

Exploring Ruthenium Nanoparticles Geometric Complexity to Boost Kellogg Advanced Ammonia
Process Through Confinement Effect

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Ammonia consumption is expected to increase in the future due to its use as a zero-carbon fuel and as a material for hydrogen storage and shipping. Among all single metal catalysts, ruthenium has the highest catalytic activity for the synthesis of ammonia. This study investigates the catalytic performance of ruthenium nanocages (CGs) towards ammonia production. Additionally, the effect of spatial constraints on reaction kinetics has been investigated using CGs with large (20 nm) and small (2 nm) confinements. The kinetic parameters for NH_3 synthesis were determined using temperature-programmed surface reaction and temperature programmed desorption experiments. The results of the ammonia production by the CGs were compared with those of control materials that would possess little to no confinement effects – nanospheres and nanoplates synthesized in the same conditions. It has been demonstrated that the uptake, activation energy and frequency factor of nitrogen desorption on ruthenium nanoparticles increases in the following order: no confinements < large confinements < large + small confinements. The nanoparticles with “small” confinements were shown to reach optimal temperatures for ammonia production at 310 °C, lower than both controls and CGs with larger confinements. The validity of attributing the potential catalytic improvement to the confinement effect, rather than to differences in morphology, structural defects, and alloying, is discussed.

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First of all, I should thank my supervisor, Anna Klinkova, for the inspiration and motivation to work and create in her lab. She is a wonderful and incredibly competent specialist who can put everything in its place in my head by asking the necessary leading questions. In her lab, I learned how to independently use a microscope and a chemisorption analyzer, stopped being afraid of working with gas cylinders, and started writing emails to people I did not know to negotiate a collaboration. Anna has also taught me how to present the material in a way that allows non-specialists in my field to understand what my research is all about. In general, Anna Klinkova's lab has brought me much closer to being a good scientist.

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I would like to thank Dr. Drew Higgins and his research group (McMaster University, Canadian Centre for Electron Microscopy) for a fruitful collaboration on the imaging and analysis of nanoparticles using in situ environmental transmission electron microscopy. This collaboration led to the discovery of previously unpublished and unstudied behavior of core-shell palladium-ruthenium nanoparticles. The work is now ongoing and we plan to publish a paper at the end of summer 2024.

I must also thank Xenia Medvedeva for introducing me to ruthenium nanoparticle synthesis and teaching me how to work with a microscope. Your love for science, your ambition, and your

determination are an excellent example for all future generations of students who will start or continue their scientific careers in Anna's lab (or in yours one day, time will tell).

Finally, thanks to my lab soulmates Nyhenflore Delva and Yujie Liu, who are continuing their graduate school journey together in Anna's lab. Thank you for the moral support, for the many funny and sad moments we shared during this time.

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List of Abbreviations

AA – ascorbic acid

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BET – Brunauer-Emmett-Teller

CGs – nanocages

EG – ethyleneglycol

EDX – Energy Dispersive X-Ray

HB – Haber-Bosch

HAADF – High-angle annular dark-field

KAAP – Kellogg Advanced Ammonia Process

NCs – nanocubes

NPIs – nanoplates

NSs – nanospheres

PVP – polyvinylpyrrolidone

TEM – transmission electron microscopy

TCD – thermal conductivity detector

TPD – temperature programmed desorption

TST – transition state theory

TPSR – temperature-programed surface reaction

SEM – scanning electron microscopy

Chapter 1

Background

1.1 Ammonia Economy and Production

Demand for ammonia has grown rapidly since the mid-20th century due to increasing demand for nitrogenous fertilizers to meet crop harvest targets to meet the requirements of an exponentially growing population.¹ In addition to fertilizer production, ammonia is used in the manufacturing of plastics, synthetic fibers, dyes, explosives, and can be found as a component of refrigerant gas and cleaning products.² Recently, ammonia has found another potential use as a renewable, cheap, and carbon-free fuel.^{3,4} In 2023, the Yara company started operating the first ammonia-fueled cargo ship, which is expected to reduce the ship's annual CO₂ emissions by 11,000 tons. Currently, Yara operates 15 vessels with this new ammonia fuel technology.⁵ Ammonia is also considered a potential chemical for the long-term storage and low-cost transportation of hydrogen (another carbon-free fuel source), because it has the highest volumetric and one of the highest gravimetric hydrogen densities compared to other potential compounds for chemical hydrogen storage (Figure 1b).⁶ When compared to transporting compressed pure hydrogen over long distances (>2,000 km), using ammonia as a hydrogen storage was found to decrease cost by at least 60% with pipeline systems and by at least 900% with ship deliveries (Figure 1c).² Once delivered to its destination, hydrogen can be regenerated by 'cracking' ammonia on the appropriate catalyst.

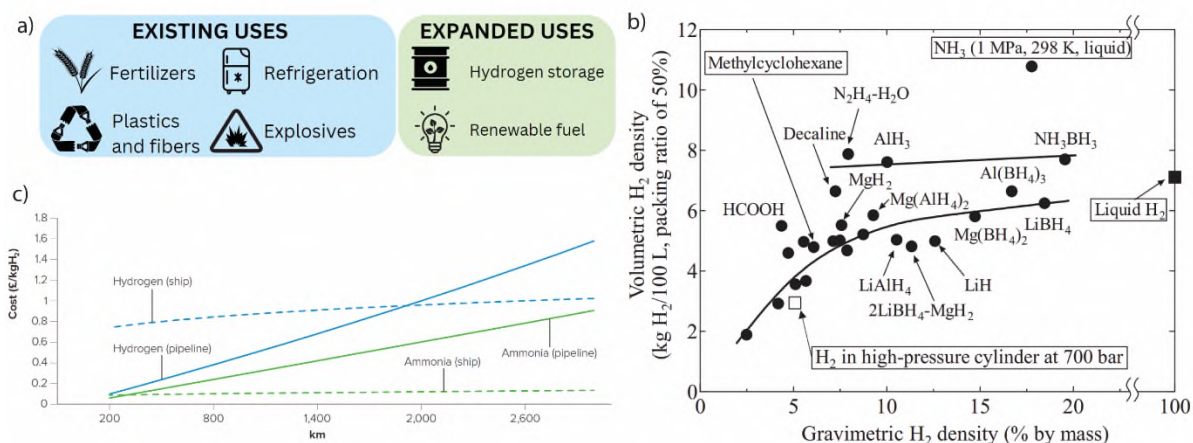


Figure 1-1. Ammonia uses and characteristics. (A) Common and future usages of ammonia. (B) Physical characteristics of ammonia important for its effectiveness as a transportation source of energy. NH₃ has the highest values for hydrogen gravimetric and volumetric density⁶. This figure is reused under the Creative Commons Attribution 4.0 International license. <https://creativecommons.org/licenses/by/4.0/> (C) Comparison of transportation costs for hydrogen and ammonia by ship and pipeline². This figure is reused under the Creative Commons Attribution 4.0 International license. <https://creativecommons.org/licenses/by/4.0/>

Today, ammonia is mostly produced by the Haber-Bosch process (or HB process), patented in 1908 by Fritz Haber and Carl Bosch, which involves the synthesis of ammonia from hydrogen and nitrogen using iron-based catalysts.¹ The advantage of this process is the low cost and availability of the catalyst components – iron, silica, and alumina. However, the synthesis runs at relatively high pressure and temperature, which leads to high energy costs and lowered efficiency – only 15% of initial mixture of nitrogen and hydrogen is converted to ammonia per cycle.⁷ According to the volcano plot for ammonia production, ruthenium is the most catalytically active metal towards ammonia production, with activity being ~100 times higher than that of iron.⁸ The Kellogg Advanced Ammonia Process (KAAP) is an alternative to the HB process, where Ru is the active component of the catalyst.^{7,9} The KAAP catalyst is prepared by the chemical vapor deposition of Ru from Ru₃(CO)₁₂ on a carbon black support (total Ru loading in carbon support is 5 wt%). The Ru-based

catalyst and a larger number of heat exchangers in the synthetic reactor allow KAAP to operate at lower temperatures and pressures, leading to higher yields per cycle compared to the HB process (Table 1). The primary disadvantage of KAAP is the high catalyst cost, which is roughly 150 times greater than that of the HB process. Reducing the amount of Ru in the catalyst and increasing its catalytic activity can lower the operational costs of KAAP process, making it more competitive with the HB process. Ru nanoparticles (NPs) are a suitable catalyst material due to their high surface area to volume ratio, which allows for a larger number of active sites to be involved in catalysis.

Table 3-1. Comparison of some characteristics of HB and KAAP processes.⁷

Characteristics	HB process	KAAP process
Catalyst composition	Fe on SiO ₂ /Al ₂ O ₃	Ru on carbon black
Maximum production yield per pass (%)	15	25
Operation temperature (°C)	400 – 650	300 – 450
Operation pressure (bar)	200 – 400	140 – 200
Maximum capacity (t·day ⁻¹)	1200	4000
Price of the catalyst (CAD·kg ⁻¹)	2.69	410
Thickness of catalytical bed (m)	0.1 – 10	10 – 100
Energy price for loop (CAD·kWh ⁻¹)	0.100 (10 t·day ⁻¹)	0.099 (10 t·day ⁻¹)
Lifetime of the catalyst (years)	>10	>10

The following two chapters detail the primary methods utilized in this thesis to improve the catalytic activity of Ru. Chapter 1.2 outlines the successes in regulating the catalytic activity of ruthenium nanomaterials by managing their morphology and phase composition. This chapter examines the experimental results and their interpretations on the enhanced catalytic activity of various hydrogenation and dehydrogenation processes. Chapter 1.3 provides the theoretical background of the confinement effect and its application in thermocatalytic processes. It summarizes the primary experimental and theoretical results for ammonia production.

1.2 Improving Ammonia Production on Ruthenium Nanoparticles Grown by Template Synthesis

In order to improve the catalytic properties of Ru nanoparticles towards ammonia synthesis it is necessary to optimize the energy of adsorption and desorption of precursors and products.⁸ This can be done by controlling the size^{10,11} and morphology^{11,12} of the NPs as well as the crystal phase¹³. Ruthenium NPs can be synthesized in two phases: hexagonal close-packed (*hcp*) and face-centered cubic (*fcc*).¹³ The latter is particularly interesting for ammonia production because theoretical calculations indicate that the activation and adsorption energies of nitrogen on *fcc* Ru surface are significantly lower (< 0.15 eV) than the *hcp* phase.^{14,15} However, the *fcc* phase of Ru is not thermodynamically stable at ambient conditions; bulk Ru *fcc* phase only exists at temperatures higher than 2,000 K.¹⁶ One of the solutions to this challenge is a colloidal template synthesis – epitaxial deposition of Ru on the surface of the NPs in *fcc* phase with the following etching of the template material.¹⁴

Currently, Pt¹⁷ and Pd hexagons¹⁸, Pd cubes^{19,20,21}, octahedra^{14,18}, truncated octahedra²², and icosahedra¹⁵ have been used as templates to grow branched *fcc* Ru NPs. The deposition rate and the amount of precipitated Ru along with facet composition of templates are crucial parameters for formation of *fcc* crystal structure. Studies showed that slow reduction of Ru at temperatures greater than 150°C on Pd cubes²¹, octahedra²⁰, and hexagons¹⁸ facilitates formation of *fcc* phase. The ideal temperature and ruthenium precursor injection rate for formation of *fcc* phase were found to be those that facilitate a diffusion rate of Ru atoms on the template surface that exceeds the reduction rate of Ru (Figure 1-2 A).²³ On Pt¹⁷ and Pd hexagons¹⁸ and octahedra²⁰, it has been demonstrated that the *fcc* shell cannot be grown infinitely. Instead, there is a limit determined by the contribution of surface energy to surface strain, caused by the difference in crystal lattice parameters of template and Ru, and defects – which arise at the interface between the *fcc* and *hcp*. When the shell thickness exceeds 10

monolayers or 8.5 nm, the *fcc* phase ceases to grow, and *hcp* Ru continues to form a crystal structure (Figure 1-2 C).¹⁸ Also, the growth of the *fcc* structure is promoted by the presence of {100} facets on the surface of the template. The {100} facet exhibits C4 symmetry, promoting the growth of the *fcc* phase of Ru and inhibiting the formation of the *hcp* phase with C3 symmetry (Figure 1-2 B).¹⁷

