CATALYSTS FOR HYDROGEN PRODUCTION BY THE AUTO-THERMAL REFORMING OF GLYCEROL

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Abstract

Due to a number of major environmental issues, essentially greenhouse gas emissions and fossil fuel reliance, the implications of hydrogen as a promising clean energy carrier have significantly increased. In this respect, the use of bio-renewable feedstock such as glycerol for hydrogen production is becoming important. The majority of natural glycerol is produced as a by-product of the bio-diesel industry. Presently, almost all crude glycerol is refined before its ultimate end use. It is the ultimate goal of the present study to develop an effective catalytic auto-thermal reforming process to convert glycerol into top value bio-based products. Glycerol can be converted to hydrogen-rich streams by steam reforming (SR), partial oxidation (POX), gasification, auto-thermal reforming (ATR), supercritical water reforming (SCWR) or aqueous-phase reforming (APR). Most of the studies have focused on SR processes for producing hydrogen over various costly noble metal-based catalysts. A portfolio of nickel-based catalysts with nominal composition 5% Ni/$Ce_{0.5}Zr_{0.33}M_{0.16}O_{2-\delta}$ [where M is the promoter element(s) selected from Mg, Ca, Y, La, or Gd] was prepared and examined for their catalyst activity for glycerol auto-thermal reforming. The catalysts' activity was evaluated using a plug flow reactor at atmospheric pressure and in the temperature range of 450°C to 700°C, steam-to-glycerol ratio of 6, 9, and 12, and oxygen-to-glycerol ratio of 0.2, 0.5, and 0.8 at atmospheric pressure in a packed bed tubular reactor (PBTR). The preliminary screening studies were carried out for a time-on-stream (TOS) of 6 hours with sampling intervals of 1 hour. The physicochemical and textural characteristics of the catalysts were investigated by means of a variety of characterization techniques such as temperature-programmed reduction (TPR), temperature-programmed oxidation (TPO),

nitrogen (N_2) physisorption, hydrogen (H_2) chemisorption, UV-Vis diffuse, thermogravimetry analysis (TGA), and X-ray diffraction (XRD). The gaseous products were analyzed by online gas chromatography equipped with a thermal conductivity detector (GC/TCD). The structural, textural, and physicochemical characteristics of the catalysts have been investigated with the help of different bulk and surface characterization techniques. Different ratios of steam/glycerol and oxygen /glycerol were employed to optimize the conditions to achieve the highest conversion as well as H_2 selectivity. Based on the above analyses, glycerol conversion and H_2 selectivity were calculated. Among all the catalyst formulations screened in the current study, the catalyst formulations prepared with Ca, Y, Mg, La, and Gd exhibit stable and steady activity even at 500°C. The catalyst formulation with Gd as a promoter element performed the best at all the investigated temperatures. Hence, it is a potential candidate for future commercialization and plausible membrane reactor applications. The thermal and catalytic effects on catalytic auto-thermal reforming were identified by performing a number of non-catalytic reaction runs and then comparing the results with the corresponding catalytic reactions.

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Nomenclatures

%	Percent
°C	Degrees Celsius
ΔH_r	Heat of reaction
APR	Aqueous-phase reforming
ATR	Auto-thermal reforming
BET	Brunauer, Emmett and Teller
C	Carbon, Coke
cc	Cubic centimetre
Ce	Cerium
CeO_2	Cerium oxide
CH_4	Methane
C_2H_5OH	Ethanol
C_3H_7OH	Glycerol
CO	Carbon monoxide
CO_2	Carbon dioxide
CPF	Carbon propensity factor
CZM	Ceria-zirconia-metal oxide
D	Internal diameter of the reactor
D_p	Particle size of the catalyst
EDS	Energy Dispersive Spectroscopy
G	Glycerol
GC	Gas chromatography
Gd	Gadolinium

GHG	Greenhouse gas
H_2	Hydrogen
ICP-MS	Inductively Coupled Plasma-Mass Spectroscopy
IUPAC	International Union of Pure and Applied Chemistry
kJ	Kilo Joule
L	Catalyst bed height
La	Lanthanum
Mg	Magnesium
mg	Milligram
Ni	Nickel
NO_x	Nitrogen oxides
O_2	Oxygen
O_2/G	Oxygen/Glycerol
PBTR	Packed Bed Tubular Reactor
pH	Negative logarithm of hydrogen ion concentration
POX	Partial oxidation
ppmv	Parts Per Million by Volume
PV	Pore volume
RWGS	Reverse water-gas-shift (reaction)
S	Steam
SA	Specific surface area
SAR	Structure activity relationship
sccm	Standard cubic centimetre per minute
SCWR	supercritical water reforming

S/G	Steam/Glycerol
S/M	Surfactant/metal
SR	Steam reforming
TCD	Thermal conductivity detector
TGA	Thermogravimetry analysis
TOS	Time on stream
TPR	Temperature programmed reduction
UHP	Ultra high purity
UV-Vis	UV-Visibale
Vol.	Volume
WGS	Water-gas-shift (reaction)
wt.	Weight
XRD	X-ray diffraction
Y	Yttrium
Zr	Zirconium

Chapter 1 Introduction

1.1. Background and Motivation

It is a well-known issue that energy demand is growing, due to the enormous rise of industries around the world, while energy resources such as fossil fuels have started to become depleted. In addition, by-products of most fossil fuels cause pollution directly affecting not only human health but also the environment and leading to many severe effects such as global warming. Owing to these serious disadvantages, it is necessary to find other alternative energy resources that are abundant and environmentally friendly. Hence, hydrogen is presumed to be a promising candidate resource to replace the presently used energy resources since hydrogen can be produced from water, which is very abundant in the world as it covers about 71% of the Earth's surface. Hydrogen can be also employed as a fuel in cars with slightly modified combustion engines. Nevertheless, combustion engines are not a sustainable solution because of their relatively low efficiency of ~25%. However, cars can be powered by fuel cells, electrochemical devices that combine hydrogen and oxygen to produce electricity. From the reaction between protons and oxygen in the fuel cell, water, non-toxic products and heat as a side product are formed. Additionally, hydrogen can be considered as one of the most important industrial chemicals due to its application to enhance the performance of petroleum products by removing organic sulphur from crude oil, as well as to converting heavy crude to lighter, easier to refine, and more valuable products. In addition, hydrogen can be used to produce other important chemicals such as methanol, ammonia, and urea.

It can be also used by pharmaceutical companies to manufacture drugs. Liquid hydrogen can be applied as rocket fuel. Hydrogen is high in energy and burns cleanly, so an engine can burn pure hydrogen and produce almost no pollution. Therefore, hydrogen as a promising clean energy resource is emerging for wide-spread future use. It is one of the best options for energy production due to its ability to dramatically decrease oil consumption, CO_2 greenhouse gas (GHG) emissions, and tail pipe pollution. Presently, fossil fuel supplies the majority of the current required energy, although it creates environmental pollution issues by releasing large quantities of greenhouse gases (GHG), mostly COx and NOx, to the atmosphere (Haga et al., 1997). Hydrogen does not emit any greenhouse gases after direct combustion in engines or use in fuel cells such as proton exchange membrane fuel cells (PEMFC) and solid oxide fuel cells (SOFC), which can be used in the electric power generation for both distributed electric power plants and electric vehicles, as well (Douvartzides et al., 2004). Thus, hydrogen energy offers one of the most interesting solutions for future energy resources owing to its great abundance and zero emissions of GHGs or any pollution products.

