Hydrogen Production from Methane Using Ceria Based Catalyst

By

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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Approved by,

(Dr. Bawadi B Abdullah)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(NUR SYAFIKA BT TAN MUSTAFAR)

ABSTRACT

Conventional processes of hydrogen production are among major producers of CO_2 emissions. CO_2-free production of hydrogen via thermocatalytic decomposition of methane as a viable alternative to the conventional processes is discussed in this paper. The technical approach is based on a single-step decomposition of methane over ceria-based catalyst with nickel or copper promoter. This approach eliminates the need for water-gas shift reactors and CO_2 removal, which significantly simplifies the process. In the case for thermocatalytic decomposition of methane, emphasis will be given on the (i) synthesizing of ceria-based catalyst with nickel or copper promoter, (ii) characterization of the catalyst, (iii) study performance of the catalyst in term of the hydrogen production.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1: INTRODUTION

1.1 Research Background

One of the major challenges posed by the continuous increase in global population and economic development is providing more energy while at the same time to limit the emission of greenhouse-gas (GHG). Increase in the concentrations of carbon dioxide, methane atmospheric temperature show that human activity holds the responsibility. The main source of GHG emissions are due to the combustion of natural gas (NG), coal and oil for heating, electricity production, transportation and industrial purposes. For example, 39% of hydrocarbon-related CO_2 emissions are from oil, 20% from NG and the remaining from the coal (Abbas & Wan Daud, 2010).

Hydrogen appears to become the sustainable solution to this problem. Hydrogen is a clean energy and suitable feeding gas when used as a fuel in fuel cells. The amount of energy produced during hydrogen combustion is higher than that evolved by other fuel on a mass basis, with a low heating that is 2.4, 2.8 or 4 times higher than that of methane, gasoline or coal, respectively (Abbas & Wan Daud, 2010). Steam reforming, partial oxidation and auto-thermal reforming of methane are the conventional processes for the production of hydrogen. These methods have a significant effects on global warming, since they release CO_x (x=1 or 2) while producing hydrogen due to mixing methane with water and oxygen (Makvandi & Alavi, 2011). Reforming is an endothermic catalytic process which requires temperatures from 800 to 950$^\circ C$ and a pressure of 3 to 25 MPa. Unlike steam reforming, partial oxidation process is carried out without the use of catalysts at higher temperatures between 800 – 1200℃ and at pressure of 3 – 25 MPa (Saraswat & Pant, 2012). Therefore, a less severe and economically process is required that can reduce or eliminate CO_2 emissions during the process.

Thermocatalytic decomposition of methane (TCD) is identified as the alternative process for hydrogen production.

$$CH_4 \rightarrow C + H_2$$

TCD eliminates the need for water gas shift reaction. Methane decomposition also produces a useful byproducts, the deposited carbon, usually as nanomaterials (Li et al., 2006). Nickel-based catalyst have been found to be an effective catalytic component in the decomposition of methane to produce hydrogen and carbon. Nickel is more active and selective than other element, as the sintering of the metal is not observed (Venugopal et al., 2007). In a literature, it has been shown that at temperature above 823 K, Ni-based catalyst exhibit stable operation for few hours, providing 2 mol of hydrogen per mole of methane reacted (Choudhary et al., 2001). In another literature, copper is reported to can increase the stability of nickel-based catalyst at high temperatures. Therefore, by making use of nickel and copper, this paper is intended to investigate the effect of these elements on ceria-based catalyst.

In this study the ceria-based catalyst was selected to be doped with nickel or copper as promoter to be conducted at a much lower temperature for producing hydrogen via thermocatalytic decomposition of methane

1.2 Problem Statement

Hydrogen is the most abundant element in the universe, but, free hydrogen does not exist naturally on earth in its gaseous form. Hydrogen must be produced from a primary source such as water, natural gas, coal, petroleum or biomass. However, the conventional processes to produce hydrogen from NG, coal and hydrocarbon emit significant amounts of greenhouse gases into the atmosphere and contributing to the global warming. Therefore, there is a need to develop a CO_x-free (x=1 or 2) process which is thermocatalytic decomposition of methane. A lot of studies reported the use of common transition metal such as nickel as a catalyst doped with various promoters. However, the operating temperature reported for these catalysts is higher in order to achieve higher conversion of methane. Hence, there is a need to develop and study a catalyst doped with promoter at a much lower temperature for producing hydrogen via a catalytic decomposition of methane

1.2 Objectives

The objectives of this study are:

1. To synthesize supported ceria based catalyst for hydrogen production.
2. To characterize the physical properties of the develop catalyst.
3. To evaluate the performance in terms of the rate and hydrogen yield of the prepared catalysts in hydrogen production.

1.4 Scope of Work

1. Synthesize 99wt% of ceria based catalyst by using three different promoter which are copper, nickel and both copper and nickel.
2. Analyze and characterize the ceria based catalyst by Temperature-Programmed Reduction (TPR).
3. Analyze the performance of the catalyst in producing hydrogen.

CHAPTER 2: LITERATURE REVIEW

2.1 Hydrogen as a Future Energy

Hydrogen is the simplest element, an atom consisting of only one proton and one electron. Being the most abundance element in the universe, hydrogen does not occur naturally as a gas on the Earth – it is always combined with other element.

Hydrogen is one of the key starting materials used in many industries. For chemicals and petrochemical industries, hydrogen is used for the production of various chemicals such as hydrogen peroxide, ammonia and methanol (Assabumrungrat, Phromprasit, & Arpornwichanop, 2012). Hydrogen is also used in reforming, one of the processes for obtaining high grade petrol and in removing sulfur compounds from petroleum in the refinery industries (CIEC Promoting Science, 2013). Sulfur contents in the petroleum would poison the catalytic converters fitted to cars if not removed. Food processing industry also uses hydrogen for hydrogenation of fats and oils.

In years to come, hydrogen itself may become one of the most important fuels for cars as the burning of hydrogen will not produce carbon dioxide. The idea of hydrogen-based energy is initiated for at least several decades ago. Interest first emerged in the early 1970s in the response to the first oil crisis and the growing concerns about environmental issues (Van Ruijven, Van Vuuren, & De Vries, 2007). Usage of hydrogen for fuel cell for transportation is receiving the most attention in research and discussions as fuel cell is claimed to be a non-polluting source of energy, and is predicted to be the “fuel of the future” (Choudhary & Goodman, 2006).

Hydrogen is an attractive alternative to carbon-based fuels. Fuel cells are a promising technology for use as a source of heat and electricity for buildings and as an electrical power source for electric vehicles as combustion of hydrogen in the engine produces almost no pollution (Momirlan & Veziroglu, 2005). All in all, hydrogen is being considered as the potential fuel in future because it can reduce global carbon dioxide CO_2 emissions and improves local air quality, ensure security of energy supply and can create a new industrial and technological energy base, which is crucial for the economic prosperity (Edwards et al., 2008).

The use of hydrogen as an energy source is likely to be in the transportation sector, where it will help reduce pollution. Internal combustion engines can be fueled with pure hydrogen, or hydrogen-rich gas. It is reported that vehicles powered with hydrogen fuel cells are three more times more efficient than a gasoline-powered engine (Momirlan & Veziroglu, 2005). Hydrogen fuel cell is a device that wills continuously recharging battery and converts hydrogen or a hydrogen-rich fuel and an oxidant directly into electricity using a low-temperature electrochemical process (Edwards et al., 2008). A fuel cell operates like a battery. Different from a battery where it only used to store energy, fuel cell does not run down or require recharging as it will produce energy in the form of electricity and heat as long as fuel is supplied (Johnston, Mayo, & Khare, 2005). Figure below shows a configuration of typical hydrogen fuel cells. The basic design of hydrogen fuel cells is it consisting of two electrodes (anode and cathode) separated by a solid or liquid electrolyte or a membrane. Hydrogen (or a hydrogen-containing fuel) and air is feed into the anode and cathode of the fuel cell, and the electrochemical reactions assisted by catalysts will take place at the electrodes. The electrolyte enables the transport of ions between the electrodes, while the electrical power is produced from the flow of excess electron through an external circuit.

