases since the beginning of the industrial revolution and their levels are expected to be rising more in the future.¹ The increasing attention to global warming and climate change caused by greenhouse gas has encouraged society and particularly engineers to mitigate the current environmental jeopardy. Hydrogen is one of the compounds that requires significant consideration in the transition towards a more sustainable society, as hydrogen has a high potential to reduce the oil dependency of the transportation sector.² Hydrogen is also a clean source of energy compared to the hydrocarbon fuels, as its consumption does not generate any undesired greenhouse gases such as carbon dioxide or nitrogen oxides. Despite the fact that hydrogen is a very promising alternative to fossil fuels, its storage has a low energy cycle efficiency.³ Hydrogen gas can only be liquefied at extreme cold temperatures or high pressures which makes its transportation expensive and energy intensive.³ Therefore, to overcome this problem an efficient hydrogen carrier is required with physical properties that allow easy transportation.⁷ From this perspective, ammonia decomposition is advantageous for hydrogen production due to ammonia's high hydrogen content and the lack of undesired decomposition products such as carbon dioxide.

Ammonia is a high value chemical and it is produced in vast amounts worldwide, as 168 million tons were produced in 2018.⁴ Approximately 80% of the total ammonia production is used for agricultural purposes, as ammonia is a key component in the fertilizers industry.⁴ However, still a considerable amount of ammonia is left for other uses such as the production of hydrogen. Ammonia can be stored as a liquid at 20 °C and at a moderate pressure of 0.87 MPa, which means that it can be transported with relative ease.⁵ Furthermore, ammonia has a high volumetric energy density, as 108 kg of hydrogen is stored in 1 m³ of ammonia.⁷ As we can see ammonia is a very attractive compound, due to its beneficial properties, however the problem of how to efficiently convert ammonia to hydrogen must be solved. To overcome this barrier, several microreactor designs for ammonia decomposition were researched in the past.⁶ There has been a wide range of catalysts that have been investigated, such as noble and non-noble metals, metal composites and transition metal carbides/nitrides.⁷ One the most exploited catalyst for this reaction involved the noble metal, ruthenium.¹⁸ Although ruthenium is relatively expensive metal compared to other transition metals, it is one of the most active single metal catalysts for ammonia decomposition.¹⁸

It is obvious that there is an urgent need for greener technologies to be utilized in the world. Therefore, how to optimize ruthenium based catalysts so that they are able to provide high ammonia conversion to hydrogen at mild reaction conditions needs to be carefully explored. Moreover, they should be able to support the possibility of scale up and thus global implementation. In the proceeding section we will

give a brief review generally on ammonia decomposition over heterogeneous catalysts and specifically on ruthenium based catalysts.

2. Literature Review and Background

In general processes heterogeneous catalysis is favoured over homogeneous catalysis in case of gaseous reactants, as it eases the steps of catalysts recovery and reactor design. When a solid catalyst is applied, the interactions between the active sites of the catalyst with ammonia and the produced nitrogen and hydrogen play a critical role in the reaction mechanism.

Generally, there are numerous heterogeneous catalysts available for ammonia decomposition.⁷ These include noble and non-noble metals, alloys and other compounds such as nitrides or carbides.⁷ The numerous metals that have been studied include Fe, Co, Ni, Ru, Rh, Ir, Pd, Pt, etc.^{8,9} As for the reaction kinetics it is stated that for non-noble metals the rate determining step is the nitrogen desorption while for noble metals it is the cleavage of the N-H bonds.⁷ For example, the suggested mechanism over the Cu(111) involves the chemisorption of ammonia to the surface, followed by three subsequent dehydrogenations and the desorption steps of nitrogen and hydrogen. The exact active metal sites where each corresponding step takes place are depicted in figure 1.⁸

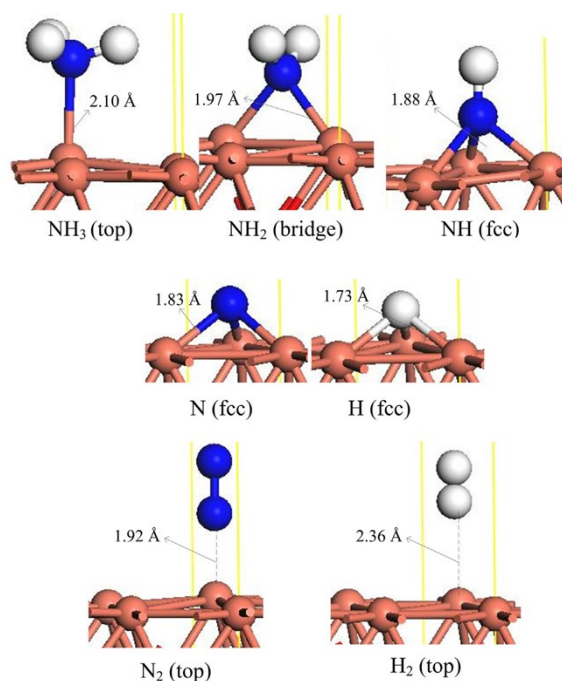


Figure 1. Decomposition of ammonia over Cu(111) catalyst. The blue balls represent nitrogen, the white balls hydrogen and the orange color the catalyst surface.⁸