Hydrogen can be produced from non-renewable fossil sources such as natural gas, naphtha, coal, etc. and renewable sources such as biomass, bio-diesel, bio-oil, biogas, solar energy etc. (Wang, 2010). It can also be produced from water. Although, if a global cycle of clean and sustainable production of energy is envisaged, a new eco-friendly reserve of hydrogen is required. In this context, glycerol can be effectively applied to produce hydrogen. Glycerol holds a series of advantages as a fuel since it is a side product of bio-diesel processing from animal fats and vegetables oils (Gerpen, 2005). The CO_2 discharged in utilizing glycerol is absorbed in the growth of the biomasses, and there

is no CO_2 released into the atmosphere. Glycerol can be converted into hydrogen through different processes such as auto-thermal reforming, partial oxidation, dry reforming, gasification, aqueous-phase reforming, and supercritical water reforming (Wang, 2010). Most studies have focused on steam reforming processes for producing H_2 by applying various noble-based metal catalysts, which are expensive. Glycerol steam reforming provides higher efficiency and better quality of reformate, although it shows some disadvantages such as high energy consumption, as well as catalyst deactivation. Very few studies are being performed on partial oxidation and auto-thermal processes. Partial oxidation presents an advantage in terms of fast start-up time due to the exothermic nature of its reaction. There is no need to apply extra heat via a heat exchanger for partial oxidation, and its reactor is more compact than that of a steam reformer. Auto-thermal processes combine the effects of steam reforming and partial oxidation by feeding fuel, air, and water together into the reactor. This process is usually carried out in the presence of a catalyst. The partial oxidation process generates heat that can be utilized in the steam reforming process. The total process can be understood as follows:

$$C_3H_8O_3\ (g) + 3/2\ H_2O + 3/4\ O_2 \rightarrow 11/2H_2\ (g) + 3\ CO_2\ (g) \quad \Delta H = -240\ KJ/mol \tag{1.1}$$

Applying auto-thermal reforming to producing hydrogen from glycerol was investigated by Dauenhauer et al., (2006) over $Rh\text{-}CeO_2/Al_2O_3$. They showed that Rh catalyst supported on CeO_2 with a ɣ- Al_2O_3 wash coat has higher H_2 selectivity. In addition, their studies showed that the addition of steam suppressed CO formation. The most important advantage of the auto-thermal process is that it should not ideally need any energy for the reaction to take place, while steam reforming is a highly endothermic process. However, the auto-thermal reforming process has disadvantages over

conventional steam reforming (Dauenhauer et al., 2006). The amount of H_2 generated from the auto-thermal reforming process would be less based on thermodynamics. The comparison between conventional steam and auto-thermal reforming of glycerol process over ɣ- Al_2O_3 supported Ni/Pd/Cu/K catalyst was performed by Swami and Abraham (2006). Their study indicates that the auto-thermal reforming process can produce higher amounts of H_2 compared to the previous studies. However, higher temperatures favour H_2 production in both auto-thermal and conventional steam reforming processes. In summary, the studies demonstrate that reforming of glycerol by the auto-thermal process can produce high selectivity to synthesize H_2 while all minor products exhibit selectivity of no more than 2% for hydrogen under optimal conditions. Glycerol can be reformed to hydrogen under auto-thermal conditions on catalyst to achieve high selectivity to H_2 by adjusting the fuel/air and fuel/steam feed ratios, as well as the catalyst. Based on these studies, auto-thermal reforming of glycerol demonstrates higher conversion, selectivity, and high H_2 yield in comparison to other processes. The auto-thermal reforming process does not need any external heat to occur since the partial oxidation reaction generates heat. Hence, there is a great interest in using auto-thermal reforming for glycerol conversion to hydrogen. Recently, the $Ce_xZr_{1-x}O_2$ mixture has been considered as a good support composition for Ni-based catalyst for reforming processes. It is found that the use of ZrO_2 to CeO_2 with a transition metal catalyst can improve the oxygen storage capacity, redox properties, thermal stability, and catalytic activity (Diagne et al., 2002; Roh et al., 2004; Erdohelyi et al., 2006). Based on the Diagne et al.,(2002) study, the Zr content has a positive effect on the structure and redox properties of the ceria–zirconia mixed oxides. Typically, there are two phases (tetragonal and cubic) in the $Ce_xZr_{1-x}O_2$ structures with

$x \leqslant 0.5$ (Roh et al., 2004). However, only a cubic fluorite phase is formed in the $Ce_xZr_{1-x}O_2$ samples while x is greater than 0.5 (Pengpanich et al., 2002). To achieve good catalytic activity, it is preferred to apply the deposition of noble metals, typically, $Ce_xZr_{1-x}O_2$, with x ranging from 0.6 to 0.8 (Terribile et al., 1998). In this formulation, Zr^{4+} ions are incorporated into the CeO_2 matrix to form a solid solution. Ce_x-$Zr_{1-x}O_2$ can be prepared by different techniques such as urea hydrolysis (Pengpanich et al., 2002), co-precipitation (Biswas and Kunzru 2008), incipient wetness impregnation (Biswas and Kunzru, 2008), sol–gel techniques (Youn et al., 2008), and surfactant-assisted procedures (Terribile et al., 1998), etc. Among the above methods, the surfactant-assisted method is the most attractive technique because of the effective soft template effect, reproducibility, and simple manoeuvrability (Terribile et al., 1998). (Kumar et al., 2008) indicated that the surfactant-assisted method can be used for preparation of solid solutions with high thermal stability and specific surface area, which favours the application of the solid solutions at high temperature. In this study, Ni-based catalyst supported on Ce-Zr-M (where M = promoter element) carriers prepared by applying the surfactant-assisted method was chosen for glycerol auto-thermal reforming. The research objectives are discussed briefly in the following section.

1.2. RESEARCH OBJECTIVES

The main objectives of this research were (1) to apply low cost, active, and stable transition metal catalysts to produce hydrogen in high yields from pure glycerol by the auto-thermal reforming process; (2) to perform catalyst characterization of fresh and used catalysts; and (3) to determine the parameters that influence the catalytic activities such as steam-to-glycerol and oxygen-to-glycerol ratios.

The overall goal was to optimize the steam/glycerol and oxygen/glycerol molar ratios, as well as temperature, in order to achieve maximum thermodynamically allowed glycerol conversion and hydrogen selectivity over the chosen Ni-based mixed oxide catalyst in auto-thermal reforming process. The main benefit of applying the auto-thermal process is that, ideally it is thermo-neutral, which means it does not require any external heat for the reaction to proceed; while other processes, such as steam reforming and dry reforming are highly endothermic and need additional energy to proceed. Another benefit of auto-thermal reforming is that it eliminates the need to employ high pressures to obtain high throughput, which makes the process cheaper in terms of cost. In addition, the auto-thermal process shows higher selectivity towards hydrogen and higher glycerol conversion efficiency, when compared to other reforming processes. Finally, catalyst deactivation on account of coking is also minimized in the auto-thermal reforming process, on account of the presence of oxygen. The other important objective of the current investigation is to establish realistic structure/activity relationships (SARs), which were devised by correlating the intrinsic physico-chemical properties of both fresh and used catalysts with the observed catalytic activity. Within the set objectives, various phases of research were undertaken, with each phase having a set of sub-objectives. These phases and their set objectives are listed below.

1.2.1. Phase I: Catalysts Preparation and Characterization

Five different catalysts were employed in this investigation. They were prepared by impregnating 5wt. % Ni over CZM (Ce-Zr-M, where, M = Ca, La, Gd, Mg, and Y) mixed oxide supports, prepared via surfactant-assisted method making use of surfactant/metal (S/M) ratio = 0.5. For the optimization of the surfactant/metal (S/M)

ratio, another two catalysts were prepared with different a S/M ratio that is 1.25 .The fresh supports and the Ni-based catalysts were characterized by Temperature Programmed Reduction (TPR), Nitrogen (N_2) Physisorption, Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS), Hydrogen (H_2) Chemisorption, and X-ray diffraction(XRD) techniques.

1.2.2. Phase II: Catalyst Screening Tests

The experimental phase was carried out in a Packed Bed Tubular Reactor (PBTR) in order to screen the catalysts and to identify the best one among the five Ni-based mixed oxide catalysts with different promoter elements. The screening tests were conducted at five different temperatures, 700°C, 600°C, 550°C, 500°C, and 450°C, for about 6 hours Time on Stream (TOS) which is typical lab scale study. In order to identify the thermal and the catalytic effects during reaction, also non-catalytic reactions were performed at six different temperatures and compared with the catalytic reactions. The effect of increased Ni loading on the catalytic performance was also evaluated.