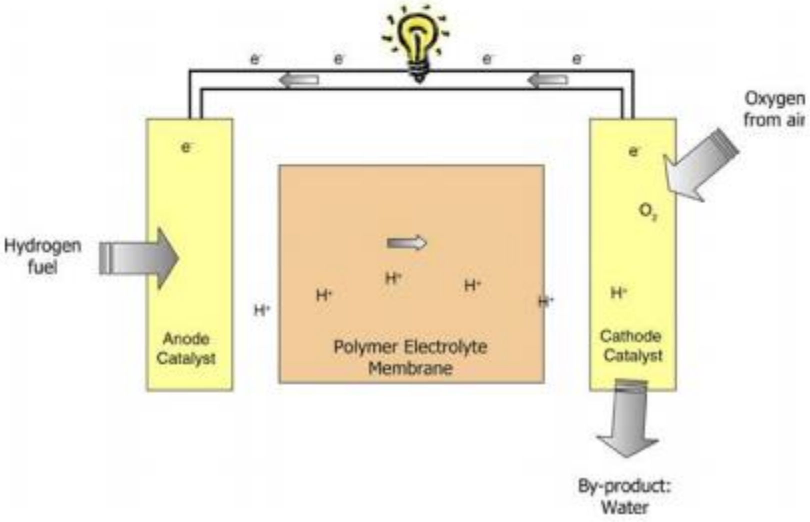
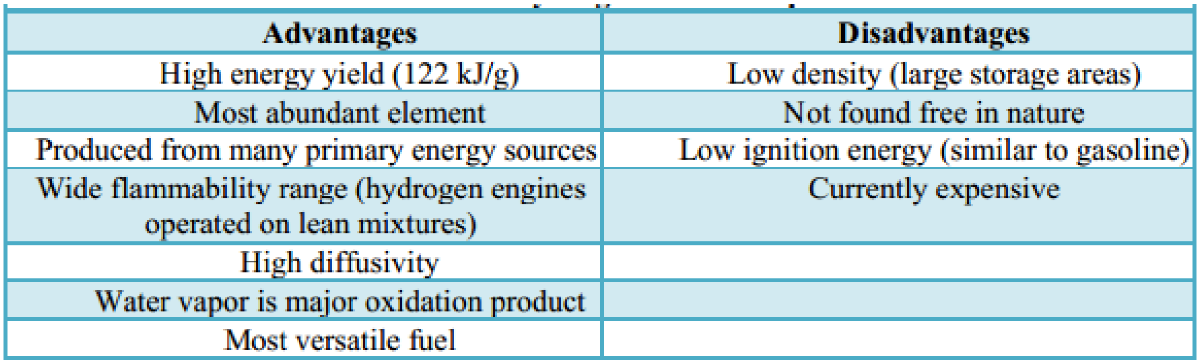


FIGURE 1: A simple view of hydrogen fuel cell

However, advantages and drawbacks of a system come together. Figure 2 shows some advantages and disadvantages with the uses of fuel cell in transportation technologies (Chamousis, 2009).



Advantages	Disadvantages
High energy yield (122 kJ/g)	Low density (large storage areas)
Most abundant element	Not found free in nature
Produced from many primary energy sources	Low ignition energy (similar to gasoline)
Wide flammability range (hydrogen engines operated on lean mixtures)	Currently expensive
High diffusivity	
Water vapor is major oxidation product	
Most versatile fuel	

FIGURE 2: Hydrogen as a transportation fuel

2.2 Hydrogen Production Technologies

Since hydrogen is not naturally available, a fuel processing technology is essential to convert many possible fuels (e.g. biomass, hydrocarbons, coals and alcohols) to hydrogen. Several technologies are already available for the industrial production of hydrogen.

Three methods are available for producing hydrogen from hydrocarbons fuels; steam reforming, partial oxidation (POX) and autothermal reforming (ATR) (Holladay et al., 2009). Steam reforming is a well-established technology that produces hydrogen from hydrocarbons and water. Nowadays, large quantities of hydrogen is produced by steam reforming of hydrocarbon (Edwards et al., 2008). This method yields CO_2 as a byproducts. However, the main problem of this method is that the hydrogen producing through steam reforming contribute significantly to greenhouse gas emissions since carbon dioxide is the dominant gas released (Johnston et al., 2005). Steam reforming is a endothermic conversion of methane and water vapour into hydrogen and carbon monoxide. It does not require oxygen, has a lower operating temperature than POX and ATR. The general reaction for steam reforming as below:

$$C_mH_n + mH_2O = mCO + (m + \frac{1}{2}n)H_2$$

$\Delta H =$ hydrocarbon dependent, endothermic

Partial oxidation (POX) converts hydrocarbon to hydrogen by partially oxidizing (combusting) the hydrocarbon with oxygen (Riis et al., 2005). No catalyst is required for the process, and it is more sulfur tolerant than the other processes. It is an exothermic reaction, hence no need for any external heating of the reactor. It occurs at high temperatures with a formation of some soot. POX proceeds with the reaction below:

$C_mH_n + \frac{1}{2}mO_2 = mCO + \frac{1}{2}H_2$ $\Delta H =$ hydrocarbon dependent, exothermic

Autothermal reforming (ATR) is a combination of both steam reforming and partial oxidation. It uses the partial oxidation to provide the heat and steam reforming to increase the hydrogen production resulting in a thermally neutral process (Holladay et al., 2009). ATR normally conducted at lower pressure than POX. Since POX is exothermic and ATR incorporates POX, these processes do not need an external heat source for the reactor. The reaction process as below:

$$C_mH_n + \frac{1}{2}mH_2O + \frac{1}{4}mO_2 = mCO + (\frac{1}{2}m + \frac{1}{2}n)H_2$$

$\Delta H =$ hydrocarbon dependent, thermally neutral

Hydrogen can also be produced from using coal as feedstock and this method is getting a lot of attention in places such as India and China (Johnston et al., 2005). As for steam reforming, the main concern is the production of carbon dioxide, where methods for sequestering the carbon released must be developed. Hydrogen from coal can be produced through gasification process (Riis et al., 2005) . In gasification process, carbon is converted to carbon monoxide and hydrogen.

$$C(s) + H_2O + heat \rightarrow CO + H_2$$

This reaction is endothermic; hence additional heat is required, as with methane reforming. The CO produced will further converted to CO_2 and H_2 through water-gas shift reaction

Water can be split to produce hydrogen through various processes, including electrolysis, photo-electrolysis, high-temperature decomposition and photo-biological water splitting (Edwards et al., 2008). In electrolysis, electrical current is applied to decompose water into hydrogen and oxygen atoms (Johnston et al., 2005). It can achieved up to 70-75% of hydrogen production

(Edwards et al., 2008). The cost of hydrogen produced through this method is high as electricity is used to split the water but this cost might be reduced if the electricity is replaced with a renewable energy source (Johnston et al., 2005). Table 1 provides a summary of the various ways to produce hydrogen.

TABLE 1: Comparison between various methods to produce hydrogen

Method	**Advantages**	**Disadvantages**
Steam reforming of hydrocarbon (e.g. methane gas)	65 -75% efficiency Economical (least expensive method) Established infrastructure	Nonrenewable resources Produces CO_2 emissions
Autothermal Reforming (ATR)	Lowest process temperature than POX	Limited commercial experience Requires oxygen or air
Partial oxidation (POX)	Decreased desulfurization requirement No catalyst required	Low H_2/CO ratio Very high process temperature Produce soot
Coal Gasification	Inexpensive resources	Produces CO_2 emissions Carbon sequestration will raise costs 45% efficiency
Electrolysis of water	Depend on electricity source	Input into production may require more energy than released Produces CO_2 if coal is energy source

2.3 Hydrogen Production from Methane

Among the various fuels, methane is a promising source of hydrogen production as it is a main component in natural gas and renewable biogas. There are many possible reaction routes to produce hydrogen from methane (Assabumrungrat et al., 2012). Reactions below summarized the routes available for methane conversion into hydrogen.