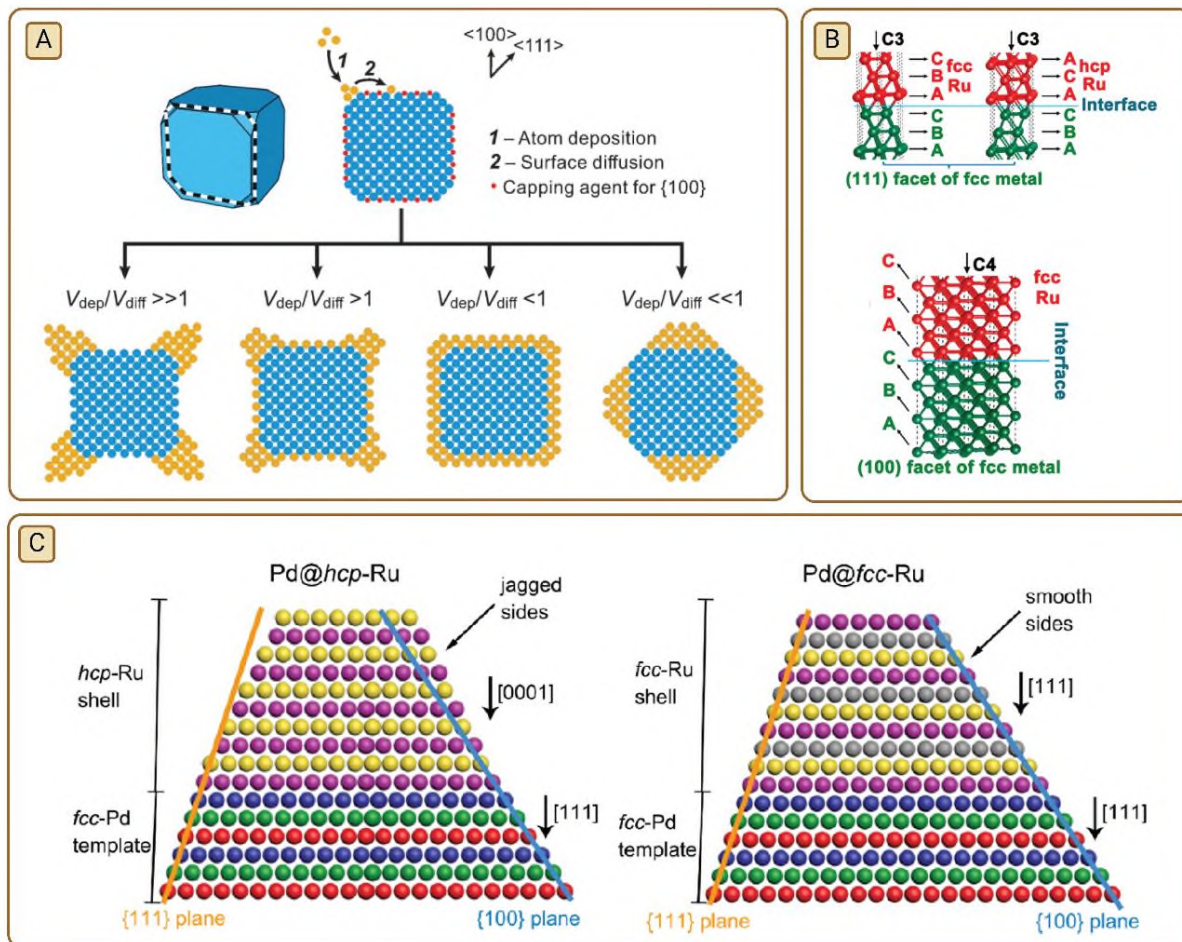


Figure 1-2 Processes during Ru growth on Pd template. (A) Ru growth on Pd cubic seeds at four different kinetic conditions. Reprinted from Xia et al.²³ (B) *Hcp* and *fcc* Ru phase growth on *fcc* seed depending on symmetry of interface. Reprinted from Zhang et al.¹⁷ (C) Jagged and smooth sides of Ru contributing to total surface defect energy and strain energy respectively. Reprinted from Xia et al.¹⁸

In current literature, the catalytic properties of branched *fcc* Ru NPs were examined experimentally for the redox reactions of reductive and oxidative reactions of organic molecules. The studied reactions can be classified into two groups: electrooxidation^{18,20} and heterogeneously-catalyzed redox reactions in aqueous solutions.^{15,19,22} All reviewed works indicate that branched *fcc* Ru NPs are significantly more active than their *hcp* analogues. However, one major limitation of these studies is the absence of a control experiment to standardize the rate of catalyzed processes based on the number of active sites on the NPs' surface, rather than the mass of the loaded metal (heterogeneous oxidation/reduction) or electrical double layer capacity (electrooxidation). In case of electrochemical reactions, performing a standard electrochemical CO-stripping procedure could prevent ambiguity in result interpretation. This method provides information on the ratio of active Ru atoms for adsorbing small molecules to the overall metal loading, which is referred to as dispersion in catalysis.²⁴ Normalizing by the dispersion of Ru removes the contribution of surface defectiveness and provides insights solely on the phase composition's contribution to the enhancement of the material's activity.

In thermocatalysis, the surface area of the catalyst is determined by Brunauer-Emmett-Teller (BET) surface area analysis. BET analysis is based on the adsorption of small gas molecules, such as N₂, on the catalyst at -179°C (the reactor with a catalyst is immersed in a Dewar with liquid nitrogen; -179°C corresponds to a thermocouple reading, however, the boiling point of liquid nitrogen is -196°C).²⁵ The adsorption occurs due to weak van der Waals forces. The amount of gas in a monolayer and the adsorption rate are used to calculate the specific surface area of a catalyst (chapter 2.2.4.3). This method enables the calculation of the physically accessible total catalyst surface (active metal and substrate) for diffusion and adsorption. The reference value for the substrate without metal is subtracted to determine the contribution of active metal adsorption only. This allows for the

normalization of catalytic activity to a surface active for adsorption, which was further used in the experimental part of this work.

1.3 Improving Ammonia Production by Confinement Effect

This work covers the confinement effect on ammonia synthesis in spatial constraints, where the diffusion and mobility of molecules are limited by the physical dimensions of the material. The confinement concept first appeared in biology as a theoretical explanation for the conditions required for life to begin and biological reactions to occur.²⁶ The nanotechnology field drew inspiration from these works and scientists started to create artificial confined systems that can be easily tuned in terms of size and composition and modelled to explain the confinement effect. Figure 1-3 shows three categories of confinement of ruthenium NPs that have been identified in the literature:

1. Encapsulated nanoparticles, where the space between the catalyst nanoparticle and the substrate provides the confinement (Figure 1-3 A);
2. Hallowed nanoparticles, where the space inside the nanoparticle provides the confinement (Figure 1-3 B);
3. Sites consisting of single atoms are created by embedding metal atoms covalently within the substrate's framework (Figure 1-3 C).

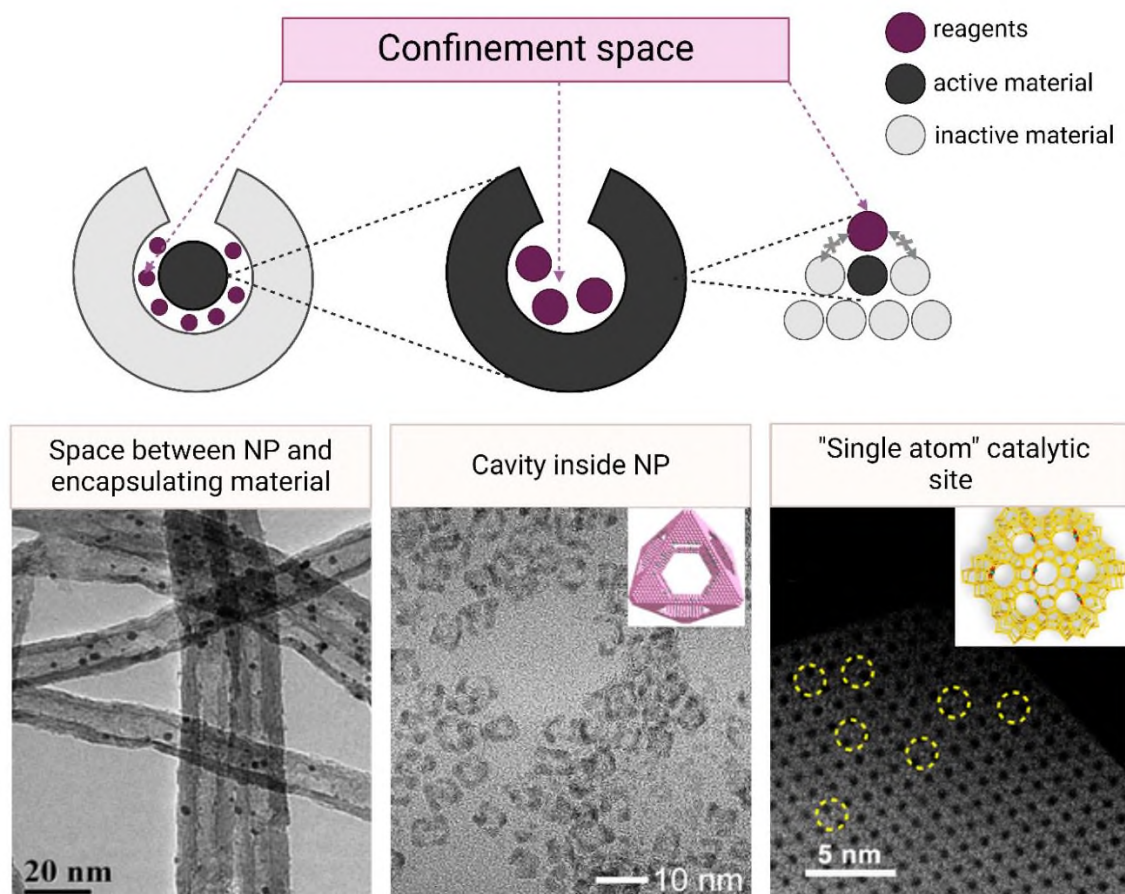


Figure 1-3. Types of spatial constraints studied by other groups. The left panel represents a catalytically active NP encapsulated in support material where confinement is the space between NP and support. The corresponding TEM image of the real system is Ru spherical NPs encapsulated in carbon nanotubes. Reprinted from Guo et al.²⁷ The middle panel shows confinement inside hollowed NP. The corresponding TEM image of the real system is Ru hollowed truncated octahedra. Reprinted from Ye et al.²⁸ The right figure shows confinement on “single atom” catalytic site where diffusion of reagents on inactive atoms of support. The corresponding TEM image of the real system is “single atom” Ru sites (circled with yellow) embedded inside zeolite structure. Reprinted from Qiu.²⁹

To describe benefits of confinement effects on performance of the heterogeneous catalyst transition state theory (TST)³⁰ can be used. The expression for rate of the reaction in TST is

$$r = \theta_A \theta_B \cdot A \cdot e^{-\Delta H^\ddagger/RT} \cdot e^{\Delta S^\ddagger/R} \quad (1)$$

where θ_A and θ_B represent reagent coverages of adsorbates A and B, A is a pre-factor constant in TST, $\Delta H^\ddagger$ is the enthalpy of the transition state, often associated with *activation energy*, $\Delta S^\ddagger$ is the entropy of the transition state, T is temperature, and R is the gas constant. When considering confinements, the TST expression analysis leads to the following conclusions:

- In a confined space, molecules are pre-oriented differently than on a bulk surface, which can decrease the entropy of transition state, $\Delta S^\ddagger$, and increase the reaction rate.
- In the event of the optimal dimensional parameters and surface morphology being met, the enthalpy of transition state in confined space, $\Delta H^\ddagger$, could decrease, resulting in an increase in the reaction rate.

The pre-factor in the TST rate expression is also influenced by the presence of a confined space. The expression for the pre-factor is as follows:

$$A = \kappa(T) \cdot \frac{k_b T}{h} \quad (2)$$

where $\kappa(T)$ is transmittance coefficient that shows ability of reactant molecules to diffuse through the catalytic surface and reach the active sites where the catalytic reaction occurs; k_b is the Boltzmann's constant; h is the Plank's constant. The analysis of the above expression leads to the conclusion that in a confined space, the transmittance factor increases as the time between the collisions decreases. This results in an increase in the frequency factor and, correspondingly, the reaction rate. In this work, chemisorption analysis is used to

experimentally determine the activation energy and pre-exponential factor of the nitrogen desorption as well as normalized total reagent uptake (local surface coverages).

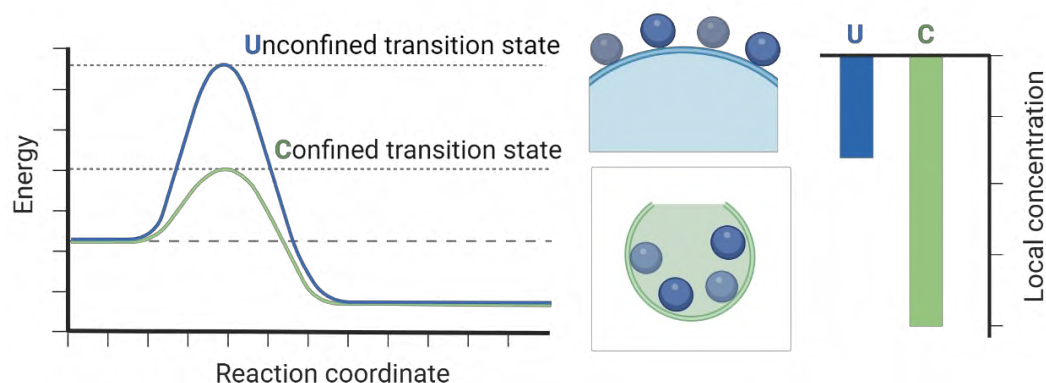
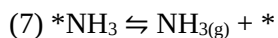
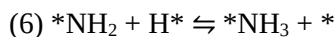
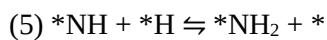
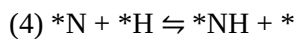
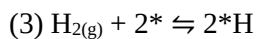
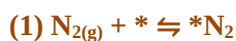


Figure 1-4. The confinement effect influence on the activation energy of the process and the local concentration of reagents.

The process of desorption of a nitrogen molecule on the surface of ruthenium-based catalysts was selected for study as a descriptor that correlates with the catalytic activity of ammonia synthesis. In order to accurately assess the validity of this choice of process, the mechanism of ammonia synthesis on the surface of bulk ruthenium (0001) must be considered⁸:



The most energy-consuming process is the breaking of the triple bond of a nitrogen molecule (step 2), which is adsorbed on the surface of the catalyst. This process is represented by the following equation: $*N_2 + * \rightarrow 2*N$ ($E_{a2} = 1.9$ eV). When carrying out the temperature-programmed desorption process (TPD), the following process is carried out: The reaction $2*N \rightarrow N_{2(g)} + 2*$ represents a combination of the reverse processes of steps 1 and 2. Since step 1 is non-activated, it can be concluded that the processes $2*N \rightarrow N_{2(g)} + 2*$ and $2*N \rightarrow *N_2 + *$ have almost the same activation energy. The processes of adsorption and desorption occur through the same transition states, and thus the reaction is completely reversible. Therefore, it can be argued that a change in the activation barrier of the process of breaking the triple bond $*N_2 + * \rightarrow 2*N$ leads to an almost identical change in the activation barrier of $2*N \rightarrow N_{2(g)} + 2*$. Consequently, a reduction in the activation energy for desorption of chemisorbed nitrogen will result in a reduction in the activation energy for ammonia synthesis and an increase in the reaction rate.