1.2.3. Phase III: Reaction Parametric Studies

In this phase, three different ratios of steam-to-glycerol (6, 9, and 12), as well as three different ratios of oxygen-to-glycerol (0.2, 0.5, and 0.8), at four different temperatures, namely, 450°C, 500°C, 550°C, and 600°C, over 5% Ni/CeZrGd applying a surfactant/metal (S/M) ratio of 0.5 were applied to achieve the highest catalytic activity for glycerol auto-thermal reforming. The surfactant/metal (S/M) ratio of 0.5 was previously optimized in our group.

Chapter 2 Literature Review

2.1. HYDROGEN AS A CLEAN ENERGY CARRIER

In the twentieth century, most of energy supplies mainly come from fossil fuel based resources such as crude oil, coal, etc. Unfortunately, these resources can generate harmful gases such as CO, CO_2, NOx and SO_2 to the atmosphere causing the environmental issues. A hydrogen economy is proposed as one of the most attractive solutions for the future energy resources owing to the fact that it is a very abundant element on the earth and produces no pollution byproducts. Another motivation regarding the hydrogen economy is that the mass energy density of hydrogen is higher than that of the current fossil fuels by about three times (Graetz, 2012).Hydrogen, then, can be considered a very promising alternative energy carrier. It undergoes a perfectly clean combustion reaction with oxygen ($2H_2$ g+ O_2 g = $2H_2O$ g) to produce energy (ΔH = 120 kJ /g) and water. Since hydrogen is a ‘‘carbon free’’ energy carrier, it presents the maximum possible energy density of any hydrogen-based fuel (Graetz,2012)..,

In a combustion reaction such as $CH_4 + 2O_2 = CO_2 + 2H_2O$, the energy contribution from hydrogen is 120 kJ/g whereas the contribution from carbon is only 33 kJ/g (Graetz, 2012). Consequently, the hydrogen-to-carbon ratio scales the energy densities of hydrocarbon fuels directly. In addition, the carbon reaction produces undesirable greenhouse gases such as CO_2. For a direct comparison, 1 kg of H_2 has the same energy as 3 kg of gasoline (or 1 gallon = 3.79 L), while the gasoline also produces approximately 9 kg of CO_2 that contribute significantly to environmental issues. (Graetz, 2012).Moreover, gasoline currently comes from oil that is a finite resource. The Fischer–

Tropsch process is the most common technique for producing gasoline from coal, but this method is costly and likely emits greater amounts of greenhouse gas (CO_2) into the atmosphere.

Hence, such a technology for clean alternative energy carriers like hydrogen need to be developed and employed today to facilitate the transition to a sustainable, carbon-neutral energy economy tomorrow.

2.2. HYDROGEN PRODUCTION TECHNOLOGIES

The main available source of hydrogen production is represented by hydrocarbons, though the interest in hydrogen production from renewable sources is increasing, due to the depletion of fossil fuels and to the possibility of introducing Third World States into hydrogen economy. However, in the middle-term vision, the presence of valid infrastructures for fossil fuels transportation makes this kind of source the best candidate for a hydrogen source by using different technologies. At present, hydrogen production from renewable sources cannot economically compete with production from fossil fuels in the near future, but hydrogen production in controlled conditions allows a reduction of pollutant emissions, especially in highly urbanized zones.

The highest combustion energy release per unit of weight of any substance belongs to hydrogen. As a result, this property makes hydrogen a promising clean energy carrier. Thus, nowadays, renewable sources are desirable sources to produce hydrogen because of their variety, regionality, abundance, and potential for sustainability.

Glycerol ($C_3H_8O_3$), a 3-carbon carbohydrate, is a main side-product of the process that produces bio-diesel via the esterification of fats or oils. During conversion of vegetable oils into methyl esters to produce bio-diesel, approximately 10 wt. % of

glycerol is produced as a side-product (Zhao et al., 2012). Currently, bio-diesel production companies purify the glycerol in order to make it acceptable for either food-grade or pharmaceutical grade, although world demand is limited. Presently, the U.S. needs almost 61 billion gallons of diesel fuel. If, in the future, bio-diesel makes up 3% of the diesel fuel pool, over 1.8 billion pounds of glycerol will be generated as a side-product that greatly surpasses the current demand of 0.49 billion pounds of glycerol (Salge, 2006). Accordingly, the production of glycerol from bio-diesel is expected to greatly reduce the chemical value of glycerol. Ethylene glycol and glycerol can also be produced by the hydrogenolysis of sorbitol (Zhao et al., 2010). Then, glycerol can be used as a source of renewable hydrogen and can be converted into hydrogen by steam reforming (Deluga et al., 2004), partial oxidation (Adhikari et al., 2009), gasification (Hashaikeh et al., 2006), auto-thermal reforming (Dauenhauer et al., 2006), supercritical water reforming (Cortright et al., 2002), and aqueous-phase reforming (Manfro et al., 2011).

There are several reforming technologies that can be applied for glycerol reforming, such as auto-thermal reforming, steam reforming, aqueous-phase reforming, partial oxidation, and supercritical water reforming. Among all these techniques, auto-thermal reforming has some advantages over the other technologies. The main benefit of applying the auto-thermal process is that, ideally, it does not require any additional energy for the reaction to occur while the steam reforming process, the most common technique for glycerol conversion to hydrogen, is a highly endothermic process and needs to receive additional energy to occur. Another benefit of auto-thermal reforming is that it does not need to employ high pressures to take place, which makes the process cheap in

terms of cost. In addition, the auto-thermal process shows higher selectivity toward producing hydrogen and higher glycerol conversion to hydrogen. Finally, catalyst deactivation and coking are minimized easily in auto-thermal reforming processes by applying reducible supports in the presence of steam and oxygen.

2.2.1. Auto-thermal Reforming

The auto-thermal process combines the effects of steam reforming and partial oxidation by feeding fuel, air, and water together into the reactor. This process is usually carried out in the presence of a catalyst. The partial oxidation process generates heat that can be utilized by the steam reforming process. The total process can be understood as follows:

$$C_3H_8O_3\ (g) + 3/2\ H_2O + 3/4\ O_2 \rightarrow 11/2H_2\ (g) + 3\ CO_2\ (g)\ \Delta H = -240\ KJ/mol \quad (2.1)$$

(Adhikari et. al, 2009)

Dauenhauer et al., (2006) produced hydrogen from glycerol by auto-thermal reforming over Rh-CeO_2/Al_2O_3. They showed that Rh catalyst supported on CeO_2 with ɣ-Al_2O_3 wash coat indicates higher H_2 selectivity. In addition, they found that the addition of steam suppressed CO formation. The most important advantage of the auto-thermal process is that it should not, ideally, need any energy for reaction to take place while steam reforming is a highly endothermic process. However, the auto-thermal reforming process has disadvantages over conventional steam reforming (Dauenhauer et al., 2006). The amount of H_2 generated from the auto-thermal reforming process would be less on a thermodynamic basis. A comparison between conventional steam and auto-thermal reforming of glycerol process over ɣ- Al_2O_3 supported Ni/Pd/Cu/K catalyst was

performed by Swami and Abraham (2006). Their study indicates that the auto-thermal reforming process can produce higher amounts of H_2 in comparison to the previous studies, although, higher temperatures favour H_2 production in both auto-thermal and conventional steam reforming processes. In summary, the studies demonstrate that reforming of glycerol by auto-thermal reforming can produce high selectivity to the synthesis of H_2 while all minor products exhibit selectivity of no more than a 2% ratio to hydrogen under optimal conditions. Glycerol can be reformed to hydrogen under auto-thermal conditions on a catalyst to achieve high selectivity to H_2 by adjusting the fuel/air and fuel/steam feed ratios, as well as the catalyst. Based on these studies, the auto-thermal reforming process of glycerol demonstrates higher conversion, selectivity, and high yield H_2 in comparison to other processes. The auto-thermal reforming process does not need any external heat to occur, since the partial oxidation reaction generates heat. Hence, there is a great interest in using auto-thermal reforming for glycerol conversion to hydrogen.