Steam Reforming $CH_4 + H_2O \leftrightarrow CO + 3H_2$ $\Delta H_{298} = +206.2\ kJ/mol$ (1)

Partial Oxidation $CH_4 + \frac{1}{2}O_2 \leftrightarrow CO + 2H_2$ $\Delta H_{298} = -38\ kJ/mol$ (2)

Dry Reforming $CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$ $\Delta H_{298} = +247\ kJ/mol$ (3)

Decomposition $CH_4 \leftrightarrow C + 2H_2$ $\Delta H_{298} = +74.8\ kJ/mol$ (4)

Steam reforming (Eq. (1)) or likely known as steam methane reforming (SMR) is conducted at a high temperature, which produce hydrogen and carbon monoxide. Partial oxidation (Eq. (2)) is an exothermic reaction and converts methane to hydrogen by reacting limited oxygen to avoid the complete oxidation that generated steam and carbon dioxide products. With the combination principle of steam reforming and partial oxidation, autothermal reforming is a promising process. However, for these processes, it produce large amounts of carbon monoxide, hence a water gas shift reactor is required after the reforming section to further convert carbon monoxide by reacting with steam to hydrogen and carbon dioxide. Methane dry reforming (Eq. (3)) is a process where both greenhouse gases (methane and carbon dioxide) are converted to synthesis gas with low hydrogen-to-carbon monoxide ratio. While methane decomposition (Eq. (4)) is an alternative route for production of CO_x-free hydrogen suitable for a low temperature fuel cell (Assabumrungrat et al., 2012).

Table below summarizes the processes and challenges of each of these three methods.

TABLE 2: Comparison between the methods of producing hydrogen from methane

	Process	Challenges
SMR	Methane react with water to produce CO and H_2	Produce CO or CO_2 as a byproducts Require WGS reaction to remove the byproducts
Partial Oxidation of methane (POX)	Methane react with oxygen to produce CO and H_2	
Dry Reforming	Combination of SMR and POX to produce CO and H_2	
Decomposition	Methane is decomposed into hydrogen and carbon under thermal or catalytic reaction	Produce CO_x-free hydrogen Not require WGS

In this review of the literature, reports relating to the direct methane decomposition process for hydrogen production are further discussed. Theoretically, methane decomposition can be represented as:

$$CH_4 \leftrightarrow C + 2H_2 \qquad \Delta H_{298} = +74.8\ kJ/mol$$

From the stoichiometric reaction, 2 moles of hydrogen is produced for every mole of methane reacted. The decomposition of methane has attracted a lot of attention since this route only produces hydrogen and carbon, hence a CO_x-free hydrogen is produced. Therefore, it does not require complex CO_x removal procedures. The main advantages of methane decomposition compared to conventional methods is the simplicity of the methane decomposition process by eliminating the high- and low- temperature water-gas-shift reactions and CO_2 removal step (Choudhary & Goodman, 2006). Besides that, the production of CO_x-free hydrogen results in an easier separation of H_2 gas from the product stream (Sy, Abella, & Monroy, 2012). However, since carbon is produced during the reaction, a gradual catalyst deactivation can be expected due to the accumulation of carbon on the catalyst (Choudhary & Goodman, 2006). The catalyst can be regenerated by removing the carbon on the catalyst in another step. Overall, hydrogen production through methane decomposition is represented as follow:

(1) $CH_4 \leftrightarrow C + 2H_2$
(2) $C + H_2O/O_2/\ CO_2 \rightarrow CO_x + H_2$ and clean catalyst surface

In one study, it has been found out that the carbon formed on the catalyst surface is a useful byproduct, usually as nanometarials where the size and texture is depends on the structure and composition of the catalyst used in the decomposition (Makvandi & Alavi, 2011).

Methane can be thermally or thermocatalytically decomposed into carbon and hydrogen without producing CO_2 (Abbas & Wan Daud, 2010), and this has attracted the attentions of researchers. By definition, thermal decomposition (TD) is a reaction in which heat is used for breaking up a chemical substance in two or more substances and this process is often an endothermic reaction. The decomposition of methane can be accelerated by increasing the reaction temperature due to endothermic feature of the reaction (Jiang et al., 2003). Abbas and Wan Daud have reported that the temperature requiring for non-catalytic thermal decomposition of methane is higher than 1200°C to obtain a reasonable yield due to a very strong C-H bond in methane (Muradov & Veziroğlu, 2005). Besides the vast usage of electrical furnaces as a source of

TCD reactor, concentrated solar energy, plasma or molten-metal bath are among the alternatives sources of heat for TCD (Abbas & Wan Daud, 2010).

By using a catalyst, the temperature can be significantly reduced, depending on the type of catalyst used (Abbas & Wan Daud, 2010). The figure below from Muradov et al summarizes the catalyst effect on reducing the reaction temperature.

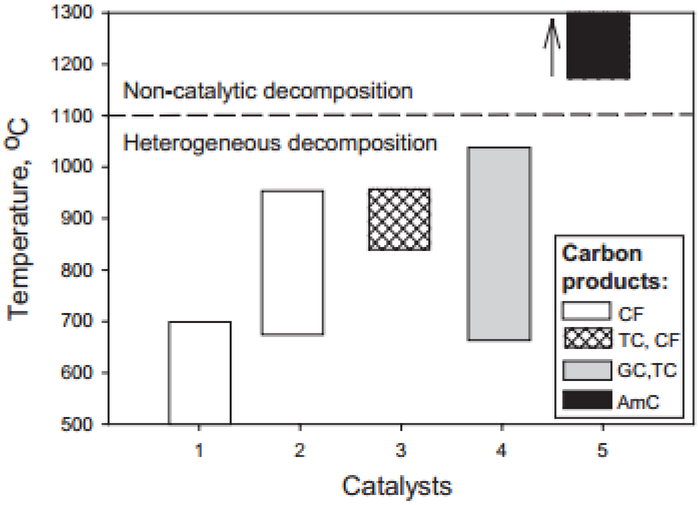


FIGURE 3: Graphical representation of the bulk literature data on catalysts. Catalysts: 1-Ni-based, 2-Fe-based, 3-carbon-based, 4-summary of data related to Co, Ni, Fe, Pd, Pt, Cr, Ru, Mo, W catalysts, 5- non-catalytic decomposition. Carbon products: CF- carbon filaments, TC- turbostratic carbon, GC- graphitis carbon, AmC – amorphous carbon

P.Kyriaki et. al. (2011) reported that ceria-based catalyst has been widely applied in hydrocarbon steam reforming and the water-gas shift reaction routes. Ceria, CeO_2 is a well-known important component for the control of automotive emissions (“three-way” catalyst) and for other environmental and energy-related applications, primarily for its intrinsic property of oxygen storage; receiving oxygen under oxidizing gas condition and releasing oxygen under reducing gas conditions. It has a major role in steam and dry reforming of hydrocarbons, and the WGS shift catalytic reactions. Many patents also claimed that ceria's thermal stability can be improved by the addition of rare-earth elements and/or zirconium. Ceria-based mixed metal oxides were also found to exhibit improved catalytic performance in comparison with pure ceria. In another literature, Ni/CeO_2 catalyst was investigated for hydrogen production from methane decomposition. Ceria (CeO_2), a fluorite-type oxide with well-known properties, has showed promising catalytic activities and selectivity in partial oxidation of methane to propene, and methane combustion (Li et al., 2006). Addition of noble metals as well as transition metals could greatly enhanced the redox features of ceria, while the improvement in catalytic performance was often attributed to the strong metal-ceria interactions and the generation of metal-ceria solid solution.

Nickel is one of the transition metals commonly used for the decomposition of methane (Ashok et al., 2007). Majority of transition metals demonstrated a remarkable activity in methane dissociation reaction including Ni, Fe Co and others (Muradov, 2000). Nickel-based catalysts have been found to be an effective catalyst for the methane decomposition and usually supported on different carriers such as Al_2O_3, SiO_2, MgO and zeolite (Makvandi & Alavi, 2011). It is also been shown that Ni-based catalyst is stable at a temperature above 823 K for a few hours (Choudhary et al., 2001). In addition, Ni-based catalysts is also reported to exhibit high activity for reforming reaction but with poor stability (Jiang et al., 2003).