The confinement effect for ammonia production has been demonstrated in several studies. The paper by Wanga & Abild-Pedersen³¹ is entirely dedicated to DFT calculations, proving how the close proximity of the catalytic sites of transition metals – "dual sites" – may facilitate the cleavage of the triple bond of a nitrogen molecule, thereby greatly reducing the activation energy of the process. Since the adsorption of nitrogen is considered to be the rate-determining step in ammonia synthesis, making it easier to break the bond between two nitrogen atoms results in significantly higher calculated reaction rates. The paper provides valuable information about the structure of a potential catalytic site and shows that the confinement effect on Ru material can be observed in spaces with an optimal length of 4.2 Å. Another work by Matito-Martos et al.³² shows Monte-Carlo simulations for ammonia production in zeolites with different sizes of pores ranging from 3.5x4.1 to 7.4x7.4 Å². In contrast to Wanga & Abild-Pedersen, this work includes the direct reaction between the reagents in

the computation, rather than just the adsorption of nitrogen. Also, the latter study considers the concentration gradient of ammonia formed in the pore, which is a quantitative measure of the reaction yield. A major drawback of this work is that the system for simulations, zeolites, does not contain metals. This makes the calculations somewhat artificial and far from real systems. In both papers, the sizes are comparable, but in the first work, the authors postulate the possibility of a confinement effect only at an optimal distance between metal atoms, while in the second work, the effect is observed to varying degrees in pores of all sizes. In this thesis, the morphology of ruthenium nanoparticles is selected on the basis of the two studies to demonstrate experimentally how confinement occurs at different levels of spatial constraint.

In the 1990s, the research group of R. Schlögl investigated the conditions of confinement^{33,34,35} described in the theoretical work by I. Matito-Martos et al. The authors reduced ruthenium salts within branched zeolites A and Y, resulting in the formation of catalysts containing highly polydisperse ruthenium nanoparticles. Based on the microscopy data, it is difficult to determine the amount of ruthenium present in the zeolite pores in the form of clusters <0.7 nm versus fairly large aggregates of ~30 nm. However, the resulting catalysts exhibit 70°C lower onset temperature of ammonia formation compared to the control experiments using Haldor Topsoe KM1, the iron-containing catalyst used in the Haber-Bosch process. Unfortunately, the choice of the control experiment in the papers is poor: the metal and the support are changed, making it impossible to draw serious conclusions about the presence of the confinement effect (and the authors do not claim it).

Recent work from 2010-2020 shows the effect of spatial confinement for "single atoms"²⁹, clusters³⁶, and spherical ruthenium nanoparticles <5 nm in diameter^{27,37,38,39}. Recent studies have provided more definitive microscopic results indicating that the vast majority of ruthenium material is indeed spatially confined. However, the substrate materials and their pore sizes vary widely, ranging

from zeolite with a pore size of 4.2-4.2 Å² to N-doped carbon with pore diameters of 125-135 nm, making it difficult to make conclusions about the sizes required for the effect to occur. When comparing the works of J. Wellenbüscher et al.³⁵ and Qui et al.²⁹ (highlighted in orange in Table 2), the only notable difference is the size of the zeolites and the dispersity of the ruthenium phase. Although the pore size of the zeolites is almost identical (with only a 0.1 Å difference), there is a significant difference in the activation energy for ammonia formation, which differs by 64.6 kJ mol⁻¹ or 0.67 eV. The theoretically predicted optimal distance of 4.2 Å between single ruthenium atoms – ‘dual sites’ – is discussed earlier³¹. However, the decrease in activation energy is only 0.3 eV (compared to the bulk surface of Ru *hcp* {0001})³¹, which is two times less than the experimentally observed value. A comparison of the studies done by U. Guntow et al.³⁴ and S.E. Sivan et al.³⁹ shows that the size of the nanoparticles is comparable (Table 2, highlighted in pink), but the confinement size of the materials is different: in one case it is a 7.4x7.4 Å² channel, in the other case it is a 1-5 nm diameter pore. The kinetic studies indicate that nitrogen desorption occurs 120°C lower in the case of the larger pores. It can be attributed to longer nitrogen retention in tighter zeolite channels that leads to the local increase of N₂ concentration and shifting ammonia formation equilibria as predicted by Monte-Carlo simulations discussed above.³² However, it is important to be cautious in drawing conclusions, as differences in the methods of synthesis and the materials used can lead to similar effects with the same degree of probability.

Table 1-4. Characteristics of ruthenium-based catalysts where catalytic activity can be attributed to confinement effect

Publication period	Particle size	Confinement material and size	Activation energy of NH ₃ production, (kJ·mol ⁻¹)	Temperature NH ₃ production, (°C)	Temperature N ₂ desorption, (°C)	Ref.
1990s	From clusters inside pores to 30 nm	Zeolite Y channels 7.4·7.4 Å ²	-	330-400	-	[33]
	From clusters inside pores to 30 nm	Zeolite A channels 4.1·4.1 Å ²	120	300-350	-	[35]
	From clusters inside pores to 3 nm	Zeolite Y channels 7.4·7.4 Å ²	-	280-330	320-430	[34]
2010s	2-5 nm	Carbon nanotubes inner diameter 4-8 nm	-	400	-	[27]
	2-3 nm	xAl ₂ O ₃ ·yMgO channels ~6 nm	-	-	-	[37]
	0.2-0.3 nm (<i>Ru-Co alloy</i>)	ZIF-8 pores 11·11 Å ²	-	-	-	[38]
	“Single atom”	Zeolite SAS – channels 4.2·4.2 Å ²	55.4	250-400	-	[29]
2020s	2.2-2.5 nm (<i>Ru-Co alloy</i>)	N-doped carbon pore – 125-135 nm	80.7	300-400	-	[36]
	1.0, 2.7, 3.6 nm	Space between NPs/CeO ₂ 1-5 nm	72, 64, 87	325-400	198-460	[39]

Most of the studies listed in Table 1-2 have a significant limitation – the absence of a reliable control to confirm the confinement effect without the influence of other factors. For instance, in the study by Qiu et al.²⁹, the primary catalyst is atomic Ru distributed in the structure of SAS zeolite, while the control material is Ru NPs supported on MgO promoted by Cs⁺ additives. The comparison of these two materials cannot establish the presence of confinement due to the completely different morphology of Ru and nature of supporting materials. One, however, could compare zeolites with different pore diameters, but with ruthenium embedded in the structure. As for the control material, silicon oxide microspheres with ruthenium distributed over the surface would be a better option. Ni et al.³⁶ used N-doped carbon spherical particles (~200 nm) without Ru NPs as a control material, which was then compared with NPs encapsulated inside. However, to conclude about the effect of confinement, the control material must contain NPs located outside of confined region. A good control in this case would be a material where NPs are on the surface of the N-doped carbon particles. A good example of a control is done Guo et al.²⁷, where the activity towards ammonia synthesis of spherical Ru NPs of the same size inside and outside carbon nanotubes of the same diameter was compared. This work aims to address the challenges of studying confinement by selecting appropriate control materials.

Table 2 shows that mechanism of ammonia production is not systematically studied on materials with the potential manifestation of the confinement effect. The nature of changes in synthesis process remains a mystery, even though the effect is observed. Some works show the activation energy for ammonia formation changes. However, the production of NH₃ is complex process, and it is crucial to determine which step of the mechanism is impacted by the spatial limitations. Therefore, the adsorption and desorption of nitrogen molecules is examined in this project, as this process is considered rate-limiting and theoretically described in the spatial limitation mode.

1.4 Scope of Thesis

This thesis investigates the impact of confinement effects on branched ruthenium nanoparticles to improve ammonia production. The aim is to show the effect of confinement through temperature-programmed techniques that can provide information on activation energy of the process, optimal temperature of ammonia production, and the local increase of reagents. Chapter 1 presents the motivation and relevant up-to-date information for this research. Chapter 2 outlines the synthetic procedures, analysis methods, and computational derivations used in this project. Chapter 3 focuses on the experimental results of ammonia production and mechanism analysis on nanoparticles with different types of confinement. Chapter 4 presents conclusions on confinement effects in investigated systems and suggests directions for future research.

Chapter 2

Methods and Materials

2.1 Catalyst Fabrication

2.1.1 Synthesis of Pd NCs

The synthesis procedure of Pd NCs was adapted from Xia et al.⁴⁰ To prepare the solution of palladium precursor, 34 mg PdCl₂, 27 mg NaCl and 3 mL MQ water were mixed and shaken in a thermomixer at r.t. for 3 h. Then, 105 mg PVP, 600 mg KBr and 60 mg AA were dissolved in 8 mL of MQ water in a 20 mL vial with stirring rod and placed in a preheated oil bath at 80°C for 10 min. Then, the entire solution of Na₂PdCl₄ was rapidly added with a pipette under vigorous stirring (900 rpm). After the reaction was continued for 3 h, the mixture was allowed to cool to r.t. The final sol of Pd NCs was washed three times by centrifugation (20,000 rcf, 5 min) and redispersion in water (twice) and in 13 mL EG for future use.

2.1.2 Synthesis of core-shell Pd@Ru

The synthesis procedure of Pd NCs was adapted from Xia et al.⁴¹ with modifications. Briefly, 50 mg PVP, 100 mg AA, and 8 mL EG were placed in a 100 mL three-necked flask and preheated to 185 °C in a heating mantle under Ar flow. Then, 4 mL solution of 19 nm Pd NCs (section 2.1.1) was added to the flask using a syringe under vigorous stirring (900 rpm). After the temperature reached 185°C, 5 mL RuCl₃·xH₂O solution in EG (2 mg/mL) was injected into the flask using a Harvard Apparatus syringe pump model '22' (the pump was pre-calibrated). and branched Ru shells were synthesized at injection rate of RuCl₃ solution 0.5mL/h and 8mL/h respectively. The reaction was allowed to continue for another 10 minutes after the injection of the RuCl₃·xH₂O solution was completed. The reaction was quenched in an ice bath. Core-shell Pd@Ru NPs were collected by

centrifugation, washed once with acetone (2:1 by volume), twice with water, and finally redispersed in 56 mL of MQ water for future use.

2.1.3 Synthesis of Ru CGs

To synthesize Ru branched and CGs, an etching procedure adapted from Xia et al⁴¹ was performed with slight modifications. The etching solution was prepared by mixing 600 mg KBr, 50 mg FeCl₃, 0.3 mL HCl (wt. 38%) and 12 mL MQ water in a 50 mL plastic tube. To the etching solution, 4 mL of as-prepared Pd@Ru NPs were added (subsection 2.1.2). The mixture was then placed in an oven pre-set at 90°C, incubated for 3 h, and left overnight. Ru CGs were collected by centrifugation (7,200 rcf, 10 min), washed three times with water, and finally redispersed in 1 mL of MQ water for future use.

2.1.4 Synthesis of Ru NPLs

The synthesis procedure of Ru NPLs was adapted from Yang et al⁴² with modifications. 100 mg of AA, 200 mg of PVP, and 14 mL of EG were placed in a 50 mL three-necked flask and preheated to 185°C in a heating mantle under Ar flow. After that, a solution of 17.26 mg RuCl₃·xH₂O in 6 mL EG was injected into the flask at a rate of 0.75 mL/h using a syringe pump (subchapter 2.1.2). After the injection, the reaction mixture was kept at 185°C to further react until it reached a total reaction time of 3 h. The reaction was quenched in an ice bath. Ru NPLs were collected by centrifugation (7,200 rcf, 25 min), washed once with acetone (2:1 by volume), twice with water, and finally redispersed in 1 mL of MQ water for future use.

2.1.5 Synthesis of spherical Ru NPs

The synthesis procedure of spherical Ru NPs was adapted from Yang et al⁴² with modifications. 100 mg of AA, 200 mg of PVP, and 14 mL of EG were placed in a 50 mL three-necked flask and preheated to 185°C in a heating mantle under Ar flow. After that, a solution of 17.26 mg RuCl₃·xH₂O in 6 mL EG was injected into the flask at a rate of 8.0 mL/h using a syringe pump (subchapter 2.1.2).

After the injection, the reaction mixture was kept at 185°C to further react until it reached a total reaction time of 3 h. The reaction was quenched in an ice bath. Ru NPs were collected by centrifugation (20,200 rcf, 15 min), washed once with acetone (2:1 by volume), twice with water, and finally redispersed in 1 mL of MQ water for future use.

2.1.6 Support of NPs on silica gel (SiO₂)

The NPs/SiO₂ catalysts were prepared using the incipient wetness impregnation method. Briefly, the initial solution of NPs in water was centrifuged and redispersed in ethanol. Next, the 5 ml of alcohol solution of NPs was added to SiO₂. The amount of SiO₂ was calculated to ensure the total ruthenium loading of 1.0 % by weight. Afterward, 5 mg of NaBH₄ was added at vigorous stirring to remove excess of PVP and chlorine ions from the surface of NPs (the method is adapted from works on Au NPs⁴³). The mixture is washed by decantation and redispersion in a fresh portion of ethanol 3 times. After washing, the suspension is left to dry in the fume hood at r. t. overnight. The residual amount of water and ethanol is removed by drying the catalyst in a vacuum at 120°C for six hours. All dried catalyst samples were crushed in a mortar.

2.2 Catalyst Characterization

2.2.1 Electron microscopy

TEM imaging was performed using a Philips CM10 operating at 80 kV at the Confocal and Electron Microscopy facility in the Biology department at the University of Waterloo. A diluted sol of NPs was dropcast onto TEM copper grids with a mesh size of 200 coated with formvar and dried at r.t.

SEM imaging was performed using a Hitachi S-5200 microscope operating at 30 kV. Samples for imaging were dropcasted onto steel stabs, dried, and treated with plasma using the digital plasma system Diener with an air flow.