2.2.2. Steam Reforming

Steam reforming is the most commonly used method to produce hydrogen in the chemical industry. In this process, glycerol is reacted with steam in the presence of a catalyst to produce hydrogen and carbon dioxide. This process is highly endothermic and the overall reaction is given by:

$$C_3H_8O_3\ (g) + 3\ H_2O \rightarrow 7H_2\ (g) + 3\ CO_2\ (g) \quad \Delta H=128\ KJ/mol \text{ (Cheng et. al, 2010)} \tag{2.2}$$

Therefore, 7 mol H_2 /mol glycerol are produced as per the reaction stoichiometry. The main concerns of glycerol steam reforming are by-product formation (e.g., CO), catalyst deactivation, and high energy consumption. Thermodynamically, the steam reforming process favours low pressure and high temperatures while water–gas shift reaction is inhibited by high temperatures and not affected by pressure. Ni, Ir, Co, Pt, Ru, and Rh-based catalysts have been investigated for steam reforming of glycerol to produce hydrogen (Adhikari et al., 2007). Iriondo et al., (2008) carried out steam reforming of glycerol over Ni catalysts supported with Al_2O_3 by applying different promoters such as Ce, Mg, Zr, and La. Their study showed that the use of Mg, Zr, Ce, and La increases the selectivity of hydrogen. Higher activities of catalysts were ascribed to higher concentration of Ni, higher stability, and higher capacity to activate steam. Cheng et al., (2010) applied bimetallic Co-Ni catalyst with alumina support for steam reforming of glycerol in a wide range of steam-to-glycerol ratios of 3 to 12 and reaction temperatures from 773 K to 823 K at atmospheric pressure. Their bimetallic 5 wt % Co-10 wt % Ni/Al_2O_3 catalyst was prepared by wet co-impregnation method. Carbon deposition during reaction proved to be the greatest reason for the loss in surface area and pore volume of the used catalysts. Carbon deposition is a strong function of glycerol partial pressure while it is rather insensitive to the presence of steam, suggesting that the carbon residue was to producing most likely not reactive with steam under the reaction conditions. Zhang et al., (2007) have studied the steam reforming of glycerol over ceria-supported Ir, Ni, and Co catalysts at the temperature range of 400°C to 550°C. They demonstrated that these catalysts are activated and selective for hydrogen production of glycerol. In particular, the Ir/CeO_2 catalyst indicated the most promising catalytic

performance among all those tested. The researchers achieved complete conversion of glycerol with more than 80% H_2 selectivity at 400°C for the steam reforming of glycerol.

Hydrogen production from glycerol via steam reforming over Ni/CeO_2, Ni/MgO, and Ni/TiO_2 catalysts was performed by Adhikari et al., (2007). They studied the effects of reaction temperatures, feed flow rates, and water/glycerol molar ratios on hydrogen selectivity and glycerol conversion. Their studies showed that Ni/CeO_2 catalyst demonstrated the best performance compared to Ni/MgO and Ni/TiO_2 under similar experimental conditions. The catalysts were synthesized by the incipient wetness technique. The catalyst performance is evaluated by H_2, CO_2, CO, and CH_4 selectivity and glycerol conversion. Their results showed that hydrogen selectivity can be increased by increasing reaction temperature. They achieved the maximum hydrogen selectivity of 66% for Ni/CeO_2, 52% for Ni/MgO, and 47% for Ni/TiO_2. Based on their study, an increase in temperature from 550°C to 600°C and 600°C to 650°C will increase hydrogen selectivity significantly. At all their experimental temperatures, a complete conversion for Ni/CeO_2, and Ni/MgO was obtained. They also found that glycerol conversion will also be increased by increasing the reaction temperature. The increase in temperature from 550°C to 600°C did not significantly increase glycerol conversion while the increase in temperature from 600°C to 650°C could considerably increase the glycerol conversion.

Buffoni et al., (2009) studied the steam reforming of glycerol over nickel catalysts supported with α-Al_2O_3 to produce hydrogen. They modified their catalyst using CeO_2 and ZrO_2 and indicated that the support affects the stability of the catalyst in steam reforming of glycerol at atmospheric pressure and in the temperature range of 450°C to 600°C. Using CeO_2 and ZrO_2 improved the oxygen storage capacity, and as a result, this

property can help carbon gasification. According to their results, the nickel catalysts are active and selective with dependence on the reaction temperature for glycerol conversion to gaseous products in steam reforming. Based on their results, 550°C is the lowest temperature needed to produce hydrogen with high selectivity. Nickel catalyst with Ce support indicated the higher stability and lower coke formation. Nichelea et al., (2012) evaluated the activity of Ni based catalysts supported with TiO_2, SBA-15, and ZrO_2 for hydrogen production by glycerol steam reforming. They performed steam reforming of glycerol in a fixed-bed quartz reactor at atmospheric pressure and at 500°C and 650°C for 20 h. Their results demonstrated that Ni-base catalysts can be promising catalysts to be employed in glycerol steam reforming because of the Ni activity in breaking C–C bonds and also in promoting the water–gas shift reaction. They highlighted that support plays a key role in designing the catalytic performance. Based on their studies, the support has a significant effect on the stability of the active phase; and as a result, the catalytic performance itself depends considerably on the reaction conditions. They reported that a strong metal–support interaction guarantees stability, activity, and selectivity of the catalyst in the steam reforming of glycerol. They also demonstrated that Ni/ZrO_2 catalyst can be the best catalyst for glycerol steam reforming; however, optimization of the reaction conditions such as higher temperature (650°C) is required to improve its performance even more. Pompeo et al., (2010) applied Pt and Ni catalysts supported on SiO_2 for glycerol steam reforming at temperature between 350°C and 450°C. According to the identification of reaction intermediates, they found that Ni and Pt include the same reaction steps. Hence, a schematic representation of the reaction pathways was proposed involving successive steps of dehydrogenation and C–C bond cleavage, which leads to H_2

and CO production. They obtained different levels of conversion, selectivity, and stability of catalysts. Pt catalysts showed more activity and stability than Ni catalysts. Ni catalysts illustrated differences in the selectivity to gaseous products as a result of the increased contribution of the water-gas shift reaction. The Pt catalysts showed a complete conversion to gaseous products at 450°C with no deactivation during the 40 hr. Gallo et al., (2010) evaluated bimetallic Ru-Sn heterogeneous catalysts supported on Mg (Al) O mixed oxide for steam reforming of glycerol. They tested the effect of tin doping on their catalysts with a different Sn loading in steam reforming of glycerol at 650 °C for 40 hr. Their catalysts showed high selectivity and activity for glycerol reforming to produce hydrogen.

Dave and Pant (2011) studied hydrogen production from steam reforming of glycerol over nickel-based catalyst promoted by zirconia and supported over ceria. They prepared the catalysts by the wet-impregnation method and evaluated them in terms of H_2 yield, selectivity, and glycerol conversion at 700°C in a tubular fixed bed reactor. The effect of glycerol concentration, feed, space, temperature, and time on stream were also studied for the catalyst $NiZrO_2/CeO_2$, and the results indicated a complete conversion of glycerol and high H_2 yield.