Meanwhile, numerous studies have reported the positive effect of copper addition on the catalytic performance of various supported Ni catalysts (Sy et al., 2012). In the study, copper addition has been found to increase the thermal stability of supported Ni catalysts by enhancing the ability of the Ni catalyst to accumulate carbon, resulting in longer catalytic lifetimes.

With the property of ceria, nickel and copper mentioned before, this paper is intended to study the catalytic activity and carbon deposition for ceria-based catalyst with the support of nickel and copper at a much lower temperature.

2.4 Catalyst for thermocatalytic decomposition of methane to hydrogen

2.4.1 Catalyst preparation

Methods of catalyst preparation are very diverse and each catalyst may be produced via different routes (Zerva & Philippopoulos, 2006). Preparation usually involves continuous step. There are three type of method in preparation of primary solid or supported catalyst which are impregnation, co-precipitation and sol-gel method. For the purpose of this paper, co-precipitation has been employed in producing the supported catalyst.

Co-precipitation method is frequently used in the preparation of single and multi-component catalyst. This method provides a good dispersion of catalytic component in the support. In precipitation, the objective is to achieve a reaction of the type:

$$\text{Metal salt solution + Support powder particle} \xrightarrow{\substack{\textit{Precipitating agent} \\ \textit{Hydroxide, carbonate}}} \text{Metal hydroxide/carbonate on support}$$

The aims for employing a precipitation process in catalyst manufacturing are the intimate mixing of the catalyst components and the formation of very small particles for high surface area. The necessary degree of mixing can be achieved either by the formation of very small crystallites, in close proximity, for the different components or by the formation of mixed crystallites containing the catalyst constituents. Hydroxide carbonates or basic carbonates are the favored precipitating agents for the following reasons:

1. The solubilities of these transition metal salt and other catalytic components are very low. Consequently, very high supersaturations, leading to very small precipitate particle sizes, can be reached.
2. The solubilities of the precursors, typically metal nitrates and sodium hydroxide or carbonate, are high, so concentrated solutions can be used, again giving high supersaturations.
3. Hydroxide and carbonates are readily decomposed, by heat, to oxides of high area without leaving catalyst poisons as, for example, sulfur residues from the calcination of sulfates.
4. Many hydroxides, carbonates and hydroxycarbonates are known, so there is good chance of getting a mixed compound of the required composition for given compoenents.
5. Environmental difficulties arising from the calcination of hydroxide and carbonates are minimal.

Conceivable, co-precipitation may occur by either adsorption of one material by another, or formation of a solid solution of microcomponent in the host lattice. In other words, co-precipitation can lead to either adsorption compounds, with the microcomponents free to diffuse through the interior of solid phase. Precipitated catalyst are generally prepared by rapid mixing of concentrated solutions of metal salts. Other procedures involved are filtration, washing, drying and calcination.

CHAPTER 3: METHODOLOGY

Methodology refers to methods/procedure used by the author to achieve the objective(s) of the project. The author need to develop the catalyst comparison in terms of composition of the catalysts.

3.1 List of Chemicals

Chemicals used in this study including their source and purity are summarized in table below.

TABLE 3: Chemicals employed in this study

Name	Chemical Formula	Supplier	Usage
Cerium (III) nitrate hexahydrate	$\mathrm{Ce(NO_3)_3.6H_2O}$	R&M Chemicals	Catalyst precursor
Copper (II) nitrate trihydrate	$Cu(NO_3)_3.3H_2O$	R&M Chemicals	Catalyst precursor
Nickel (II) nitrate hexahydrate	$Ni(NO_3)_3.6H_2O$	R&M Chemicals	Catalyst precursor
Sodium carbonate decahydrate	$Na_2CO_3.10H_2O$	R&M Chemicals	Precipitating agent

3.2 Experimental Procedure

The experimental procedure involved: (i) preparation and characterization of the catalysts and (ii) methane decomposition experiments.

3.2.1 Preparation of Catalyst

The source for ceria, copper and nickel was obtained from cerium (III) nitrate hexahydrate [$Ce(NO_3)_3.6H_2O$], copper (II) nitrate trihydrate [$Cu(NO_3)_3.3H_2O$] and nickel (II) nitrate hexahydrate [$Ni(NO_3)_3.6H_2O$]. Precipitating agent used was sodium carbonate decahydrate [$Na_2CO_3.10H_2O$].

TABLE 4: List of chemical composition (wt%)

Sample	Composition (wt%)		
	$Ce(NO_3)_3.6H_2O$	$Ni(NO_3)_3.6H_2O$	$Cu(NO_3)_3.3H_2O$
A	99	1	-
B	99	-	1
C	99	0.5	0.5

TABLE 5: List of chemical weight composition (g)

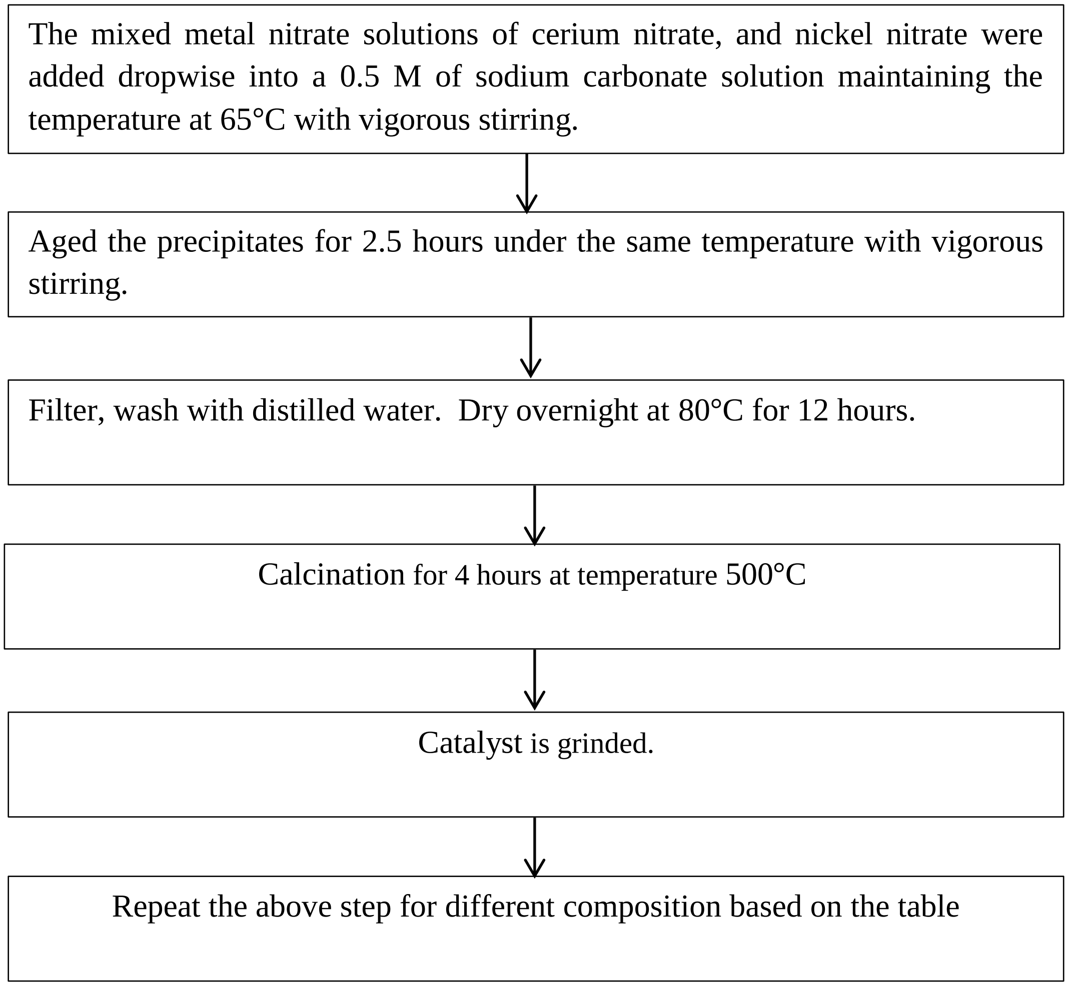
Sample	Composition (g)		
	$Ce(NO_3)_3.6H_2O$	$Ni(NO_3)_3.6H_2O$	$Cu(NO_3)_3.3H_2O$
A	19.8	0.2	-
B	19.8	-	0.76
C	19.8	0.1	0.5