In terms of the noble metal Ir, the mechanism involves in total seven possible steps. Six of these are identical to the ones presented previously for the Cu based catalyst. Besides that, Ir does not form strong bonds with nitrogen, therefore the recombination of two NH molecules to form N₂ and H₂ (step 5 of figure 2) is more thermodynamically feasible.¹⁰ The depiction of the proposed decomposition model on Ir is shown in figure 2.¹⁰

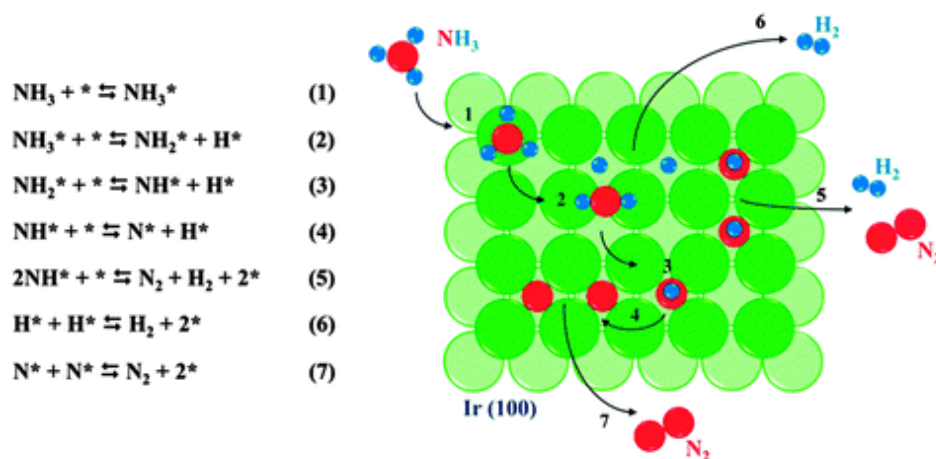


Figure 2. Proposed decomposition mechanism of NH₃ over Ir(100) based catalyst supported on carbon.¹⁰

Catalytic systems involving iron have been also studied due to its known role in ammonia synthesis.⁷ Wide range of iron-based composites include Fe-MO_x (M = Ce, Al, Si, Sr, and Zr).¹¹ The hybridization between iron and the oxides aims to prevent agglomeration of the catalyst powder, as the oxides can retard crystal growth of iron.¹¹ Vanadium carbide as a catalyst was also studied in the past.⁷ The electronic states of vanadium carbide compared to pure vanadium are modified, as the 3d states of vanadium strongly interact with the 2p states of carbon, changing the electronic structure at the fermi level.⁷ The modified electronic structure resembles the ones of precious metals, so the carbide form can be used as a catalyst.⁷ Thus, they had activities similar to Pt, but not as high as Ru.⁷ One of the most promising alternative catalyst to ruthenium is lithium amide.⁷ However, lithium amide turns into lithium imide above 310 °C, so the stability of the catalyst is an issue.⁷ Overall other metal catalysts did not reach the activity of ruthenium under similar reaction conditions,⁷ but they could be an interesting aspect of further research, as they can be much cheaper.

2.1. Ruthenium catalyst systems

Ruthenium was reported as a catalyst for ammonia decomposition, as early as the 1950s.¹² At that early stage the conversion of ammonia was somewhere in between the range of 7 - 10% over 0.5 wt.% Ru catalyst supported on alumina.¹² The reaction conditions were employed at temperatures between 350 and 400 °C, atmospheric pressure and ammonia flow rate of 300 cm³/min.¹² The mentioned study at that time focused on the determination of kinetics and activation energies of ammonia adsorption and nitrogen desorption. An inhibitory trend from the increased hydrogen partial pressure on the overall reaction was observed and nitrogen desorption was found to be the rate determining step.

With technological advancement it was observed in a journal from the 1970s that the reaction mechanism of ammonia decomposition over ruthenium catalyst is temperature dependent.¹³ To clearly elucidate, below 377 °C the rate is determined by the recombination of nitrogen adatoms, whereas above 477 °C the rate is determined by ammonia adsorption on the catalyst surface.¹⁴ Studying experimental results of ammonia decomposition where nitrogen desorption was the rate limiting step, it seems that Langmuir-Temkin-Pyzhev model is quite reliable to describe the observations. However, only at higher temperatures than 285 °C and at moderate ammonia adsorption levels.¹³

Also, in the early 2000s ruthenium catalysts became more and more the focus of scientific research.¹⁵ In a later paper magnesium aluminium oxides spinel were used as catalyst support, this particular support has advantageous properties, such as resistance to high temperatures and to reductive chemical species.¹⁵ The experiments were conducted at around 400 °C, atmospheric pressure.¹⁵ The alkaline promoters are able to donate electrons to the antibonding electronic states of the Ru catalyst, by which the bonding between the metal and nitrogen is weakened.⁷ Hence, the desorption rate of nitrogen can be further enhanced by the addition of alkaline cesium nitrate.¹⁵ The difference in activity between the promoted and unprompted catalyst exceeded a factor of 10.¹⁵