Cheng et al., (2010) employed alumina-supported cobalt-based catalyst, CO/Al_2O_3, in a fixed bed reactor at atmospheric pressure and temperature range of 450 °C and 550 °C to produce hydrogen from glycerol steam reforming. They used different feed compositions (30 to 60 wt. % glycerol mixture) to compare their data with the stoichiometric values of H_2:CO_2 and received close stoichiometric values. They also obtained a consumption rate of (0.1) order for the glycerol and 0.4 order, respectively, for

the steam partial pressure by applying the power-law model. Dou et al., (2009) evaluated the catalytic steam reforming of glycerol for H_2 production in a continuous flow fixed-bed reactor under atmospheric pressure within a temperature range of 400–700°C by a commercial Ni-based catalyst. They applied a dolomite sorbent to remove the produced CO_2 in glycerol steam reforming. Their results showed that H_2 productivity can be significantly increased with increasing temperature and the formation of CH_4 by-product becomes insignificant at temperatures higher than 500°C. They also suggested an optimal temperature of 500°C for the glycerol steam reforming with in situ CO_2 removal, based on their achievements. Araquea et al., (2011) performed glycerol steam reforming over CZCo and CZCoRh mixed oxides as catalysts at temperatures of 450°C, 550°C and 650°C. They found that the increment of temperature will favour the activity and stability of both catalysts. Their results showed that at 650°C, the CZCoRh performed the best for H_2 production reaching 95% of the predicted thermodynamic value (6.5 molH_2 molGly.in^{-1}). In the long duration tests, they found that the introduction of Rh favoured the production of gaseous products at the expense of the liquid products (<1%). They obtained an average production of H_2 of 6.7 mol H_2 molGly.in $^{-1}$ for CZCoRh catalyst over 16 h, whereas CZCo catalyst showed stability for only 1 h. According to their study, when deactivation happens, the formation of C_2H_4 can be observed, representing the loss of the C–C bond breaking capacity.

2.2.3. Partial Oxidation

In the partial oxidation process, glycerol reacts with oxygen at sub-stoichiometric ratios. The heat and high temperature are generated by the oxidation reaction. As a result, the partial oxidation process does not need indirect addition of heat through a heat

exchanger (Zhang et al., 2007). It can be conducted with or without catalysts. The objective of partial oxidation reforming in the presence of the air is to balance the energy, which is essential for the process, by oxidizing the glycerol. If excess air is applied, all glycerol can be oxidized and will generate CO_2 and H_2O. Glycerol oxidation at various temperatures and C/O ratio over Pt/ɣ-Al_2O_3 has been studied by Dauenhauer et al., (2006).

2.2.4. Steam Gasification

In the gasification process, different steam-to-glycerol molar ratios are applied at high temperatures in order to produce hydrogen. The steam gasification of crude and pure glycerol at 800°C at different steam-to-glycerol molar ratios with and without catalyst has been studied by Valliyappan et al., (2008). They showed that hydrogen and total gas production was higher from crude glycerol than from pure glycerol. This was attributed to the presence of potassium in the crude glycerol that comes from the production of bio-diesel by an alcohol and base catalyzed by potassium hydroxide. The presence of potassium in crude glycerol tends to support the gasification process. Catalysts are shown to deactivate in the gasification process of crude glycerol in comparison to pure glycerol.

2.2.5. Aqueous-phase Reforming

Aqueous-phase reforming is a relatively new process that was developed by Cortright et al., (2002). In this process, the conversion is achieved at higher pressures, ~60 bar, and at low temperatures, ~ 270°C, in comparison to steam reforming, which occurs at atmospheric pressure and higher temperatures, ~ 500°C. The most important advantage of this method is that it is a liquid phase process in contrast to all the other

available techniques being gas phase processes, except supercritical water, and most biomass-based liquids are hard to vapourize. The process is, thus, unique in that the reforming is carried out in the liquid phase. It generates H_2 without volatilizing the water, which shows major energy saving in comparison to gaseous phase reactions. Another advantage of this process is that it produces less CO. Navarro et al., (2007) operated the APR process over Ni catalysts supported with Al_2O_3 applying different promoters such as Ce, Mg, Zr, and La. Ni catalysts deactivated due to gradual transformation from metallic to oxidized state (Swami and Abraham 2006). The highest glycerol conversion to hydrogen was attained with La promoted catalysts at 37% (Iriondo et al., 2008).

2.2.6. Supercritical Water Reforming

In supercritical water reforming process, water is heated and then compressed at its critical temperature (374˚C) and pressure (22.1 Mpa).This process operates under the critical temperature and pressure. Water is supplied as a dense solvent as well as a reactant. Byrd et al., (2008) studied the conversion of glycerol to hydrogen in supercritical water over Ru/ Al_2O_3 catalysts applying low feed concentration (5wt% glycerol in water), 6.5 mol of hydrogen/ mol of glycerol at 800˚C and pressure of 241 bar. Based on their research, supercritical water can be a promising method for the reforming of glycerol to produce hydrogen at high pressures in a short reaction time.

2.3. CATALYSTS

In a chemical reaction, catalysts are those substances that influence the reaction without being consumed during it. In this particular process, an effective catalyst accelerates the reaction by increasing the reaction rate, increasing the hydrogen

selectivity, decreasing coke and methane formation, and influencing the water-gas shift reaction. Most of the studies have focused on steam reforming processes for producing H_2 in which are utilized various noble-based metal catalysts, which are expensive. Very few studies have been performed on partial oxidation and auto-thermal processes. Studies indicate that Pt, Rh, and Pd-based materials are effective catalysts, but they are expensive. This makes their use to produce H_2 from glycerol costly. The objective of the current investigation is to use low cost and more stable catalysts based on transition metals instead of noble metals to produce hydrogen from pure glycerol. In this study, 5% Ni/ $Ce_{0.5}Zr_{0.33}M_{0.16}O_2$ (where M= Gd, Ca, and Mg, etc.) catalysts were tested for the ATR of pure glycerol. Different catalysts have been employed in the literature for the auto-thermal reforming of glycerol. The high cost of the precious noble metals such as Rh, Ru, Pd, Ir, and Pt limits their industrial use although they perform well (Liguras et al. , 2003; Vaidya et al. , 2006). Use of base metals, such as nickel (Ni), overcomes this limitation due to their low cost. The base metals show the same level of activity as noble metals, and they have been widely studied (Navarro et al., 2007), but, the challenge associated with Ni is coke formation (Bartholomew et al., 2001; Kauppi et al., 2010; Penkova et al., 2011). To decrease the coke formation, the employ of supports with the Ni catalyst has been investigated. Metal oxides, mixed oxides, carbides, sulphides, molecular sieves, zeolites, etc. can be considered as supports. (Ni et al., 2007; Vaidya and Rodrigues, 2009).

2.3.1. Catalysts for Auto-thermal Reforming of Glycerol

2.3.1.1. Noble Metal Catalysts

Auto-thermal reforming of glycerol has been investigated with supported noble metal catalysts such as Pt and Rh (Dauenhauer et al., 2006). Rh-based catalysts have presented high selectivity for syngas from oxygenated compounds by auto-thermal reforming (Liguras et al., 2003).

2.3.1.2. Base Metal Catalysts

Base metals, such as Ni, have been widely used for steam reforming of glycerol under various operating conditions. Adhikari et al., (2008) used CeO_2, MgO, and TiO_2-supported Ni catalyst to perform glycerol steam reforming and found that catalysts show high stability at higher temperature. According to their results, Ni/CeO_2 and Ni/MgO showed the highest conversion and H_2 selectivity at higher temperature, but Ni/CeO_2 performed the best compared to Ni/MgO and Ni/TiO_2. Glycerol conversion was more than 99% at 600°C over Ni/TiO_2. The comparison between conventional steam and auto-thermal reforming of the glycerol process over ɣ- Al_2O_3 supported Ni/Pd/Cu/K catalyst was performed by Swami and Abraham (2006). Their study confirms that the auto-thermal reforming process can produce higher amounts of H_2 compared to other reforming processes, although, higher temperatures favour H_2 production in both auto-thermal and conventional steam reforming processes.