Basis: 20g

Precipitating agent use: Sodium carbonate decahydrate , $Na_2CO_3.10H_2O$

Catalysts with different weight percentage based on table above were prepared by using co-precipitation method from metal nitrate precursors and $Na_2CO_3.10H_2O$ as the precipitating agent. Three solutions, each containing appropriate quantities of the metal nitrate precursors of ceria, copper and nickel were prepared. The mixed metal nitrate solution according to the composition stated in table above were added dropwise into a 0.5 M of sodium carbonate solution maintaining the temperature at 65°C with vigorous stirring. The precipitates were aged for about 2.5 hours under the same temperature with vigorous stirring. Then, the precipitates were filtered and washed several times with water to remove Na^+ and NO^{-3} ions then filtered and dried at 80°C for 12 hours. The dried precipitate was calcined at 500°C for 4 h. Finally, the resulting catalysts were grinded.

This procedure is for 1wt% of Ni.



The mixed metal nitrate solutions of cerium nitrate, and nickel nitrate were added dropwise into a 0.5 M of sodium carbonate solution maintaining the temperature at 65°C with vigorous stirring.

Aged the precipitates for 2.5 hours under the same temperature with vigorous stirring.

Filter, wash with distilled water. Dry overnight at 80°C for 12 hours.

Calcination for 4 hours at temperature 500°C

Catalyst is grinded.

Repeat the above step for different composition based on the table

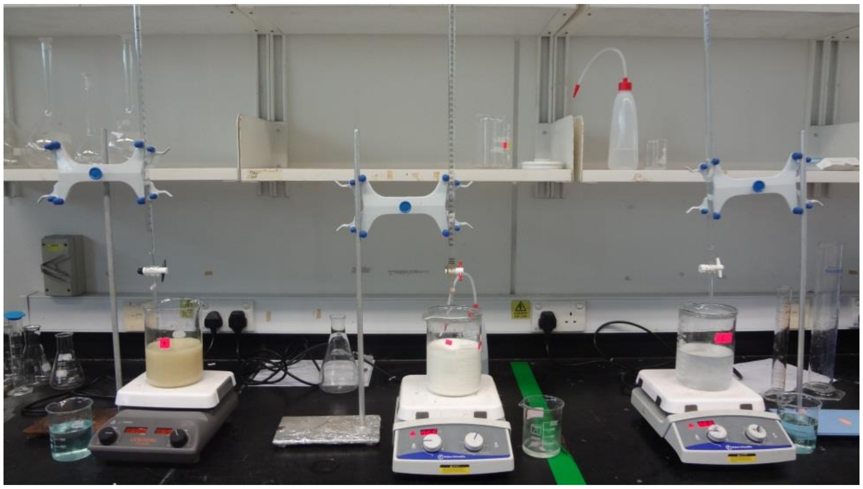


FIGURE 4: Titration of mixed metal nitrate with sodium carbonate for sample A, B and C respectively with vigorous stirring

FIGURE 5: Catalyst after 12 hours of drying

FIGURE 6: Catalyst after 4 hours of calcination

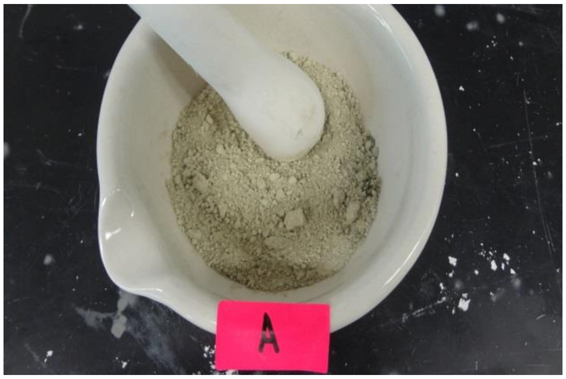


FIGURE 7: Grinding of the catalyst

FIGURE 8: The catalyst produced

3.2.2 Catalyst Characterization

The prepared catalysts were characterized by Temperature-programmed reduction (TPR). Figure below shows the TPR profile for the catalysts.

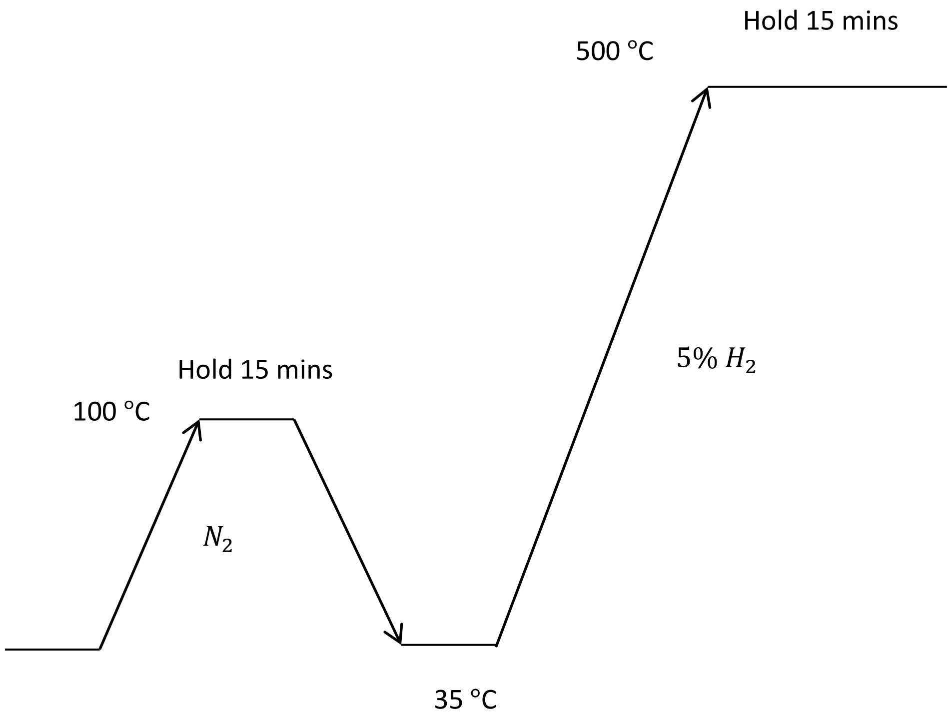


FIGURE 9: TPR profile for the catalysts characterization

3.3 Methane Thermocatalytic Decomposition Experiments

The methane decomposition reactions were performed in a fixed-bed reactor. The experiment were carried out at 350°C and 500°C, and then the catalyst were tested using TPR and the outlet gas were collected at the mentioned temperature to be analyzed using Gas Chromatography (GC). Small catalyst samples (1 gram) were placed in the reactor.