Cesium promoted catalyst on carbon support showed a factor of 10 times higher activity than cesium promoted catalyst on magnesium aluminium oxide spinel. Furthermore, the carbon supported catalyst had a higher activation energy. This can seem as a contradiction, but the explanation is that Cs has different forms on the two surfaces.¹⁵ When applied to the carbon support Cs is in its atomic form, whereas if applied onto aluminium oxide it forms caesium oxides.¹⁵ The zero valent Cs on carbon is a more efficient electronic promoter than the Cs_xO_y compounds on magnesium aluminium oxide, thus the observed difference in activities.¹⁵ However, it is still unknown why are the activation energies higher for the modified carbon supported Ru catalysts.¹⁵

Another important characteristic of Ru catalyst is the different roles that metal active sites played in the reaction. In case of ammonia decomposition, García-García et al. proposed that the site responsible for enhancement of nitrogen desorption is referred to as a Ru B₅ site, which consists of three ruthenium atoms in one layer and another two in an internal layer, as shown in figure 3. It is suggested that B₅ sites have a modified electronic state compared to the bare surface, thus the increased activity. B₅ sites are more abundant at a relatively large nanoparticle size in the range of 3 - 5 nm.¹⁶

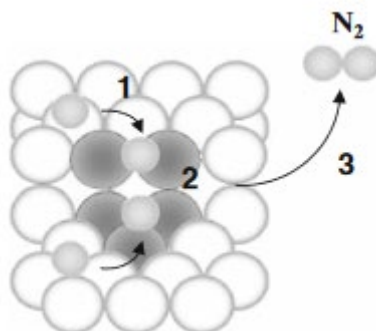


Figure 3. Scheme of associative adsorption of the two N atoms to form N₂ molecule in a B₅-type metal active site: (1) N atoms diffusion to the B₅-type site, (2) association of N atoms to form a N₂ molecule and (3) desorption of the N₂ molecule.¹⁶

In the same aforementioned article, the promotion effect of sodium was also tested. The support used was activated carbon and the conversion of the prepared catalysts was measured between approximately 227 and 577 °C. Although the catalysts with sodium had a lower density of B₅ sites, it showed higher activity due to the dominant effect of strong electron promoting capacity of valent sodium. Moreover, sodium can also help stabilize Ru nanoparticles during calcination and thus resulting in an average Ru nanoparticle size below 2 nm. Inspired by this, an interesting aspect of research could be on how to apply alkaline promoters such that the crystal size of ruthenium would fall in the optimal range of 3 - 5 nm.¹⁶

The decomposition model of NH₃ over Ru was researched together with the previously mentioned decomposition model over Ir.¹⁰ Despite the fact that both of these metals are noble metals, the mechanism of ammonia decomposition differ for the two metals. The model over Ru resembles the model over Cu. Based on the observations, Ru makes stronger bonds with nitrogen than Ir. Therefore, the main difference in the models is that the recombination of NH over Ru is thermodynamically unfavoured.¹⁰ The six steps of the decomposition model for Ru catalyst are depicted in figure 4.

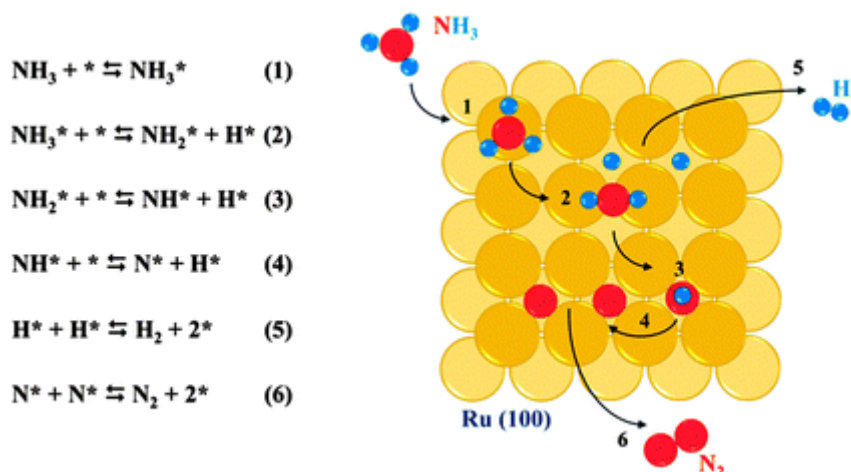


Figure 4. Proposed decomposition model of NH₃ over Ru(100) based catalyst supported on carbon.¹⁰

Another possible way to improve ruthenium based catalysts is by doping the carbon nanotubes (CNT) support by nitrogen. The experiments were conducted by increasing temperature up to 550 °C and using a gas hourly space velocity of 6000 cm³_{NH₃} g_{cat}⁻¹ h⁻¹.¹⁷ Results show that catalytic activity is increased after nitrogen doping, but changes in the activation energies are not significant which indicates that nitrogen doping does not modify the type of ruthenium active sites.¹⁷ The effects of nitrogen doping, that enhanced the activity include improved support basicity, electronically promoting ruthenium sites and strengthening the interaction between the metal and the support. Examining the particle size of ruthenium showed that the most active catalyst doped with nitrogen has a particle size lower than the optimum size which is between 3 and 5 nm. This result is in agreement with the experimental findings of García-García and coworkers.

