การสังเคราะห์คาร์บาเมตจากคาร์บอนไดออกไซด์โดยใช้ตัวเร่งปฏิกิริยานิกเกิล-ซีเรียมเซอร์โคเนียมออกไซด์

นายพีรยุธ เจริญธมะสุข

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SYNTHESIS OF CARBAMATES FROM CARBON DIOXIDE USING Ni/CeO_2-ZrO_2 CATALYST

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A Thesis Submitted in Partial Fulfillment of the Requirements
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Field of Study	Petrochemistry and Polymer Science
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พีรยุธ เจริญธมะสุข: การสังเคราะห์คาร์บาเมตจากคาร์บอนไดออกไซด์โดยใช้ตัวเร่งปฏิกิริยานิกเกิล-ซีเรียมเซอร์โคเนี่ยมออกไซด์. (SYNTHESIS OF CARBAMATES FROM CARBON DIOXIDE USING Ni/CeO_2-ZrO_2 CATALYST) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.ศุภวรรณ ตันตยานนท์, 64 หน้า

ตัวเร่งปฏิกิริยา นิกเกิลบนตัวรองรับซีเรียม -เซอร์โคเนี่ยม ออกไซด์ ซึ่งถูกเตรียมด้วย วิธีการตกตะกอนร่วมแบบมีสารลดแรงตึงผิว ถูกตรวจสอบสมบัติตัวเร่งปฏิกิริยาที่ได้ด้วยเทคนิคการดูดซับทางกายภาพด้วยไนโตรเจน การเลี้ยวเบนรังสีเอกซ์ และ การรีดักชันแบบโปรแกรมอุณหภูมิ จากผลการทดลองพบว่า ตัวเร่งปฏิกิริยาที่เตรียมด้วยวิธีตกตะกอนร่วมแบบมีสารลดแรงตึงผิวเป็น นิกเกิลบนตัวรองรับซีเรียม -เซอร์โคเนี่ยม ออกไซด์ ซึ่งยืนยันด้วยเทคนิค การเลี้ยวเบนรังสีเอกซ์ เพื่อเป็นการพิสูจน์เอกลักษณ์ของตัวเร่งปฏิกิริยา จึงทำการพิจารณาอุณหภูมิการเกิดรีดักชั่นจากวิธีการรีดักชันแบบโปรแกรมอุณหภูมิ และทำการศึกษาพื้นผิวของตัวเร่งปฏิกิริยาโดยเทคนิคการดูดซับทางกายภาพด้วยไนโตรเจน ตัวเร่งชนิดนี้ได้ถูกนำมาใช้ในการสังเคราะห์คาร์บาเมต ซึ่งในปฏิกิริยาที่ใช้นั้นประกอบไปด้วยสารประกอบเอมีน สารประกอบบิวทิวโบรไมด์ ร่วมกับ ก๊าซคาร์บอนไดออกไซด์ การทดลองนี้ทำที่อุณหภูมิ 70, 80 และ 90 องศาเซลเซียส และทำการเปลี่ยนค่าของความดันที่ 2 ถึง 5 บาร์ เมื่อครบ 4 ชั่วโมง ตัวเร่งปฏิกิริยาถูกแยกออกและทำการแยกผลิตภัณฑ์ออกมาโดยเทคนิคคอลัมน์โครมาโทกราฟี เพื่อการศึกษาปัจจัยต่างๆที่มีผลต่อปฏิกิริยา เช่น อุณหภูมิ , ความดัน , ปริมาณของตัวเร่งปฏิกิริยา และชนิดของสารประกอบเอมีนที่ถูกใช้ในระบบ ปฏิกิริยาการสังเคราะห์ดังกล่าวนี้ก๊าซคาร์บอนไดออกไซด์ถูกนำมาใช้และไม่ต้องใช้สารละลายใดๆในการทำปฏิกิริยาทั้งสิ้น

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PEERAYUT JAREONTHAMASUK: SYNTHESIS OF CARBAMATE FROM CARBON DIOXIDE USING Ni/CeO_2-ZrO_2 CATALYST.
ADVISOR: ASSOC. PROF. SUPAWAN TANTAYANON, Ph.D., 64 pp

Ni/CeO_2-ZrO_2 catalyst prepared by impregnation of Ni on CeO_2-ZrO_2 synthesized by surfactant-assisted templating route was characterized by N_2 physisoption, XRD, and TPR. The results showed that the catalyst prepared by surfactant-assisted templating route was Ni/CeO_2-ZrO_2 by X-ray diffraction technique. To confirm characteristic of Ni/CeO_2-ZrO_2 catalyst followed by considering The reduction temperature of catalyst from Temperature reduction program method. And it was studied on surface area of catalyst by N_2 physisoption technique. It was used to catalyze for the synthesis of carbamates in the reaction of amine and n-butyl bromide with gaseous carbon dioxide. These experiments were conducted at temperature of 70, 80 and 90 ^oC and the pressure of carbon dioxide was varied from 2-5 bars. After 4 hours of each reaction, the catalyst was removed and the product was separated by column chromatography. To study about many factor that influence to the reaction such as temperature, pressure, amount of catalyst and types of amines, that were used in the system. However, in this synthesis carbon dioxide was consumed and no solvent was required.

Field of Student: Petrochemistry and Polymer Science Student"s Signature............................
Academic Year: 2011 Advisor"s Signature...........................

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LIST OF ABBREVIATIONS

°C : Degree Celsius

h : Hour

g : Gram

mg : Milligram

K : Kelvin

cm^{-1} : Wavenumber

ppm : Parts per million

TOF : Turnover frequency

CHAPTER I

INTRODUCTION

1.1 Introduction

Carbon dioxide (CO_2) is the major „„greenhouse‟‟‟ gas. It constantly circulates in the environment through a variety of processes known as the carbon cycle. Both volcanic eruptions and the decay of plants release CO_2 into the atmosphere. Oceans, lakes, and rivers absorb CO_2 from the atmosphere. Upon burning the fossil fuels, oils, coal and natural gas and wood, huge amounts of CO_2 are released into the atmosphere. As a result of these activities and growing CO_2 concentration, an imbalance persists in the atmosphere. There are several motivations for producing chemicals from CO_2 whenever possible: CO_2 is a cheap, non-toxic and inflammable feedstock that can frequently replace toxic chemicals such as phosgene or isocyanates. There is a new routes to existing chemical intermediates and products could be more efficient and economical than current methods [1]. We report here efficient, solid, reusable catalysts for the synthesis of carbamates using CO_2 instead of phosgene [2]. Whether the use of CO_2 in these types of reactions contributes to global CO_2 problems or not is, however, debatable. But its application as a replacement for toxic chemical like phosgene in chemicals synthesis can possibly leads to eco-friendly technologies [3]. The chemical utilization of carbon dioxide as a raw material in the synthetic chemical industry has so far been limited [4].

Organic carbamates ($R_1NHCO_2R_2$) are another class of important materials widely used in pharmaceuticals, pesticides and herbicides and more generally for the production of intermediates for fine and commodity chemicals. Commercially, carbamates are synthesized by aminolysis of chloroformate esters, derived from phosgene and an alcohol. This method is hazardous. To improve this drawback. Many alternative routes, such as catalytic carbonylation of nitroaromatics and oxidative carbonylation of amines have also been developed. However, these reaction requires a strong donor solvent like DMF. The reaction of amines, CO_2 and alkyl halides is an eco-friendly method for the production of carbamates. And this synthesis carbon dioxide was consumed and no solvent was required [3,5,15].

Ni/$Ce_{0.6}Zr_{0.4}O_2$ catalyst is very active for reforming reactions that was used of carbon dioxide in the system, and compared to noble metals, are low-priced. Ceria is known for its high oxygen storage, its has ability to release oxygen under oxygen poor environment and quickly reoxidize under oxygen rich environment. Zr stabilizes ceria, forming a ceria–zirconia solid solution to improving textural features, thermal resistance, catalytic activity at lower temperatures and, most important, oxygen storage/transport properties.Although, Ni/$Ce_{0.6}Zr_{0.4}O_2$ catalyst is very active for reforming reactions that was used of carbon dioxide in the system, and compared to noble metals, are low-priced. Ceria is known for its high oxygen storage, its has ability to release oxygen under oxygen poor environment and quickly reoxidize under oxygen rich environment. Zr stabilizes ceria, forming a ceria–zirconia solid solution to improving textural features, thermal resistance, catalytic activity at lower temperatures and, most important, oxygen storage/transport properties [6].

In this study, We report that various carbamates can be synthesized in the absence of any solvent by using the reaction of amine, alkyl halide and CO_2 using Ni/CeO_2-ZrO_2 catalyst. We estimate to use Ni-based catalysts in this reaction, because it has shown good potential as a catalyst for the reforming of methane that uses carbon dioxide same as the reaction of carbamate. The kind of product was varied by changing the starting material " amine group " (hexylamine, cyclohexylamine and aniline). The influence of temperature, pressure, amount of catalyst were discussed.

1.2 Objectives of Research

The objectives of this research work are:

1. To reduce carbon dioxide and uses for change into the highly chemical production costs.
2. To synthesize and investigate the activity of Ni/CeO_2-ZrO_2 in the synthesis of carbamates from CO_2.

3. To obtain the optimum condition of the synthesis of carbamates from CO_2 using Ni/CeO_2-ZrO_2.

1.3 Scope of Research

The stepwise investigation was gone through as follows:

1. Literature survey for related research work
2. To synthesize carbamates by the reaction of amine, alkyl halide and CO_2. The kind of amine group was varied by hexylamine, cyclohexylamine and aniline. The temperature was varied between 70, 80 and 90°C, the pressure was varied between 2, 3, 4 and 5 bar, the amount of Ni/CeO_2-ZrO_2 catalyst was varied between 40, 50 and 60 mg. And characterization by FT-IR, ^1H NMR and column chromatography
3. To investigate the influence of temperature, pressure, amount of catalyst and the various of amine on the Conversion, selectivity, yield% of carbamates.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Theory

2.1.1 Carbon Dioxide

Carbon dioxide (CO_2) is the major „greenhouse“ gas [3]. It constantly circulates in the environment through a variety of processes known as the carbon cycle. Both volcanic eruptions and the decay of plants and animals release CO_2 into the atmosphere. Oceans, lakes, and rivers absorb CO_2 from the atmosphere. Upon burning the fossil fuels, oils, coal and natural gas and wood, huge amounts of CO_2 are released into the atmosphere. As a result of these activities and growing CO_2 concentration. The CO_2 level in the atmosphere has risen by 31% over the last 250 years and this concentration may double or even triple in the next century. Carbon dioxide recovered from flue stacks or the atmosphere can be sequestered in oceans in an effort to mitigate atmospheric CO_2 increases. Alternatively, recovered CO_2 can be used for producing chemicals, fuels and other useful products [7,8]. However, due to inert nature of CO_2, its activation and incorporation into organic substrates still remains a difficult target. There are several motivations for producing chemicals from CO_2 whenever possible: (1) CO_2 is a cheap, non-toxic and non-flammable feedstock that can frequently replace toxic chemicals such as phosgene or isocyanates; (2) CO_2 is a totally renewable feedstock compared to oil or coal; (3) the production of chemicals from CO_2 can lead to totally new materials such as polymers; (4) new routes to existing chemical intermediates and products could be more efficient and economical than current methods; and (5) the production of chemicals from CO_2 could have a small but significant positive impact on the global carbon balance. Totally, only 0.7–1.0% of the produced CO_2 is used, and the consumption of chemical industries is 0.1%. Approximately 110 megatonnes of CO_2 are currently used for chemical synthesis annually [7].

2.1.2 Carbamates

Organic carbamates ($R_1NHCO_2R_2$) are another class of important compounds widely used for pharmaceuticals, pesticides and herbicides, and more generally, for the production of intermediates for fine and commodity chemicals [9,10]. Carbamates are precursors for polyurethanes. They are commercially manufactured with the use of toxic phosgene and isocyanate intermediates [16,17]. Commercially, carbamates are synthesized by aminolysis of chloroformate esters, derived from phosgene and an alcohol [9]. Many alternative routes, such as catalytic carbonylation of nitroaromatics and oxidative carbonylation of amines, have also been developed [12,13,14] (involves separation of methanol-DMC azeotrope, an expensive operation) all have significant disadvantages [15]. The reaction of amines, CO_2 and alkyl halides is an eco-friendly method for the production of carbamates

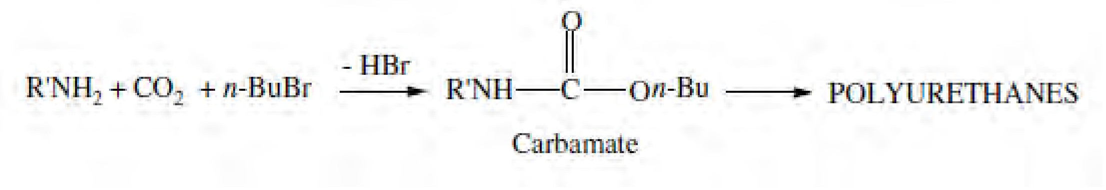
2.1.2.1 Reactions of Carbamates

Several methods were used for synthesis of carbamates namely such as catalytic carbonylation of nitroaromatics and oxidative carbonylation of amines. However, the reductive carbonylation route (using platinum group metal catalysts) is economically not viable; only one-third of CO could be utilized effectively and the separation of CO from CO_2 increases the operation cost [3,5]. Most importantly, the presence of redox-active co-catalysts (ferrous chlorides) results in corrosion problems and makes recovery of the catalyst difficult. The second oxidative carbonylation route involving the handling of hazardous (CO + O_2) mixtures at harsh conditions (50–400 bar; 443 K) is also not satisfactory (scheme1) [15,18,26]. Nevertheless, the reaction of amines, CO_2 and alkyl halides is used for the synthesis of carbamates because of reaction condition and good yields. However, these methods have drawback such as unwanted side-product, and longer reaction time [5].

$$R'NO_2 + 3CO + ROH \longrightarrow R'NHCOOR + 2CO_2 \quad (1)$$

$$R'NH_2 + CO + O_2 + ROH \longrightarrow R'NHCOOR + CO_2 \quad (2)$$

Scheme 2.1 Chemical synthesis of carbamates (1) Reductive carbonylation of nitro aromatics (2) Oxidative carbonylation of amines



Scheme 2.2 Chemical synthesis of carbamates by utilizing CO_2 as a raw material instead of phosgene [5]

2.1.2.2 Reaction of Carbamate mechanism

Carbamates can be formed via the reaction of amine, CO_2 and butyl bromide. CO_2 reacted at a surface of catalyst. And it was reacted with amine readily forms the carbamic acid. Further the reaction of this carbamate anion with n-BuBr yields the corresponding alkyl carbamate Finally, this reaction generates the carbamates [18].

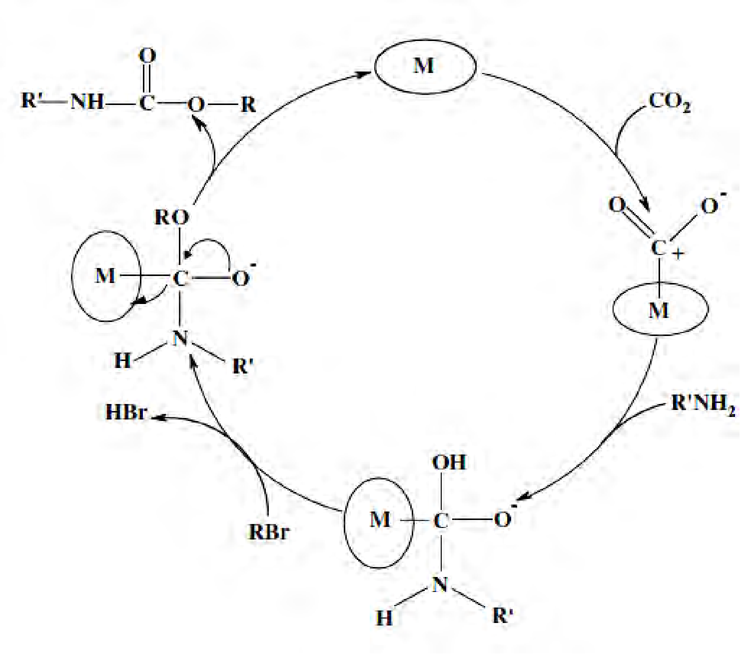


Figure 2.1 A tentative reaction scheme for carbamate synthesis

2.1.3 E1cB elimination reaction

2.1.3.1 The mechanism of E1cB elimination reaction

The E1cB elimination reaction is a special type of elimination reaction in organic chemistry. This reaction mechanism explains the formation of alkenes from (mostly) alkyl halides through a carbanion intermediate given specified reaction conditions and specified substrates. The abbreviation stands for Elimination Unimolecular conjugate Base. The reaction takes place around a sp^3 - sp^3 carbon to carbon covalent bond with an α-acidic hydrogen atom substituent and a β-leaving group. This leaving group can be a halide or a sulfonic acid ester such as a tosyl group. A strong base abstracts the α proton generating a carbanion. The electron pair then expel

s the leaving group and the double bond is formed. When the first step to the carbanion is slow and the second step fast the reaction is irreversible and named (E1cB)i. When the first step is fast and the deprotonation reversible then the reaction mechanism is (E1cB)r. In the (E1cB)anion variation the carbanion is especially stable with a rapid first step and a slow second step. A named reaction displaying E1cB elimination mechanism is the Boord olefin synthesis.