In situ TEM was performed at the Canadian Centre for Electron Microscopy (McMaster University). *In situ* TEM observation was performed with a JEOL ARM-200FTH microscope operated at 200 kV. NPs were dispersed in EtOH. A drop of the resulting solution was placed on a special E-chip and dried at room temperature. The E-chip was mounted in an *in situ* heating holder (Fusion, Protochips) or a gas cell holder (Atmosphere, Protochips). The samples were heated in the temperature range of 25-650°C to study the morphology changes of NPs under the reducing environment of 10% H₂/Ar (corresponding to the pretreatment procedure for chemisorption analysis). The pressure was maintained at 500 Torr. To minimize the effect of electron beam irradiation, the current density was kept below 16 pA/cm².

2.2.2 X-ray diffraction analysis (XRD)

Powder XRD patterns of NPs supported on SiO₂ were collected on a Malvern Panalytical Aeris Benchtop XRD at r.t. operating at 40 kV. The instrument was equipped with a copper anode. The incident beam was collimated by a 1.52 mm divergence slit and the diffraction angle range was set between 0° and 90°.

2.2.3 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The SiO₂-supported NPs catalysts (100 mg) were dissolved in 2 mL of aqua regia for 48 hours in glass vials. Two dilutions were performed using a mixture of 3% HCl and 2% HNO₃ to achieve a final total Ru concentration ranging from 100-1000 ppb. The samples were then submitted to the Metal Isotope Geochemistry Laboratory in the Earth Science department at the University of Waterloo.

2.2.4 Chemisorption analysis

All chemisorption studies were performed using an AMI 300-Lite chemisorption analyzer equipped with a TCD detector. For each experiment, ~100 mg for TPD or ~150 mg for TPSR and BET of 5 wt% NPIs/SiO₂ samples were placed in a quartz U-tube reactor between two plugs of quartz wool. For all experiments, the pretreatment procedure was a reduction of the sample in 10% H₂/Ar at a flow rate of 30 sccm at 650°C for 2 h. Calibration procedures were performed for each experiment using corresponding gases to convert TCD signal values to moles of desorbed gases. The time between injections for the calibration procedure was 240 seconds, with data collection lasting 180 seconds and a flow rate of 30 sccm. The loop (515 µl) was calibrated by Altamira company.

2.2.4.1 Temperature programmed desorption (TPD)

After reduction and cooling in an Ar flow, N₂ or H₂ (10%H₂/Ar) adsorption was performed for 2 h at 400°C and 30 sccm. The system was cooled to 50°C and flushed with Ar for 1 h to remove the physisorbed nitrogen or hydrogen. Samples were then heated in He (N₂-TPD) or Ar (H₂-TPD) from 50°C to 250°C with a hold time of 2 h (ramp rates of 1, 3, 7, 20°C/min).

2.2.4.2 Temperature surface programmed reaction (TSPR) of NH₃ production

After reduction and cooling in an argon flow, NH₃-TPSR was performed in a mixture of nitrogen and hydrogen (1:3 vol.) in the temperature range of 50°C to 450°C, with ramp rates of 1, 3, 7, and 20°C/min. The optimal temperature for NH₃ production was selected based on the TSPR results. NH₃ synthesis was then carried out for 12 hours, during which a sulfuric acid solution was used to trap the produced ammonia. The concentration of ammonium ions was analyzed using ionic chromatography.

2.2.4.3 BET surface area measurements

The BET surface area of the catalyst was determined using the dynamic BET method. The sample was reduced and cooled in an Ar flow before being purged with a mixture of nitrogen and hydrogen

(1:3 vol.). The U-tube was then immersed in a Dewar vessel filled with liquid nitrogen (-179°C) to condense nitrogen on the surface of the catalyst. The BET expression was used to analyze the results²⁵

$$\frac{p}{V(p_0 - p)} = \frac{1}{v_m C} + \left(\frac{C-1}{v_m}\right) \frac{p}{p_0} \quad (3)$$

where p and p_0 – actual partial pressure of adsorbate and the equilibrium (saturation) vapor pressure of the gas at the adsorption temperature (-179°C) respectively (p_0 indicates the maximum pressure at which the gas can exist in the vapor phase under a given set of conditions), V – volume of nitrogen purged through system at the adsorption temperature, v_m – volume of adsorbed N₂ monolayer, and C – constant determined from the experiment. To derive BET surface area (m²·g⁻¹) data from the experiment – slope ($\frac{C-1}{v_m}$) and intercept $\frac{1}{v_m C}$ – are converted to formula

$$BET \text{ surface} = \frac{\frac{v_m}{V_m} \cdot N_A \cdot a}{m} \quad (4)$$

where V_m – molar volume of gas at the adsorption temperature, N_A – Avogadro's constant, a – cross-section of one nitrogen molecule (16.2 Å²), and m – mass of the catalyst (active component + support) in the reactor.

In BET model gases treated as ideal and only monolayer of adsorbed gas is assumed.

2.2.4.4 TGA-analogue experiment in chemisorption reactor

For temperature-programmed experiments, it is necessary to ensure that the surface of the NPs is free of PVP and chlorine ions, which can be achieved by treatment with NaBH₄ and heating them in a reductive atmosphere of 10% H₂/Ar from 50 to 650°C. The efficiency of ligands removal was confirmed using chemisorption analysis, as TGA analyzers were out of order in all University of Waterloo facilities. The samples were treated with TCD on (usually off by default for treatment procedure) and the signal was recorded. The system was cooled down using He flow, and the same

treatment was repeated. Typically, a significant amount of signal from removed ligands is observed during the first round of treatment, while subsequent rounds result in near-zero TCD signal across all temperature ranges. The procedure is summarized in the figure below.

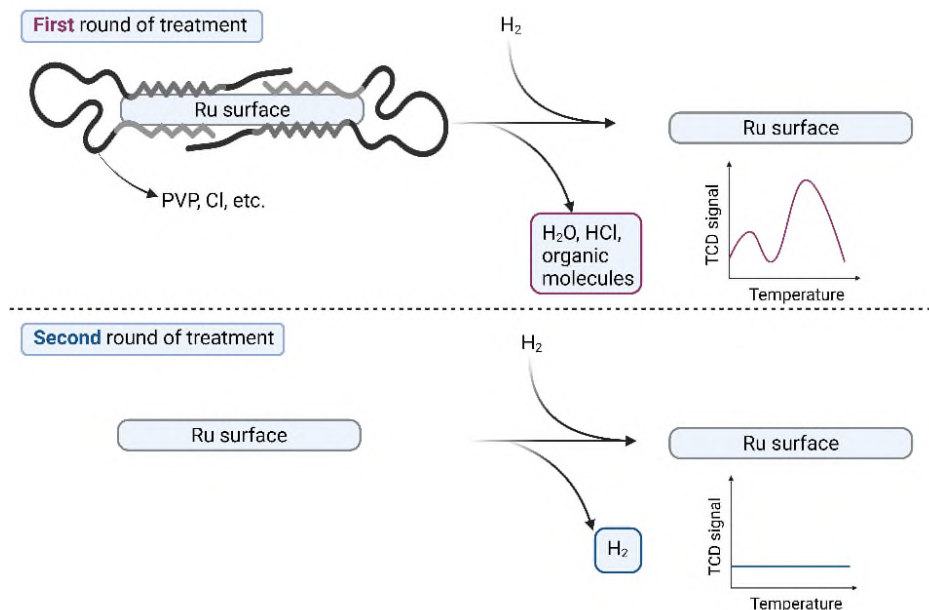


Figure 2-1 The scheme of TGA-analogue experiment using chemisorption analyzer

2.2.5 Kinetic analysis

The activation energies of N₂ and H₂ desorption, as well as NH₃ production, were calculated using the Kissinger equation in first-order approximation⁴⁴

$$\ln \frac{\beta}{T_{max}^2} = -\frac{E_a}{RT_{max}} + \ln \frac{A \cdot R}{E_a} \quad (5)$$

The Kissinger equation is utilized for heterogeneous reactions or processes. It is based on a series of experiments where the temperature is ramped at several rates (β), while recording the peak temperature (T_{max}) of the TCD signal. By plotting the graph with coordinates $\ln \frac{\beta}{T_{max}^2}$ vs $\frac{1}{T_{max}}$, the values of activation energy, E_a , and frequency factor, A , can be determined.

Chapter 3

Experimental Results

3.1 Synthesis and characterization of ruthenium nanoparticles supported on silica gel

The aim of this work is to demonstrate the difference in catalytic activity towards ammonia synthesis of confined regions of Ru NPs. For the “big confinement” model, a cubic cavity of approximately 20 nm is used (Figure 3-1). This type of confinement is found in branched and Ru CGs. NPs with a branched shell formed by a random ensemble of 2D nanoplates are used as a model of “small confinement” (~2 nm). Branched Pd@Ru and branched Ru CGs are characterized by the type of confinement. It has been discussed in Chapter 1 that the study of the confinement effect requires proper selection of the materials for the control experiments. In this work, control experiments are performed on both NSs and 2D NPLs to ensure that the morphology and size of the control NPs are the same as those with confined spaces. The presence of the confinement effect can be determined by a comparative analysis of the confined and control materials.

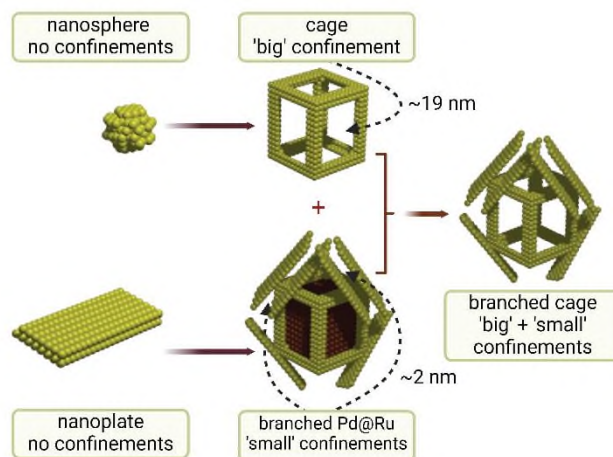
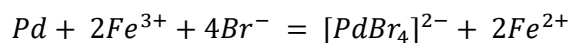


Figure 3-1. Pictorial representation of nanoparticles with confinements and controls studied in this project.

The standard seed-mediated method was used to synthesize branched and CGs, using palladium cubes as seeds. Palladium cubes were synthesized in an aqueous environment in the presence of excess bromide ions, which drive palladium nanocrystal growth along the {100} plane (Figure 3.2A). The seeds were then transferred to an organic phase using ethylene glycol. A ruthenium shell was grown on the template by dropwise adding a solution of RuCl₃ to the solution of seeds alongside AA. The rate of injection of the ruthenium precursor determines whether a smooth or branched shell is obtained. At an injection rate of 8 mL/h, ruthenium forms a branched shell with 2D nanoplates on the surface, arranged in a chaotic order, between which nanometer-sized spaces can be observed (Figure 3.2 B). At a lower injection rate of 0.5 mL/h, a smoother shell of ruthenium phase is formed (Figure 3.2 D). TEM results show that ruthenium initially forms an epitaxial layer directly on the surface of the palladium template before transitioning to the island growth mode. This phenomenon was previously described in Section 2.2; it occurs when the number of shell monolayers surpasses the critical threshold, causing the total surface energy of defects between the *hcp* and *fcc* phases of ruthenium to become lower than the energy of the strain between *fcc* Pd and Ru, which halts epitaxial growth. However, in this study, this type of shell is considered. Following the synthesis of core-shell nanocrystals, the etching procedure is performed. Based on canonical studies on branched ruthenium nanocrystals, the inner core of palladium can be oxidized by iron chloride in the presence of potassium bromide, as shown in the following equation:



Microscopy images for branched and CGs are shown in Figures 3.2C and 3.2E, respectively. The TEM images indicate that the etching procedure was effective, as lighter spots are observed at the sites of the core compared to the original core-shell NPs, implying the loss of palladium from the core. To determine quantitatively the etching efficiency, ICP-MS is performed. The palladium content

of the final CGs is found to be 5.2% and 4.8% for and branched CGs, respectively (Appendix A, Table 1A).

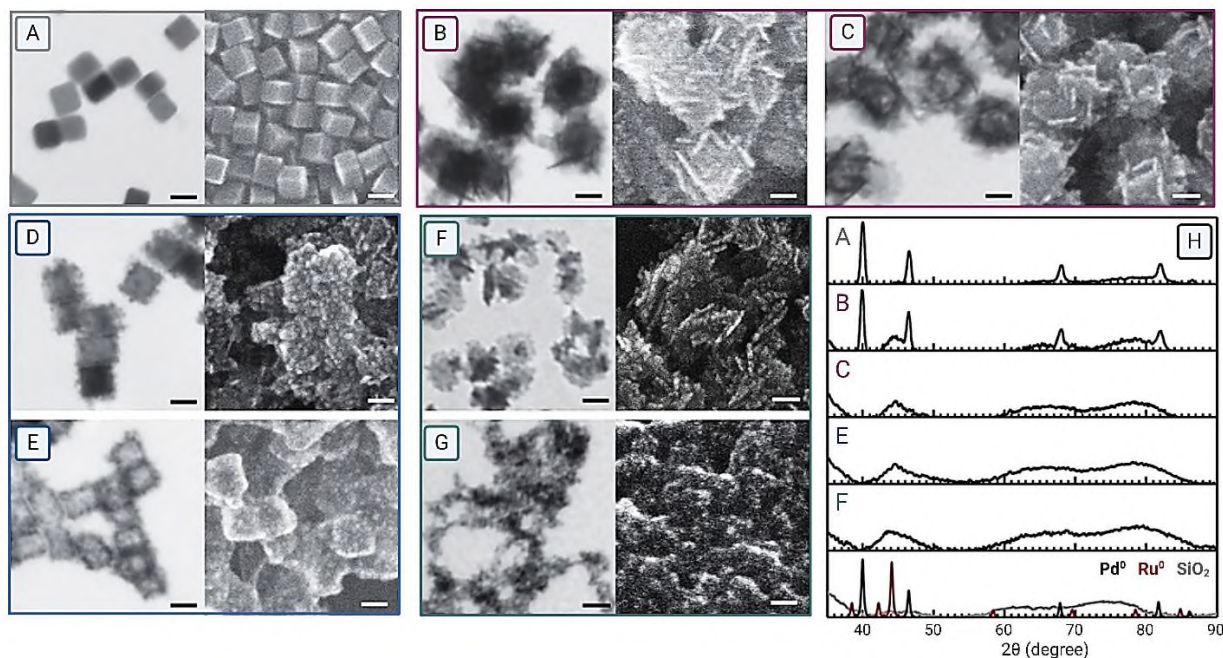


Figure 3-2. EM and XRD characterization of synthesized NPs. TEM and SEM images of Pd NCs (A), branched Pd@Ru (B), branched Ru CGs (C), Pd@Ru (D), Ru CGs (E), Ru NPLs (F), and Ru NSs (G). Scale bar is 20 nm. XRD data for Pd NCs, branched Pd@Ru, branched and Ru CGs, and Ru NPLs (H). The bottom panel represents XRD for reference materials: black line – fcc-Pd (JCPDS No. 05-0685), dark red line – hcp-Ru (JCPDS No. 06-0663), and grey line – silica gel (obtained experimentally).