A very recent study²² from 2020 reported a high activity on Ru-Sr bimetallic catalysts supported on K promoted Al₂O₃. The amount of K was kept constant at 12wt.%. The sum of the Ru-Sr catalyst weight percentages was kept constant at 4% and Sr was varied between 0 and 3%. Sr being electropositive weakens the bonding to the absorbed species, thus increasing the activity.²² For comparison purposes a recent study from 2019 was displayed in table 1 with monometallic Ru catalyst supported on LiOH promoted Al₂O₃.¹⁹ Similarly to Sr LiOH is also electropositive so it can enhance the activity for the same reason.

To conclude, different routes were studied in order to develop a catalyst system which is able to provide high conversion of ammonia at low temperature (below ~ 450 °C).⁷ There are overall four main factors that can beneficially influence the activity: (1) The density of the specific Ru active sites play an important role.¹⁶ (2) Type of support used for the catalyst system also plays a role, as strongly basic and good conductors in general can enhance activity.²² (3) Alkaline promoters can enhance the activity by electron donation and improving metal dispersion on the surface.⁷

Lastly, bimetallic catalysts based on ruthenium showed more promising activity for ammonia decomposition compared to the monometallic variant.²² The turn over frequency values (TOFs) are very useful to compare the activities of different catalysts. TOF is defined as the total number of reactants converted by one gram of catalyst per unit time divided by the number of active sites per one gram of catalyst.¹⁹ The most recently reported TOF values for numerous Ru catalyst systems are summarized in table 1.

Table 1. Recent TOF values for numerous Ru based catalysts. (* not stated in the article)

Ref. #	Support	Promoter	TOF (s ⁻¹)	Temp. (°C)	Pressure (bar)	Catalyst loading (w.t%)	GHSV (cm ³ g ⁻¹ h ⁻¹)
15	MgAl ₂ O ₄	Cs	0.54	400	1	4.6	*
15	C	Cs	5.1	400	1	4.6	*
17	CNT	-	0.051	400	*	7	6000
17	CNT	N doping	0.072	400	*	7	6000
20	MgO	-	2.5	450	1	2.1	30000
20	MgO	-	4.7	450	1	3.5	30000
21	Ca(NH ₂) ₂	-	0.174	300	1	10	3000
21	MgO	Cs	0.467	300	1	5	3000
21	MgO	-	0.012	300	1	10	3000
21	Al ₂ O ₃	-	0.002	300	1	10	3000
22	Al ₂ O ₃	-	0.14	400	1	4	5400
22	Al ₂ O ₃	K	0.33	400	1	4	5400
22	Al ₂ O ₃	K	0.88	400	1	3	5400
22	Al ₂ O ₃	K	1.38	400	1	2	5400
22	Al ₂ O ₃	K	1.78	400	1	1	5400
19	Al ₂ O ₃	LiOH	1.6	350	1	1	*

The absolute TOF values have to be looked at critically as each study might have used different equipment and techniques or even had mistaken in the calculations. Nevertheless, certain trends can be extracted from the gathered data such as the advantageous effects of alkaline promoters, increasing catalyst loadings and generally higher activity at higher temperatures. Furthermore, C and MgO supports with promoters seem to be promising options to achieve high catalyst activity.

3. Proposed research

A previous study from our group involved the use of Ru on a series of alumina/silica supports.²³ Acidity of the supports were tested by ammonia temperature programmed desorption (NH₃-TPD) with a thermal conductivity detector (TCD).²³ After loading the Ru nanoparticles onto the supports and running the NH₃-TPD measurements, interestingly a sharp peak was observed at around 280 °C as shown in figure 5.²³ Later an NH₃-TPD measurement with mass spectrometry showed that after temperature increased to 300 °C only nitrogen was detected.²³ Combined with TCD results, it suggested that ammonia decomposes on the Ru catalyst. This is a relatively low temperature for ammonia decomposition,⁷ so these findings inspired the focus of the research.