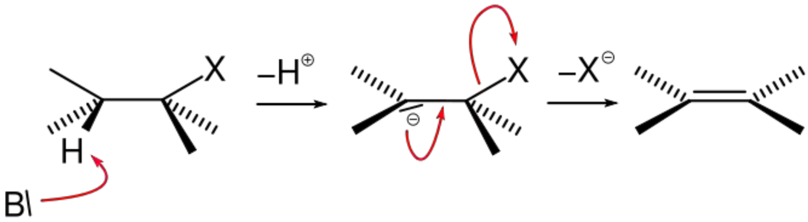


Figure 2.2 The E1cB reaction mechanism.

E1cB is an elimination reaction which looks similar to E2, only the leaving group can be a hydroxide, which cannot be the case in E2 elimination. Negative charges are stabilized by conjugation with carbonyl groups. The proton which is removed using a strong base is adjacent to a carbonyl group, which makes the proton rather acidic, and can therefore be removed by the base without the leaving group departing at the same time. The resulting anion is stable enough to exist due to delocalization on to the carbonyl group. Although the anion is stabilized by the carbonyl group, it still prefers to lose a leaving group and become an alkene, which forms the rate-determining step for the elimination. This is an example of an E1cB reaction which shows the formation of acrolein [19].

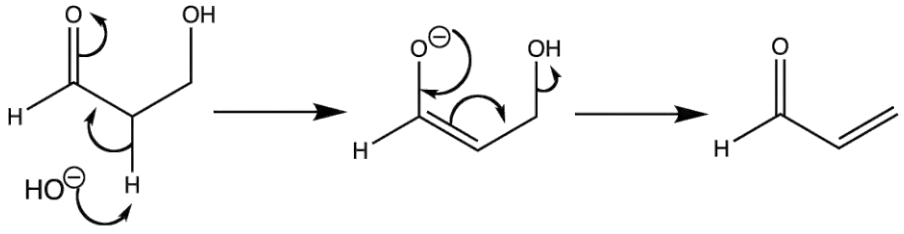


Figure 2.3 Example of an E1cB reaction showed the formation of acrolein [20]

2.1.4 Ni/CeO_2-ZrO_2 catalyst

Many preparation methods have been applied for the preparation of CeO_2–ZrO_2 solid solution for catalytic applications. These include the high-temperature firing or high-energy milling of a mixture of the oxides, sol–gel techniques, and conventional precipitation, and surfactant assisted templating routes. However the catalysts prepared by surfactant-assisted templating route exhibited higher activity and stability than co-precipitation method. These catalysts also exhibited remarkable stability even at low temperature.

2.1.4.1 Support and catalyst preparation

Many preparation methods have been applied for the preparation of CeO_2–ZrO_2 solid solution for catalytic applications. These include the high-temperature firing or high-energy milling of a mixture of the oxides, sol–gel techniques, and conventional precipitation, and surfactant assisted templating routes.

2.1.4.1.1 Precipitation methods [21]

In this procedure, the solutions containing the metal salt and a salt of a compound that will be converted into the support are contacted under stirring with a base in order to precipitate as hydroxides and/or carbonate. After washing, these can be transformed to oxides by heating. Typical examples of industrial catalysts prepared by this procedure are Ni/Al_2O_3 and Cu-Zn oxide/alumina, both used in large scale productions: the first in the steam reforming process and the second in the methanol synthesis and in low temperature shift. The choice of the salts and/or alkali depends mainly on availability at a moderate cost, the solubility in the solvent (water), and, most important, on avoiding the introduction of compounds that can cause negative effects in the final catalyst. Nitrate is inexpensive and particularly soluble in water, but calcination has to be controlled because of the exothermic evolution of nitrogen oxides. As for the base, Na^+, K^+, NH_4^+ hydroxides, carbonates and bicarbonates can be used as precipitating agents, although ammonium hydroxide is often preferred because of the absence of cation residue. By co-precipitation a uniform distribution on a molecular scale of the different active species in the final catalyst could be attained, at least in principle. Many variables have to be controlled: very important is an efficient mixing, the procedure and order of addition of the different solutions, the temperature, the ageing time of the precipitate (which may help filtration by transferring a gelatinous precipitate into a more crystalline one), the filtering and washing procedure (during washing the precipitate may peptize, i.e. redisperse into a colloidal gel difficult to filter). Precipitation is the preferred procedure for preparing supported catalysts with a metal loading higher than 10-15%.

Surfactant-assisted templating route, a modified co-precipitation assisted with the surfactant, can be used to prepare the solid solutions with high surface area and thermal stability, which favors the application of the solid solutions in the high temperature.

2.1.4.1.2 Impregnation methods

This procedure requires that the support is contacted with a certain amount of solution of the metal precursor, usually a salt, and then it is aged, usually for a short time, dried and calcined. According to the amount of solution used, two types of impregnation can be distinguished: one called incipient “incipient wetness”" or “dryimpregnation” because the volume of the solution containing the precursor does not exceed the pore volume of the support. In the simplest way, the impregnating solution is sprayed on the support which is maintained under stirring and has been previously evacuated. By removing the air trapped in the inner pores, a deeper penetration of the solution is allowed and a consequent more uniform distribution of the metal precursor should be attained. In principle this method appears to be simple, economic (especially when using solutions of costly active components) and able to give a reproducible metal loading which is however limited by the solubility of the metal precursor. However, when higher concentration of the metal are required, this limitation can be overcome by carrying out consecutive impregnation steps. The other type of impregnation, called “wet” or “soaking”, involves the use of an excess of solution with respect to the pore volume of the support. The system is left to age for a certain time under stirring, filtered and dried. This procedure is applied especially when a precursor-support interaction can be envisaged. Therefore, the concentration of the metal precursors on the support will depend not only on the concentration of the solution and on the pore volume of the support, but also on the type and/or concentration of adsorbing sites existing at the surface

2.1.4.1.3 Drying

After impregnation, the material undergoes a drying treatment which is generally performed at temperatures between 80 ^{o}C and 200 ^{o}C in order to eliminate the solvent used in the previous impregnation step. Different variables such as the rate of heating, final temperature and time of treatment, type of atmosphere, can influence the process and have to be selected according to the different systems. It has been pointed out that this step can affect, even severely, the results obtained during the impregnation procedure (in case of weak or no interaction between the metal precursor and the carrier surface) in terms of distribution of the active precursor. The significant factors which influence the process and make the redistribution of the metal compounds possible are different and complex: for instance, the rate of nucleation, rate of heating, degree of liquid saturation, viscosity, volume and forms of pores, distribution of pore size, etc. If the drying rate is very slow the evaporation of the solvent (usually water), which starts at the external surfaces, allows the diffusion of the salt into the liquid deeper in the pore resulting in an increase of concentration of the solution in the inner pore: after precipitation the metal precursor is mainly located at the bottom of the pore. On the contrary, too high drying rates will generate temperature gradients and will force the solution towards the outer layer of the particles, where the precipitation will occur. In order to obtain a uniform distribution, the rate of drying has to be higher than the rate of homogenization of the solution. In practice the situation is more complicated because we are dealing with a complex porous system.

2.1.4.1.4 Calcination

This treatment consists of heating the catalysts in oxidizing atmosphere at a temperature usually as high as or a little higher than that encountered during reaction. Calcination has the purpose of decomposing the metal precursor with formation of an oxide and removal of gaseous products (usually water, CO_2) and the anions (Cl^-, NO_3^-, etc) which have been previously introduced. In the case of industrial production, calcination is useful for the removal of extraneous materials, like binders or lubricants, which have been used during the previous forming operations (extrusion, tabletting, etc.). Besides decomposition during the calcinations are (i) a sintering of the precursor or of the formed oxide, and (ii) a reaction of the oxide with the support can occur. In fact, in case of alumina as the support, a calcination performed at temperatures around 500-600 ^oC, can give rise to reaction with divalent metal (Ni, Co, Cu) oxide with consequent formation on the surface of metal aluminates which are more stable than the oxides and so might require a higher temperature of reduction than that needed for the oxides. However, this is not a problem if the reduction temperature is not going to cause excessive sintering: in fact after reduction, the final catalysts will be well dispersed due to this textural effect. When dealing with bimetallic catalysts, a severe control of calcination temperature is required in order to avoid the formation of two separate oxides or segregation of one of the component.

2.1.4.1.5 Reduction

With this operation the metal oxide, or sometimes the metal precursor, is transformed into a metal by thermal treatment in hydrogen (or diluted hydrogen) flow. In some catalysts the reduction is performed in solution by chemical reagent such as formaldehyde or hydrazine. As in the previous thermal treatments, variables like the rate of heating, final temperature and time of reduction, hydrogen concentration and flow have to be carefully chosen depending on the type of metal, catalytic system and reaction to be performed. The quality of the reduction gas or mixture is very important: water vapor has to be as low as possible because it can be detrimental for a high dispersion of the metal. For the same reason hydrogen flow has to be high enough to remove from the support the water formed during the reduction. Direct reduction of the metal precursor, for instance metal chlorides, is avoided although the latter are more easily reduced than the corresponding oxides: the hydrochloric acid would be very corrosive in the presence of small amounts of water vapor. Usually the catalysts are reduced to metals by the manufacture and stabilized before shipping, by oxidation of a thin film of metal which can be easily removed in the reactor. This stabilization is usually performed with a diluted oxidant mixture (1-2% O_2 in inert gas like N_2). A commonly used technique to study the reduction process is the temperature programmed reduction (TPR).

2.1.4.2 Catalyst characterization

2.1.4.2.1 X-ray diffraction spectroscopy (XRD)

The X-ray diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance. The powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phases. An electron in an alternating electromagnetic field will oscillate with the same frequency as the field. When an X-ray beam hits an atom, the electrons around the atom start to oscillate with the same frequency as the incoming beam. In almost all directions we will have destructive interference, that is, the combining waves are out of phase and there is no resultant energy leaving the solid sample. However the atoms in a crystal are arranged in a regular pattern, and in a very few directions we will have constructive interference. The waves will be in phase and there will be well defined X-ray beams leaving the sample at various directions. Hence, a diffracted beam may be described as a beam composed of a large number of scattered rays mutually reinforcing one another.

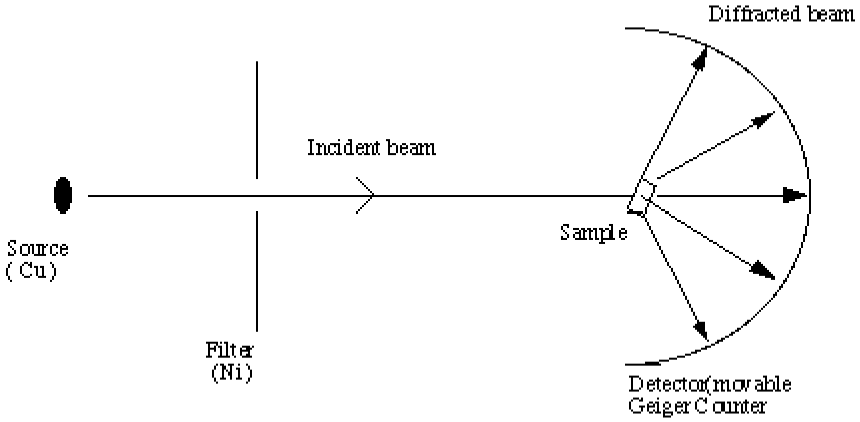


Figure 2.4 Schematic of an X-ray powder diffractometer.

The orientation and interplanar spacings of these planes are defined by the three integers h, k, l called indices. A given set of planes with indices h, k, l cut the a-axis of the unit cell in h sections, the b axis in k sections and the c axis in l sections. A zero indicates that the planes are parallel to the corresponding axis. e.g. the 2, 2, 0 planes cut the a– and the b– axes in half, but are parallel to the c– axis In X-ray diffraction work we normally distinguish between single crystal and polycrystalline or powder applications. The single crystal sample is a perfect (all unit cells aligned in a perfect extended pattern) crystal with a cross section of about 0.3 mm. The single crystal diffractometer and associated computer package is used mainly to elucidate the molecular structure of novel compounds, either natural products or man made molecules. Powder diffraction is mainly used for “finger print identification” of various solid materials, e.g. asbestos, quartz. In powder or polycrystalline diffraction it is important to have a sample with a smooth plane surface. If possible, we normally grind the sample down to particles of about 0.002 mm to 0.005 mm cross section. The ideal sample is homogeneous and the crystallites are randomly distributed (we will later point out problems which will occur if the specimen deviates from this ideal state). The sample is pressed into a sample holder so that we have a smooth flat surface. Ideally we now have a random distribution of all possible h, k, l planes. Only crystallites having reflecting planes (h, k, l) parallel to the specimen surface will contribute to the reflected intensities. If we have a truly random sample, each possible reflection from a given set of h, k, l planes will have an equal number of crystallites contributing to it. We only have to rock the sample through the glancing angle THETA in order to produce all possible reflections.

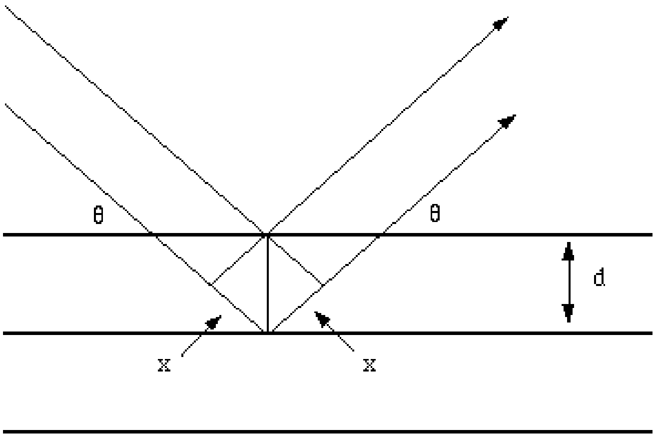


Figure 2.5 Reflection of x-rays from two planes of atoms in a solid [22]

Using this method, Braggs"s law is able to determine the interplanar spacing of the samples, from diffraction peak according to Bragg angle.

$$n\lambda = 2d \sin \theta \qquad \text{.......} (2.12)$$

Where the integer n is the order of the diffraction beam, λ is the wavelength, d is the distance between adjacent planes of atoms (the d-spacings), and θ is the angle of between the incident beam and these planes [23].

2.1.4.2.2 Nitrogen adsorption/ desorption technique: BET [24]

Many solid and powder materials both natural and manufactured contain a certain void volume of empty space. This is distributed within the solid mass in the form of pores, cavities, and cracks of various shapes and sizes. The total sum of the void volume is called the porosity. The type and nature of porosity in natural materials depend on their formation while in man-made materials depend on their manufacturing and generally it can be controlled. Porosity strongly determines important physical properties of materials such as durability, mechanical strength, permeability, adsorption properties, etc. The knowledge of pore structure is an important step in characterizing materials, predicting their behavior. There are two main and important typologies of pores: closed and open pores. Closed pores are completely isolated from the external surface, not allowing the access of external fluids in neither liquid nor gaseous phase. Closed pores influence parameters like density, mechanical and thermal properties. Open pores are connected to the external surface and are therefore accessible to fluids, depending on the pore nature/size and the nature of fluid. Open pores can be further divided in dead-end or interconnected pores. Further classification is related to the pore shape, whenever is possible to determine it.

The characterization of solids in terms of porosity consists in determining the following parameters:

(a) Pore size: pores are classified according to three main groups depending on the access size as shown in Table 1

Table 2.1 IUPAC Classification of pores

Pore Type	Pore Diameter (nm)
Micropores	less than 2 nm
Mesopores	between 2 and 50 nm
Macropores	larger than 50 nm

(b) Specific pore volume and porosity: the internal void space in a porous material can be measured. It is generally expressed as a void volume (in cc or ml) divided by a mass unit (g).

(c) Pore size distribution: it is generally represented as the relative abundance of the pore volume (as a percentage or a derivative) as a function of the pore size.

(d) Bulk density: bulk density (or envelope density) is calulated by the ratio between the dry sample mass and the external sample volume.

(e) Percentage porosity: the percentage porosity is represented by ratio between the total pore volume and the external (envelope) sample volume multiplied by 100.

(f) Specific surface area: the surface area of a solid material is the total surface of the sample that is in contact with the external environment. It is expressed as square meters per gram of dry sample. This parameter is strongly related to the pore size and the pore volume i.e. the larger the pore volume the larger the surface area and the smaller the pore size the higher the surface area. The surface area results from the contribution of the internal surface area of the pores plus the external surface area of the solid or the particles (in case of powders). Whenever a significant porosity is present, the fraction of the external surface area to the total surface area is small.

Adsorption is defined as the concentration of gas molecules near the surface of a solid material. Adsorption is a physical phenomenon (usually called physisorption) that occurs at any environmental condition (pressure and temperature) but only at very low temperature it becomes measurable. Thus physisorption experiments are performed at very low temperature, usually at the boiling temperature of liquid nitrogen at atmospheric pressure.

Adsorption takes place because of the presence of an intrinsic surface energy. When a material is exposed to a gas, an attractive force acts between the exposed surface of the solid and the gas molecules. The result of these forces is characterized as physical (or Van der Waals) adsorption, in contrast to the stronger chemical attractions associated with chemisorption. The surface area of a solid includes both the external surface and the internal surface of the pores.

Due to the weak bonds involved between gas molecules and the surface (less than 15 KJ/mole), adsorption is a reversible phenomenon. Gas physisorption is considered non-selective, thus filling the surface step by step (or layer by layer) depending on the available solid surface and the relative pressure. Filling the first layer enables the measurement of the surface area of the material, because the amount of gas adsorbed when the mono-layer is saturated is proportional to the entire surface area of the sample. The complete adsorption/desorption analysis is called an adsorption isotherm. The six IUPAC standard adsorption isotherms are shown below, they differ because the systems demonstrate different gas/solid interactions.

