



UNIVERSITI PUTRA MALAYSIA

***COPPER-BASED CATALYSTS SUPPORTED ON NITROGEN-DOPED
REDUCED GRAPHITE OXIDE FOR DEHYDROGENATION OF
CYCLOHEXANOL TO CYCLOHEXANONE***

ALYAA KHADHIER MAGEED

FK 2018 25



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By

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**Thesis Submitted to the School of Graduated Studies, Universiti Putra
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Philosophy**

October 2017

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DEDICATION

I would like to dedicate my thesis to my great family...

A great feeling of gratitude to my great mother...whom God placed paradise under her feet...

My great husband...who's always introduce a great support... for me he is the oxygen of my life...mollions thanks for God because he sent this great man for me...

For my cute kids (Adian and Thulfiqar)...despite of they are still little girl and boy, But they gave me the strength to get the PhD degree...

For my lovely father, sister and brothers...with love



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Doctor of Philosophy

COPPER-BASED CATALYSTS SUPPORTED ON NITROGEN-DOPED REDUCED GRAPHITE OXIDE FOR DEHYDROGENATION OF CYCLOHEXANOL TO CYCLOHEXANONE

By

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October 2017

Chairman : Dayang Radiah Bt. Awang Biak, PhD
Faculty : Engineering

Copper based catalysts have industrial importance in different hydrocarbons reactions especially in the synthesis of cyclohexanone from dehydrogenation of cyclohexanol. Fast deactivation of the copper based catalysts at operating conditions is one of the significant problems in the industrial process. The objectives of the present work are to formulate the catalyst support (nitrogen doped reduced graphite oxide N-rGO) and two types of the supported catalysts namely supported copper (Cu/N-rGO) and supported tri metals alloy (CuNiRu/N-rGO) in paper forms, to analyse the properties of the synthesised catalyst support (N-rGO) and the synthesised catalysts as well as to investigate the catalytic performance of the two supported catalysts in the dehydrogenation of cyclohexanol to cyclohexanone, to evaluate the suitable kinetics and model that represents the catalysts behaviour in the dehydrogenation of cyclohexanol to cyclohexanone. All experiments on the catalytic performance were conducted at moderate temperatures (200-270°C) and at 1 atm. The support and the catalysts were synthesised using chemical reduction of the graphite oxide (GO) in NH₄OH solution followed by a thermal treatment with N₂. The morphological, structural, chemical, surface, thermal and crystallinity analyses as well as phase determination were performed. The performances of the catalysts were evaluated in the gas phase dehydrogenation of cyclohexanol to cyclohexanone. The reaction was performed in a fixed bed reactor. The products and by products of the process were analysed using the gas chromatography (GC).

N-rGO provides more than 63% surface area based on BET analysis than that provides by GO. Moreover, N-rGO is thermally more stable than GO by 40°C. Single catalyst (Cu/N-rGO) showed dispersion of the metal particles with diameter approximately ranged from 5 nm to 50 nm and trimetallic catalyst (CuNiRu/N-rGO) has a particle size in the range of 1 nm to 10 nm. CuNiRu/N-rGO catalyst has bigger

surface area up to 75% compare to Cu/N-rGO. In Addition, CuNiRu/N-rGO catalyst exhibits better thermal stability. After reaction, the detected particle sizes ranged from 5 nm to 20 nm for the CuNiRu/N-rGO catalyst and 100 nm to 200 nm for Cu/N-rGO catalyst. The conversion of the cyclohexanol using CuNiRu/N-rGO is 4% higher than using the Cu/N-rGO. The selectivity for cyclohexanone in case of the Cu/N-rGO catalyst is about 83.88%, whilst, the CuNiRu/N-rGO showed approximately 6% better performance. The yield of the cyclohexanone using the Cu/N-rGO is about 78%, while with the improvement of the Cu/N-rGO by adding the Ni and Ru as promoters the yield of cyclohexanone was improved by 8%. The significant improvement posed by the CuNiRu/N-rGO is the duration of the steady state period that was proposed up to 7 times (from 60 minute to 380 minute). CuNiRu/N-rGO performs much better in terms of higher conversion, better selectivity, longer steady state period and better resistance for deactivation. The kinetics behaviour was fitted based on the Langmuir-Hinshelwood (L-H) models presented with different mechanisms models. Using fitting techniques, the single active site mechanism of the H₂ adsorption and its dissociation on the surface reaction suits the experimental data for Cu/N-rGO catalyst. However, the H₂ adsorption without dissociation on the surface reaction mechanism suits CuNiRu/N-rGO catalyst better. This indicates that the catalyst exhibit dual active site mechanism.