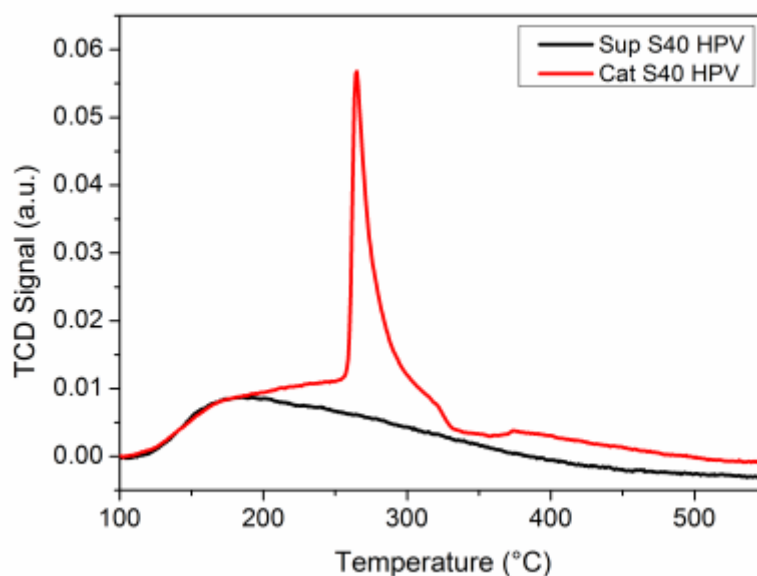


Figure 5. NH₃-TPD measurements results with bare support and catalyst.²³

3.1 Experimental Part

3.1.1 Materials

All alumina/silica supports were kindly provided by Sasol. They are alumina/silica mixtures with silica content ranging from 5 to 70% by weight and they have different surface area and thus different acidity. Chemicals such as the catalyst precursor (ruthenium(III) chloride hydrate, 35-40 wt.% Ru) and the urea (purity > 98%) are commercially available from Sigma-Aldrich and were used as received. The hydrochloric acid (37-38 wt.%) shall be purchased from Boom. The nitrogen gas (purity > 99.9%) and 1% NH₃ in helium (v/v) are available from Linde Gas. Deionized H₂O was available at University of Groningen. Ammonia (purity > 99.9%) and argon (purity > 99.9%) would be provided by Linde gas.

3.1.2 Catalyst Preparation

It is suggested that Ru would be applied to the support surface by homogeneous deposition precipitation method (DP) using ruthenium(III) chloride hydrate as the precursor, as shown in figure 6.²³ This method involves the precipitation of the ruthenium(III) chloride hydrate onto the support surface by gradually increasing the pH via the addition of urea to the solution.²³ Typical conditions for the DP includes heating the suspension of support in water up to 90 °C while lowering the pH to 3 using hydrochloric acid.²³ After urea and the precursor are added, the mixture is to be stirred for another 6 hours at constant temperature, pH is monitored every 30 minutes.²³ After the stirring is stopped the mixture is filtered and washed with water and finally dried overnight at around 120 °C.²³ It is suggested that the prepared catalysts are to be calcined under nitrogen for 8 hours at 500 °C with a ramp increase of 4 °C/min.²³

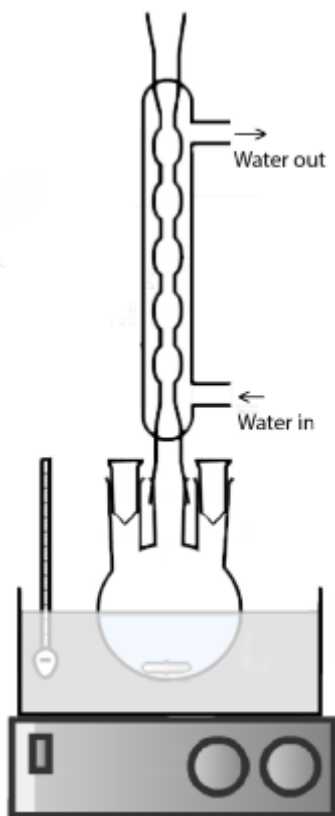


Figure 6. Suggested setup for catalyst preparation.²³

3.1.3 Characterization methods

The prepared catalysts shall be characterized by five techniques. X-ray diffraction (XRD) to examine the crystalline structure and NH₃-TPD to determine the acidity of the catalysts.²³ Furthermore, inductively coupled plasma (ICP), transmission electron microscopy (TEM) and nitrogen physisorption are techniques that also will be used.²³ ICP, TEM and nitrogen physisorption measurements can be used to measure Ru content, dispersion of Ru nanoparticles and textural properties, respectively.²³

3.1.3.1 X-ray diffraction (XRD)

A Bruker D8 advance shall be used to perform XRD experiments. The measurements are suggested to be performed between 10 and 90° using Cu K α radiation ($\lambda=1.5405 \text{ \AA}$) operated at 35 kV and 25 mA at standard conditions.²³

3.1.3.2 Ammonia temperature programmed desorption (NH₃-TPD)

For the NH₃-TPD measurements the Micromeritics AutoChem II 2920 shall be employed. In order to remove any impurities prior to the measurements, thermal pretreatment under continuous helium flow is performed.²³ Samples (typically 0.1 g) are to be heated up to 550 °C with a ramp increase of 10 °C/min and kept at that temperature for 1 hour.²³ Then, the temperature is reduced to 100 °C and 1% (v/v) NH₃ in He is flown to the catalyst for 1 hour.²³ This is followed by the removal of physisorbed NH₃ by He flow for another hour.²³ Then the measurements can be performed between 100 °C and 550°C with a ramp increase of 10 °C/min.²³ Helium is employed as carrier gas for ammonia and measurements are taken by thermal conductivity detector (TCD).²³