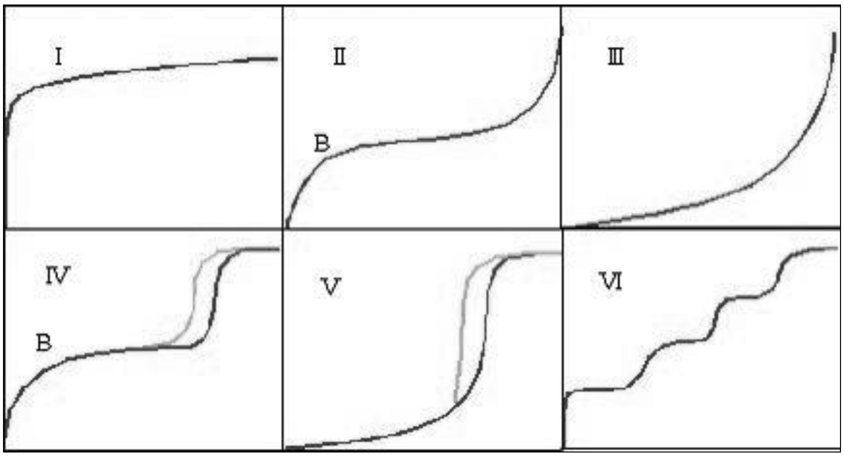


Figure 2.6 The IUPAC standard adsorption isotherms.

The Type I isotherm is typical of microporous solids and chemisorption isotherms. Type II is shown by finely divided non-porous solids. Type III and type V are typical of vapor adsorption (i.e. water vapor on hydrophobic materials). Type VI and V feature a hysteresis loop generated by the capillary condensation of the adsorbate in the mesopores of the solid. Finally, the rare type VI step-like isotherm is shown by nitrogen adsorbed on special carbon.

BET is a rule for the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. In 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller published an article about the BET theory in a journal for the first time; “BET” consists of the first initials of their family names. The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses: (a) gas molecules physically adsorb on a solid in layers infinitely; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each lyer.

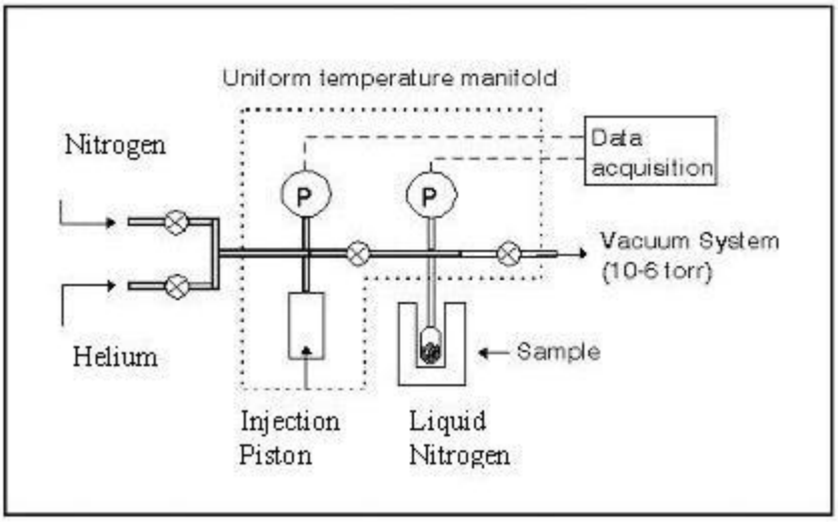


Figure 2.7 A schematic of the N_2 adsorption instrument.

2.1.4.2.3 Temperature programmed reduction (TPR)

This useful technique is mainly used for investigation and characterization of metal catalysts. In principle, during the TPR experiment, a reducing mixture (5% H_2/N_2) flows through a fixed amount of catalyst [B] (where the active metal is in its oxidic or other reducible form) contained in a reactor which is linearly heated. The amount of hydrogen consumed during the reaction is given by the difference of its concentration in the mixture before and after reduction and is measured by a TCD detector [A]. In order to obtain quantitative data, the gas mixture leaving the reactor passes through a cold trap [C] before going to the TCD detector, to remove H_2O or other reduction products and a proper calibration has to be performed, for instance by injecting known amounts of H_2 through a sampling valve [D]. The change in hydrogen concentration and temperature with time are recorded: a typical TPR profile shows one or more peaks for each different reduction process. In order to avoid artifacts in the TPR profile, care has to be taken to control such experimental parameters as gas flow rate, mass of sample, particle size, and heating rate. TPR experiments provide very useful information to decide the proper reduction conditions of the metal oxide precursor and to recognize the presence of different precursor phases, their oxidation state and their interaction with the support. So TPR patterns can be used to study and optimize catalyst pretreatment. In the industrial laboratories TPR is used as a quality control device to determine the efficacy of the preparation procedures. In case of bimetallic catalysts, TPR is very useful to characterize the state of the metallic components, giving information on their mutual effect and on the factors which influence the formation of an alloy.

Temperature programmed reduction (TPR) with hydrogen is a widely used technique for the characterization of reducible solids and catalysts. In TPR, a reducible catalyst or catalyst precursor is exposed to a flow of a reducing gas mixture (typically a few vol.% of hydrogen in an inert gas) while the temperature is linearly increased. The rate of reduction is continuously followed by measuring the composition (H_2 content) of the reducing gas mixture at the outlet of the reactor. The experiment permits the determination of the total amount of hydrogen consumed, from which the degree of reduction and thus, the average oxidation state of the solid after reduction can be calculated [25].

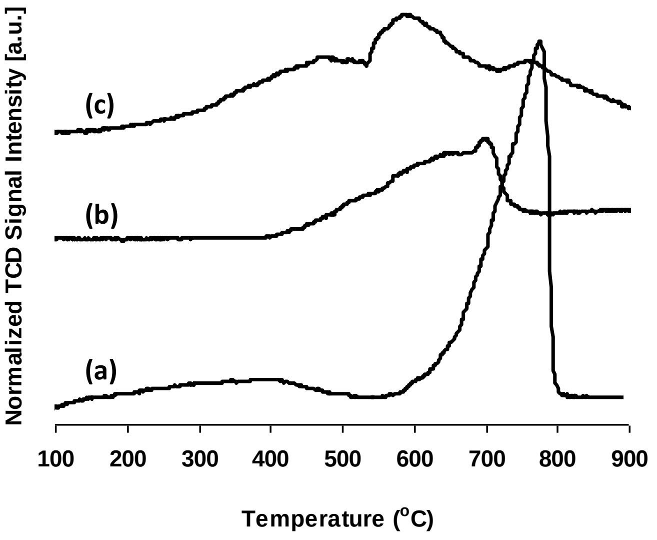


Figure 2.8 TPR spectra of of the ternary mixed oxide support and catalyst calcinated at 650 °C (a) CaO (b) CeZrCa (c) Ni/CeZrCa.

2.2 Literature Reviews

In 2004, Srivastava *et al.* [26], Alkyl and aryl carbamates are synthesized in high yields (80%) at mild reaction conditions by reaction of the corresponding amine, CO_2 and alkyl halides over either titanosilicate molecular sieves or metal phthalocyanine complexes encapsulated in zeolite-Y. The catalysts could be reused with little or no loss in activity. In contrast to hitherto known catalysts for carbamate synthesis, the zeolite-based catalysts of the present study do not require additional onium salts as co-catalysts.

In 2005, Srivastava *et al.* [3], As-synthesized zeolite-beta exhibits high catalytic activity for the synthesis of cyclic carbonates and alkyl and aryl carbamates by a phosgene-free route, utilizing the greenhouse effect gas CO_2. The reaction occurs with high yields of the desired products at mild conditions and without using any solvent or cocatalyst. Cyclic carbonates are synthesized by cycloaddition reaction of CO_2 with oxiranes (epichlorohydrin, propene oxide, styrene oxide and n-butene oxide) at 393 K and 6.9 bar. Alkyl and aryl carbamates are synthesized by the reaction of the corresponding amines, CO_2 and n-butyl bromide at 353 K and 3.4 bar. The as-synthesized zeolite-beta containing the encapsulated quaternary ammonium ions is not only reusable in several recycling experiments, but also shows superior activity to that of the corresponding homogeneous, quaternary ammonium halide salt generally used in the commercial synthetic practice. The microporous silica (inorganic) acting in concert with the encapsulated organic component constitutes an efficient, recyclable catalyst for this reaction.

In 2006, Srivastava *et al.* [5], As-synthesized MCM-41 was used as a reusable, heterogeneous catalyst for the eco-friendly synthesis of cyclic carbonate precursors of polycarbonates via a cycloaddition reaction of CO_2 with epoxides. This catalyst is also efficient for the synthesis of alkyl and aryl carbamate precursors of polyurethanes via the reaction of amines, CO_2 and alkyl halides. Both these reactions were carried out under mild conditions and without using any solvent or co-catalyst. CO_2 is utilized as a raw material replacement for toxic phosgene in the conventional synthesis of these chemicals.

In 2001, Shi *et al.* [14], synthesis of carbamates by oxidative carbonylation of amines over a $PdCl_2(RuCl_3)/ZrO_2–SO_4^{2-}$ catalyst system can proceed with high conversion and selectivity, especially for aromatic amines. This catalyst system is relatively simple and can be further optimized. To our knowledge, it is the first time that such a catalyst system has been used for the oxidative carbonylation of amines. The role of $ZrO_2–SO_4^{2-}$ and the synergism between homogeneous $PdCl_2(RuCl_3)$ and heterogeneous $ZrO_2–SO_4^{2-}$ is now under further investigation.

In 2004, Kuznetsova *et al.* [27], The surface and bulk oxygen mobility and reactivity of ceria-based solid solutions as related to the process of methane conversion into syngas can be tuned in a broad limits by bulk and surface promoters. Variation of the surface/bulk real structure of those complex oxides and their strong interaction with the surface promoters (Pt, Ni) appear to be responsible for those effects.

In 2008, Kumars *et al.* [28], Carbon dioxide reforming of methane (CDRM) to synthesis gas was studied over various Ni-based catalysts. It is shown that the mixed oxide supports CeO_2-ZrO_2, CeO_2-Al_2O_3, and La_2O_3-Al_2O_3, prepared using surfactant, exhibit a high catalytic activity and stability for CDRM. Temperature program reduction (TPR) results demonstrate that the presence of CeO_2, ZrO_2, or La_2O_3 leads to the enhancement of the Ni reducibility compared to Al_2O_3, which is an important indicator of high activity and stability of these Ni catalysts for CDRM. Our thermodynamic calculations indicate that CeO_2 could react with CH_4 to produce synthesis gas, and then CO_2 might reoxidize CeO_{2-x} to its oxidation state. Furthermore, CeO_2 might help in gasification of deposited carbon to inhibit the carbon formation and therefore improve catalyst stability. The presence of alumina tends not to affect the stability of the catalyst as well.

In 2011, Sukonket *et al.* [6], A series of ceria−zirconia mixed oxide supports with nominal composition “$Ce_{0.6}Zr_{0.4}O_2$” were synthesized by two different routes, namely, a surfactant-assisted route and a coprecipitation route. Among the supports obtained by the surfactant-assisted route, different surfactant/metal molar ratios (namely, 1.25, 0.8, and 0.5) were employed to study the influence of the surfactant amount on the catalyst performance. A nominal 5 wt % Ni was impregnated on the supports by a wet impregnation method. These catalysts were evaluated for CO_2 reforming of CH_4 in both the presence and absence of steam. The textural, structural, and physicochemical characteristics of the catalysts were thoroughly investigated with the help of various bulk and surface characterization techniques. The activity results indicate the superior nature of the catalysts obtained by the surfactant-assisted route over the one obtained by coprecipitation. Also, within the limits of the surfactant ratios used, the amount of surfactant employed during the course of support preparation seems to affect the activity, with catalysts prepared with the higher surfactant/metal molar ratio exhibiting better activity and enhanced stability. Structure−activity relationships (SARs) were formulated for some of the characteristics in order to explain the marked difference in activity between the catalysts obtained by the surfactant-assisted and coprecipitation methods and between the catalysts prepared by the surfactant-assisted route but with different surfactant/metal molar ratios. The SARs helped to identify that high oxygen storage capacity, high surface area, high reducibility, higher nickel surface area, better nickel dispersion, and higher surface nickel content are necessary for good performance in the CO_2 reforming of CH_4. On the whole, catalysts obtained by the surfactant-assisted route exhibit a reasonably good performance in the CO_2 reforming reaction but were prone to deactivation in the presence of steam. The inherent hydrophilic nature of the ceria−zirconia support is the main cause for the apparent deactivation in the presence of steam.

CHAPTER III

EXPERIMENTAL

3.1 Materials Chemicals, Glassware & Equipments and Instruments

3.1.1 Materials Chemicals

1. Cerium (III) nitrate hexahydrate $Ce(NO_3)_3.6H_2O$, 99%: Aldrich
2. Zirconyl nitrate hydrate $ZrO(NO_3)_2.xH_2O$, 99.99%: Aldrich
3. Cetyltrimethyl ammonium bromide (CTAB) $C_{19}H_{42}N.Br$: Aldrich
4. Nickel (II) nitrate hexahydrate $Ni(NO_3)_2.6H_2O$, 99.999%: Aldrich
5. Hexylamine ($CH_3(CH_2)_5NH_2$), 99%: Aldrich
6. Cyclohexylamine ($(CH_2)_5CHNH_2$), 99%: Aldrich
7. Aniline ($C_6H_5NH_2$), 99%: Panreac sintesis
8. 1-Butyl bromide ($CH_3(CH_2)_3Br$), 99%: Aldrich
9. Dichloromethane (CH_2Cl_2), Commercial grade: Carlo Erba Reagents
10. Methanol (CH_3OH), Commercial grade: Merck kGaA
11. Acetone (CH_3COCH_3), Commercial grade: Merck kGaA
12. Chloroform ($CHCl_3$), Commercial grade: Carlo Erba Reagents
13. Chloroform-D1 [$CDCl_3$], 99.8% for NMR: Merck kGaA
14. Silica gel [SiO_2], 0.040-0.063 mm: Merck kGaA
15. Carbon dioxide gas: Praxair
16. Nitrogen gas: Praxair
17. Hydrogen: Nitrogen (5%:Balance): Praxair

3.1.2 Glasswares & Equipments

1. 1000 ml , beaker
2. 5000 ml , beaker
3. Regulator pressure: Harris calorific

4. Pressure reactor: Parr instrument Co.
5. Refrigerated/Heating circulator: F-33, Julabo
6. Rotary evaporator: RII ,Buchi
7. Vacuum pump: model 2025, Welch
8. Water bath: B-480, BUCHI

3.1.3 Instruments

1. Fourier transform infrared spectrometer (FTIR): Perkin-Elmer (Spectrum One) infrared spectrophotometer
2. Nuclear Magnetic Resonance (NMR) Spectrometer: Varian, model Mercury-400 nuclear magnetic resonance spectrometer (USA) operating at 400 MHz.
3. Temperature- programmed reduction (TPR): ChemBET 3000 TPR/TPD, Quantachrome
4. X-ray diffraction (XRD): Bruker รุ่น X8 APEX
5. Surface and porosity: Micromeritics ASAP 2010

3.2 Experimental procedure

3.2.1 Ni-based catalyst preparation

3.2.1.1 Support preparation

In order to prepare the $Ce_{0.6}Zr_{0.4}O_2$ mixed oxide support by surfactant-assisted templating route, appropriate quantities of $Ce(NO_3)_3.6H_2O$ and $ZrO(NO_3)_2.H_2O$ precursor salts were dissolved in deionized water. Separately, a calculated amount of cetyltrimethyl ammonium bromide (CTAB) was dissolved in deionized at 60 °C. The above two solutions were mixed together to obtain a resultant mixture solution. The molar ratio of [CTAB]/[Ce+Zr] as 1.25. Aqueous ammonia (25 vol.%) was gradually added to the aforementioned mixture solutions under vigorous stirring until precipitation was complete (pH 11.8). The addition of ammonia induced the precipitation of gelatinous yellow–brown colloidal slurry. The slurry was stirred for

60 min in a glass reactor, subsequently transferred into pyrex glass bottles, sealed and aged *"hydrothermally"* in autogenous pressure conditions for 5 days at 90 °C. After this time frame, the mixture was cooled and the resulting precipitate was filtered and washed repeatedly with warm DI water. The resulting cakes were oven-dried at 120 °C overnight and finally calcined at 650 °C for 3 h in air environment [6].

3.2.1.2 Supported-nickel catalyst preparation

A nominal 5 wt.% Ni was loaded over the above prepared supports by standard wet impregnation method. In a typical impregnation 14.25 g of catalyst support was immersed in 127.75 ml of 0.1 M $Ni(NO_3)_2$ solution. The mixture was subjected to slow heating under constant stirring in a hot water bath, so as to remove the excess water; the dried powders thus obtained were calcined at 650 °C in air for 3 h. The calcined catalysts were reduced *in situ* during the course of reaction in order to reduce the NiO species to metallic Ni species. The reduction was carried out at 710 °C for 3 h in flowing $5\%H_2/bal.N_2$ [6].

3.2.2 Catalyst Characterization

All of the catalysts were further characterized using different analytical techniques. Micromeritics ASAP 2010 was used for Brunauer-Emmett-Teller (BET) surface area and chemisorption (using H_2) measurements, whereas temperature-programmed reduction (TPR; Chembet 3000, Quantachrome), and X-ray diffraction (XRD; Bruker, AXS) were used to evaluate other characterizations of the received catalysts.