This research shows that the N-rGO has the potential to be an excellent support due to its excellent flexible interstices that provide the macro and microporous active catalytic sites. Furthermore, this study shows that the CuNiRu/N-rGO catalyst provides the suitable and selective active sites for the dehydrogenation of cyclohexanol to cyclohexanone reaction.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

**PEMANGKIN-BERASASKAN TEMBAGA DISOKONG-PADA GRAFIT
OKSIDA TERTURUN UNTUK PENYAHHIDROGENAN SIKLOHEKSANOL
KEPADA SIKLOHEKSANON**

Oleh

ALYAA KHADHIER MAGEED

Oktober 2017

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Pemangkin bahan tembaga mempunyai kepentingan industri dalam pelbagai tindak balas hidrokarbon yang berbeza terutamanya dalam sintesis sikloheksanon daripada penyahhidrogenan sikloheksanol. Penyahaktifan cepat pemangkin berasaskan tembaga pada keadaan operasi adalah salah satu masalah utama dalam proses perindustrian. Tujuan kajian ini adalah untuk menghasilkan penyokong pemangkin (nitrogen grafit oksida, N-rGO) dengan dua jenis pemangkin sokongan yang dinamakan tembaga sokongan (Cu/N-rGO) dan aloi logam (CuNiRu/N-rGO) dalam bentuk kertas; untuk mencirikan sifat-sifat penyokong pemangkin (N-rGO) dan pemangkin yang disintesis, untuk menyelidik prestasi dua pemangkin tersokong dalam proses penyahhidrogenan sikloheksanol kepada sikloheksanon dan untuk menilai kinetik dan model yang bersesuaian bagi mewakili perilaku pemangkin dalam proses penyahhidrogenan sikloheksanol kepada sikloheksanon. Semua eksperimen terhadap prestasi pemangkin dilaksanakan pada suhu sederhana (200-270°C) dan 1 atm. Penyokong dan pemangkin disintesis dengan menggunakan tindakbalas penurunan kimia grafit oksida (GO) dalam larutan NH₄OH diikuti dengan rawatan haba dalam persekitaran N₂. Analisis morfologi, struktur, kimia, permukaan, haba dan struktur kristal serta penentuan fasa telah dijalankan. Prestasi pemangkin tersebut dilaksanakan dalam tindak balas fasa gas penyahhidrogenan sikloheksanol dalam reaktor lapisan tetap. Produk dan produk sampingan proses tersebut dianalisa menggunakan kaedah kromatografi (GC).

N-rGO menyediakan lebih daripada 63% kawasan permukaan berdasarkan analisis BET daripada yang disediakan oleh GO. Selain itu, N-rGO adalah termal lebih stabil daripada GO oleh 40°C. Pemangkin tunggal (Cu/N-rGO) menunjukkan penyebaran zarah logam dengan anggaran diameter sepanjang 5 nm sehingga 50 nm dan pemangkin trilogan (CuNiRu/N-rGO) mempunyai saiz zarah dalam 1 nm sehingga