Ni was selected as the active metal due to its extensive documentation and wide applicability to the reforming process. Based on the literature, Ce-Zr-mixed oxide support was selected in order to reduce the coke formation and increase the thermal stability of

the catalyst. For the catalyst preparation method, a surfactant-assisted method was chosen to achieve the maximum possible specific surface area for better Ni dispersion of the active metals and to provide more catalytic-active sites for the auto-thermal reforming process, as well. Different elements, such as Mg, Gd, La, Y, and Ca, have been selected as promoter elements due to their noticeable performance in reforming of glycerol (Sengupta, 2011).

Chapter 3 Experimental Section

In this chapter, the experimental equipment, procedures, and materials used in all studies in this thesis research are described. The safety protocols are attached in appendix D.

3.1. CATALYST PREPARATION

3.1.1. Support Preparation

The ternary oxide supports were prepared with the help of surfactant-assisted method under basic conditions. The nominal compositions of each support were $Ce_{0.5}Zr_{0.33}M_{0.17}O_{2-\delta}$ (CZM), where M is a transition (Ts.), non-Ts., or inner-Ts. metal ion such as Ca, Gd, La, Mg, or Y. To prepare all of the above catalysts, Cerium (III) nitrate hexahydrate [$Ce(NO_3)_3$. $6H_2O$, 99%: Aldrich]; Zirconium oxynitratedihydrate [$ZrO(NO_3)_2.2H_2O$, 99.99%: Alfa Aesar]; and Gadolinium (III) nitrate hydrate [$Gd(NO_3)_3.xH_2O$, 99.99%: Alfa Aesar] precursors were used. In a typical preparation, the calculated amount of nitrate precursors of different metal ions for preparing 10 grams of support were dissolved separately in 500 mL deionized (DI) water under rigorous stirring and were, hence, mixed together. In a separate beaker, a predetermined amount of surfactant - cetyltrimethyl ammonium bromide (CTAB $C_{19}H_{42}NBr$: Sigma) was dissolved in 1000 mL DI water at 60°C under rigorous stirring. Then, these two solutions were mixed together to obtain a resultant mixture solution. The molar ratio of surfactant to metal (Ce + Zr + M) was kept constant at 0.5. Aqueous ammonia [ACS-Pure: Fisher (30% w/w)] (25 vol. %) was slowly added to the aforementioned mixture solutions under

vigorous stirring (450 rpm) at 60°C until precipitation was complete (pH 11.8). The addition of ammonia induced the precipitation of gelatinous yellow–brown colloidal slurry. The pH of the solution was measured time-to-time by applying a micro-fine pH paper (pHydrine microfine, Micro Essential Laboratory, USA. Then, the slurry was stirred for 30 min in a glass container and subsequently transferred into Pyrex glass bottles, sealed, and aged hydrothermally under autogenous pressure conditions in an air-circulated oven for 5 days at 90°C. Next, the mixture was cooled, and the resultant precipitate was filtered using 2, Qualitative, Circles, 110mm Dia, Whatman on separating funnel(Ceramic, 50245, CoorsTex) and washed repeatedly with warm DI water. The resulting cakes were dried in the oven at 120°C for 12 hours and, in the end, calcined in a ceramic crucible at 650°C for 3 hours in an air environment.

In addition, to proving that S/M=0.5 is the optimum surfactant/metal molar ratio, two other $Ce_{0.5}Zr_{0.33}M_{0.17}O_{2-\delta}$ supports were prepared using the same procedure mentioned above by increasing the surfactant-to-metal (Mg, and Ca) molar ratios to 1.25.

3.1.2. Active Metal Incorporation

A nominal 5 wt. % Ni was loaded over the prepared CZM supports applying a standard wet impregnation technique to achieve the final 5N/CeZrM ($5\%Ni/Ce_{0.5}Zr_{0.33}M_{0.17}O_{2-\delta}$, where M = Ca, Gd, La, Mg, and Y) catalysts. Typically for the nickel impregnation, 2.85 g of catalyst support was immersed in 25.55 ml of 0.1 M $Ni(NO_3)_2$ [99.999%: Aldrich]solution in a 50 ml round-bottomed flux. Then, the mixture was heated in a silicon oil bath at 80°C under constant stirring (240 rpm) using hot plate, Gyratherm IIa, VWR Scientific Inc. in order to remove the excess water. The dried

powders, which were obtained later, were calcined at 650°C on a ceramic crucible in an air environment for 3 hours. Next the powders were ground to a fine grain size and from the powders, palates were made applying a hydraulic press [model 3912, Carver]. Finally in order to obtain the desire 0.80 mm particle size catalyst, the sieving was performed. The theoretical elemental compositions of the final catalysts are given in table 3.1 and table 3.2.

Table 3.1 : Elemental compositions of final Ni-based catalysts (nominal, mass fraction)

Catalyst (xNCZM)	**Ni (%Mass Fraction)**	**Ce (%Mass Fraction)**	**Zr (%Mass Fraction)**	**M (%Mass Fraction)**	**O (%Mass Fraction)**
5N/CeZrCa	3.98	16.37	10.81	5.24	63.60
5N/CeZrGd	4.33	15.80	10.42	5.06	64.39
5N/CeZrLa	4.41	15.77	10.41	5.05	64.36
5N/CeZrMg	3.92	16.40	10.82	5.25	63.61
5N/CeZrY	4.27	16.46	10.87	1.58	66.82

Table 3.2 : Elemental compositions of final Ni-based catalysts (nominal, mole fraction)

Catalyst (xNCZM)	Ni (% Mole Fraction)	Ce (% Mole Fraction)	Zr (% Mole Fraction)	M (% Mole Fraction)	O (% Mole Fraction)
5N/CeZrCa	4.93	48.40	20.79	4.43	21.45
5N/CeZrGd	4.93	42.97	18.46	13.63	19.99
5N/CeZrLa	4.93	42.17	18.11	15.14	19.64
5N/CeZrMg	4.93	49.31	21.18	2.74	21.84
5N/CeZrGd	4.93	42.97	18.46	13.63	19.99
5N/CeZrY	4.93	45.35	19.49	9.21	21.02

3.2. CATALYST CHARACTERIZATION

3.2.1. Specific Surface Area and Pore Size Distribution Analysis

The pore size distribution and specific BET surface area of all catalysts were measured by N_2 physisorption at liquid N_2 temperature applying a Micromeritics ASAP 2010 apparatus. Prior to analysis, all the samples were degassed for 4 hours at 180°C under a vacuum. Pore size distribution and average pore volume were measured using the desorption branch of the N_2-isotherm.

3.2.2. Metallic Surface Area and Metal Dispersion Measurements

The metal dispersion and metallic surface area in the catalyst samples were measured using hydrogen chemisorption at 35°C using a Micromeritics ASAP 2010 instrument. The catalyst samples were dried at 120°C prior to analysis and then reduced in situ in flowing H_2 gas (UHP grade) at 700°C for 2 hours (in order to have the reduced

state formed during the course of a typical catalytic run), followed by evacuation at 700°C for 1 hour before cooling down to 35°C. The metallic surface area (*S*Ni) was calculated with the help of the following expression:

$$SNi = 13.58 \times 10^{-20} NM\ (m^2/gcat.) \quad (3.1)$$

where N_M shows the number of hydrogen molecules adsorbed in the monolayer per gram of catalyst. By considering the surface occupied per atom of nickel as 6.79 $Å^2$ per atom (considering the density of nickel as 8.91 g/cm^3 and a face-centred cubic lattice), the above expression was derived and the adsorption stoichiometry was 2 surface nickel atoms per hydrogen molecule. The nickel dispersion (*D* %) was then estimated as the percentage of surface nickel atoms with respect to total nickel atoms in the catalysts (Iglesia and Boudart, 1983; Tsay and Chang, 2000).

3.2.3. TPR Measurements

The H_2-TPR measurements of support and catalyst sample were performed on a Quantachrome ChemBET 3000 unit equipped with a thermal conductivity detector (TCD). Prior to TPR measurements, a 50 mg sample was degassed at 180°C in an inert atmosphere (N_2 UHP grade) for 2 hours. The reducibility of the support and the catalyst prepared in the current study was studied using the TPR technique in a temperature range from ambient to 1050°C at a heating rate of 15°C/min using 5%H_2/balance N_2 as the reactive gas (flow rate = 45 mL/min). The total reactive gas consumed during TPR analysis was measured. The H_2 uptake as a function of TCD response vs. temperature was used to plot the TPR profile. For reference purposes, the TPR profiles of pristine NiO and CeO_2 were also studied.