3.2.2.1 Surface area and pore size distribution analysis

The BET surface area and pore size distribution analyses for all catalysts were obtained by N_2 physisorption at liquid N_2 temperature using a Micromeritics ASAP 2010 apparatus. Prior to analysis, all the samples were degassed overnight at 180 ^{o}C under vacuum. Pore size distribution and average pore volume were analyzed using the desorption branch of the N_2-isotherm.

3.2.2.2 X-ray diffraction spectroscopy: XRD

Powder XRD patterns were recorded on a Bruker Discover diffractometer using nickel-filtered Cu $K\alpha$ (0.154056 nm) as the radiation source. The intensity data were collected over a 2θ range of 10–90° with a step size of 0.02° using a counting time of 1 s per point. Crystalline phases were identified through comparison with the reference data from ICDD files. The average crystallite size was estimated with the help of Debye–Scherrer equation using the XRD data of all prominent lines.

3.2.2.3 Temperature-programmed reduction: TPR

H_2-TPR of various catalyst samples was performed on a Quantachrome ChemBET 3000 unit equipped with a thermal conductivity detector (TCD). Prior to TPR measurements, the samples were degassed at 150 °C in an inert atmosphere (N_2 UHP grade) for 4 h. The TPR experiments were performed between ambient to 1000 °C at a heating rate of 15 °C/min. Approximately 5 vol.% H_2 in N_2 bal., was used for reduction at the flow rate of 45 mL/min (STP). The total reactive gas consumption during TPR analysis was measured.

3.2.3 Carbamate Synthesis

In a typical reaction, Amine (10mmol), N-butyl bromide (10mmol) and Ni/CeO_2-ZrO_2 catalyst (50mg) were charged into 300 ml Parr reactor. The reactions were conducted at temperature of 70, 80 and 90 ^{o}C and the pressure of carbon dioxide was varied from 2-5 bars. After 4 hours of each reaction. It was cooled down to room temperature and CO_2 was vented out. The catalyst was filtered off and rinsed with dichloromethane. The product was then separated by column chromatography and analyzed by ATR-IR and ^{1}H NMR. Other carbamates Cyclohexylamine and Aniline, were synthesized and characterized in a manner similar to that described above. In some case, the products were isolated by column chromatography (silica gel 60–120 mesh; 100% petroleum ethyl acetate mixture as eluent).

3.2.3.1 Spectral characteristics of N-butyl-n-hexylcarbamate

ATR-IR (cm^{-1}): 3444, 1583 (N-H), 1735 (C=O), 1040 (Bu-O); ^1H NMR ($CDCl_3$), d (ppm): 4.1 (t, 2H) , 2.9 ppm (t, 2H), 1.4-1.3(m, 4H), 0.9(t, 3H).

3.2.3.2 Spectral characteristics of N-butyl-n-cyclohexylcarbamate

ATR-IR (cm^{-1}): 1583 (N-H), 1733, 1380 (C=O), 1045 (Bu-O); ^1H NMR ($CDCl_3$), d (ppm): 4.1(t, 2H), 3.0(m, 1H), 1.6-2.0(m, 10H), 1.3,1.2(m, 4H), 0.9(t, 3H).

3.2.3.3 Spectral characteristics of N-butyl-n-phenylcarbamate

ATR-IR (cm^{-1}): 3406, 1596 (N-H), 1725, 1221 (C=O), 1095 (Bu-O); ^1H NMR ($CDCl_3$), d (ppm): 7.2(m, 2H), 6.6(m, 3H), 3.2(t, 3H), 2.1(m, 2H), 1.5,1.3(m, 4H), 0.9(t, 3H).

3.2.4 Carbamate Characterization

All of carbamates were further characterized using Perkin-Elmer (Spectrum One) infrared spectrophotometer was used for Fourier-Transform Infrared Spectrometer (FT-IR) and Nuclear Magnetic Resonance (NMR) Spectrometer (Varian, model Mercury-400 nuclear magnetic resonance spectrometer (USA)) were used to evaluate other characterizations of the received products.

3.2.4.1 Attenuated Total Reflection Infrared (ATR-IR) spectroscopy

Attenuated total reflection infrared (ATR-IR) spectra were performed on a Perkin-Elmer (Spectrum One). ATR-IR spectroscopy technique is used to analyze material surface. It is also suitable for characterization of material which are either too thick or too strong absorbing to be analyzed by transmission.

3.2.4.2 Nuclear Magnetic Resonance (NMR) Spectrometer

^1H NMR spectra of carbamates were recorded using a Varian, model Mercury-400 nuclear magnetic resonance spectrometer (USA) operating at 400 MHz. Carbamates was dissolved in solution of $CDCl_3$.

Figure 3.1 Schematic of the experimental setup for the utilizing CO_2 of amine, butyl bromide, using parr reactor, PBTR.

3.2.5 Equations used for calculating conversion, selectivity and yield.

The conversions of $R\text{-}NH_2$ (Amine) and $CH_3(CH_2)_3Br$ (1-Butyl bromide), Carbamates yield and selectivity of Carbamates are defined as follows:

$$2R\text{-}NH_2 + CO_2 + 2Bu\text{-}Br \longrightarrow \underset{\text{(Carbamate)}}{R\text{-}NH\text{-}COO\text{-}Bu} + 2HBr + R\text{-}NH\text{-}Bu$$

$$2R\text{-}NH_2 + CO_2 + Bu\text{-}Br \longrightarrow \underset{\text{(Carbamic acid)}}{R\text{-}NH\text{-}COOH} + R\text{-}NH\text{-}Bu + HBr$$

Equation:

$$\% \text{ RNH}_2 \text{ conversion} = \frac{(\text{RNH}_{2\,\text{in}}) - (\text{RNH}_{2\,\text{out}})}{(\text{RNH}_{2\,\text{in}})} \times 100 \qquad \text{------ (1)}$$

$$\% \text{ Bu-Br conversion} = \frac{(\text{Bu - Br}_{\text{in}}) - (\text{Bu - Br}_{\text{out}})}{(\text{Bu - Br}_{\text{in}})} \times 100 \qquad \text{------ (2)}$$

$$\% \text{ RNHCOOBu yield} = \left(\frac{\text{RNHCOOBu}_{\text{out}}}{\text{RNH}_{2\,\text{in}}}\right) \times 100 \qquad \text{------ (3)}$$

$$\% \text{ RNHCOOBu selectivity} = \left(\frac{(\text{RNHCOOBu}_{\text{out}})}{[\,(\text{RNH}_{2\,\text{in}}) - (\text{RNH}_{2\,\text{out}})\,]}\right) \times 100 \qquad \text{------ (4)}$$

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis and characterization of Ni/CeO_2-ZrO_2 catalyst

After Ni-based catalyst was prepared by the surfactant-assisted templating route as explained in chapter 3, it was characterized the crystalline type by X-ray diffraction (XRD), surface area and pore size distribution by BET and reduction temperature by TPR to assure that‟s Ni/CeO_2-ZrO_2 catalyst.

4.1.1 X-ray diffraction

The XRD patterns of NiO and CeO_2 standard and Ce-ZrO_2(CZ) and 5%Ni/$CeZrO_2$(NCZ) prepared by co-precipitation method are shown in Figure 4.1.

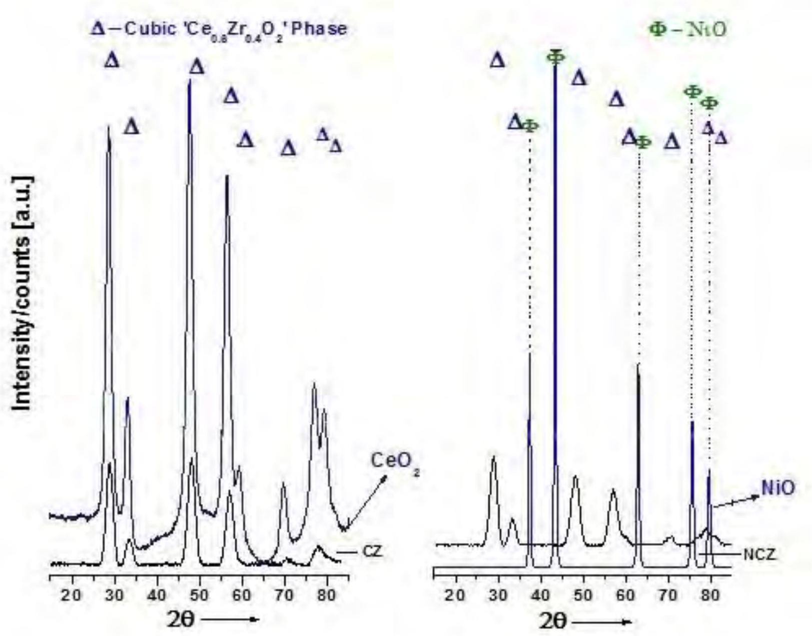


Figure 4.1 X-ray diffraction patterns of $Ce_{0.6}Zr_{0.4}O_2$ support and 5%Ni/$Ce_{0.6}Zr_{0.4}O_2$ catalyst.

The typical XRD patterns of samples (CZ, NCZ) are shown in Figure 4.1 along with the XRD profiles of pristine ceria and nickel oxide samples. The diffraction patterns observed show the existence of a single phase cubic fluorite-type structure for all the CZ supports similar to what is observed in the case of pristine ceria sample. A distinct shift towards higher two theta values could be noted in the case of ceria-zirconia samples ($2\theta \sim 29.0°$), when compared with pure CeO_2 ($2\theta = 28.65°$). The shift in the peak positions can be attributed to the substitution of the smaller Zr^{4+} ions (0.84 Å) in place of Ce^{4+} ions (0.97 Å) in the cubic fluorite lattice resulting in the formation of solid solution with structural distortion [29]. The XRD pattern of pristine NiO was used to indicate the presence/absence of crystalline NiO features in the Ni-impregnated catalyst samples (Figure 4.1). The XRD patterns of catalysts obtained by surfactant route are similar to diffraction patterns of the supports, signifying the presence of single phase cubic fluorite Ce/Zr solid solution and absence of any crystalline NiO structures. The fact that NiO crystallites were not observed in the above samples indicates that the surfactant assisted route imparts special characteristics to the support resulting in the better dispersion of active NiO species.

4.1.2 BET surface area and pore size distribution analyses

The textural characteristics of the supports as well as that of catalysts prepared by co-precipitation and surfactant-assisted route are summarized in Table 4.1.

Table 4.1 Characteristics of support and catalyst after calcination at 650 °C for 3 h.

Sample	BET SA ($m^2 g^{-1}$)	Pore Volume ($cc\ g^{-1}$)	Avg. Pore Diameter (Å)	Pore Vol/ BET SSA (10^{-9} m)
$Ce_{0.6}Zr_{0.4}O_2$				
: from ref [4]	201.0	0.26	40.8	1.28
: as prepared	202.5	0.24	39.5	1.20
5%Ni/ $Ce_{0.6}Zr_{0.4}O_2$				
: from ref [4]	184.5	0.23	41.0	1.25
: as prepared	186.0	0.21	41.8	1.13

WI = Wet impregnation route; SA = Surfactant Assisted route

For Table 4.1. it was observed that the specific surface area and pore volume of $Ce_{0.6}Zr_{0.4}O_2$ support and5%Ni/ $Ce_{0.6}Zr_{0.4}O_2$ catalyst prepared by surfactant assisted route were similar results as Thitinat et al. [4]. The large surface areas obtained as a result of the interaction of hydrous mixed metal hydroxide gel with cationic surfactants under basic conditions was explained as follow.

At pH ≥ 11.0, the surface hydroxyl protons ($CeZr\text{-}O^-H^+$) are exchanged by the cetyltrimethylammonium cation ($(C_{16}H_{33})N^+(CH_3)_3$), resulting in the incorporation of the surfactant cations into hydrous ceria-zirconia mixed oxide gel. This incorporation decreases the interfacial energy and eventually decreases the surface tension of water that exists in the hydrous support pores. As a result, the degree of shrinkage and pore collapse that would occur in the hydrous support during drying and calcination is reduced, which consequently, imparts higher surface area to the sample.

4.1.3 Temperature program reduction

The reducibility of the support as well as that of catalysts prepared in the current study, were studied by TPR technique in the temperature range from ambient to 1050 ^oC using 5%H_2/bal.N_2 as the reactive gas. For reference purposes, TPR profiles of pristine NiO and CeO_2 are included in Figure 4.2. The H_2 uptake as a function of TCD response vs. temperature is plotted.

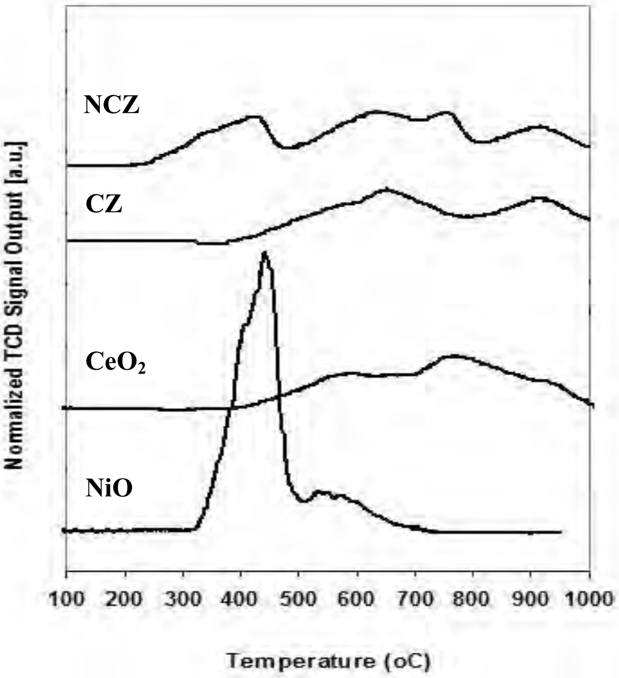


Figure 4.2 TPR profiles of NiO, CeO_2, $Ce_{0.6}Zr_{0.4}O_2$, 5%Ni/ $Ce_{0.6}Zr_{0.4}O_2$ calcined at 650 °C.

Pure NiO shows a sharp reduction peak at about 440 °C, which can be attributed to the transformation of Ni^{2+} to Ni^0 species. In the case of pure CeO_2, the one at the lower temperature (T_{max} ~ 600 °C) was ascribed to the reduction of the surface oxygen species, and the other two broad peaks at higher temperatures (T_{max} ~780 and 950 °C) were due to the reduction of bulk oxygen species [27]. The higher mobility of the surface oxygen ions helps in the removal of lattice oxygen during the reduction process. The coordinately unsaturated surface capping oxygen ions can be easily removed in the low temperature region. However, bulk oxygen requires to be transported to the surface before their reduction. Consequently, the bulk reduction takes place at a higher temperature compared to the surface reduction. The bulk reduction begins only after the complete reduction of the surface sites [27]. Pure ZrO_2 does not show any sign of reduction below 900 °C, due to its refractory nature [28]. By similar reasoning, ceria and ceria-zirconia solid solutions exhibit two distinct reduction zones; the former at lower temperatures pertains to surface shell reduction, while the later at higher temperatures pertains to the bulk reduction. In the case of CZ, the reduction of CeO_2 occurs at higher temperatures, compared to that in the case of pure CeO_2. This result indicates that Zr incorporation into the CeO_2 make CZ more thermal stable.

In the case of NCZ catalyst, a reduction peak at about 440 ^{o}C is associated with the reduction of NiO to Ni and the other peaks at the higher temperature are associated with the surface and bulk reduction of Ce^{+4} to Ce^{+3} species. The low temperature reduction peak corresponding to CZ of the NCZ catalyst shifted to the lower temperature than CZ itself indicating that Ni incorporation into the CZ makes CeO_2 more reducible, which helps produce mobile oxygen during the reforming reaction. This result agrees with the report of Dong et al [28].

4.2 The study of carbamate formation by using 5% Ni/ $Ce_{0.6}Zr_{0.4}O_2$ catalyst

Several research group reports that various alkyl and aryl carbamates could be synthesized under mild conditions from the corresponding amines, CO_2 and n-butyl bromide (n-BuBr) by using another catalyst. In all these works involved organic solvent such as methanol and ethanol [14]. Moreover, not only N,N-dimethylformamide (DMF) used as a solvent but co-catalyst was introduced in the system for producing the carbamate [26,35]. However, both solvent and co-catalyst were not necessary to be used in this research.

4.2.1 Synthesis and characterization of N-butyl-n-hexylcarbamate

After hexylamine reacted with CO_2 and n-butyl bromide at 70 ^{o}C and 2 bar for 4 hour, the catalyst was removed by using dichloromethane as solvent and the product was separated by column chromatography. The results were shown as Table 4.2.

Table 4.2 Effect of catalyst, support and N-butyl bromide from the reactions of hexylamine and N-butyl bromide with CO_2.

Entry	**5%Ni/ $Ce_{0.6}Zr_{0.4}O_2$ (g)**	**N-Butyl bromide (g)**	**Time (Hr)**	**Product**
1	0.05	2.7406	4	Carbamic acid
2	-	2.7406	4	-
3	$Ce_{0.6}Zr_{0.4}O_2$(0.05)	2.7406	4	-
4	0.05	-	4	-

Reaction condition: Hexylamine : N-butyl bromide1:1; pressure 2 bar; temperature 70 °C; catalyst amount 50 mg.

It was found that the reaction could not be taken place if without 5%Ni/ $Ce_{0.6}Zr_{0.4}O_2$ catalyst and N-butyl bromide. Moreover, this experiment also proved that the CeO_2ZrO_2 used as a support for 5%Ni/ $Ce_{0.6}Zr_{0.4}O_2$ catalyst could not produce the carbamate product.