10 nm. Pemangkin CuNiRu/N-rGO mempunyai luas permukaan yang lebih besar sehingga 75% berbanding dengan Cu/N-rGO. Dalam Penambahan, pemangkin CuNiRu/N-rGO mempamerkan kestabilan terma yang lebih baik. Selepas tindakbalas, zarah yang dihasilkan bersiaiz di antara 5 nm sehingga 20 nm bagi pemangkin CuNiRu/N-rGO dan 100 nm sehingga 200 nm bagi pemangkin Cu/N-rGO. Penukaran sikloheksanol menggunakan pemangkin CuNiRu/N-rGO adalah 4% lebih tinggi berbanding penggunaan Cu/N-rGO. Kememilihan mangkin kepada sikloheksanon ialah 83.88% bagi Cu/N-rGO. Pemangkin CuNiRu/N-rGO menunjukkan prestasi 6% lebih efektif. Hasil sikloheksanon menggunakan Cu/N-rGO ialah 78%, dan apabila di tambah baik dengan Ni dan Ru sebagai penggalak, hasil sikloheksanon meningkat lebih 8%. Penambahbaikan ketara yang ditunjukkan oleh CuNiRu/N-rGO adalah perlanjutan mass stabil pemangkin di mana tempoh stabil dianggarkan sehingga 7 kali ganda (dari 60 minit ke 380 minit). CuNiRu/N-rGO melakukan lebih baik dari segi penukaran yang lebih tinggi, pemilihan yang lebih baik, tempoh keadaan mantap yang lebih lama dan rintangan yang lebih baik untuk penyahaktifan. Ciri-ciri kinetik pemangkin yang dihasilkan adalah berdasarkan model Langmuir-Hinshelwood (L-H) berasaskan beberapa mekanisme. Menggunakan teknik pemasangan, mekanisme tapak aktif tunggal penjerapan H₂ dan penyisihannya pada reaksi permukaan sesuai dengan data eksperimen untuk pemangkin Cu/N-rGO. Walau bagaimanapun, penjerapan H₂ tanpa pemisahan pada mekanisme tindak balas permukaan sesuai dengan pemangkin CuNiRu/N-rGO yang lebih baik. Ini menunjukkan bahawa pemangkin mempamerkan mekanisme tapak dua aktif.

Kajian ini menunjukkan bahawa N-rGO mempunyai potensi sebagai penyokong pemangkin disebabkan struktur ruang antaranya yang anjal yang boleh menyeleksi tapak mangkin aktif berbilang bersaiz mikro dan makro. Tambahan pula, kajian ini menunjukkan bahawa pemangkin CuNiRu/N-rGO memberikan tapak aktif yang sesuai dan mempunyai kememilihan bagi tindakbalas penyahhidrogenan sikloheksanol kepada sikloheksanon.

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I certify that a Thesis Examination Committee has met on 26 October 2017 to conduct the final examination of Alyaa Khadhier Mageed on her thesis entitled "Copper-Based Catalysts Supported on Nitrogen-Doped Reduced Graphite Oxide for Dehydrogenation of Cyclohexanol to Cyclohexanone" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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LIST OF ABBREVIATIONS

rGO	Reduced graphite oxide
GO	Graphite oxide
N-rGO	Nitrogen doped reduced graphite oxide
X _{OL}	Conversion of cyclohexanol
S _{NONE}	selectivity of cyclohexanone
NR	Not Reported
FESEM	Field Emission Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
FTIR	Fourier Transform Infrared Analysis
EDX	Energy dispersive X-ray
TPD-NH ₃	Temperature-programmed desorption
XPS	X-ray photoelectron spectroscopy
BET	Surface Area and Porosity Analysis
IUPAC	International Union of Pure and Applied Chemistry
H ₂ -TPR	Temperature Programmed Reduction
TGA	Thermogravimetric analysis
XRD	X-ray diffraction
D	The crystallite size
K	The Scherrer constant, being generally 0.94
λ	The wavelength of the X-ray, being 0.154 nm
β	The full width at half maximum (FWHM)
θ	The angle at the position of the peak
n	the order of the diffraction, being generally 1,
d	is the interlayer spacing,
at %	Average atomic percent
GC	Gas chromatography
FID	flame ionization detector
TCD	thermal conductivity detector
n _{in}	moles of reactant in inlet stream (mol)
n _{out}	moles of reactant in the outlet stream (mol)
WHSV	Weight hourly space velocity (hour ⁻¹)
GHSV	Gas hourly space velocity (hour ⁻¹)