In this work, a modified etching process was used to eliminate the need for chloride-containing salts (FeCl_3 , HCl), as Cl^- can poison for ruthenium-based catalysts. The presence of chloride ions on the surface of nanoparticles can significantly inhibit the process of ammonia synthesis^{45,46}. Instead, iron nitrate and nitric acid were explored to be used as replacements for the corresponding chlorides. However, the palladium core in the core-shell particles is not oxidized when etched in a solution containing nitrates (Appendix A). This observation suggests that chloride ions also participate in the

etching process when oxidizing and removing the Pd phase. Alternatively, under these conditions, the exposed palladium surface may become passivated, preventing its removal from the core-shell NPs.

XRD analysis was performed on SiO₂-supported NPs to confirm the presence of Pd⁰ and Ru⁰ phases. The Pd NCs exhibited 5 distinct reflections at 40.2°, 46.1°, 67.8°, 81.4°, and 86.4°, which correspond to the reference values from the database (Figure 3.2 H). When growing the branched shell of ruthenium, the reflections of palladium are preserved, except for one with the lowest intensity at 86.4°. Additionally, a shoulder is observed in the range of 42-45°, which corresponds to the superimposed signals of ruthenium at 41.9° and 43.7°. Due to the low crystallinity of the shell, the two signals are not separated, resulting in a broad shoulder signal. After the etching procedure, all reflexes corresponding to the Pd⁰ phase disappeared for both types of CGs. Only a broad peak at 42-50° remains, corresponding to Ru⁰. An increase in the signal is also observed at higher values of diffraction angles. This may be an artifact due to the background subtraction procedure or the small contribution of the 58.3°, 69.2° and 78.2° reflections of ruthenium phase.

For control experiments, ruthenium NPLs and NSs are synthesized. The synthesis is carried out under the same conditions as CGs, using an EG as the organic solvent, RuCl₃ as a ruthenium precursor, AA as a reducing agent, and PVP as a stabilizer. The only difference between the systems was the absence of Pd seeds in the reaction mixture. The same conditions enable the synthesis of CGs, NPLs, and NSs with the same surface chemical composition. This simplifies data analysis and allows for comparison of NPs activity. The morphology of the NPs can be controlled by regulating the injection rate of the ruthenium chloride solution (similar to branched and CGs). When a ruthenium solution is rapidly added at a rate of 8 ml/h, polydisperse 0D nanoparticles are formed. These nanoparticles, when dried on a TEM grid, form aggregates (Figure 3-2 G). On the other hand, when a 0.75 ml/h ruthenium precursor solution is slowly added dropwise, 2D nanoplates are formed. XRD analysis

reveals the formation of a semicrystalline ruthenium phase similar to CGs, with a broad signal of 42-50 (Figure 3-2 H).

TEM images are analyzed to quantitatively describe confined spaces. Figure 3-3 A shows a representative HAADF TEM image of a branched Pd@Ru, highlighting the main dimensional parameters that can influence the catalytic performance. The size of the “big confinement” is determined by the edge length of the Pd NCs (Figure 3-3 B). According to the microscopic analysis results, the edge length and, correspondingly, the internal cavity size of CGs is 17.6 ± 2.3 nm. Secondly, the dimensions of the “small confinement” are determined by the distance between the NPLs in their ensemble. The measured parameters are the distance between parallel NPLs (Figure 3-3 E) and the angle between two non-parallel NPLs (Figure 3-3 G). The average distance between parallel NPs is found to be 2.3 ± 0.5 nm. The rotation angles of the NPLs are 30° , 45° , 60° , 90° , and 120° . NPLs growth that originated on the ruthenium *hcp* phase (hexagonal structure) likely exhibits angles of 30° , 60° , and 120° . The epitaxial fcc phase of ruthenium (cubic structure) facilitates the rotation of NPLs by 45° and 90° . The structural data will be used to construct particles and simulate the ammonia synthesis reaction in the COMSOL program (not presented in this work, but planned for the future publication).

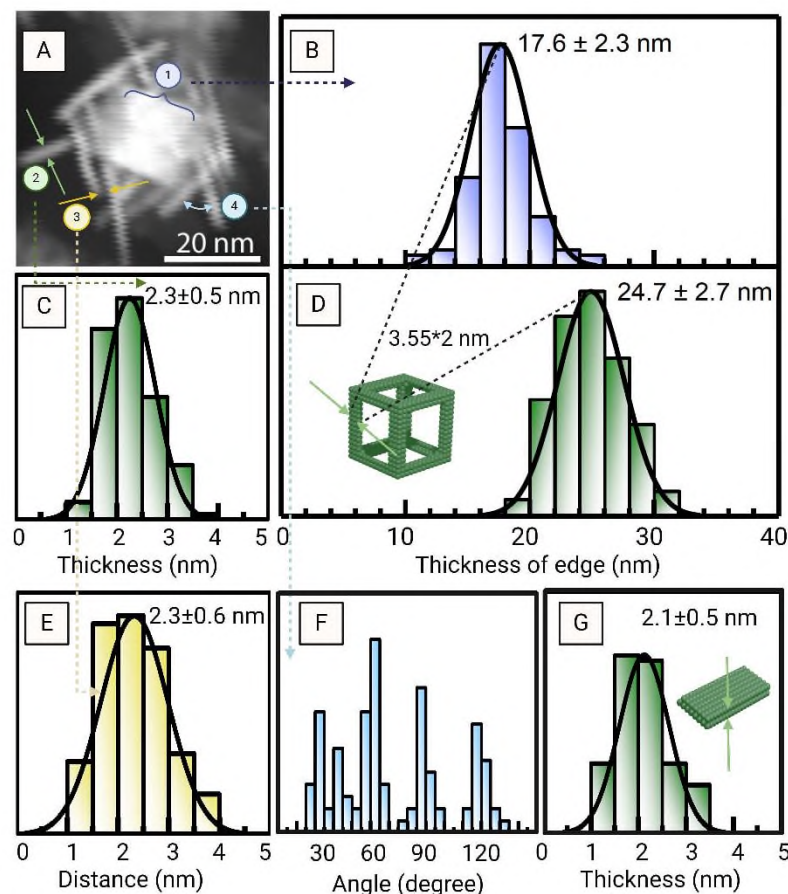


Figure 3-3. Structural characterization of NPs and confined regions. (A) HAADF image of branched Pd@Ru. The labels represent: 1 – size of the core (‘big confinement’); 2 – thickness of Ru NPLs in the shell, 3 – distance between Ru NPLs in the shell (‘small confinement’), 4 – angle between two Ru NPLs in the shell. (B) Size distribution of Pd NCs. (C) Thickness distribution of Ru NPLs in the branched Pd@Ru shell. (D) Size distribution of Pd@Ru. The inset represents the thickness of Ru CGs. (E) Distance distribution between parallel Ru NPLs in the branched Pd@Ru shell. (F) Angular distribution between non-parallel Ru NPLs in the branched Pd@Ru shell. (G) Thickness distribution of Ru NPLs. The number of counts for each histogram is 200.

Since morphology affects the catalytic activity of nanomaterials, it is important to analyze the morphology of the NPs used in this study. To do this, the comparison of the thickness of NPLs in branched NPs (Figure 3-3 C), frame of NCs (Figure 3-3 D), and individual NPLs – the control material (Figure 3-3 G). The thicknesses of individual NPLs and those in of branched Pd@Ru and Ru CGs are similar in value, differing by only 0.2 nm or 0.5 monolayers. However, the thickness of the frame of

Ru CGs differs significantly from all of them, with a difference greater than 1 nm. Since the value of the frame thickness was obtained by subtracting the length of Pd NCs from the length of the Pd@Ru edge, it must be treated with caution (in future plans, taking HRTEM images and clarifying the value of the frame thickness). In any case, all three thicknesses are of the same order of magnitude, which means that the morphology makes the same contribution to the catalytic activity of NPLs, and branched Ru CGs.

To further investigate the catalytic activity of materials, it is essential to examine their thermal stability during chemisorption analysis and ammonia synthesis. The catalyst undergoes a pre-treatment procedure for chemisorption analysis, involving heating in a reducing atmosphere of 10%H₂/Ar at 650°C for 2 hours. This process removes surface ligands – mainly PVP⁴⁷ and Cl⁴⁶ – from the NPs, activating them. To examine the thermal stability of NPs, a sample was placed on a copper TEM grid and introduced into a U-tube. The pre-treatment procedure was then conducted using a chemisorption analyzer. The grid was removed and TEM images were taken. Appendix A, Figure 4-3, displays images of branched Ru CGs before and after heating at 650°C, demonstrating the thermal stability of NPs with small and big confinements for further chemisorption and kinetic analysis.

NPs were deposited on a silica gel substrate for chemisorption and kinetic analysis. This support was selected for its convenience of use, as it does not crumble like γ -alumina and does not stain like carbon black. Additionally, it is commercially available, does not significantly reduce the catalytic activity of ruthenium, and does not produce volatile carbon-containing products when heated in a reducing atmosphere. The latter factor is especially important for TPD analysis because hydrocarbons can interfere with the ammonia signal. Also, silica gel does not have XRD peaks that overlap with the Ru phase (Appendix A, Figure 4-4). The nanoparticles were transferred from water to ethanol, which

readily evaporates at high temperatures in a vacuum. Next, sodium borohydride was added to a suspension of silica gel and an ethanol solution of nanoparticles. This step removes excess ligands from the surface of the nanoparticles, causing them to deposit onto the silica gel particles. The ethanol is removed by heating under vacuum at 120°C for 6 hours to obtain the black catalyst powder, which is further used in chemisorption analysis.

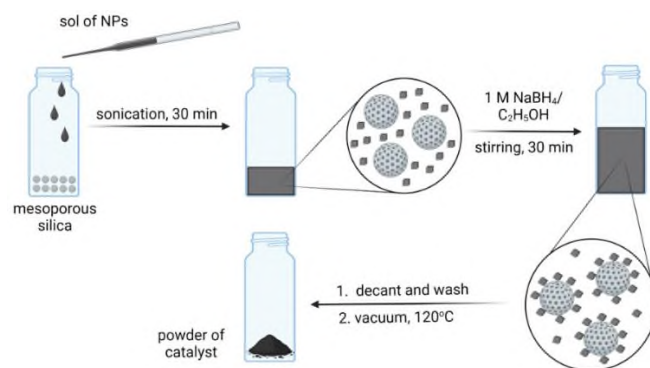


Figure 3-4. Process of NPs impregnation on silica gel support.

Ru content of supported catalysts were analyzed with ICP-MS. The procedure includes soaking the catalyst in aqua regia for 48 h to ensure that all metals are dissolved. The total amount of one batch of each catalyst type is ~2 g. The results of quantitative analysis show that all catalysts contain ~5% of Ru by mass which means that comparison of their chemisorption and kinetic behaviour is reliable.

Table 5-1 ICP-MS data for five types of Ru catalysts.

Metal	NSs/SiO ₂	NPIs/SiO ₂	Branched Pd@Ru/SiO ₂	Ru CGs/SiO ₂	Branched Ru CGs/SiO ₂
Ru (wt. %)	4.9	4.8	5.2	5.3	4.9
Pd (wt. %)	0	0	1.7	0.3	0.2

3.2 Chemisorption analysis of supported NPs

The chemisorption analysis in this work comprises various experiments. The first experiment is temperature-programmed desorption (TPD), which enables one to determine the temperature and activation energy of desorption of nitrogen and hydrogen from the catalyst surface, as well as the number of molecules that can be adsorbed on the catalyst. In TPD, the catalyst is placed in a quartz U-tube between two pieces of quartz wool (Figure 3-5, A). In a chemisorption analyzer, the sample is exposed to either nitrogen or hydrogen. As the reactor temperature increases, adsorbates are removed from the surface of the catalyst, and a signal is detected on the TCD (Figure 3-5, B). The final signal is determined by the difference in thermal conductivity between pure carrier gas and the carrier gas that has passed through the U-tube at varying temperatures. To convert TCD signal values to the amount of desorbed gas, a calibration procedure is necessary, which requires the analyzer to be equipped with a calibration loop.