3.1.3.3 Textural properties by nitrogen physisorption

The nitrogen adsorption–desorption measurements of the samples were performed at 77 K on a Micromeritics Tristar 3000 analyzer, utilizing Brunauer–Emmett–Teller (BET) calculations for surface area. About 0.5 g of each sample were used for the analysis and they were pretreated on a stream of N₂ at 423 K overnight before carrying out the measurements. The textural properties and specific surface area data (m²/g) was also determined for all samples.²⁵ The pore size distribution can be determined by the Barrett-Joyner-Halenda (BJH) model.²³

3.1.3.4 Transmission electron microscopy (TEM)

TEM measurements are suggested to be taken by CM12 microscope, operating at 120 keV.²³ For the determination of metal dispersion, it is suggested that the catalyst samples are first suspended in ethanol.²³ Then, the suspension is placed on carbon coated copper grids and measurements can be taken by a slow scanning charge-coupled device (CCD) camera at standard conditions.²³

3.1.3.5 Inductively coupled plasma (ICP)

The exact Ru wt.% can be measured by ICP using the Optima 7000 DV.²³ The catalyst samples are suggested to be digested in a mixture of nitric, hydrochloric and hydrofluoric acids.²³ The samples are to be thermally treated at 200 °C for 1 hour before the measurements can be taken.²³

3.1.4 Catalytic fixed-bed setup

Catalytic experiments are suggested to be performed in a fixed bed reactor setup as shown in figure 7.

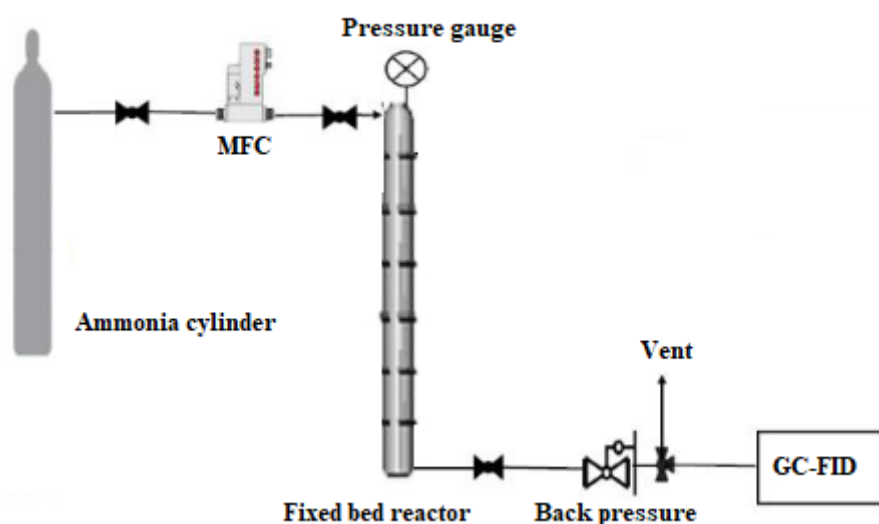


Figure 7. Schematic illustration of the bench scale fixed-bed catalytic unit used for NH_3 decomposition.

The catalytic tests took place in a bench scale setup, as depicted in figure 7. All lines were kept at the desired reactor temperature. The NH_3 flow rate to the reactor was controlled using a Brooks mass flow controller (MFC). The product gases from the reactor were continuously analysed using an online GC-FID, as shown in figure 8, in order to determine the NH_3 conversion and assess the catalyst decomposition activity.



Figure 8. GC-FID equipment.

The reaction temperature is suggested to be varied between 200 and 350°C, ammonia GHSV could be varied in between 5000 and 60000 cm³g⁻¹h⁻¹ by the mass flow controller (MFC). The pressure is suggested to be kept atmospheric during the experiments. In each of the experiment the mass of the catalyst is fixed to 0.06 g. Experiments shall be repeated two times to reproducibility confirmation.

3.1.5 Suggested procedure

The prepared catalysts would be charged into the fixed bed setup. Primarily to the start of the experiments the inlet tubing to the reactor shall be heated to 200 °C. After reaching this temperature, the needle valve on the inlet can be opened and the gas hourly space velocity (GHSV) would be set to the lowest value of 5000 cm³g⁻¹h⁻¹. Subsequently, the measurements by the GC-FID shall be started. Following the start of the experiment, the temperature can be further increased to 350 °C with an increase of 5 °C/min. By monitoring the product gases, the lowest temperature where ammonia decomposes on the catalyst can be determined. Following this, the GHSV can be steadily increased through the range up to 60000 cm³g⁻¹h⁻¹ with continuously monitoring the product gases. By these experiments the conditions at which ammonia decomposes at the lowest possible temperature with the highest conversion and GHSV can be determined. In order to evaluate catalyst performance, the turnover frequencies (TOF) and conversions shall be calculated by the equations shown below.¹⁸ The number of active sites in all catalysts can be calculated from H₂ chemisorption experiments.

$$\text{TOF} = \frac{\text{number of NH}_3 \text{ molecules decomposed g}^{-1} \text{ catalyst s}^{-1}}{\text{number of active sites g}^{-1} \text{ catalyst}}$$

$$\text{Conversion} = \frac{\text{NH}_3 \text{ outlet concentration}}{\text{NH}_3 \text{ inlet concentration}} \times 100\%$$

After running the experiments, the catalytic activities of the samples can be compared. The catalyst performances can be gathered in a table and patterns in activity are expected to show up as a function of support acidity. The primary hypothesis regarding the support activities would be that decreasing support acidity would result in higher catalytic activity.