r	The reaction rate (mol/s.g _{cat.})
F	The molar flow rate (mol/s)
X	The reaction conversion
W	Catalyst weight (g)
ΔG	Gibbs free energy, J/mol
ν_j	stoichiometric coefficient
ΔH_{fj}	enthalpy of formation of compound j , J/mol
ΔS_j	entropy of compound j , J/mol K
T	absolute temperature, K
R	gas constant, J/mol K
K_p	equilibrium constant for reaction (atm)
y_{OL}	molar fraction of cyclohexanol
y_{ONE}	molar fraction of cyclohexanone
y_{H_2}	molar fraction of H ₂
P_T	the total pressure (atm)
P_{OL}	Partial pressure of cyclohexanol (atm)
P_{ONE}	Partial pressure of cyclohexanone (atm)
P_{H_2}	Partial pressure of hydrogen (atm)
k	reaction rate constant for reaction (mol/atm g _{cat} s)
A	frequency factor for reaction (mol/atm g _{cat} s)
E_a	activation energy for reaction (kJ/mol)
K_{OL}	adsorption constant of CYNOL (atm ⁻¹)
K_{ONE}	desorption constant of CYNONE (atm ⁻¹)
K_{H_2}	desorption constant of hydrogen(atm ⁻¹)
R^2	Correlation factor
CYNOL	Cyclohexanol
CYNONE	Cyclohexanone

CHAPTER 1

INTRODUCTION

1.1 Background

The formation of cyclohexanone from the catalytic dehydrogenation of cyclohexanol is a significant industrial process for the production of caprolactam (Pramod et al., 2012). Besides the production of caprolactam, cyclohexanone is also used for the production of other valuable chemicals such as adipic acid (Simón et al., 2012). Both caprolactam and adipic acid are important raw materials for the production of polymeric materials such as nylon-6 and nylon-6-6 (Zhang et al., 2013). Due to the unique properties of cyclohexanone such as high solvent capability and reactivity, it finds wide applications in several industries such as solvent for paints and dyes, in pesticides and pharmaceuticals (Lin et al., 2015). The production of cyclohexanone from dehydrogenation of cyclohexanol is an endothermic process, with a reaction temperature of 200-450°C, which requires about 65 kJ/mol of energy (Tangale et al., 2013). The process is always associated with high temperature and energy intensive. The conventional process utilized zinc oxide and calcium carbonate as catalyst and performed at an elevated temperature of 200-500°C. The conversion of cyclohexanol and the selectivity of cyclohexanone were obtained as 70% and 99%, respectively (Briicker et al., 2000). In such a condition, the shelf life of the catalyst is greatly reduced due to the catalysts deactivity at highly operating temperatures. In order to alleviate this problem, several attempts had been made to improve and enhance the efficiency of the dehydrogenation of the cyclohexanol at moderate temperature namely between 150-300°C (Tangale et al., 2013). Hence, the performance of the catalysts were investigated and improved.