Then the reaction was carried out by using equimolar of hexylamine and N-butyl bromide (1:1), pressure 2 bar, temperature 70°C, and 50 mg of 5%Ni/ $Ce_{0.6}Zr_{0.4}O_2$ catalyst for 4 hours. After 4 hours the product was further investigated by Attenuated Total Reflection Infrared spectroscopy (ATR-IR) and Nuclear Magnetic Resonance (NMR) technique, respectively.

From Figure 4.3, the ATR-IR spectra exhibited the IR absorption bands of –NH group at 3438 cm^{-1}, 1580 cm^{-1} and carbonyl group (-C=O) at 1715 cm^{-1}. From Figure 4.4, ^{1}H-NMR spectrum showed chemical shift at 8.9(s, 1H, -COOH), 2.9(t, 2H, $-NH-CH_2-$). It exhibited clearly that the obtained product using this reaction condition was N-butyl-n-hexylcarbamic acid. It could be concluded that this condition was not suitable for producing carbamate.

In order to find the right condition for carbamate, the reaction time was the first factor to be observed as shown in Table 4.3.

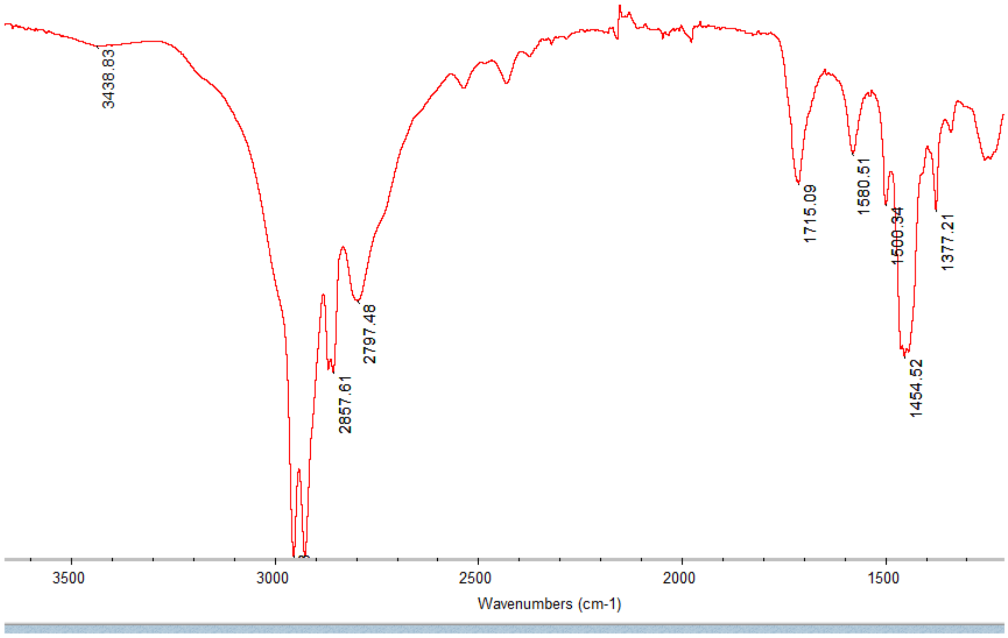


Figure 4.3 ATR-IR of the product from the reaction of hexylamine and N-butyl bromide over Ni/CeO_2-ZrO_2 at 3 bar and 90°C for 4 hours.

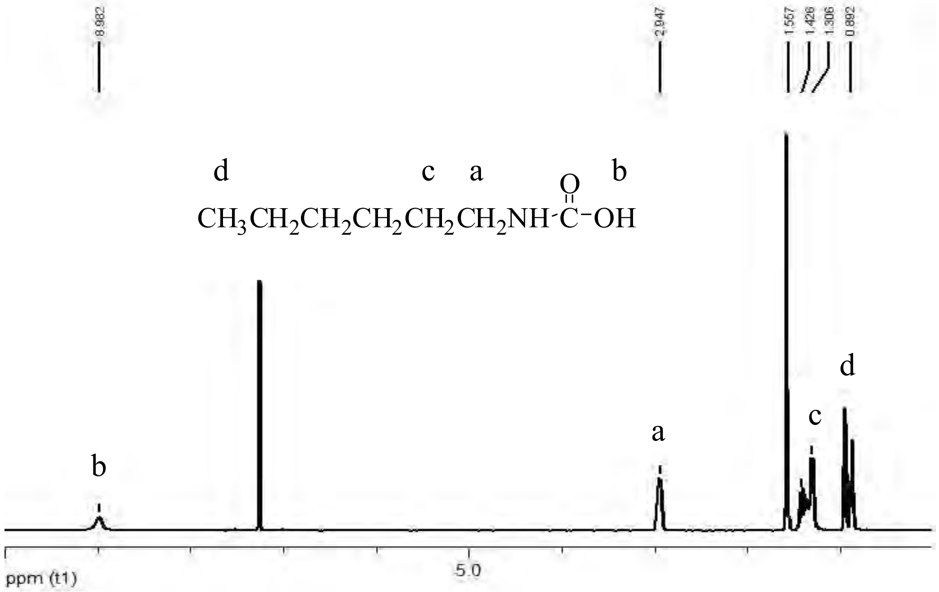


Figure 4.4 NMR of the product from the reaction of hexylamine and N-butyl bromide over Ni/CeO_2-ZrO_2 at 3 bar and 90°C for 4 hours.

Table 4.3 Effect of time from the reactions of hexylamine and N-butyl bromide with CO_2.

Entry	**5%Ni/ $Ce_{0.6}Zr_{0.4}O_2$ (g)**	**N-Butyl bromide (g)**	**Time (Hr)**	**Product**
1	0.05	2.7406	4	Carbamic acid
2	0.05	2.7406	2	Carbamate

Reaction condition: Hexylamine : N-butyl bromide1:1; pressure 2 bar; temperature 70 °C; catalyst amount 50 mg.

Then the product from Entry #5 was investigated by using ATR-IR and ^{1}H-NMR, respectively. From Figure 4.5, the IR absorption bands were shown at 3444 cm^{-1} and 1583 cm^{-1} presenting -NH group and at 1735 cm^{-1}for carbonyl (-C=O) of ester group. ^{1}H-NMR experiment was also investigated as shown in Figure 4.6. the chemical shift was obtained at 4.1 [t, 2H, (–O=C-O-CH_2)] , 2.9 ppm [t, 2H, (-CH_2NHC=O)], 1.4-1.3(m, 4H, -CH_2-CH_2-), 0.9(t, 3H, -CH_3). It was concluded that Carbamate could be obtained once the reaction was carried out for 2 hours. However, if the reaction was carried longer than 2 hours, the carbamate product will be converted to carbamic acid. It might because of the formation of hydrogen bromide inside the system as shown in Figure 4.7.

The mechanism of forming the carbamic acid is proposed via E1cB elimination mechanism as shown in Figure 4.8 [17,18]. It appears that E1cB elimination reaction starting with the fact that the acidic proton from Hydrogen bromide is attacked by lone pair electron of the oxygen group and electrons isolation of nitrogen may shift towards to the carbonyl group appeared electron on the oxygen group. That made the elimination of the structure to produce the isocyanate and alcohol. Afterwards the moisture in the system that attack at the carbonyl group is made up of electron at the nitrogen group to receive the proton within the system to forms “ N-butyl-n-hexylcarbamic acid “.

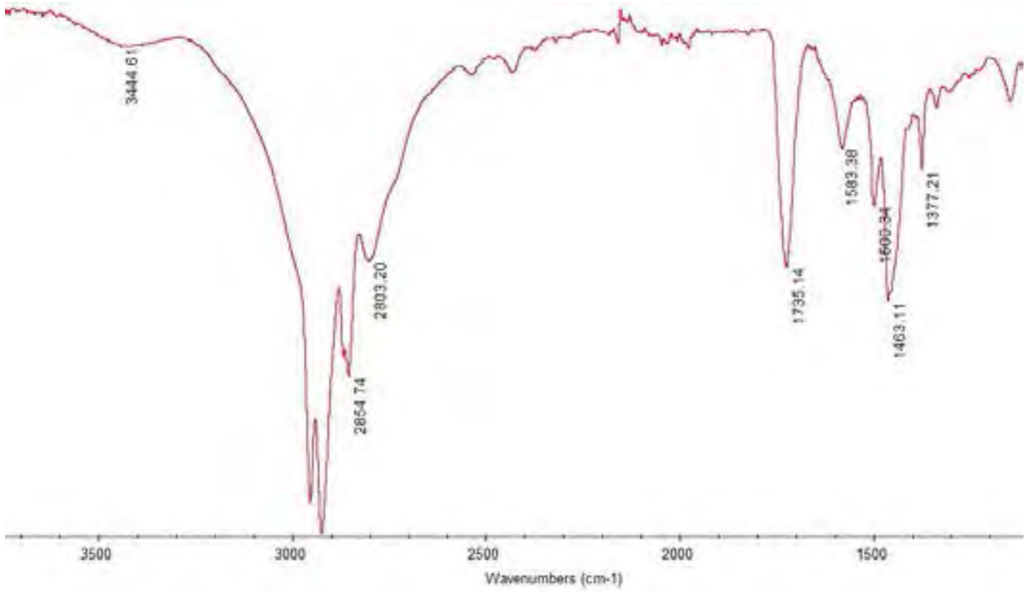


Figure 4.5 ATR-IR of the product from the reaction of hexylamine and N-butyl bromide over Ni/CeO_2-ZrO_2 at 3 bar and 90°C for 2 hours.

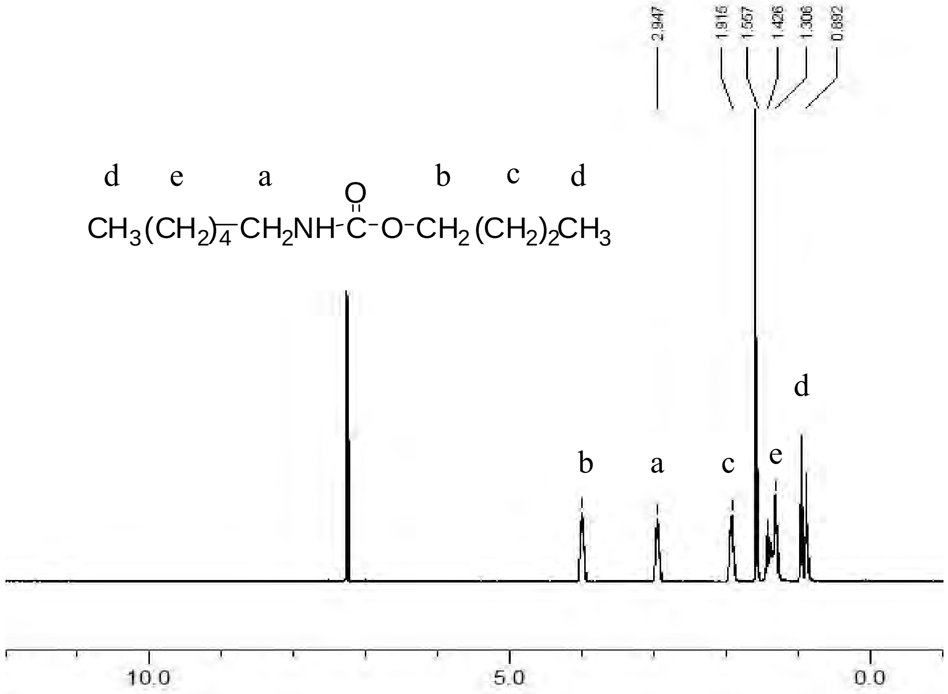


Figure 4.6 NMR of the product from the reaction of hexylamine and N-butyl bromide over Ni/CeO_2-ZrO_2 at 3 bar and 90°C for 2 hours.

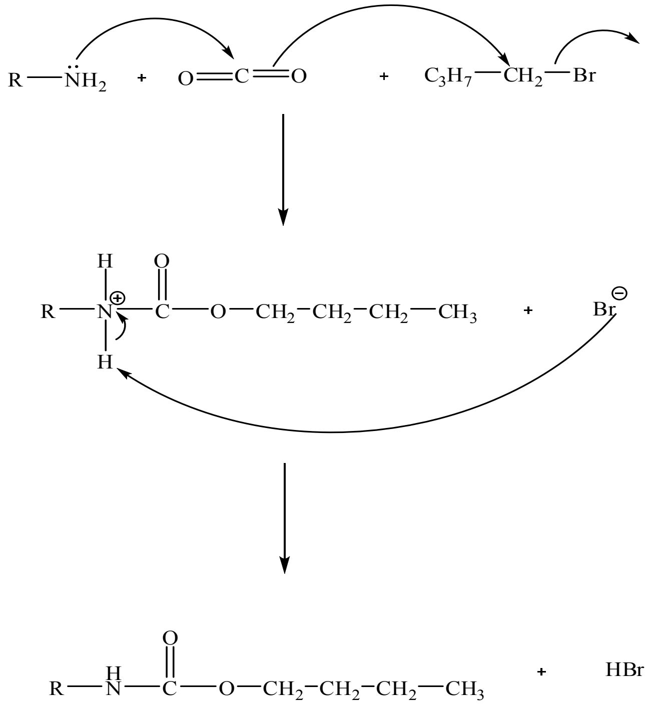


Figure 4.7 Mechanism of carbamates from the reaction Amine, CO_2 and N-butyl bromide.

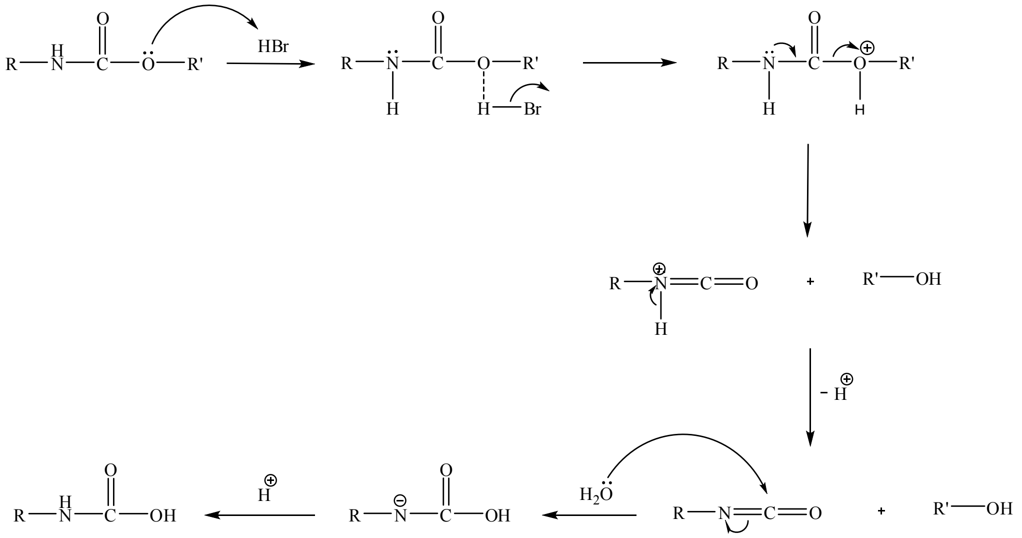


Figure 4.8 Mechanism of the E1cB elimination reaction from the reaction of hexylamine and N-butyl bromide over Ni/CeO_2-ZrO_2.

To identify the products from the reaction, gas chromatography (GC) technique was introduced. Moreover, the amine conversion, carbamates selectivity, and %yield in this reaction were also observed by using this technique. Initially, the crude product was injected into GC to determine its composition as shown in Figure 4.9. Then the N-butyl-n-hexylcarbamate purified and confirmed by using column chromatography and ATR-IR and ^{1}H-NMR, respectively, was introduced into GC in order to be used as a standard. From Figure 4.10, it was found that the retention time at 28 min was a N-butyl-n-hexylcarbamate. In addition, the substrate, hexylamine, was also introduced into GC. From chromatogram shown in Figure 4.11, the retention time at 6 min was hexylamine and the peak of retention time below 5 min was dichloromethane used as a solvent.

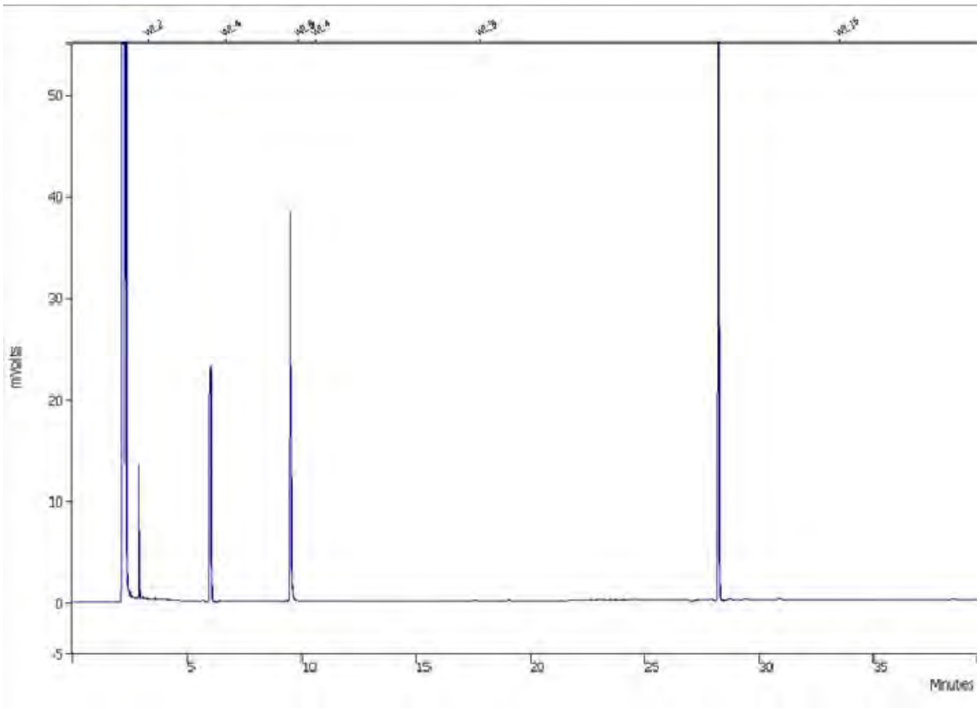


Figure 4.9 Chromatogram of the mixture from the reaction of hexylamine and N-butyl bromide over Ni/CeO_2-ZrO_2.