3.2.4. X-ray Diffraction Studies

Powder XRD patterns were recorded on a Bruker Discover diffractometer using Ni-filtered Cu Kα (0.154056 nm) as the radiation source. The intensity data were collected over a 2θ range of 10 to 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 International Centre for Diffraction Data (ICDD) files.

3.2.5. UV-Vis diffuse reflectance analysis

The Shimadzu UV-probe (UV-2600/2700) instrument was used to obtain the information on the electronic structure of the support and catalyst(CZGd and 5N/CeZrGd).This investigation was done based on the reflection of light in the ultraviolet and visible regions (200-800 nm) for both CZGd and 5N/CeZrGd powders.

3.2.6. Thermogravimetry Analysis (TGA)

When a substance is subjected to a programmed heating and cooling, in general, it goes through physical, chemical, or mechanical changes. The gain or loss in weight of a catalyst as a function of temperature is measured by thermogravimetry. It is a very useful technique to measure the amount of carbon deposited on the catalyst during reforming processes. The measuring instrument is composed of an ultra-sensitive weighing device. The changes in the mass of the catalyst clearly imply evolution or uptake of carbon by the catalyst. All the TGA curves represented in this study were obtained on a Shimadzu TGA/Fc-60A instrument. The samples were heated from ambient temperature to 1050°C under 4.87%O_2/bal.N_2 flow at a flow rate of 20 mL/min and heating rate of 15°C/min.

3.3. AUTO-THERMAL REFORMING OF GLYCEROL

3.3.1. Catalytic Activity Evaluation

Activity evaluation studies were carried out in a packed bed tubular reactor (PBTR) (1/2" I.D.) made of Inconel 625(homemade reactor). The reactor was placed vertically inside a programmable tubular furnace that was heated (electrically [ZCP 386, Zesta Engineering, Ltd.). The catalyst bed temperature was measured by means of a sliding thermocouple (Type-K, AFEU0AQ180UK05X-2, Zesta Engineering, Ltd.) dipped inside the catalyst bed, the top of which was placed on the center of the bed. The sieved catalyst particles were between 710 µm and 850 µm in size. In each reaction, 250 mg of the catalyst particles were mixed with 7.6 grams of 0.78 mm sized α-Alumina beads ((0.8mm, Lot: M4919, Space: Z600100, Sasol) to achieve a catalyst bed height of 4.5 cm. Prior to each run, the catalyst bed was pre-reduced at 700°C for 2 hours while applying a reducing gas mixture of 5%H_2 balance N_2(Praxair, CGA 350) . The flow gas was regulated by a digital flow controller (DFC 26, 0-500 mL/min, Aalborg). The catalyst pre-treatment involved the partial reduction of nickel oxide (NiO) to metallic nickel species (Ni), and enough care was applied to avoid over-reduction and sintering of metallic 'Ni' species. All the gases were regulated through pre-calibrated mass flow controllers with a digital readout unit. The feed was composed of different mixtures of glycerol ($C_3H_8O_3$, 99.5+%, A.C.S. reagent: Sigma-Aldrich) and water ratios. Six, nine, and twelve times the stoichiometric amount of water was added to the feed in the current research so that enough steam could be provided to prevent coking but not so much as to increase the volume of the liquid product. The steam-to-glycerol ratios were 6, 9, and 12 and oxygen-to-glycerol ratios were 0.2, 0.5, and 0.8. The feed flow rate was regulated at

a rate of 150 µL/min through a motorized syringe pump(Kd Scientific, Holliston, MA, USA). A 100 mL stainless steel (SS) syringe was used to inject feed to the reactor. Pure N_2 was passed through the reactor at a flow rate of 100 mL/min. The activity evaluation tests were performed at five different temperatures, namely 700°C, 600°C, 550°C, 500°C, and 450°C. Specific operating criteria were employed in order to approach plug flow conditions and minimize back mixing and channelling. Consequently, the ratio of catalyst bed length to catalyst particle size (L/Dp) was 56.25, and the ratio of the inside diameter of the reactor to particle size (D/Dp) was 15.88. The product reformate stream coming from the reactor was passed through a double pipe heat exchanger where product mixture was passed inside the inner tube while water, at 16°C, was passed through the outer tube. This was followed by an ice-cooled metal separator (knockout trap) to condense the liquid product. At the end of process, the liquid product was collected. The product gases coming from the knockout trap were analyzed with an online GC/TCD (Agilent 6890 N, Canada.) equipped with Hayesep Q and Molecular Sieve A columns. The schematic of the experimental setup is shown in figure 3.1.

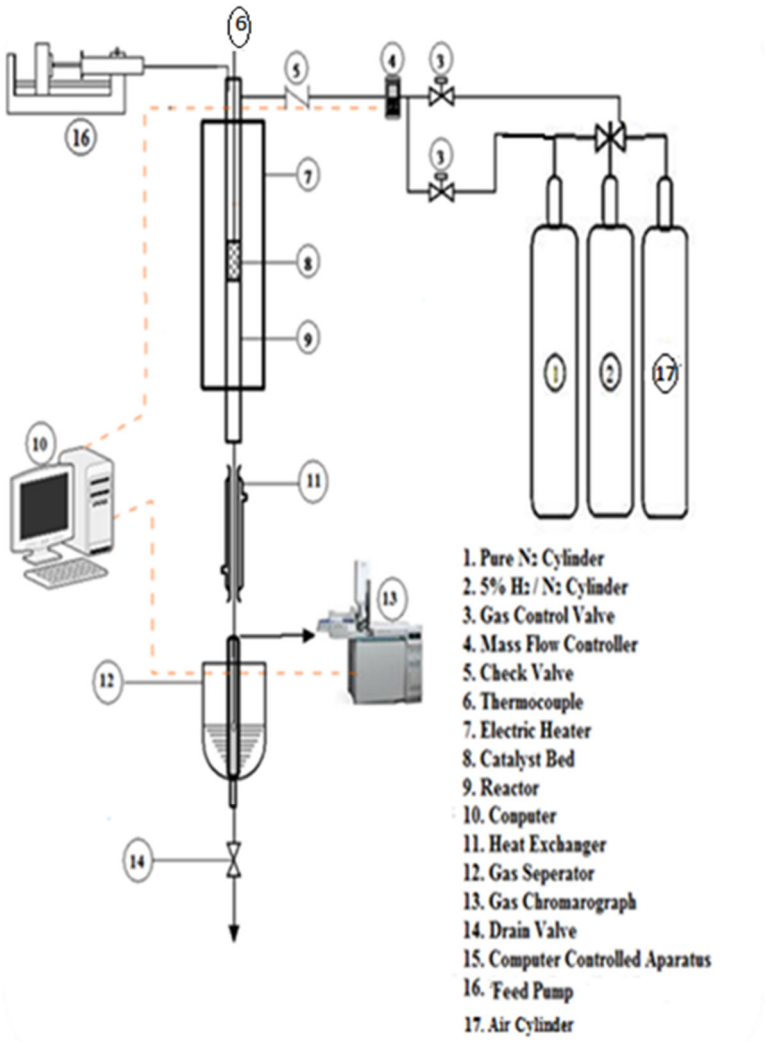

Figure 3.1 Schematic diagram of the experimental setup for Auto-thermal reforming of glycerol in a packed bed tubular reactor (PBTR).