The dehydrogenation of the cyclohexanol to cyclohexanone is a very traditional petrochemical processing, so various researches had been done to improve this kind of process. Improving and optimizing the process parameters, i.e., the process flow rates, the time on stream (reaction time) and the catalysts, are the main interest. This industrial process is generally catalyzed using Cu-catalysts such as Cu/SiO₂ (Jeon et al., 1996), Rh-Cu/Al₂O₃ (Mendes et al., 1997), Cu-ZnO/SiO₂ (Ji et al., 2007) CuCr₂O₄ (Romero et al., 2011 a), Cu-Al₂O₃ and Cu/SiO₂ (Popova et al., 2012) at operating temperature range between 200-300°C. The results from the named studies showed that the conversion of the cyclohexanol to cyclohexanone and selectivity for the cyclohexanone are dependent on the degree of dispersion of Cu⁰ metallic in the catalysts. However, Fridman et al. (2000 and 2004) has described that monovalent metal is a better state for this kind of reaction.

In this way, Jenness and his colleagues highlighted the importance of selecting suitable support for the metal catalyst (Jenness et al. 2013). Based on their pioneering work, they found that the selection of the support affected dispersion degree of the metal. In this manner, it is very important to note that the interaction

between the metal nanoparticles and the supports determine the activity of the catalysts.

One advantage of using graphene based materials as catalysts supports is the functional groups present in the structures of these materials, such as oxygen or nitrogen functional groups which act as anchor sites for the metal particles. For example, using reduced graphite oxide (rGO) as a support is the abundant functional groups present on the surface of the graphite oxide (GO) which act as anchor sites for the metal particles. The dispersion of the metal nanoparticles on the rGO often leads to an improved catalytic activity (Chien et al., 2006). In this way, the rGO nanosheet has been used as a support for dispersion of Cu catalysts in oxygen reduction reaction which the prepared catalyst was in powder form (Ania et al. 2015). It was found that copper atoms formed 3D framework with rGO with specific chemistry homogeneously distributed on the surface (Ania et al. 2015).

1.2 Problem statement

The dehydrogenation of the cyclohexanol to cyclohexanone is an important industrial process for the production of chemical intermediates for several applications. From the industrial point of view, the production of the cyclohexanone is still limited due to:

- High reaction temperature lead to much faster catalyst deactivation rate due to faster coke formation rate (Simón et al., 2013)
- High reaction temperature will cause the sintering of copper particles (Popova et al., 2012). Several reports described the works which have been done on various metal based catalysts such as cobalt based catalysts (Liu et al., 2001), copper based catalysts (Fridman et al., 2004) and chromium based catalysts (Zapata et al., 2016), which has been found that copper is the best option as a metal catalyst for the dehydrogenation of cyclohexanol to cyclohexanone process. However, copper has fast deactivation problem due to its fast sintering behaviour in high temperature reaction processes.
- Reduction in the yield and selectivity of the cyclohexanone due to the formation of byproducts (Romero et al., 2011).

Researchers had come up with various attempts to:

- avoid catalysts coking by preventing the sequential dissociation of absorbed cyclohexanol and controlling the mechanism of the coke formation (Simón et al., 2013).
- prolong the catalysts activity by improving the catalyst properties using suitable supports and promoters (Bai et al., 2008; García-Rosado et al., 2017).

- prevent the byproducts formation by providing suitable monovalent copper active sites which are responsible for the dehydrogenation process of cyclohexanol to cyclohexanone (Romero et al., 2011).

Various supports had been investigated such as CNT (Liu et al., 2001), Al₂O₃ and SiO₂ (Popova et al., 2012). However, it has been found that copper dispersed on Al₂O₃ tend to the produce highly acidic monovalent copper compound which might prefer the formation of the byproducts (cyclohexene). Therefore, it is important to find a suitable support which will lead to the formation of the lower acidic monovalent copper compounds for the production of cyclohexanone. Nitrogen-doped reduced graphite oxide (N-rGO), as a kind of novel carbonaceous derived materials which has gained much more attention due to its abundant properties, such as much larger functional surface area and more chemically active sites for further functionalization with metal NPs (García-Rosado et al., 2017). Handling the catalysts in powder form is quite difficult in case of the reactors donot have distributors to avoid the catalysts losing with the products. Using glass wool inside the reactors might not be able to keep the catalysts since the catalysts particle sizes are very small. Therefore, prepare the catalyst in a sheet/paper form will reduce the handling problem, especially if the catalysts in paper form have the cleavages that help the metals settle at the surface as well as between the layers of the support. This will reduce the limitations of mass transfer. Moreover, adding the other metals as promoters can also significantly enhance the dispersion and increase the resistance to coking (Bai et al., 2008).