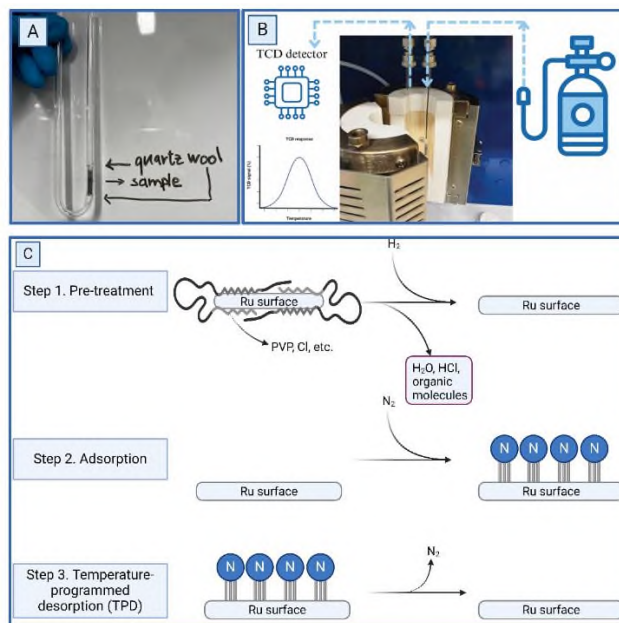


Figure 3-5 Temperature-programmed desorption analysis. (A) Quartz U-tube with a sample. (B) Simplified set-up of chemisorption analyzer with main parts: gas cylinder (gas source), reactor (U-tube), and thermal conductivity detector (TCD). (C) Typical steps of a standard TPD experiment.

The TPD procedure typically involves three steps: pre-treatment, gas adsorption, and TPD. Pre-treatment in a reducing atmosphere can remove residual amounts of PVP and chlorine from Ru NPs, activating them. It is important to determine the temperature range of the pre-treatment procedure to ensure maximum removal of surface ligands without overheating the catalyst and destroying the nanoparticles. The activation temperature of a catalyst is usually determined through thermogravimetric analysis. However, all TGA analyzers on the campus were out of order for a prolonged period, so a similar procedure was invented using a chemisorption analyzer. The catalyst was heated in a flow of 10% H_2 /Ar, with the TCD turned on, in the temperature range of 25-650°C at a ramping rate of 1C/min and held for 30 minutes. Subsequently, it was cooled in a stream of helium and subjected to a second heating procedure in a flow of 10% H_2 /Ar (Figure 2-1 in Chapter 2). Figure 3-6 displays the TCD signals after the first and second round of calcination. The result indicates that the ligands are effectively removed by one pre-treatment procedure. However, it is recommended to avoid conducting similar experiments in the future, as the TCD is susceptible to damage when exposed to excessive amounts of HCl or H_2O .

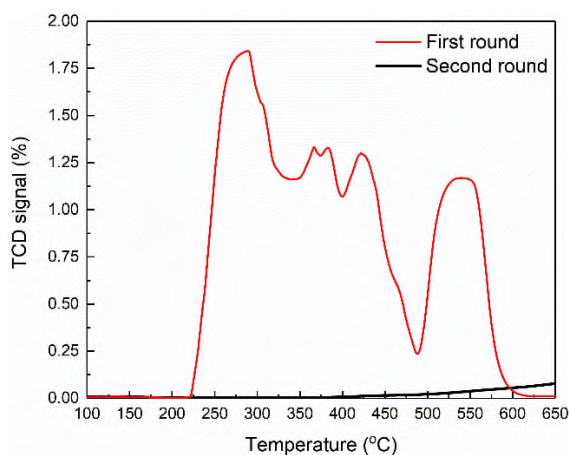


Figure 3-6. TGA-analogue experiment in chemisorption analyzer. Ru NSs supported on silica gel treated in 10% H_2 /Ar flow. The experiment was conducted in two rounds, represented by red and black lines for the first and second rounds, respectively.

After the determination of the pretreatment conditions, a series of N₂-TPD experiments were performed to determine the activation energy, frequency factor, and the uptake of N₂. The Kissinger plots show that the activation energy for nitrogen desorption decreases in the following order: branched Ru CGs > Ru NSs > Ru NPLs > branched Pd@Ru. The difference between activities of NSs and NPLs has been shown experimentally before⁴⁸, and the following DFT studies have revealed that a higher surface abundance of B5 sites (ensemble of five Ru atoms on a step defect of *hcp* phase) on a 2D NPLs facilitates interaction with nitrogen molecules. If 2D NPLs are arranged and form “small” confinements in branched Pd@Ru the activation energy decreases by 27.1 kJ mol⁻¹ or 0.28 eV. This value is very close to the value described in Chapter 1 (0.3 eV), where the theoretical calculations were discussed, which showed the possibility of the realization of the confinement effect. Thus, it can be assumed that the “small” confinement effect can be observed in the case of the nitrogen sorption-desorption process on branched Pd@Ru catalyst (however, this conclusion is challenged in chapter 3.3). The activation energies for nitrogen desorption in branched Ru CGs and reference NSs are nearly identical. This suggests that the “big” confinement has a negative impact on the activation of the nitrogen molecule. However, the nitrogen desorption temperature for branched Ru CGs is approximately 50°C higher than for NSs. This suggests that the branched structure with confined spaces contributes to the retention of nitrogen atoms on the ruthenium surface. A more robust conclusion regarding the impact of “big” confinement on the interaction between ruthenium and nitrogen will be made after conducting N₂-TPD on the Ru CGs catalyst.

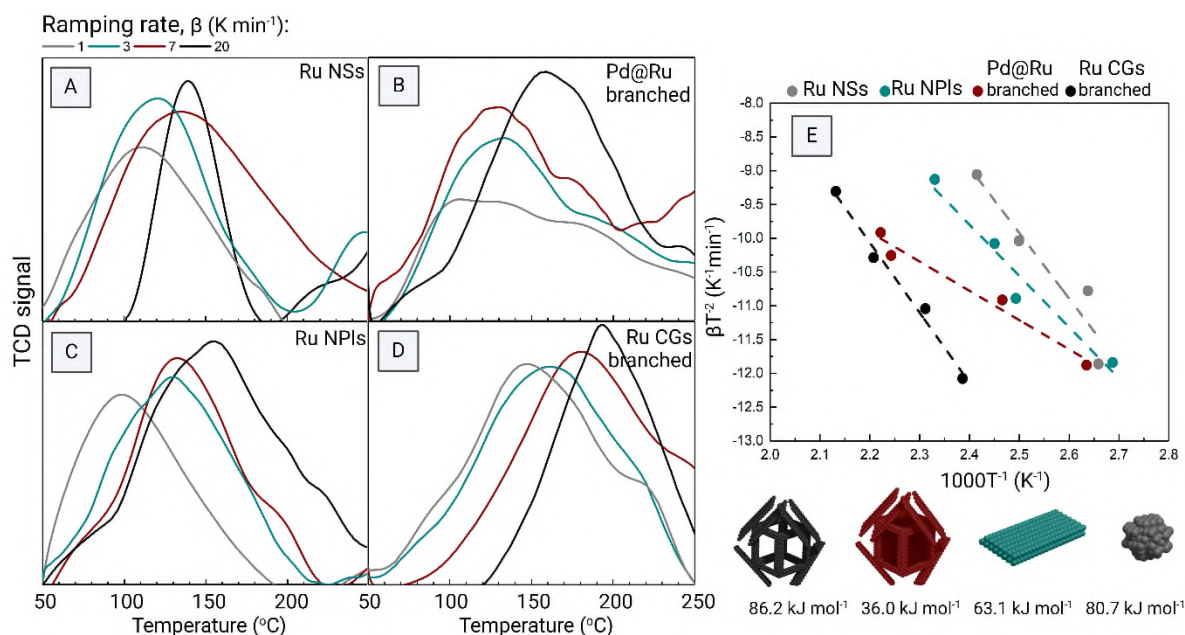


Figure 3-7. N₂-TPD analysis of the catalysts. (A) N₂-TPD on Ru NSs supported on SiO₂. (B) N₂-TPD on branched Pd@Ru supported on SiO₂. (C) N₂-TPD on Ru NPLs supported on SiO₂. (D) N₂-TPD on branched Ru CGs supported on SiO₂. On panels A-D ramping rates 1, 3, 7, and 20 K·min⁻¹ are represented by grey, green, red, and black lines respectively. Panel (E) shows Kissinger plots for Ru NSs (grey), Ru NPLs (green), branched Pd@Ru (red), and branched Ru CGs (black). Bottom part of the panel represents catalysts and corresponding values of activation energy of N₂ desorption obtained from linear fitting of Kissinger plots.

Another kinetic parameter, the frequency or pre-exponential factor, can be obtained from the analysis of the Kissinger plots (Table 4). The experimentally determined frequency factor values decrease in the following order: branched Pd@Ru > Ru branched CGs > Ru NPLs > Ru NSs. The frequency of collisions depends on the number of molecules and the volume in which they are distributed. Therefore, in cases of “small” confinement (or volume), the frequency of sorption and desorption events is at least three orders of magnitude greater than without it. The normalized N₂-uptake values do not entirely support this conclusion, as the amount of nitrogen molecules desorbed from the surface of the branched Pd@Ru catalyst is relatively low. Normalization of N₂-uptake to the total amount of ruthenium may not be entirely correct, particularly in the case of branched Pd@Ru. The

inner ruthenium layer at the interface with palladium is inaccessible and inactive for adsorption. A more accurate approach in this case is to normalize to the BET-surface area, which represents the catalyst surface active to surface reactions. In this case, the N₂-uptake on branched Pd@Ru is the largest, which agrees with the fact that these particles also have the largest frequency factor.

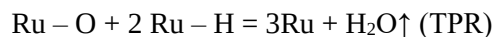
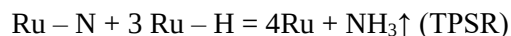
Table 3-2. Characteristics of silica gel supported Ru catalysts.

	Ru spherical	Ru NPIs	Ru CGs	branched Pd@Ru	Ru branched CGs
BET surface area* (m ² ·g _{Ru/Silica} ⁻¹)	398	6686	7981	808	9633
N ₂ uptake (μmol·g _{Ru} ⁻¹)	0.45	6.72		2.59	18.6
N ₂ uptake (μmol·g _{Ru/Silica} ·m ⁻²)	0.11	0.10	TBD**	0.32	0.19
Frequency factor for N ₂ desorption (s ⁻¹)	1.64·10 ⁷	2.58·10 ⁸		2.89·10 ¹¹	2.18·10 ⁹

*data provided for adsorption experiment. Comparison of adsorption and desorption BET see in Appendix 1A.

**to be determined after conducting series of N₂-TPD experiments

The following stage of the research involves determining the net activation energy for ammonia synthesis on various catalysts. To achieve this, an analysis known as temperature-programmed surface reaction (TPSR) was conducted. This analysis comprises two stages: pre-treatment and TPSR. The pre-treatment procedure is identical to that of TPD. TPSR is conducted in a flow of a mixture of 25% N₂ and 75% H₂, with the temperature of the U-tube reactor ramping up from 100 to 450°C. The analysis of signals in this experiment is complex due to the simultaneous process of ammonia formation and Ru reduction (temperature-programmed reduction, TPR), which interacts with the oxygen atoms of silica gel:



Literature data analysis indicates that the TCD signal of NH_3 -TPSR on ruthenium catalysts is typically a main peak with a shoulder or two unresolved peaks corresponding to the signals from water molecules ($<300^\circ\text{C}$) and ammonia ($>300^\circ\text{C}$).^{37,39} To determine the temperature peak value of ammonia production, the TCD signal must be decomposed into two Gaussian curves. Figure 3-8 displays the first series of NH_3 -TPSR experiments at a ramping rate of $1^\circ\text{C}/\text{min}$. The analysis reveals that the temperature of ammonia formation and the activation energy of nitrogen desorption correlate with each other. The branched Pd@Ru exhibits the lowest peak value of the NH_3 signal at 310°C as well as the lowest activation energy of nitrogen desorption. Also, NH_3 -TPSR experiments were conducted at a ramping rate of $20^\circ\text{C}\cdot\text{min}^{-1}$. The results indicate that nanoparticles with “small” and “large” confinement have a lower activation energy for ammonia formation than reference materials (Appendix A, Figure 4-5). The next stage of research will involve synthesizing ammonia under optimal conditions and quantitatively determining the yield using ion chromatography.

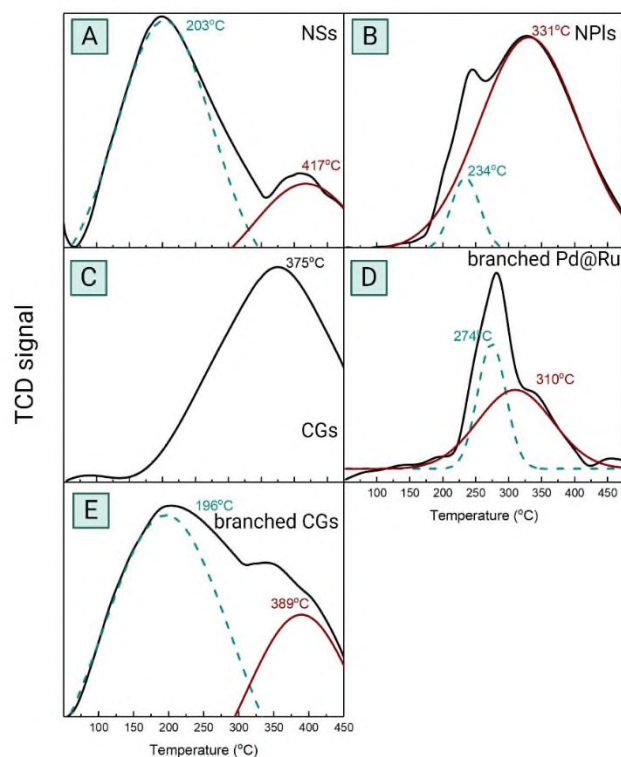


Figure 3-8. NH₃-TPSR analysis of the catalysts. (A) NH₃-TPSR on Ru NSs supported on SiO₂. (B) NH₃-TPSR on Ru NPIs supported on SiO₂. (C) NH₃-TPSR on Ru CGs supported on SiO₂. (D) NH₃-TPSR on branched Pd@Ru supported on SiO₂. (E) NH₃-TPSR on branched Ru CGs supported on SiO₂. On each panel full TPSR curve, deconvoluted peak of H₂O production and peak of NH₃ production are represented by bulk black, dashed green, and bulk red lines respectively. All experiments are performed at ramping rate 1C · min⁻¹.