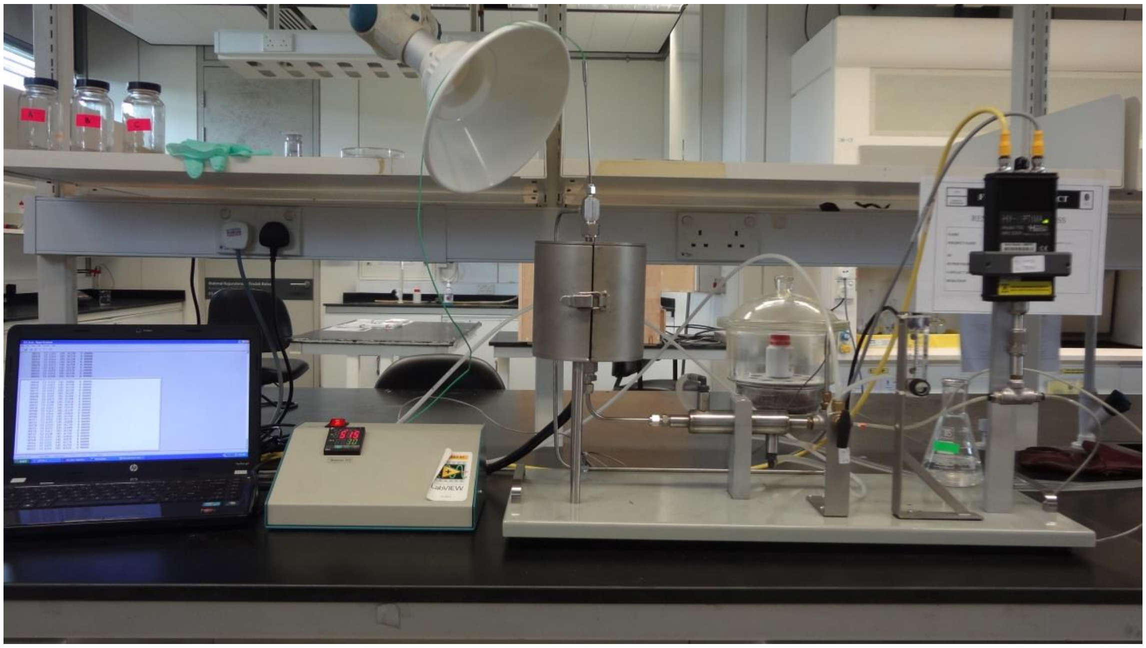


FIGURE 10: Experimental set-up for the methane decomposition

Detailed of the reactor profile for the can experiment can be seen as figure below.

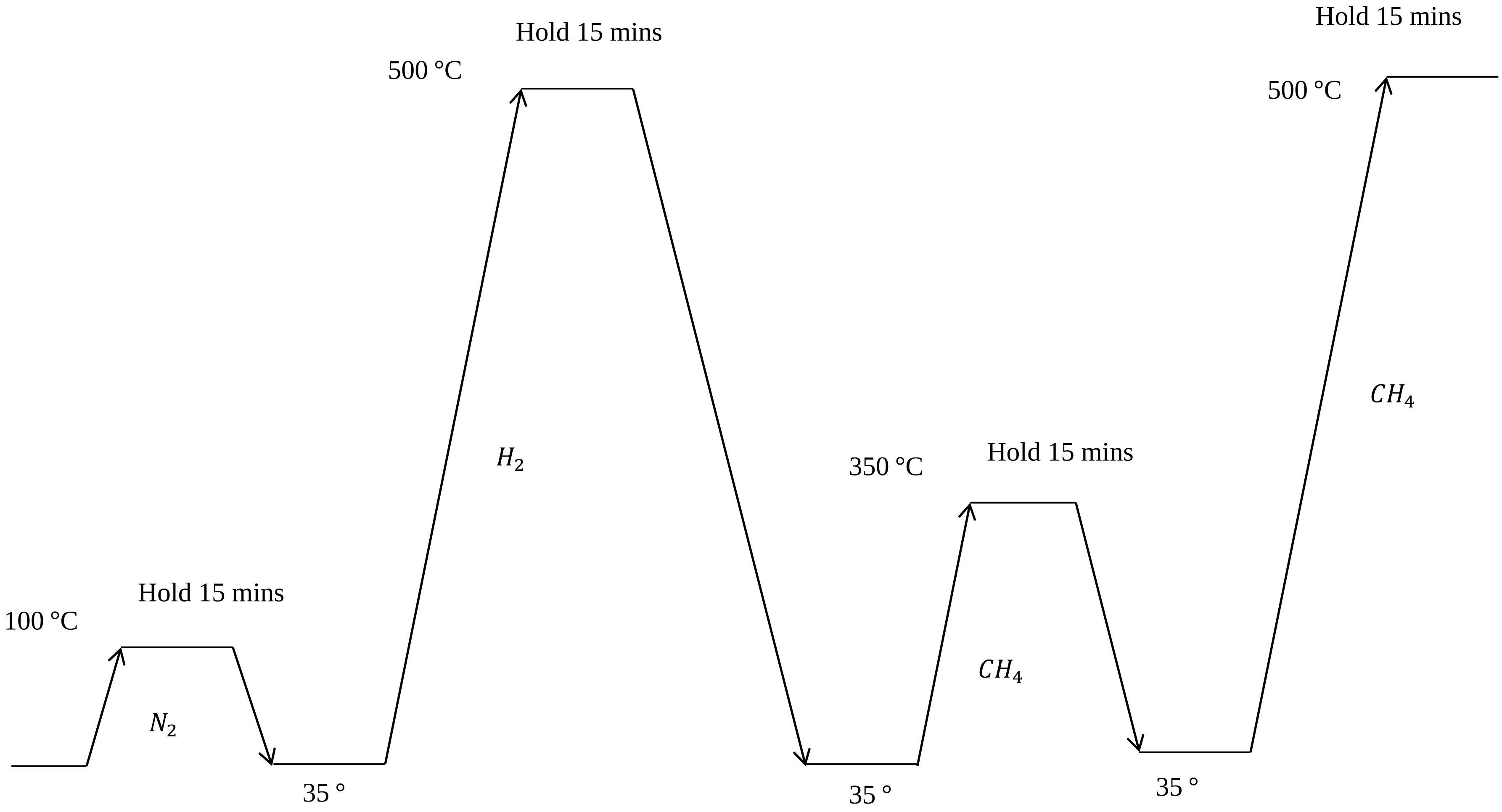


FIGURE 11: Reactor profile for methane decomposition

3.4 Gantt Chart and Key Milestone

TABLE 6: Gantt Chart of final year project

Project activities	Week No																												
	MAY			JUNE				JULY				AUG			SEPT		OCT				NOV				DEC/JAN				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Selection of project topic	🟨	🟨																											
Preliminary research work		🟧	🟧	🟧	🟧																								
Submission of extended proposal						●																							
Proposal defense							🟥	🟥	🟥																				
Fine-tuning research methodology										🟫	🟫	🟫																	
Submission of interim draft report													●																
Submission of interim report														●															
Arrival of experimental apparatus															●														
Catalyst preparation															🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦							
Submission of progress report																						●							
Data post-processing																						🟦	🟦	🟦					
Data analysis and documentation																								🟩	🟩	🟩			
Pre-SEDEX																									●				
Submission of draft report																										●			
Submission of dissertation																											●		
Submission of technical paper																												●	
Oral presentation																													●
Submission of project dissertation																													X

CHAPTER 4: RESULT AND DISCUSSION

4.1 Catalyst Characterization

4.1.1 Temperature programmed reduction

The TPR profiles of Ce supported Cu, Ni and Cu and Ni are shown in Figure 12, Figure 13 and Figure 14 respectively.