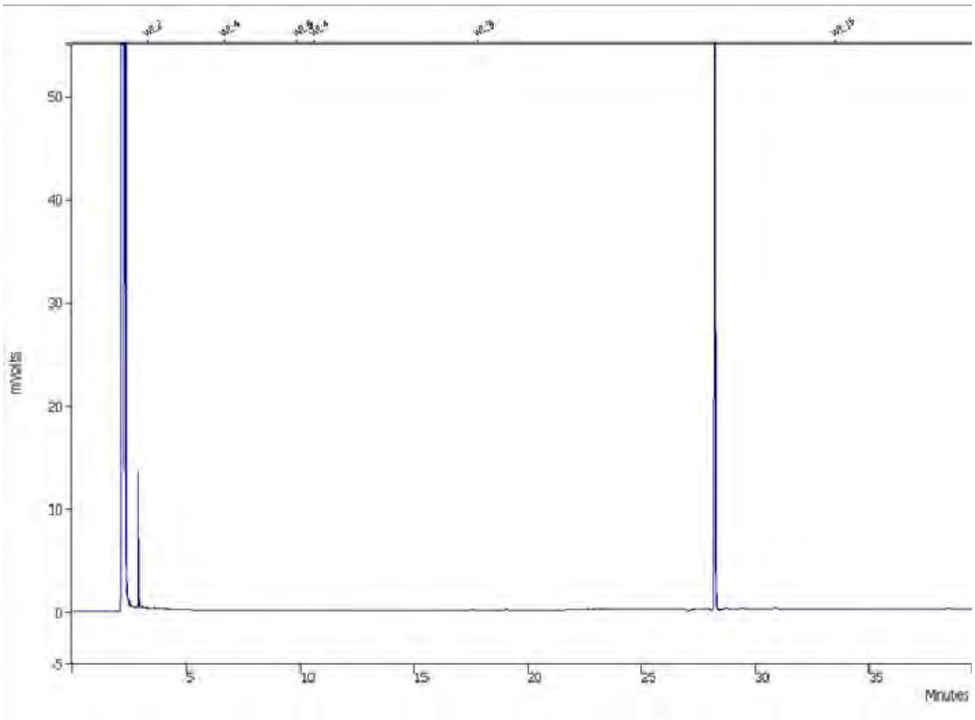


Figure 4.10 Chromatogram of pure N-butyl-n-hexylcarbamate from the reaction of hexylamine and N-butyl bromide over Ni/CeO_2-ZrO_2.

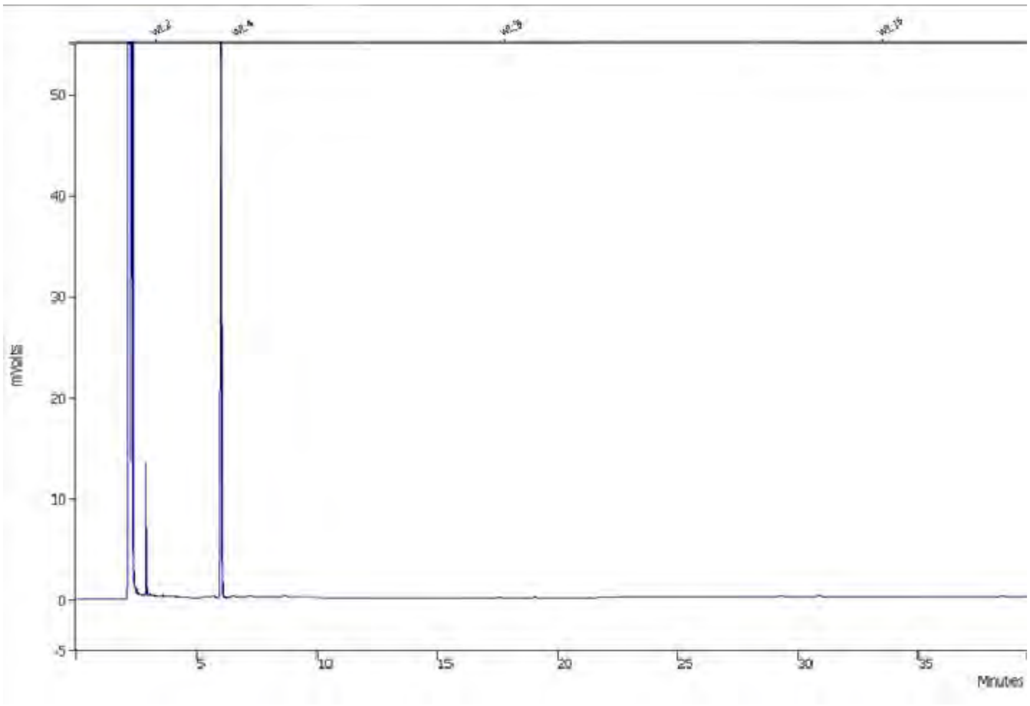


Figure 4.11 Chromatogram of hexylamine.

4.2.2 Synthesis and characterization of N-butyl-n-cyclohexylcarbamate

From Figure 4.12, the IR absorption bands were shown at 1583 cm^{-1} presenting –NH group, 1733 and 1380 cm^{-1} for carbonyl group (-C=O) and at 1045 cm^{-1} for (–O-Bu). ^{1}H NMR experiment was also investigated as shown in Figure 4.13 the chemical shift was obtained at 4.1(t, 2H, -O-CH$_2$-), 3.0(m, 1H, Ali-NH), 1.6-2.0(m, 10H, Ali-H), 1.3,1.2(m, 4H, -CH$_2$-CH$_2$-), 0.9(t, 3H, -CH$_3$).

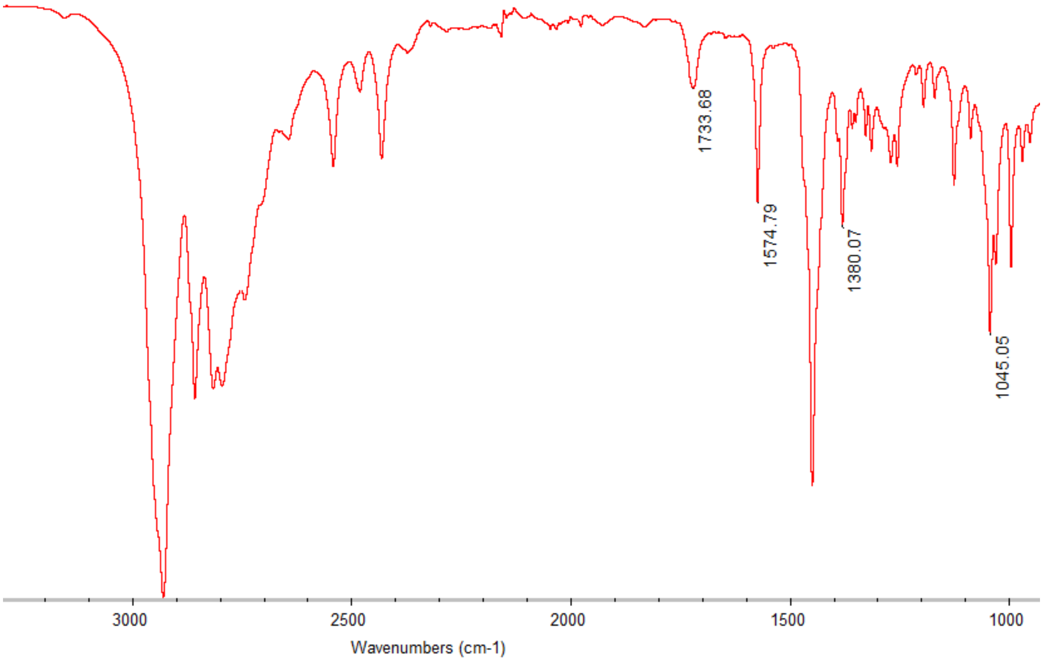


Figure 4.12 ATR-IR of the product from the reaction of cyclohexylamine over Ni/CeO$_2$-ZrO$_2$ catalyst at 3 bar and 90°C for 4 hours.

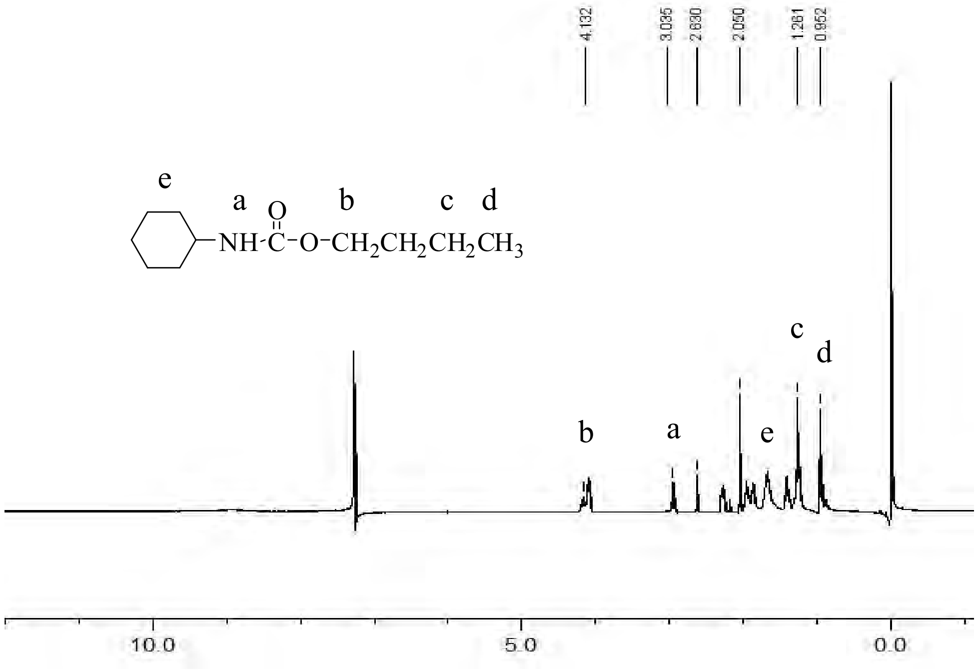


Figure 4.13 NMR of the product from the reaction of Cyclohexylamine and N-butyl bromide over Ni/CeO_2-ZrO_2 catalyst at 3 bar and 90°C for 4 hours.

4.2.3 Synthesis and characterization of N-butyl-n-phenylcarbamate

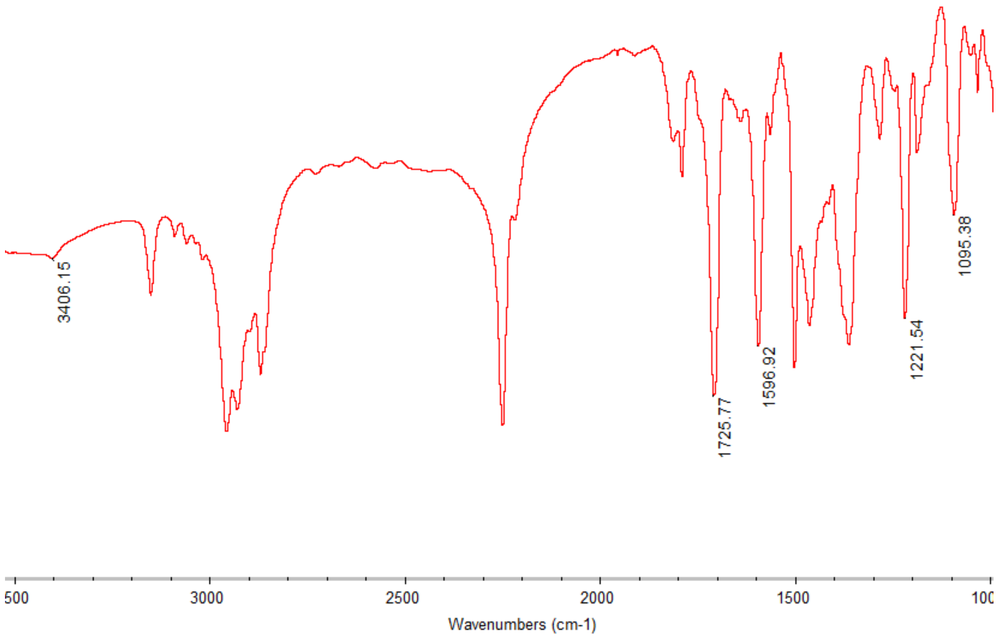


Figure 4.14 ATR-IR of the product from the reaction of aniline over Ni/CeO_2-ZrO_2 at 3 bar and 90°C for 4 hours.

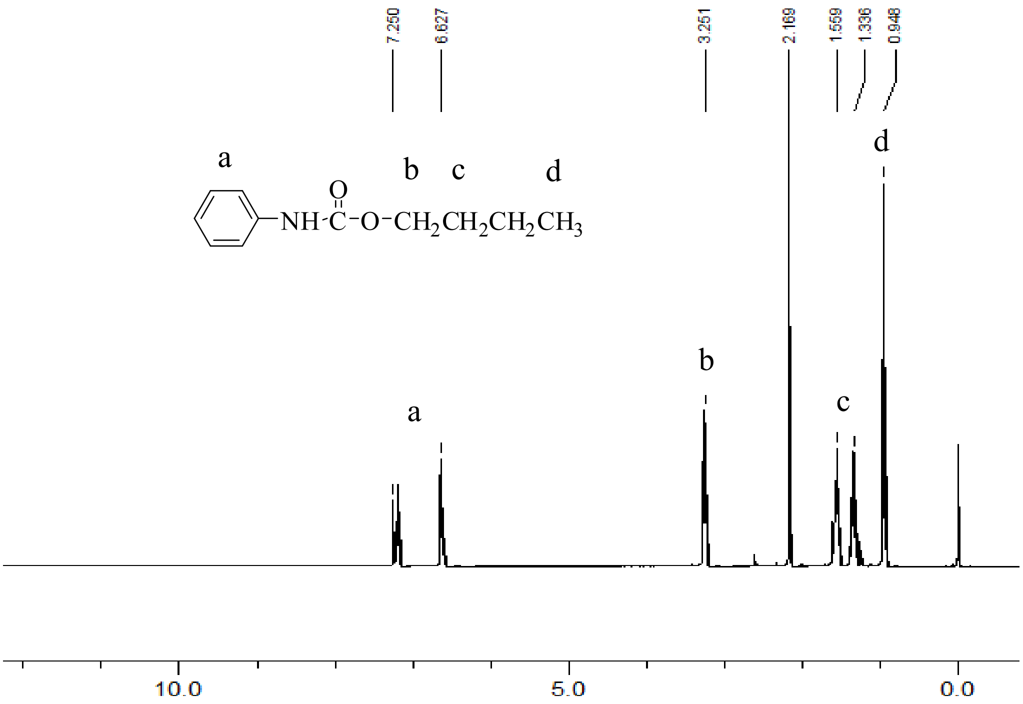


Figure 4.15 NMR of the product from the reaction of aniline and N-butyl bromide over Ni/CeO_2-ZrO_2 at 3 bar and 90°C for 4 hours.

From Figure 4.14, the IR absorption bands were shown at 3406 and 1596 cm^{-1} presenting –NH group, 1725 and 1221 cm^{-1} for carbonyl group (-C=O) and at 1095 cm^{-1} for (–O-Bu). ^{1}H NMR experiment was also investigated as shown in Figure 4.15 the chemical shift was obtained at 7.2(m, 2H, Ar-H), 6.6(m, 3H, Ar-H), 3.2(t, 3H, O-CH_2-), 2.1(m, 2H, Ar-NH), 1.5,1.3(m, 4H, -CH_2-CH_2-), 0.9(t, 3H, -CH_3). Similar results were reported by Srivastava et al[1].

4.3 Effect of reaction parameters

4.3.1 Effect of temperature and pressure

Hexylamine and N-butyl bromide were used as model substrates. When the %yield of product was varied pressure and temperature in the reaction, followed by CO_2 0.693 g(350 ml). N-butyl-n-hexylcarbamate was obtained. The influence of pressure and temperature were investigated and the results are given in Table 4.4 and Figure 4.16.

Table 4.4 Effect of temperature and pressure with yield (%) from the reactions of hexylamine and N-butyl bromide over Ni/CeO_2-ZrO_2[a].

Entry	**Pressure (Bar)**	**Temperature (°C)**	**Amine conversion**	**Yield (%)**	**TOF (h^{-1})[b]**
5	2	70	26.7	15	17.2
6	2	80	37.4	21	24.2
7	2	90	62.3	35	40.2
8	3	90	90.7	51	58.6
9	4	90	85.4	48	55.0
10	5	90	80.0	45	51.6

[a]Reaction condition: Hexylamine : N-butyl bromide1:1; reaction pressure 2 bar; time 2 hours; catalyst amount 50 mg.