3.2 Future experiments

In case the experiments give promising results for low temperature ammonia decomposition, possible further improvement of supports could be considered as a future research aspect. Reaction conditions could be optimized by more detailed experiments. Furthermore, some papers^{17,21} in the literature part suggest that alkaline metal promoters might be advantageous, the currently used supports might be improved by alkaline metal promotion.

3.3 Safety evaluation

Ammonia has a very strong unpleasant odour and it is known to be a toxic gas if inhaled in high concentrations.²⁶ Generally, it is not considered to be flammable, but it can ignite at certain vapor pressure with strong ignition.²⁶ Nitrogen and hydrogen (the products of ammonia decomposition) are not harmful if inhaled, but hydrogen is explosive. Hydrogen air mixtures can form combustible mixtures with hydrogen volume content between 4 and 75%.²⁷ Furthermore, hydrogen has a very high deflagration index of 550 which is 10 times higher than that of methane.²⁷ The auto ignition temperature of hydrogen is 572 °C,²⁷ since this is higher than the proposed temperature of the reaction auto ignition during the experiments will be unlikely.

The most important safety measurement that has to be taken is to ensure that there is no leakage in the fixed bed setup. Therefore, it is important to run a pressure test on the setup by an inert gas such as argon prior to the experiments. Anyhow, experiments should be run in a fume hood to reduce the risk of hydrogen buildup to the minimum.

Acids such as nitric, hydrochloric and hydrofluoric used during the experiments need to be handled carefully as they are toxic and corrosive. Naturally, standard lab safety guidelines need to be followed at all times.

4. Conclusion

In this theoretical thesis a deep review was given on the previously reported researches on ruthenium catalyst systems for the decomposition of ammonia. Furthermore, a proposed research method was discussed on a series of possible ruthenium catalysts that were previously researched at the university. These catalysts were supported on alumina/silica composites with silica content ranging from 5% to up to 70% by weight. Pore sizes of the supports are also differed as high pore volume variants were included among them. The product stream from the fixed bed setup following the supposed ammonia decomposition is suggested to be analyzed by GC-FID. The various supports and the catalysts based on them would be characterized by TEM, X-ray diffraction, ammonia temperature-controlled desorption, nitrogen physisorption and inductively coupled plasma.²³

The earlier reported properties of supports regarding total acidity suggests the possibility that there will be a pattern in catalytic activity as a function of total acidity. If it is so, we will be able to gain understanding on the role of acidity during the decomposition of ammonia. If the performed experiments give promising results for the low temperature decomposition of ammonia, further research might be conducted on how to further improve the suggested catalyst systems.

Acknowledgments

At the end of this thesis I would like to give special thanks to my supervisors. Sincere thanks to my principal supervisor Dr. Khaled O. Sebakhy and my cosupervisor Qingqing Yuan for the continuous support and assistance throughout this project. I also would like to thank the board of examiners and professors of this university for working out an alternative for the practical lab work that allowed students to complete their diploma from abroad in these challenging times.