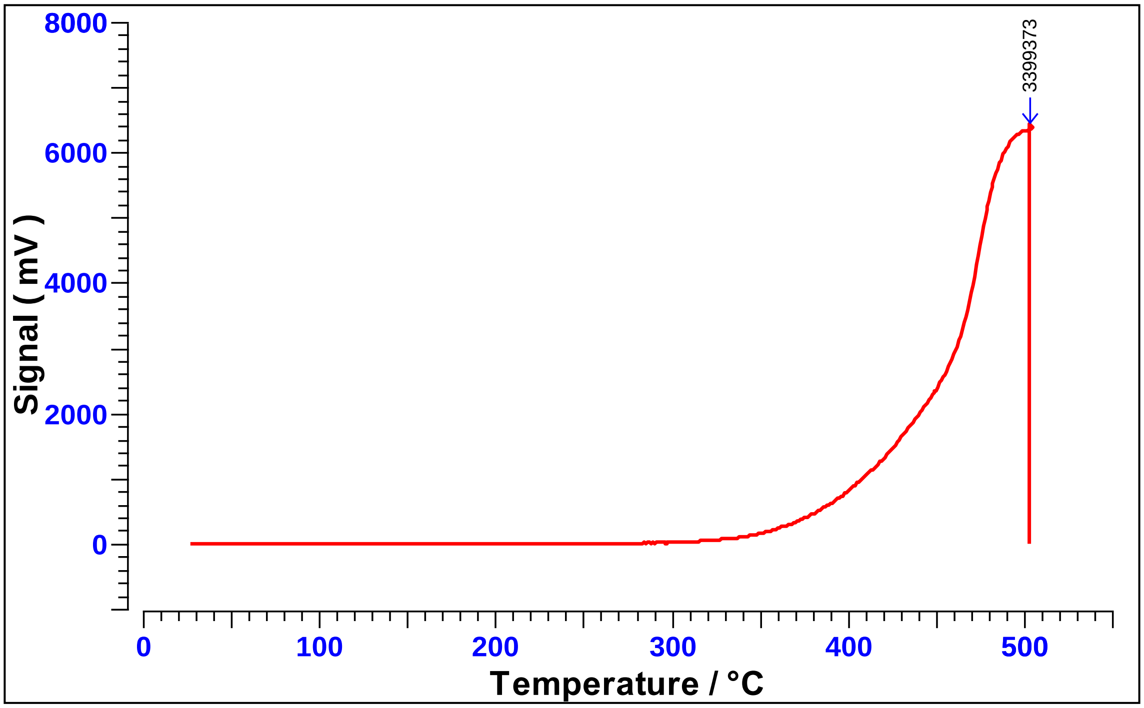


FIGURE 12: TPR profile of 1wt% of Ni over CeO_2

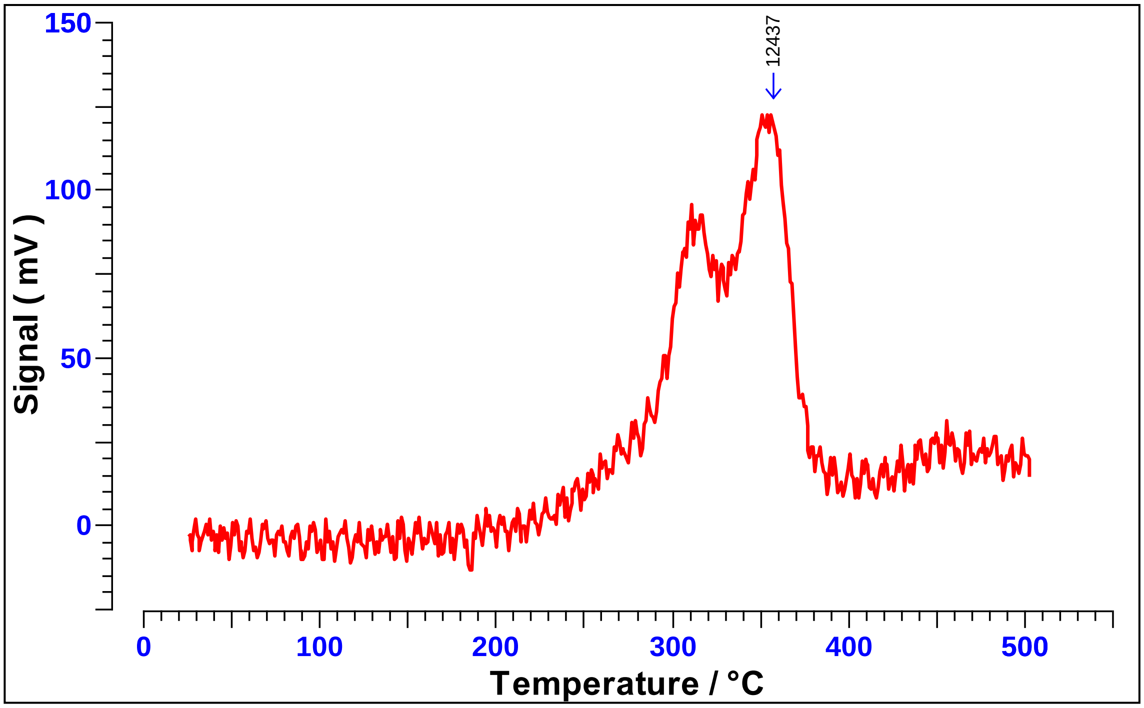


FIGURE 13: TPR profile of 1wt% of Cu over CeO_2

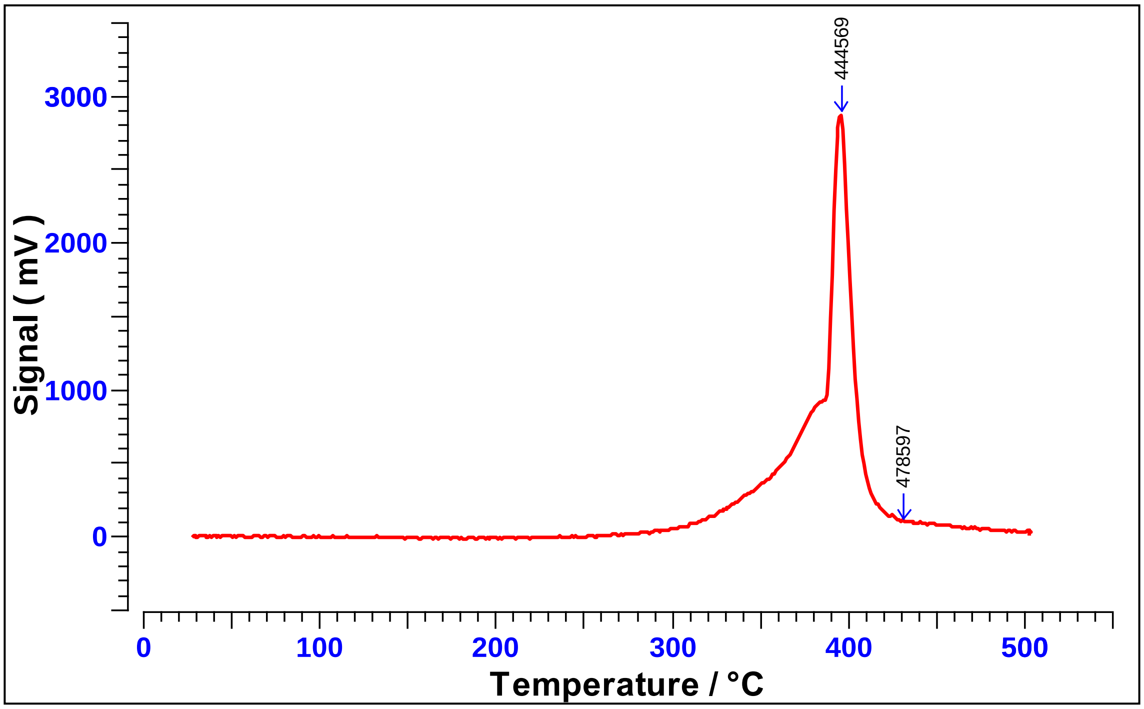


FIGURE 14: TPR profile of 0.5wt% of Ni and 0.5wt% over CeO_2

The TPR analysis was conducted with a maximum temperature of $500^{\circ}C.$ It is clearly evident from the patterns that the Ce catalysts exhibit a very different reduction behavior. At $500^{\circ}C$, there are still major and significant peaks recorded for both Ce/Ni and Ce/Cu catalysts. This shows that these catalysts have not been reduced completely to its metallic state. Thus, not ready to catalyze the reaction at the highest temperature of the experiment, which is $500^{\circ}C.$ No hydrogen is expected to be produced from by these catalysts. The experimental thermocatalytic decomposition of methane for these catalysts further confirmed these findings.

However, it is clearly evident from the profile that the catalyst with 0.5wt% Ni and 0.5wt% Cu exhibit a very different reduction behavior. The maximum temperature for large peak area is around 400°C. Only this catalysts show single reduction peaks. This indicate that the catalyst is ready to catalyze the thermocatalytic decomposition of methane to hydrogen for a temperature around 400°C. In addition, it has been reported that the pure ceria shows a major reduction region around 800°C. This is again able to indicate that the addition of Ni and Cu to the ceria has been greatly reduced the reduction temperature of pure ceria, from 800°C to 400°C.