[b]Turnover frequency (TOF) = moles of amine converted per mole of quaternary ammonium ion (template) in Ni/CeO_2-ZrO_2 catalyst per hour.

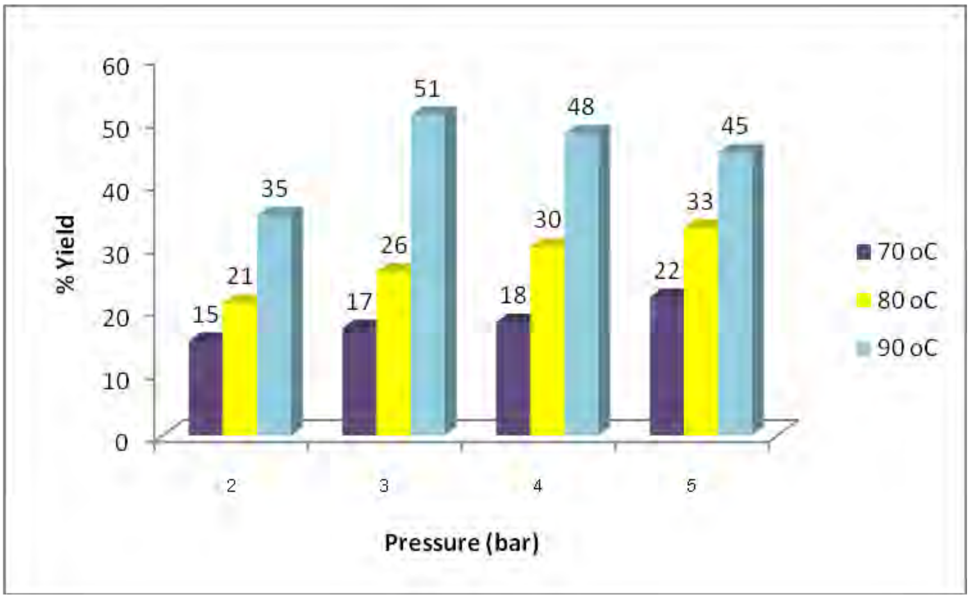


Figure 4.16 Effect of temperature with yield (%) from the reactions of hexylamine and N-butyl bromide over Ni/CeO_2-ZrO_2.

At pressure 2 bar, when the temperature of the reaction was increasing from 70-90°C, the yields of N-butyl-n-hexyl carbamate were low to moderate (entries 5, 6 and 7). Increasing the pressure from 2 to 3 bar gave the corresponding carbamate quantitatively (entry 7 and 8) whereas the desired carbamates was obtained only in moderate yield at 90°C (entry 8). However, when the pressure was increased to 4 and 5 bar at 90°C, the yield of the desired product was decreased (entry 9 and 10) because of the formation of side products. Finally, The optimum condition was 3 bar at 90°C which obtained highest carbamates yield% is 51%.

Table 4.5 Effect of temperature and pressure with yield(%) from the reactions of cyclohexylamine and Aniline[a].

Entry	**Amine**	**Pressure (Bar)**	**Temperature (°C)**	**Amine conversion**	**Yield (%)**
11	Cyclohexylamine	2	70	79.8	33
12	Cyclohexylamine	2	80	85.4	45
13	Cyclohexylamine	2	90	90.6	52
14	Cyclohexylamine	3	90	94.2	78
15	Cyclohexylamine	4	90	92.9	70
16	Cyclohexylamine	5	90	91.7	64
17	Aniline	2	70	33.7	8
18	Aniline	2	80	42.8	14
19	Aniline	2	90	45.3	19
20	Aniline	3	90	50.8	31
21	Aniline	4	90	48.2	26
22	Aniline	5	90	47.1	23

[a] Reaction condition: Cyclohexylamine or Aniline : N-butyl bromide1:1; reaction pressure 2 bar; time 4 hours; catalyst amount 50 mg.

The reaction results from Table 4.5. were shown yield% of carbamates was increased by increasing temperature (entries 11-13) and for N-butyl-n-phenylcarbamate (entries 17-19). Increasing pressure showed the yield% of carbamates was increased whereas the yield% of carbamates was decreased above 3 bar at 90°C because the formation of side products was increased when it obtains a high pressure. Finally, The optimum condition was 3 bar at 90°C which obtained highest carbamates yield% is 78% (N-butyl-n-cyclohexylcarbamate), 31% (N-butyl-n-phenylcarbamate).

4.3.2 Effect of catalyst content

Table 4.6 Effect of varied amount of Ni/CeO_2-ZrO_2 catalyst with yield(%) and amine conversion from the reactions of hexylamine and N-butyl bromide[a].

Entry	Amount of catalyst(mg)	Amine conversion	Carbamate selectivity	Yield (%)
23	40	85.2	24.0	41.0
8	50	90.7	56.2	51.0
24	60	94.7	60.2	57.0

[a] Reaction condition: Hexylamine : N-butyl bromide1:1; reaction pressure 3 bar; Temperature 90 °C, time 2 hours.

At temperature 90 °C and pressure 3 bar, when the amount of Ni/CeO_2-ZrO_2 catalyst was increased from 40-60 mg (Table 4.6), the amine conversion of N-butyl-n-hexylcarbamate were increased (entries 10, 7 and 11). Increasing the amount of Ni/CeO_2-ZrO_2 catalyst to 60 mg gave the corresponding carbamate quantitatively (entry 24) whereas the desired carbamate was obtained only in moderate yield at 90 °C (entry 24).

Table 4.7 Effect of varied amount of Ni/CeO_2-ZrO_2 catalyst with yield(%) and amine conversion from the reactions of cyclohexylamine and Aniline[a].

Entry	**Amine**	**Amount of catalyst(mg)**	**Amine conversion**	**Carbamate selectivity**	**Yield (%)**
25	Cyclohexylamine	40	88.5	75.4	66.0
14	Cyclohexylamine	50	94.2	82.7	78.0
26	Cyclohexylamine	60	97.8	89.2	81.0
27	Aniline	40	45.4	50.6	23.0
20	Aniline	50	50.8	61.0	31.0
28	Aniline	60	53.5	67.3	36.0

[a] Reaction condition: Amine : N-butyl bromide1:1; reaction pressure 3 bar; Temperature 90 °C, time 4 hours.

All of the results from Table 4.7 was based on the direction of hexylamine in Table 4.6. At temperature 90 °C; pressure 3 bar, when the amount of Ni/CeO_2-ZrO_2 catalyst was increasing from 40-60 mg (Table 4.7), the amine conversion of N-butyl-n-cyclohexylcarbamate (entries 25, 14 and 26) and N-butyl-n-phenylcarbamate (entries 27, 20 and 28) were increased. Increasing the amount of Ni/CeO_2-ZrO_2 catalyst to 60 mg gave the corresponding carbamates quantitatively (entry 26, 28) whereas the desired carbamates was obtained only in moderate yield at 90 °C (entry 26, 28).

4.3.3 Effect of various amine

Table 4.8 Effect of various amine with %yield, conversion and selectivity of carbamates over Ni/CeO_2-ZrO_2[a].

Entry	Amine	Amine conversion	Carbamate selectivity	Yield (%)	TON[b]	TOF (h^{-1})[c]
26	Cyclohexylamine	97.8	89.2	81.0	105.2	26.3
24	Hexylamine	94.7	60.2	57.0	102.0	51.0
28	Aniline	53.5	67.3	36.0	57.6	14.4

[a] Reaction condition: Amine, 10 mmol n-butyl bromide, 10 mmol; reaction pressure 3 bar; Temperature 90 °C; catalyst amount 0.06 g.

[b] Turnover number (TON) = moles of amine converted per mole of Ni/CeO_2-ZrO_2 catalyst.

[c] Turnover frequency (TOF) = moles of amine converted per mole of quaternary ammonium ion (template) in Ni/CeO_2-ZrO_2 catalyst per hour.

Both aliphatic and aromatic amines could be converted into their carbamates by this method. With different amines, the carbamate yields varied in the order: cyclohexylamine > hexylamine > aniline (Table 4.8). Aliphatic amines can be more easily converted to their corresponding carbamates as compared to aromatic amines. Similar results were reported by Srivastava et al [3]. Interestingly, when Ni/CeO_2-ZrO_2 catalyst were used, carbamate product formed with high selectivity (60–90%) without any solvent.

Turnover number (abbreviated TON) was used to refer the maximum molecules of substrate could be converted into product per catalytic site The term turnover frequency (abbreviated TOF) was used to refer to the turnover number per unit time. As a result, Ni/CeO_2-ZrO_2 catalyst provided higher rate in all of carbamates than the report of Srivastava and et al [3]. Moreover, TON and TOF of Ni/CeO_2-ZrO_2 catalyst, which indicated the maximum molecules of substrate could be converted into product per amount of catalyst, were 51.0, 26.3 and 14.4 h^{-1}, respectively. According to these results, Ni/CeO_2-ZrO_2 catalyst was an appropriate catalyst for this experiments.

CHAPTER V

CONCLUSIONS AND SUGGESTIONS

The synthesis of carbamates was synthesized in good yields over Ni/CeO_2-ZrO_2 catalyst utilizing CO_2. The reaction proceeds at mild conditions and without using any solvent. Three types of amine was used to synthesis of carbamates were prepared. Surprisingly, in the reaction of hexylamine was found that occurs N-butyl-n-hexylacarbamate for 2 hours but if it hold on the reaction time to 4 hours. The product of this reaction was N-butyl-n-hexylcarbamic acid by the E1cB elimination reaction. By the way, it can gives the high turnover frequency of Ni/CeO_2-ZrO_2 catalyst in this reaction. Then, if we compared by the type of amine that were used in this reaction. It was found that an aliphatic amine give highly quantitative compared with an aromatic or linear amine of the same catalyst content. And the yield of carbamates was increased follow by increasing of temperature and pressure in this system. But the optimum pressure was 3 bar which the pressure was increased over 3 bar, the yield of carbamates was decreased by the formation of side products. Finally, the optimum condition of this reaction was 3 bar and 90 ^{o}C.

5.1 Further works

Synthesis of carbamate with the reaction of amine, n-butyl bromide and CO_2 using the different amine and recovery of the catalyst should be studied and compared with this work.

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APPENDICES

APPENDIX A

Calculations

The amount of amine group required to react with n-butyl bromide and any other is calculated in order to obtain the chemically stoichiometric equivalents.

Amine and alkyl halide value

The molecular weight of hexylamine is 101.19, n-butyl bromide is 136.9. We obtain the chemically stoichiometric equivalents for 10 mmol.

Example:

$$\text{Hexylamine} = \frac{101.19 \times 10}{1000} = 1.019 \text{ g.}$$

$$\text{N-butyl bromide} = \frac{136.9 \times 10}{1000} = 1.369 \text{ g.}$$

Turnover frequency

Turnover frequency were moles of starting material converted per moles of catalyst per hour and this value is obtained from the following formula:

$$\left(\frac{\text{Amine conversion}}{\text{Mw of Amine}} / \text{Moles of Ni/CeO}_2\text{ZrO}_2\right) = \text{Turnover number}$$

or

$$\frac{(\text{\% conversion of Amine x Mol of substrate})}{\text{Moles of Ni/CeO}_2\text{ZrO}_2} = \text{Turnover number}$$

$$\text{Turnover number/Hours} = \text{Turnover frequency}$$

APPENDIX B

GC/FID Analysis

A Phenomenex ZB-5 (15m x 0.25mm id x 1.00˘m df) capillary column (Torrance, CA) was installed in an Hewlett Packard 6890 Gas Chromatograph (Little Falls, DE) equipped with a flame ionization detector. The column was installed into a Cold-On-Column (COC; Hewlett Packard, Palo Alto, CA) inlet suitable for a 0.25mm I.D. column. This column was conditioned at 300 °C overnight to ensure it was clean. Blank runs were made before any samples were injected to further ensure that the system was stable and uncontaminated.

Temperature Program	50°C (1 min hold) to 280°C (5 min hold) @20°C/min
Carrier Gas	Helium-59cm/sec
Injection Volume	1μL,manual injection
Inlet Setting	Oven Tracking
Detector	FID at 250°C

Table B-1 GC condition of hexylamine.

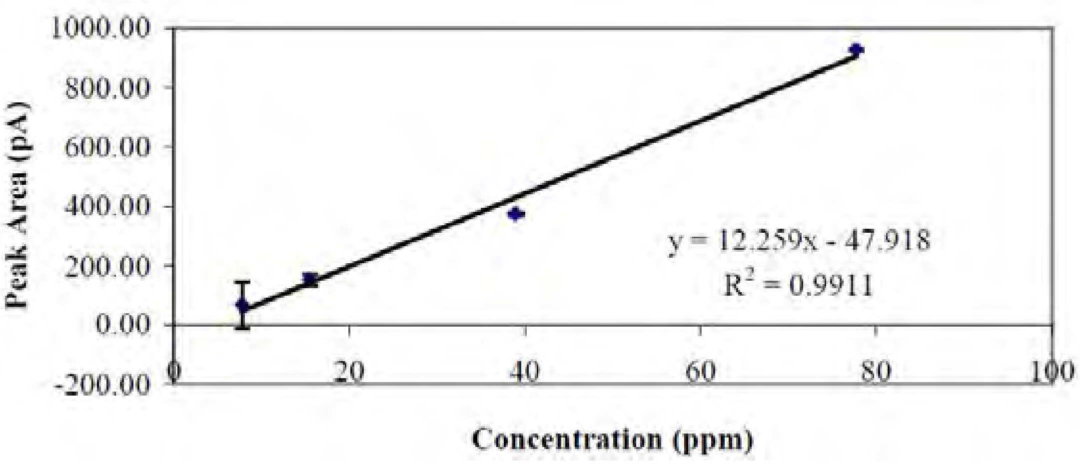

Figure B-1 Calibration curve of hexylamine.

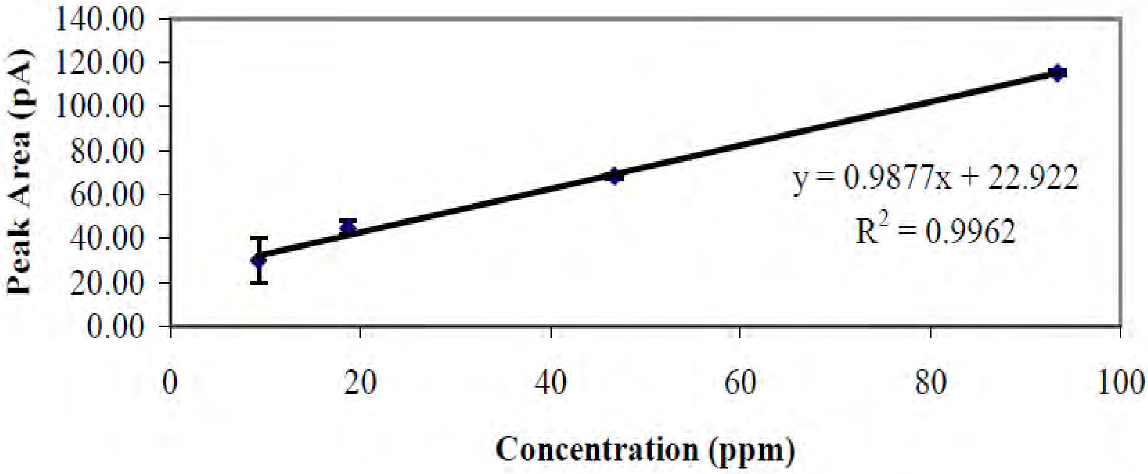

Figure B-2 Calibration curve of aniline.

Gas chromatography condition of cyclohexylamine

Injection size: 1 µL

Flow rates (mL/min)	**Temperatures (°C)**
Nitrogen (make-up): 30	Injector: 180
Hydrogen(carrier): 2	Detector: 220
Hydrogen(detector): 60	Column: 70° for 2 min then
Air: 450	10°/min to 150° for 3 min

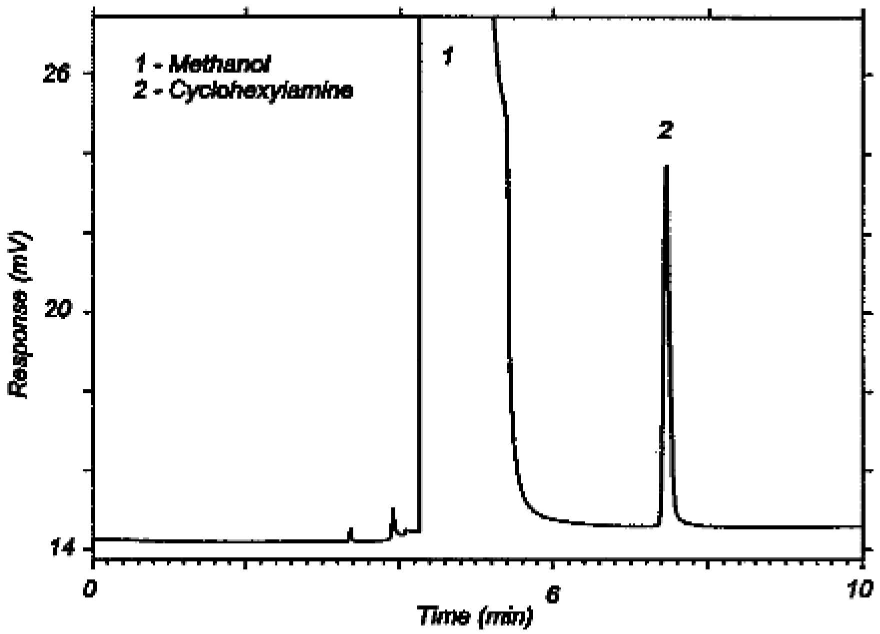

Figure B-2 Chromatogram of cyclohexylamine.