3.3 Thermal evolution of branched core-shell nanoparticles

For NPs to be used as catalysts, they must be thermally stable during synthesis. Classical TEM and SEM can be used to observe NPs morphological changes, but these methods do not allow for *in situ* imaging because microscopes operate under ultrahigh vacuum. Therefore, this work utilized an imaging modification called environmental *in situ* TEM. This method involves loading a sample of NPs (without support material) onto a pair of thermal E-chip and window E-chip (Figure 3-9 A, B). Electrodes patterned onto the E-chips create a circuit (see Figure 3-9 A). When current is applied, the

SiC membrane on the thermal E-chip undergoes resistive heating. The holder is equipped with inlets for gases (see Figure 3-9 C), allowing for catalytic reactions between gases to be performed and the evolution of the catalyst to be observed *in situ* at different temperatures.

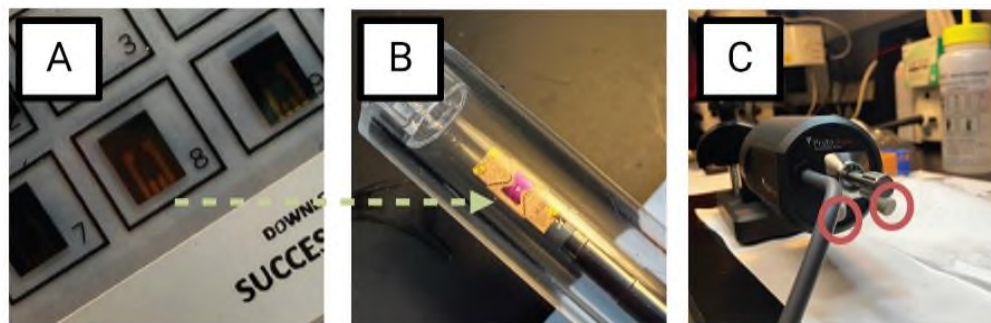


Figure 3-9. Atmosphere AX TEM Holder Preparation set up. (A) The thermal E-chip with patterned electrodes. (B) Assembled pair of thermal and window electrodes on the holder. (C) The back side of the holder with circled in red inlets for gases.

The previous study demonstrated the thermal stability of branched Ru CGs when heated to 650°C in a reducing atmosphere of 10% H₂/Ar (Chapter 3-1 and Appendix A, Figure 4-3). However, in an attempt to reduce experiment time, the decision was made to only study the thermal stability of branched Ru CGs, despite the potential interest in studying other particle behaviours. However, during the thermal stability test of branched Pd@Ru using *in situ* environmental TEM, the particles displayed atypical behaviour upon heating. As shown in Figure 3-10, when the temperature was raised to 300-400°C, the Pd core of the particles melted and diffused into the Ru shell, without significantly altering the structure of the latter (better-resolved image provided in Appendix C). The reason for this behaviour is that Pd has lower melting and Tamman temperatures than Ru (700°C⁴⁹ and 350°C⁵⁰, respectively), which allows for high atom mobility at lower temperatures. Previous studies have observed changes in the core-shell structure, but the recrystallization of particles resulted in the formation of spherical alloy particles with uniform

distribution of metals, as opposed to diffusion out of the core while maintaining original morphology.⁵¹ The effect of CG structure formation upon the heating of core-shell particles requires separate consideration and study as it has not been observed in previous literature.

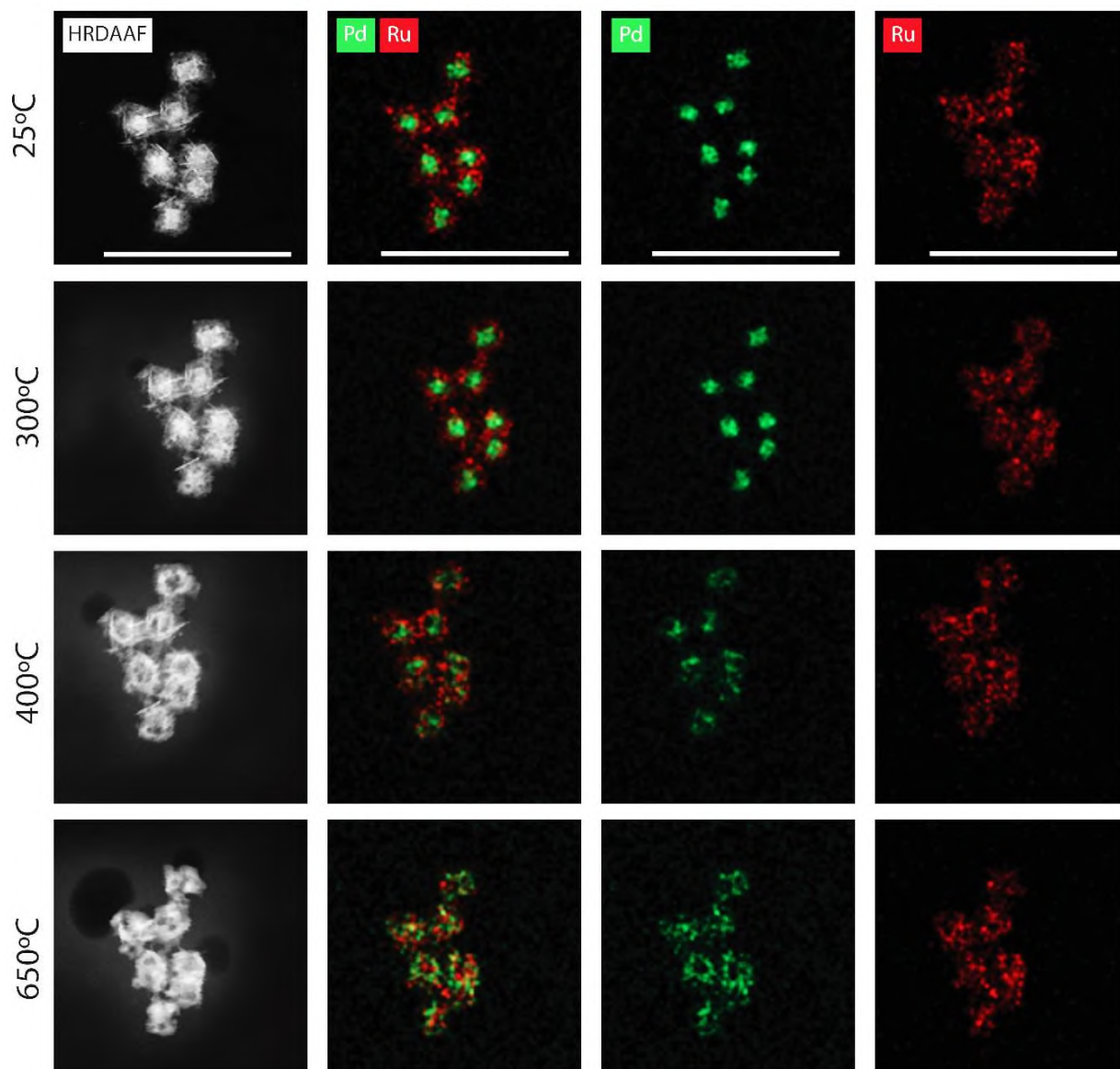


Figure 3-10. Thermal evolution of the Pd@Ru NPs in a flow of 10% H₂/Ar. HAADF and EDX images of Pd@Ru NPs at 25, 300, 400, and 650°C. Scale bar is 200 nm.

As a result of studying the potential impact of confinement on the enhancement of ammonia synthesis, a new phenomenon of cage-like structure formation of core-shell NPs was discovered. However, upon obtaining the data, it became apparent that conclusions regarding the beneficial effects of the “small” confinements on the activation energy of nitrogen desorption may be incorrect. This is because the alloy structure may also affect the interaction of NPs with N_2 . The original papers on the synthesis of Ru cage-like structures include DFT studies that showed that alloying Ru and Pd could significantly reduce the activation energy for nitrogen adsorption.^{52,53} Therefore, it is recommended to exclude branched Pd@Ru as the studied material for confinement and, potentially, replace them with another type of control core-shell NPs that have a higher melting core material.

Chapter 4

Conclusions and Outlook

This work presents a systematic analysis of the effect of confinement size on the ammonia synthesis process. Ru NPs with two types of confinements – 2 nm and 20 nm – were studied as well as two control materials. The preliminary data indicate that the activation energy of nitrogen desorption is lowest ($36 \text{ kJ}\cdot\text{mol}^{-1}$) for NPs with small confinement branched Pd@Ru. N_2 -TPD and NH_3 -TPSR experiments show, that the higher the activation energy of N_2 desorption, the higher the temperature required for NH_3 synthesis. Additionally, the experimentally determined frequency factor values change in the following series: branched Pd@Ru > Ru branched CGs > Ru NPLs > Ru NSs. The values for branched Pd@Ru and Ru NPLs differ by as much as three orders of magnitude, which may indicate the influence of confinement.

The results of section 3.3 have brought changes to the further development of the confinement project. NPs with “small” confinement cannot be considered purely Ru as they form a cage-like structure alloy during the pre-treatment procedure. Therefore, future experiments will include control particles, annealed Pd@Ru, that do not have elongated Ru branches on the surface, but have Pd/Ru alloyed cage (“big” confinement). This will allow us to check the influence of alloy formation on the studied processes.

Currently, we continue to collaborate with McMaster University to conduct experiments on synthesizing ammonia. The experiments will involve *in situ* mass spectrometry analysis to quantify the ammonia yield and calculate the synthesis rate.

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Phase-Controlled Synthesis of Ru Nanocrystals via Template-Directed Growth: Surface Energy versus Bulk Energy

Author: Annemieke Janssen, Zhiheng Lyu, Marc Figueras-Valls, et al

Publication: Nano Letters

Publisher: American Chemical Society

Date: May 1, 2022

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Figure 4-1 Processes during Ru growth on Pd template. Ru growth on Pd cubic seeds at four different kinetic conditions (A).



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Robust Phase Control through Hetero-Seeded Epitaxial Growth for Face-Centered Cubic Pt@Ru Nanotetrahedrons with Superior Hydrogen Electro-Oxidation Activity

Author: Jun Gu, Yu Guo, Ying-Ying Jiang, et al

Publication: The Journal of Physical Chemistry C

Publisher: American Chemical Society

Date: Aug 1, 2015

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Figure 4-2 Processes during Ru growth on Pd template. *Hcp* and *fcc* Ru phase growth on *fcc* seed depending on symmetry of interface (B).

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Figure 4-3 Processes during Ru growth on Pd template. Jagged and sides of Ru contributing to total surface defect energy and strain energy respectively (C).

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Figure 4-4. Types of spatial constraints studied by other groups. The left panel represents a catalytically active NP encapsulated in support material where confinement is the space between NP and support. The corresponding TEM image of the real system is Ru spherical NPs encapsulated in carbon nanotubes.



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**Ru Nanoframes with an fcc Structure and Enhanced Catalytic Properties**

Author: Haihang Ye, Qingxiao Wang, Massimo Catalano, et al

Publication: Nano Letters

Publisher: American Chemical Society

Date: Apr 1, 2016

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Figure 4-5. Types of spatial constraints studied by other groups. The middle panel shows confinement inside branched NP. The corresponding TEM image of the real system is Ru branched truncated octahedra.

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Figure 4-6. Types of spatial constraints studied by other groups. The right figure shows confinement on “single atom” catalytic site where diffusion of reagents on inactive atoms of support. The corresponding TEM image of the real system is “single atom” Ru cites (circled with yellow) embedded inside zeolite structure.

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Appendices

Appendix A

Synthesis and analysis of ruthenium cages

Table 6. ICP-MS results for and branched NPs

Metal	Pd@Ru	Ru CGs	Pd@Ru branched	Ru CGs branched
Pd (wt. %)	30.9	6.2	24.6	4.8
Ru (wt. %)	69.1	94.8	75.4	95.2

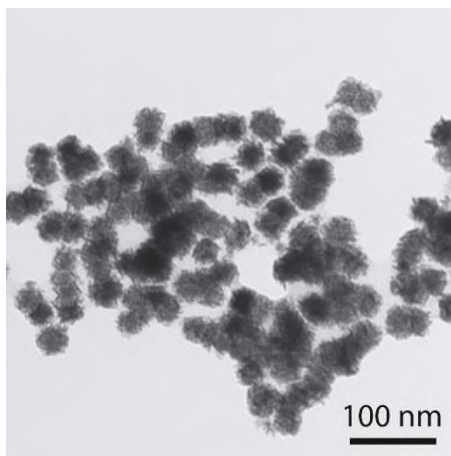


Figure 4-7. TEM image of NPs obtained after etching the branched Pd@Ru in a mixture of $\text{Fe}(\text{NO}_3)_3$ and HNO_3 .

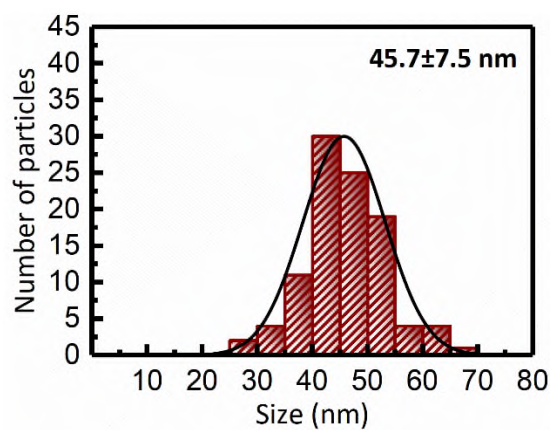


Figure 4-8. Size distribution of branched Pd@Ru.