4.2 Methane Thermocatalytic Decomposition Experiments

Figure 14 shows the formation rates over the Ce/Ni/Cu catalyst during methane decomposition. Obviously based on the TPR results, the Ce/Ni/Cu catalyst showed much higher hydrogen formation rates compared to the other two catalysts, where the TPR of the catalysts showed that the catalysts has yet been reduced completely, thus not able to catalyze the methane decomposition to hydrogen. Starting from 400°C, the hydrogen evolution increased rapidly with temperature, with the maximum hydrogen formation at 500°C.

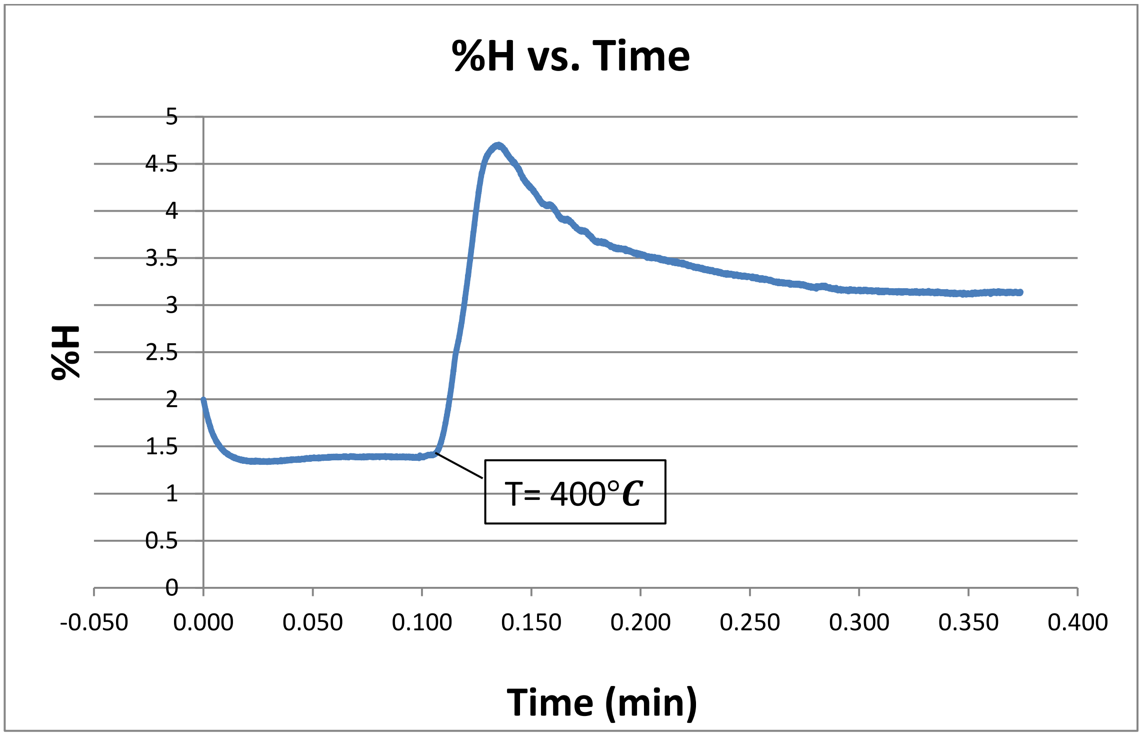


FIGURE 15: Percentage of hydrogen production over time during the thermocatalytic decomposition of methane

Figure 15 shows the composition of the outlet gas collected during the methane decomposition by Ce/Ni/Cu catalyst at 500°C with a holding time of 15 minutes. The sample collected was analyzed by the Gas Chromatography (GC). At this temperature, the outlet gas consists mainly of methane gas, about 90mol% and the remaining is the hydrogen gas. This shows that methane has not been fully decomposed into hydrogen at 500°C and a holding time of 15minutes.

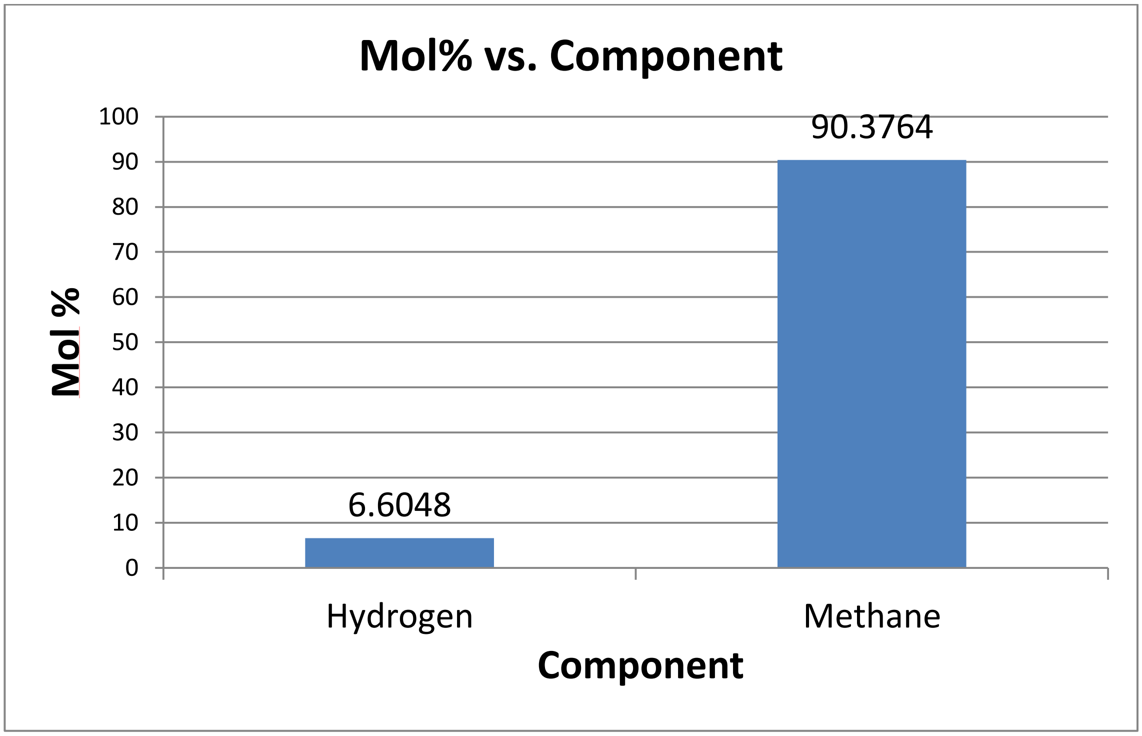


FIGURE 16: Outlet gas composition of Ce/Ni/Cu catalyst produced at 500°C

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

Thermocatalytic decompsoition (TCD) of methane has received considerable attention in recent years. This process is proven to be a CO_x-free emission unlike the other conventional methods (steam reforming and partial oxidation). The right selection of catalyst is essential in producing high production of hydrogen from methane as well as to be able to conduct the reaction at a lower temperature.

The ceria-based catalyst which are ceria supported with nickel, copper has the potential in producing hydrogen from thermocatalytic decomposition of methane at a lower temperature of 500°C. However, no hydrogen formation were recorded for the ceria with nickel and ceria with copper at a temperature of 500°C.

As a recommendation, the continuation of this project should be done at a higher temperature. With the limiting temperature of the reactor used in this research (maximum 500°C), the methane TCD over the Ce/Ni and Ce/Cu catalysts are unable to be carry out and to be analyzed. According to the TPR results, even at 500°C these catalyst are are not yet been completely reduced to their metallic state, hence unable to catalyze the decomposition. Besides that, the holding time for methane TCD over Ce/Ni/Cu catalyst should be longer instead of 15minutes to study the deactivation of the catalyst through the methane decomposition.

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