References

- (1) Harvey, L. D. D. *Global Warming*; Routledge: London, **2015**.
- (2) Eriksson, E.; Gray, E. Optimization and Integration of Hybrid Renewable Energy Hydrogen Fuel Cell Energy Systems – A Critical Review. *Applied Energy* **2017**, *202*, 348-364.
- (3) Krasae-in, S.; Stang, J.; Neksa, P. Development of Large-Scale Hydrogen Liquefaction Processes from 1898 to 2009. *International Journal of Hydrogen Energy* **2010**, *35*, 4524-4533.
- (4) Markets, R. and. Global Ammonia Market to 2024 - Increasing Usage for the Production of Explosives. <https://www.prnewswire.com/news-releases/global-ammonia-market-to-2024---increasing-usage-for-the-production-of-explosives-300894091.html> (accessed May 4, 2020).
- (5) Demirhan, C.; Tso, W.; Powell, J.; Pistikopoulos, E. Sustainable Ammonia Production Through Process Synthesis and Global Optimization. *AIChE Journal* **2018**, *65*, 1-23.
- (6) Chiuta, S.; Everson, R.; Neomagus, H.; van der Gryp, P.; Bessarabov, D. Reactor Technology Options for Distributed Hydrogen Generation Via Ammonia Decomposition: A Review. *International Journal of Hydrogen Energy* **2013**, *38*, 14968-14991.
- (7) Mukherjee, S.; Devaguptapu, S.; Sviripa, A.; Lund, C.; Wu, G. Low-Temperature Ammonia Decomposition Catalysts for Hydrogen Generation. *Applied Catalysis B: Environmental* **2018**, *226*, 162-181.
- (8) Jiang, Z.; Qin, P.; Fang, T. Mechanism of Ammonia Decomposition on Clean and Oxygen-Covered Cu (111) Surface: A DFT Study. *Chemical Physics* **2014**, *445*, 59-67.
- (9) Yin, S.; Xu, B.; Zhou, X.; Au, C. A Mini-Review on Ammonia Decomposition Catalysts for on-Site Generation of Hydrogen for Fuel Cell Applications. *Applied Catalysis A: General* **2004**, *277*, 1–9.
- (10) García-García, F. R.; Guerrero-Ruiz, A.; Rodríguez-Ramos, I.; Goguet, A.; Shekhtman, S. O.; Hardacre, C. TAP Studies of Ammonia Decomposition over Ru and Ir Catalysts. *Physical Chemistry Chemical Physics* **2011**, *13*, 12892-12899.
- (11) Itoh, M.; Masuda, M.; Machida, K.-I. Hydrogen Generation by Ammonia Cracking with Iron Metal-Rare Earth Oxide Composite Catalyst. *Materials Transactions* **2002**, *43*, 2763–2767.
- (12) Amano, A.; Taylor, H. The Decomposition of Ammonia on Ruthenium, Rhodium and Palladium Catalysts Supported on Alumina. *Journal of the American Chemical Society* **1954**, *76*, 4201-4204.
- (13) Takezawa, N.; Mezaki, R. Langmuir-Temkin-Pyzhev Rate Models for Ammonia Decomposition Reaction. *The Canadian Journal of Chemical Engineering* **1970**, *48*, 428-431.
- (14) TSAI, W.; WEINBERG, W. Cheminform Abstract: The Steady-State Decomposition Of Ammonia On The Ru(001) Surface. *ChemInform* **1987**, *91*, 5302–5307.
- (15) Szmigiel, D.; Raróg-Pilecka, W.; Miśkiewicz, E.; Kaszukur, Z.; Kowalczyk, Z. Ammonia Decomposition Over the Ruthenium Catalysts Deposited on Magnesium–Aluminum Spinel. *Applied Catalysis A: General* **2004**, *264*, 59-63.
- (16) García-García, F.; Guerrero-Ruiz, A.; Rodríguez-Ramos, I. Role of B5-Type Sites in Ru Catalysts Used for The NH₃ Decomposition Reaction. *Topics in Catalysis* **2009**, *52*, 758-764.

- (17) Bell, T.; Zhan, G.; Wu, K.; Zeng, H.; Torrente-Murciano, L. Modification of Ammonia Decomposition Activity of Ruthenium Nanoparticles By N-Doping of CNT Supports. *Topics in Catalysis* **2017**, *60*, 1251-1259.
- (18) Lamb, K. E.; Dolan, M. D.; Kennedy, D. F. Ammonia for Hydrogen Storage; A Review of Catalytic Ammonia Decomposition and Hydrogen Separation and Purification. *International Journal of Hydrogen Energy* **2019**, *44*, 3580–3593.
- (19) Lamb, K.; Hla, S. S.; Dolan, M. Ammonia Decomposition Kinetics over LiOH-Promoted, α -Al₂O₃-Supported Ru Catalyst. *International Journal of Hydrogen Energy* **2019**, *44*, 3726–3736.
- (20) Ju, X.; Liu, L.; Yu, P.; Guo, J.; Zhang, X.; He, T.; Wu, G.; Chen, P. Mesoporous Ru/MgO Prepared by a Deposition-Precipitation Method as Highly Active Catalyst for Producing CO_x-Free Hydrogen from Ammonia Decomposition. *Applied Catalysis B: Environmental* **2017**, *211*, 167–175.
- (21) Kishida, K.; Kitano, M.; Inoue, Y.; Sasase, M.; Nakao, T.; Tada, T.; Abe, H.; Niwa, Y.; Yokoyama, T.; Hara, M.; et al. Large Oblate Hemispheroidal Ruthenium Particles Supported on Calcium Amide as Efficient Catalysts for Ammonia Decomposition. *Chemistry - A European Journal* **2018**, *24*, 7976–7984.
- (22) Mccullough, K.; Chiang, P.-H.; Jimenez, J. D.; Lauterbach, J. A. Material Discovery and High Throughput Exploration of Ru Based Catalysts for Low Temperature Ammonia Decomposition. *Materials* **2020**, *13*, 1869.
- (23) M.F. de Jong. The relationship between acidic supports and the catalytic performance of levulinic acid during hydrogenation. *University of Groningen* **2018**.
- (24) Sasol, Sasol performance chemicals. *Brochure*, **2017**.
- (25) Leofanti, G.; Tozzola, G.; Padovan, M.; Petrini, G.; Bordiga, S.; Zecchina, A. Catalyst Characterization: Characterization Techniques. *Catalysis Today* **1997**, *34*, 307–327.
- (26) Ammonia <https://pubchem.ncbi.nlm.nih.gov/compound/Ammonia#section=Hazard-Classes-and-Categories> (accessed Jun 8, 2020).
- (27) Crowl, D.; Jo, Y. The Hazards and Risks of Hydrogen. *Journal of Loss Prevention in the Process Industries* **2007**, *20*, 158-164.