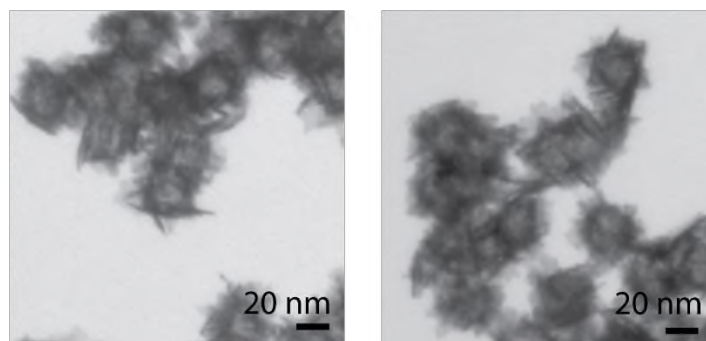


Figure 4-9 Thermal stability test of branched Ru CGs. Left and right panels represent CGs before and after heating procedure.

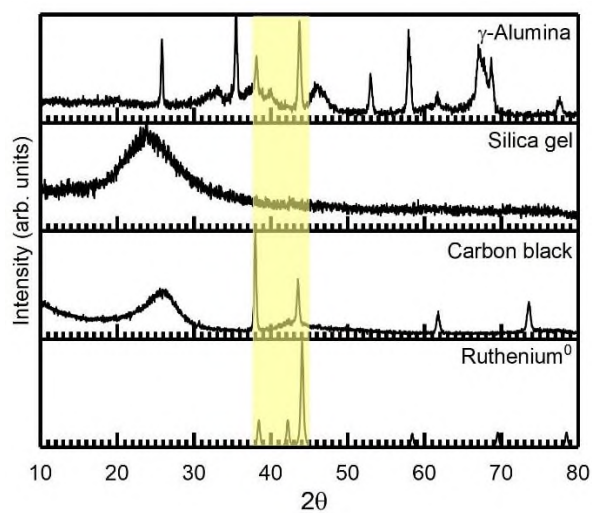


Figure 4-10 Choice of support for Ru catalysts. Silica gel is preferred over γ -alumina and carbon black as it does not overlap with signals from the Ru phase, making it possible to analyze the catalysts using XRD.

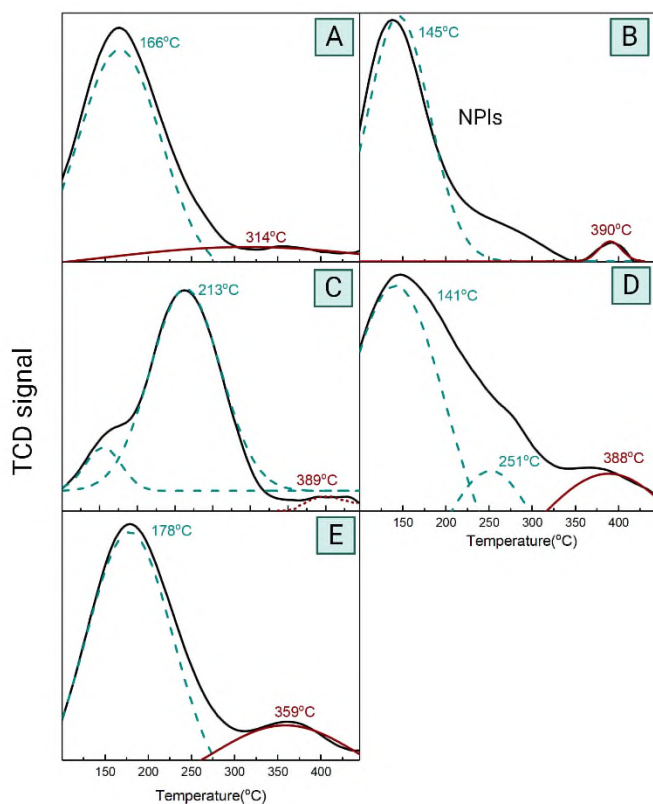


Figure 4-11. NH_3 -TPSR analysis of the catalysts. NH_3 -TPSR on Ru NSs supported on SiO_2 (A). NH_3 -TPSR on Ru NPIs supported on SiO_2 (B). NH_3 -TPSR on Ru CGs supported on SiO_2 (C). NH_3 -TPSR on branched Pd@Ru supported on SiO_2 (D). NH_3 -TPSR on branched Ru CGs supported on SiO_2 (E). On each panel full TPSR curve, deconvoluted peak of H_2O production and peak of NH_3 production are represented by bulk black, dashed green, and bulk red lines respectively. All experiments are performed at ramping rate $20\text{C} \cdot \text{min}^{-1}$.

Appendix B

Chemisorption analysis of catalysts

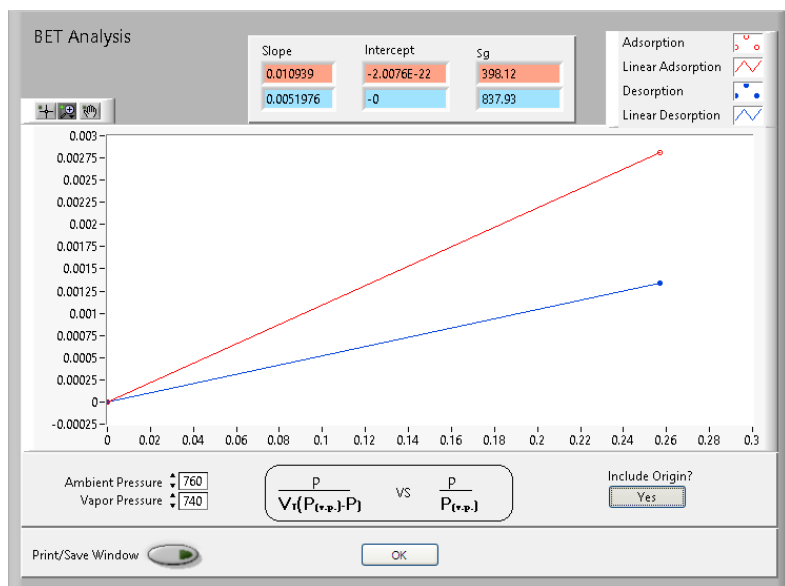


Figure 4-12 BET analysis data for Ru spherical NPs supported on SiO₂
BET surface measurements data

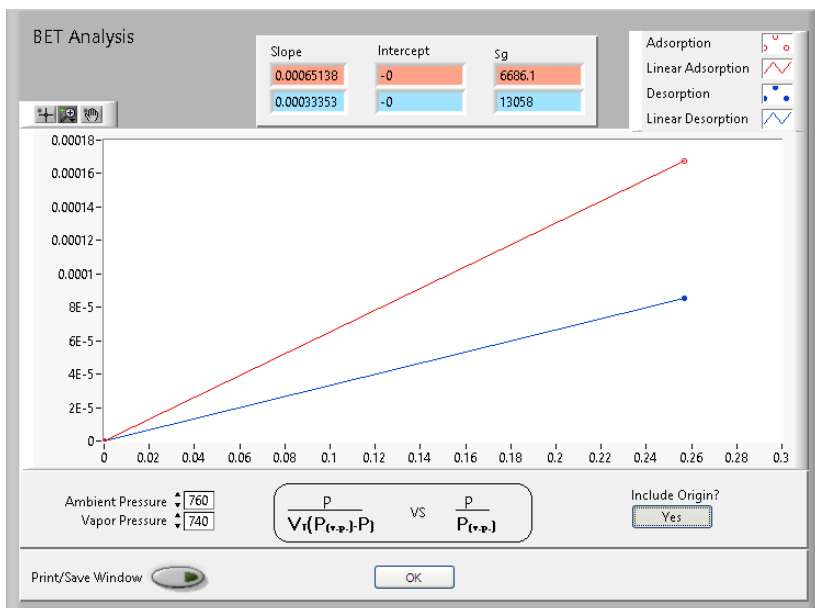


Figure 4-13 BET analysis data for Ru NPLs supported on SiO₂

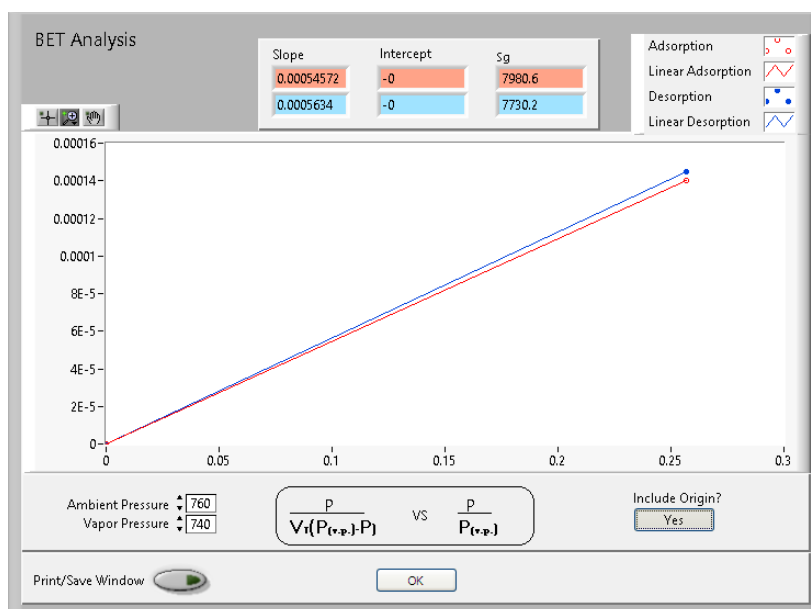


Figure 4-14 BET analysis data for Ru branched CGs supported on SiO₂

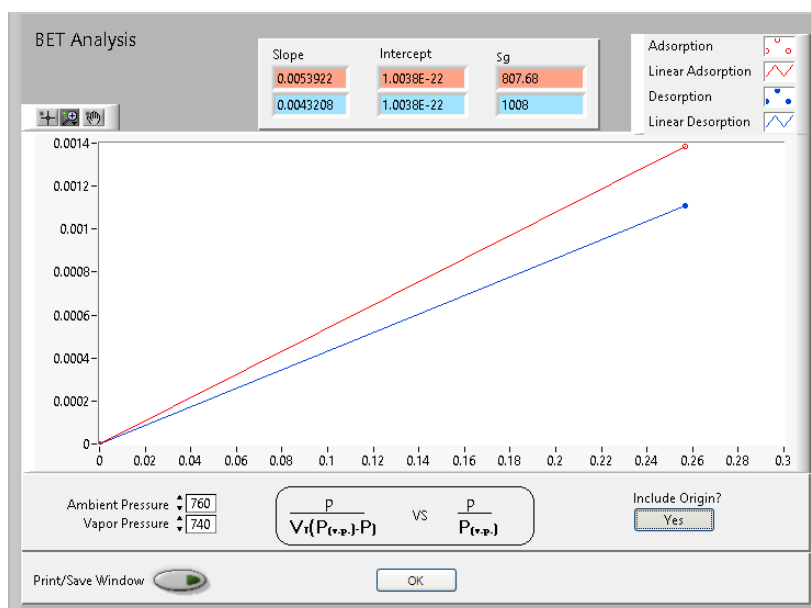


Figure 4-15 BET analysis data branched Pd@Ru NPs supported on SiO₂

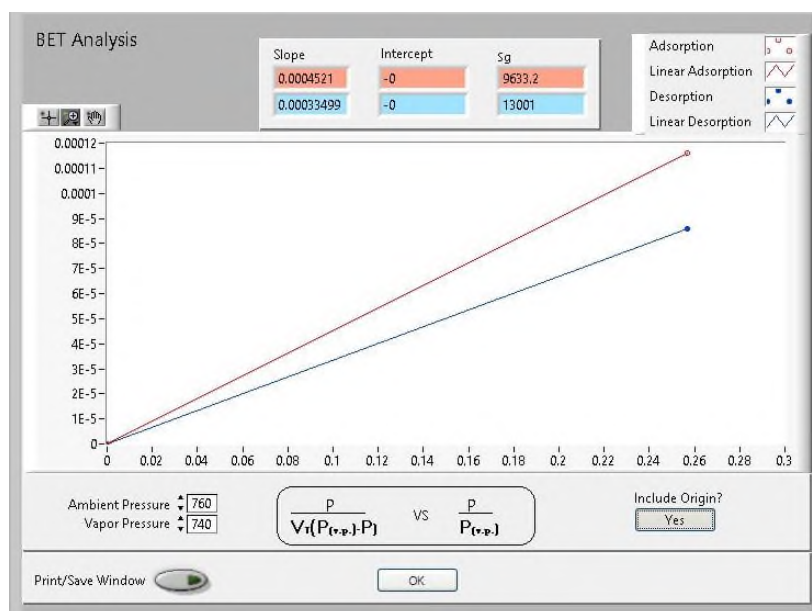


Figure 4-16 BET analysis data for Ru CGs supported on SiO₂

Appendix C Thermal evolution of Pd@Ru nanoparticles

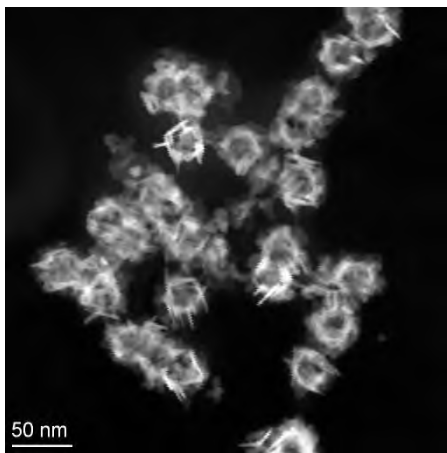


Figure 4-17. HAADF image of annealed at 650°C branched Pd@Ru. The image clearly indicates annealing leads to cage-like structure where Pd atoms are distributed in preserved Ru shell.