1.3 Objectives of the study

The significant objectives of the present study are:

1. To formulate the catalyst support (nitrogen doped reduced graphite oxide N-rGO) and two types of supported catalysts namely supported copper (Cu/N-rGO) and supported tri metals alloy (CuNiRu/N-rGO) in paper forms, using Cu/Al₂O₃ as a basis.
2. To analyse the properties of the synthesised catalyst support (N-rGO) and the synthesised catalysts.
3. To investigate the catalytic performance of the supported catalysts in the dehydrogenation of cyclohexanol to cyclohexanone.
4. To evaluate the suitable kinetics and model that represents the catalyst behaviour in the dehydrogenation of cyclohexanol to cyclohexanone.

1.4 Scope of the research

1. To achieve objective (1), nitrogen doped reduced graphite oxide (nitrogen doped graphene) is prepared using chemical reduction of graphite oxide (GO) in NH_4OH solution followed by a thermal treatment with N_2 and the catalysts prepared by the incipient wetness impregnation method.
2. To accomplish objective (2), the physical (include morphological), chemical and thermal properties of the synthesised samples are analysed before and after the reaction to distinguish the effects of the modification process of copper catalysts.
3. To support objective (3), the performances of the catalysts and the role of support (N-rGO) were evaluated in the gas phase dehydrogenation of cyclohexanol in a fix bed reactor. All experiments were performed at various operating conditions of $T=200, 225, 250, 260$ and 270°C , $P=1\text{ atm}$, liquid flow rate of reactant= 0.1, 0.2, 0.3, 0.4 and 0.5 ml/minute, gas flow rate of carrier (N_2 gas) = 25 ml/minute, and time of reaction ~ 8 hour. The products and by products of the process were analysed using gas chromatography (GC) FID and TCD.
4. The experimental data was fitted into a kinetic model to find the best fit theoretical model that is able to describe the mechanism of the catalytic reaction process.

The overview of the methodology of this study is presented in Figure 1.1.