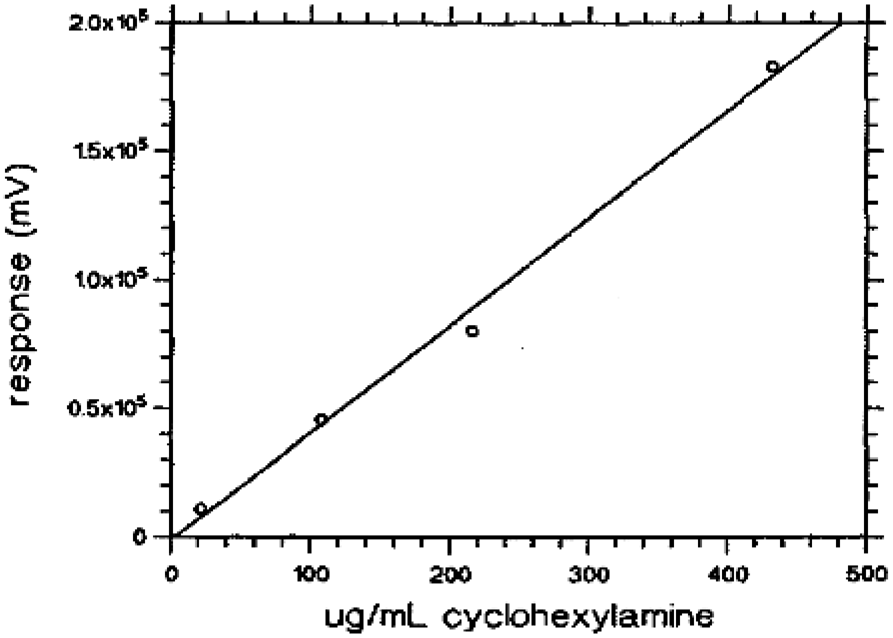

Figure B-3 Calibration curve of cyclohexylamine.

APPENDIX C

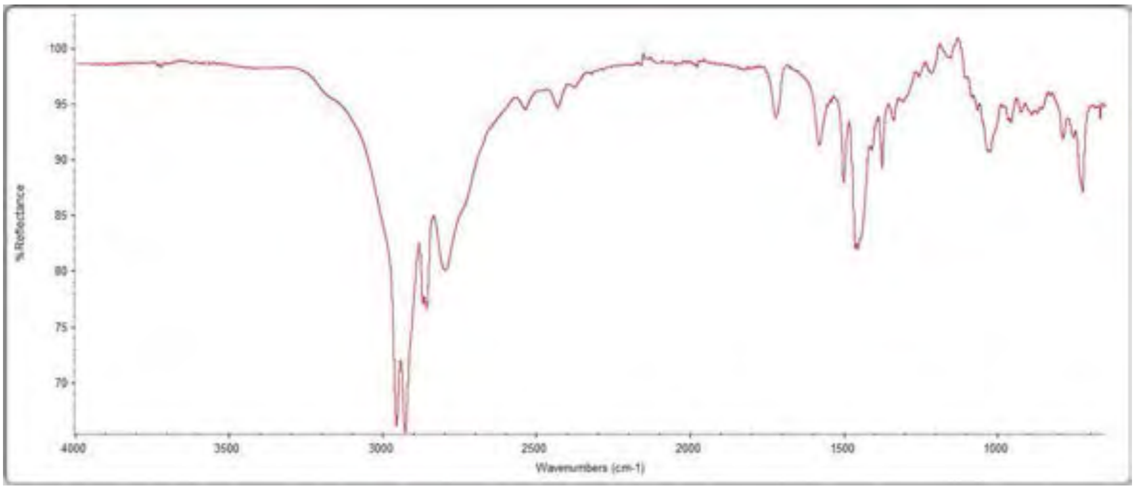

Figure C-1 ATR-IR spectrum of N-butyl-n-hexylcarbamate at 2 bar 90 ^{o}C.

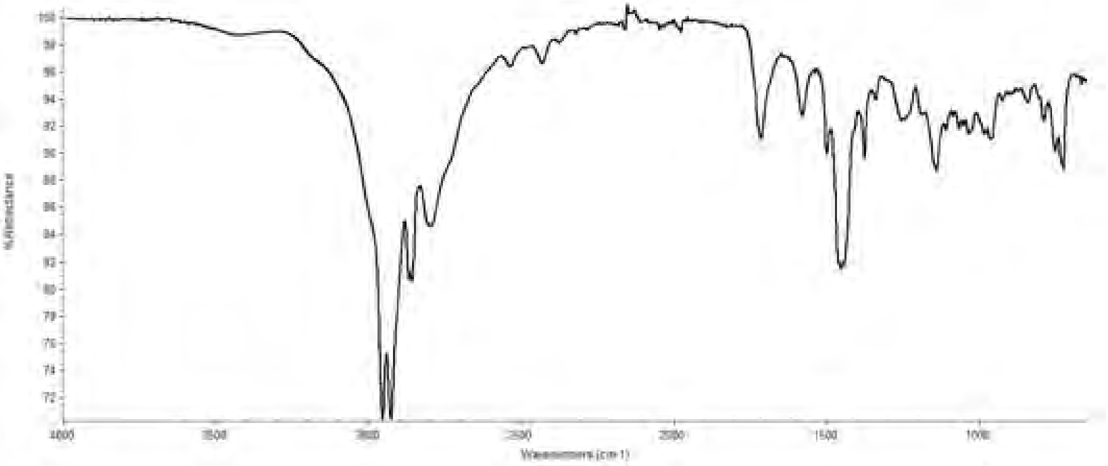

Figure C-2 ATR-IR spectrum of N-butyl-n-hexylcarbamate at 4 bar 90 ^{o}C.

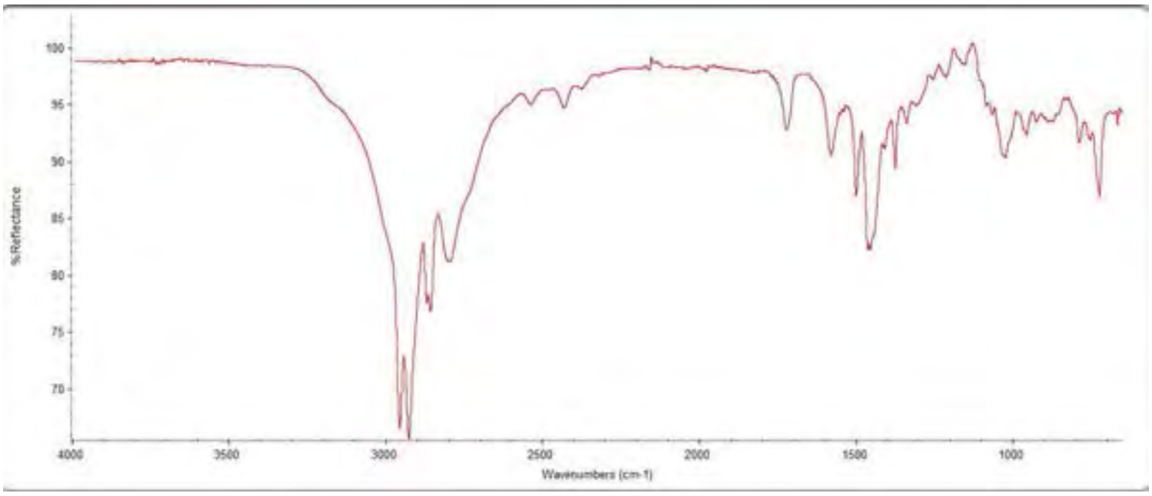

Figure C-3 ATR-IR spectrum of N-butyl-n-hexylcarbamate at 5 bar 90 ^{o}C.

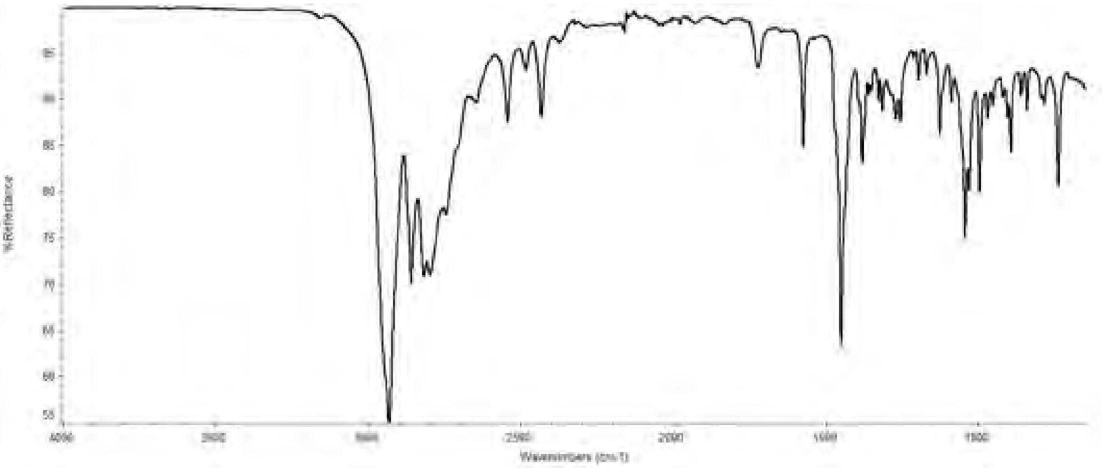

Figure C-4 ATR-IR spectrum of N-butyl-n-cyclohexylcarbamate at 4 bar 90 ^{o}C.

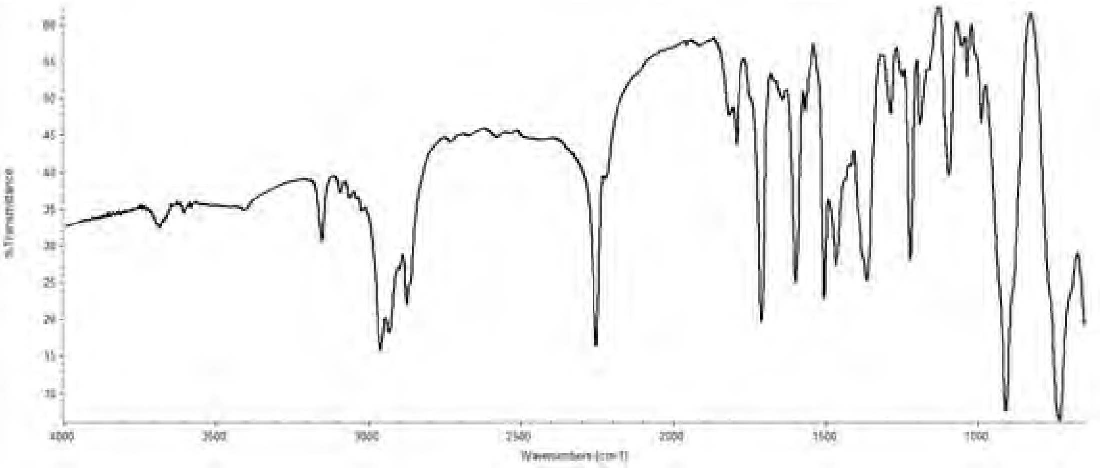

Figure C-5 ATR-IR spectrum of N-butyl-n-phenylcarbamate at 4 bar 90 °C.

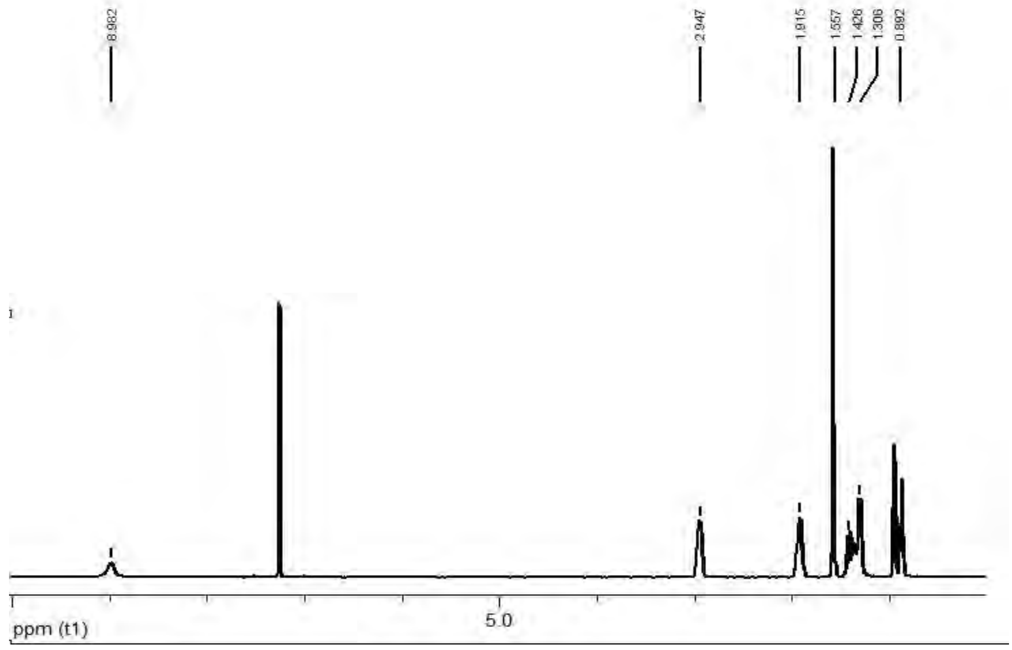

Figure C-6 ^{1}H NMR of N-butyl-n-hexylcarbamic acid at 3 bar 90 °C.

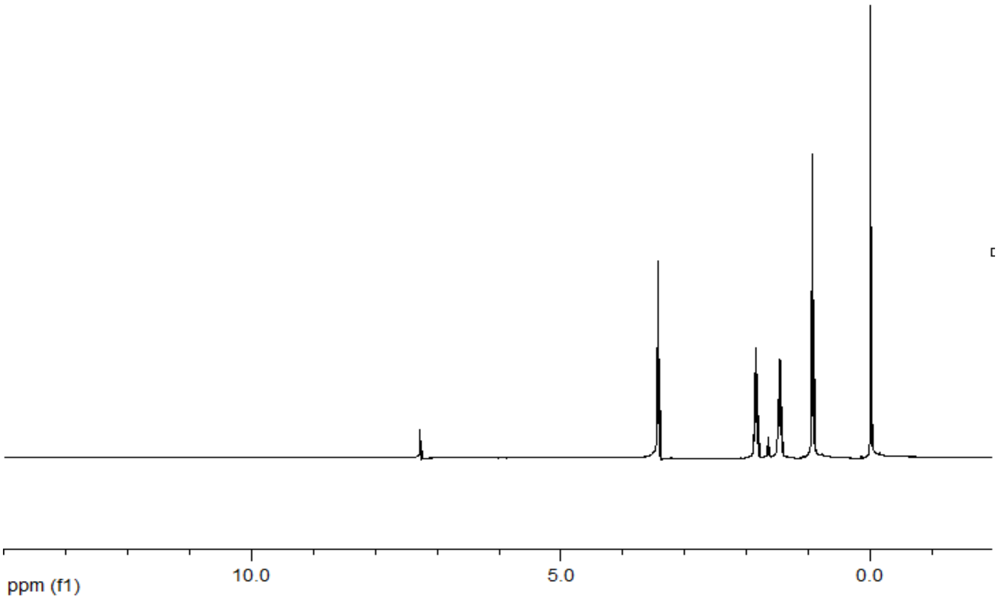

Figure C-7 ^{1}H NMR of N-butyl bromide.

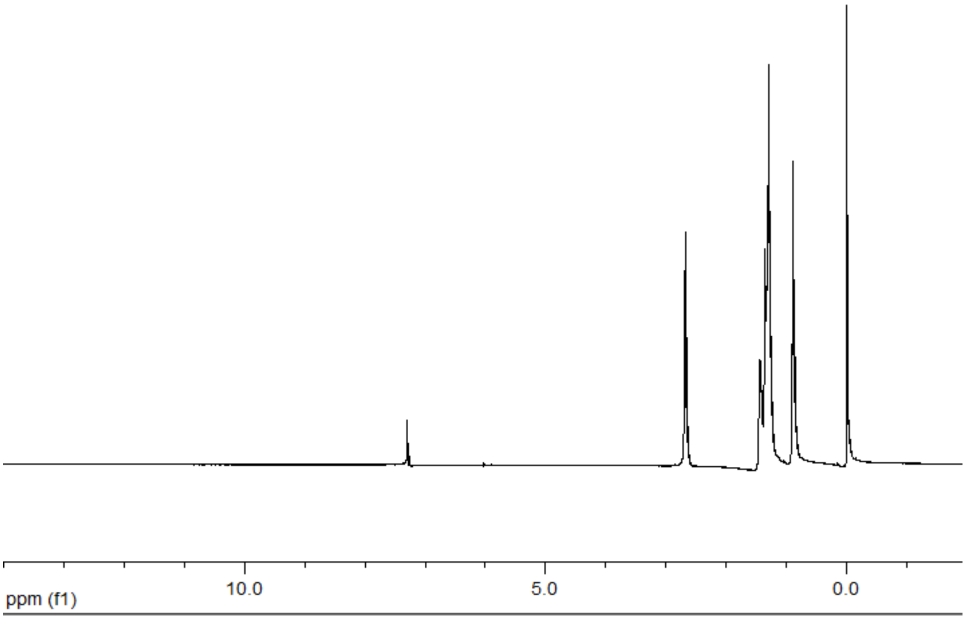

Figure C-8 ^{1}H NMR of hexylamine.

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