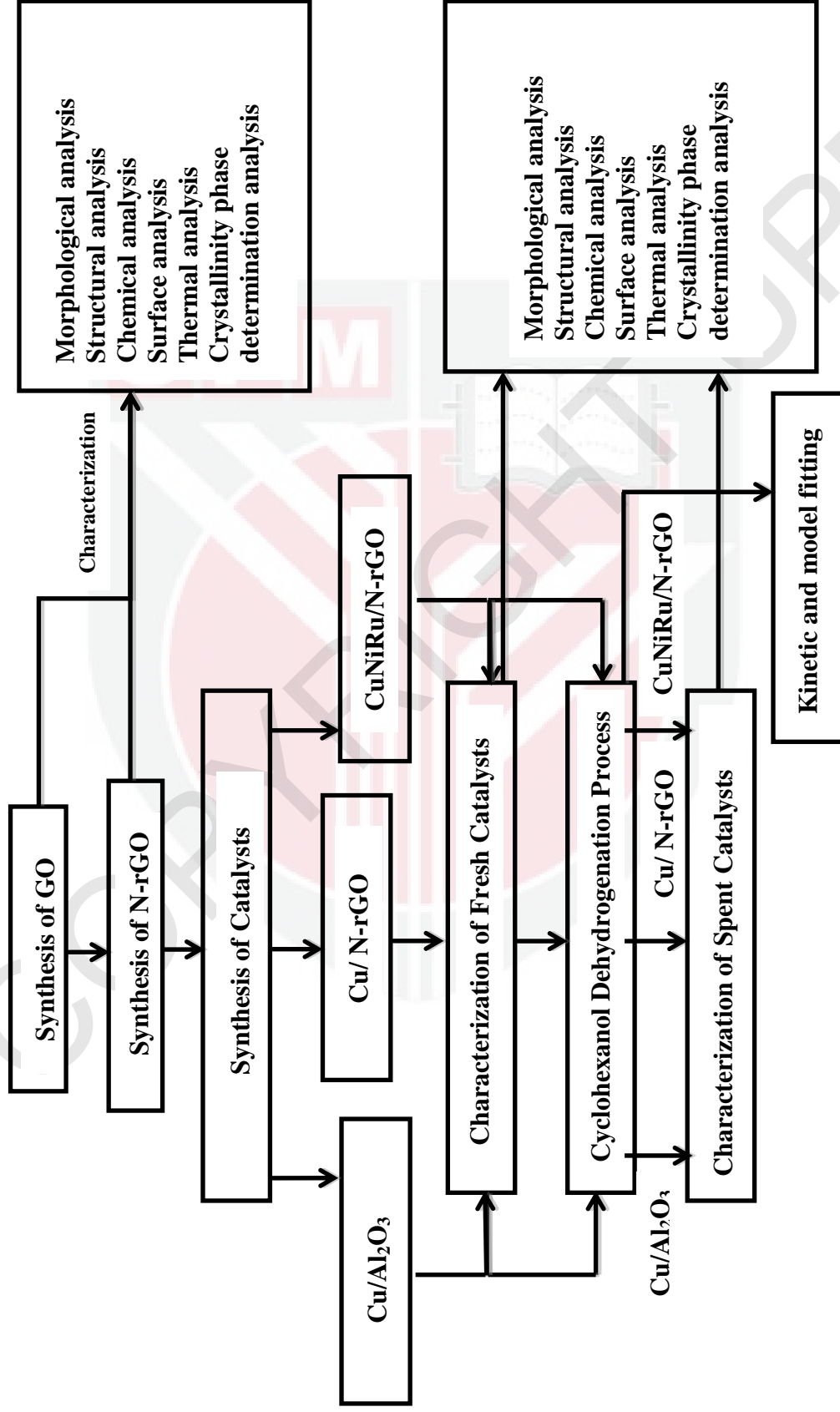


Figure 1.1: Overview of the Methodology

1.5 Research contributions

This study is contributing the knowledge on the:

1. Utilization of new nanomaterial converting from powder into sheets which are much easier to handle.
2. Deposition of the metal catalyst on the prepared nanomaterial, to improve the dehydrogenation process.
3. Provision of information on the synergistic effect of the metal nanoparticles on the catalyst performance for the dehydrogenation process.
4. Assessment of kinetics on the catalyst surface for the dehydrogenation of cyclohexanol to cyclohexanone.

1.6 Organization of thesis

The thesis is arranged in a way that describes the study from all aspects. These have been divided into seven chapters. Chapter 1 introduces the subject matter combined with the objectives of the research. Chapter 2 discusses the literature review which includes brief information about the catalysts and supported catalysts. The literature review also presents general information about the importance of both support and the promoters for the catalysts and how they are affect the chemical reactions. Furthermore, the literature review describes brief information of the kinetic study for the catalysts with the models fitting. Chapter 3 illustrates the experimental approach as well as the findings with respect to the synthesis of the support and catalysts with the elaborated discussion for characterization of the support and different catalysts before reactions analyse the activation part. Chapter 4 presents the experimental procedure for the performance of the catalysts at different operating conditions. The performances of the catalysts at optimum conditions were tested and compared. The deactivation characteristics were also analysed in this chapter. Chapter 5 presents the kinetic and model fitting works. Here, three different models were analysed and compared. Finally, Chapter 6 refers to the overall conclusions based on the finding obtained in this study, and recommendation part for future work are also given in this chapter.

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