3.3.2. Non-Catalytic Activity Evaluation

Non-catalytic (thermal) reactions were carried out in the same set-up used for the catalytic reactions. To maintain the same residence time for the thermal reactions as that of the catalytic reactions, a 4.5 cm packed bed height was maintained using 0.78 mm sized α-Alumina (inert material). The feed flow rate was regulated at 150 µL/min (steam-to-glycerol ratio=6) through the motorized syringe pump. Pure air was passed through the reactor at a flow rate of 45 mL/min to adjust the ratio of oxygen-to-glycerol as 0.5. The non-catalytic reactions were performed at six different temperatures, namely, 700°C, 600°C, 650°C, 550°C, 500°C, and 450°C. The gaseous products were separated from the reformate stream by the same method employed for the catalytic reaction and analyzed with the online GC/TCD (Agilent 6890 N) equipped with Hayesep Q and Molecular Sieve A columns.

3.3.3. Activity Evaluation Criteria

The stoichiometric balance reactions used in this work for the auto-thermal reforming of glycerol are shown in the following equations and the calculated ΔH_r are given in appendix B:

$$C_3H_8O_3 + 6H_2O + 0.5\ O_2 \leftrightarrow 2CO_2 + CO + 5H_2 + 5H_2O \quad (3.2)$$

$\Delta H_r\ (25^oC) = -77.8KJ/mol$

$$C_3H_8O_3 + 6H_2O + 0.8\ O_2 \leftrightarrow 2CO_2 + CO + 4.4H_2 + 5.6H_2O \quad (3.3)$$

$\Delta H_r\ (25°C) = -222.8KJ/mol$

$$C_3H_8O_3 + 6H_2O + 0.2\ O_2 \leftrightarrow 2CO_2 + CO + 4.6H_2 + 5.4H_2O \quad (3.4)$$

ΔH_r (25°C) = -174.52KJ/mol

$$C_3H_8O_3 + 9H_2O + 0.2\ O_2 \leftrightarrow 2CO_2 + CO + 5.6H_2 + 7.4H_2O \quad (3.5)$$

ΔH_r (25°C) = +67.28.8KJ/mol

$$C_3H_8O_3 + 9H_2O + 0.5\ O_2 \leftrightarrow 2CO_2 + CO + 5H_2 + 8H_2O \quad (3.6)$$

ΔH_r (25°C) = -77.8KJ/mol

$$C_3H_8O_3 + 9H_2O + 0.8\ O_2 \leftrightarrow 2CO_2 + CO + 4.4H_2 + 8.6\ H_2O \quad (3.7)$$

ΔH_r (25°C) = -222.8KJ/mol

$$C_3H_8O_3 + 12H_2O + 0.2\ O_2 \leftrightarrow 2CO_2 + CO + 5.6H_2 + 10.4H_2O \quad (3.8)$$

ΔH_r (25°C) = +67.28KJ/mol

$$C_3H_8O_3 + 12H_2O + 0.5\ O_2 \leftrightarrow 2CO_2 + CO + 5H_2 + 11H_2O \quad (3.9)$$

ΔH_r (25°C) = -77.8KJ/mol

$$C_3H_8O_3 + 12H_2O + 0.8\ O_2 \leftrightarrow 2CO_2 + CO + 4.4H_2 + 11.6H_2O \quad (3.10)$$

ΔH_r (25°C) = -228.8KJ/mol

The hydrogen yield is defined as follows:

$$\text{Hydrogen yield} = \frac{(\text{Molar flow rate of } H_2)_{\text{out}}}{(\text{Molar flow rate of } H_2)_{\text{Theoritical}}} \times 100\ [\%\text{mole}] \quad (3.11)$$

where the theoretical molar flow rate of hydrogen represents the moles of hydrogen expected from the feed at absolute glycerol conversion (100%) with no side reaction(s). The conversion is defined as follows:

$$\text{Conversion} = \frac{(\text{Molar flow rate of C atom in products})_{\text{out}}}{(\text{Molar flow rate of C atoms in feed})_{\text{in}}} \times 100\ [\%\text{mole}] \quad (3.12)$$

Here, the C-out components found in the gas products are CO_2, CO, and C_2H_6. However, the hydrogen selectivity is defined as follows:

$$\text{Hydrogen selectivity} = \frac{(\text{Molar flow rate of } H_2)_{out}}{\text{Conversion} \times (\text{Molar flow rate of } H_2)_{Theoritical}} \times 100 \ [\%\text{mole}] \quad (3.13)$$

Chapter 4 Results and Discussion

4.1. CATALYST CHARACTERIZATION

4.1.1. N_2-Physisorption

The specific surface area, specific pore volume, and pore size of all different CZM supports and 5N/CeZrM catalysts (where M = Ca, Gd, and, Mg) were measured using N_2 physisorption technique. The N_2 isotherms of the catalysts were obtained by physisorption technique. The isotherms belong to the 'Type IV' category, which is characteristic of mesoporous materials with strong adsorption affinity (IUPAC Recommendations, 1994; Rouquérol, 1999). The Type IV isotherms also exhibit characteristic hysteresis between the N_2 adsorption and N_2 desorption branches. IUPAC has classified hysteresis loops on the basis of their symmetry. With only the exception of CZY, the hysteresis loops observed in the current work belong to type H_2, indicating a complex mesoporous structure (IUPAC Recommendations, 1994; Rouquérol, 1999). Type H2 is associated with a more complex pore structure in which network effects are important. In the case of CZY, type H3 hysteresis was noted, which is characteristic of materials with pillared structure (plate-like), such as clays. The type H3 loop does not exhibit any limiting adsorption at high relative pressure, which is a clear indication of the absence of well-defined mesoporous structures.

The specific surface area, specific pore volume, and average pore diameter analysis of all the catalysts and supports employed in the present research are listed in

table 4.1. All support samples prepared by surfactant-assisted method with surfactant/metal (S/M) ratios of 0.5 exhibit reasonably high specific surface areas (> 116 m^2/g). The results clearly show that the use of surfactant for catalyst preparation significantly improved the specific surface area. The average pore diameter varied in the range of 60-95 Å (mesopore), and cumulative specific pore volume varied from 0.23 to 0.53 cc/g (cat).

The development of higher specific surface areas can be attributed to the technique, which was applied for catalyst preparation in this work (Terribile, 1998). The surface hydroxyl protons $[CeZrM(O^{-}–H^{+})_4]$ are exchanged with the cetyltrimethylammonium-cation $[(C_{16}H_{33})N^{+}(CH_3)_3]$ at pH > 11.0. Thus, the surfactant cations were incorporated into a hydrous ternary mixed hydroxide oxide gel. The interfacial energy is decreased because of this incorporation and eventually reduces the surface tension of water that exists in the hydrous support pores. As a result, it helps to reduce the degree of shrinkage and pore collapse that would occur in the hydrous support during drying and calcination, thereby imparting a high specific surface area to the sample. After impregnation of a nominal 5 wt. % Ni over the surface of supports, the specific surface areas and cumulative specific pore volume decreased. This is a common phenomenon observed in the case of supported catalysts when an active component is impregnated over its surface. This observed decrease is generally because of penetration of the dispersed nickel oxide into the pores of the support. The estimations of pore volume per unit surface area are also presented in table 4.1. The catalysts possessing higher pore volume per surface area (>19.8 x 10^{-10} m) demonstrated remarkably good performance. From table 4.1, it is clear that catalyst 5N/CeZrGd has the highest specific

BET surface area and specific pore volume. Catalyst 5N/CeZrCa shows the lowest value for specific BET surface area and specific pore volume.

Table 4.1 Specific BET Surface Area, Specific Pore Volume and Pore Size of the catalysts and supports obtained by N_2-Physisorption.

Catalyst (xN/CeZrM) Surfactant/Metal = 0.5	**Specific BET Surface Area (m^2/g)**	**Specific Pore Volume (cm^3/g)**	**Pore Size (A^0)**	**Pore V. / S. Area (A^0)**
5Ni/CeZrCa	116.4	0.23	60	19.8
5Ni/CeZrGd	197.4	0.53	94.71	26.8
5Ni/CeZrMg	154.65	0.45	73.52	29.1

4.1.2. H_2-Chemisorption and ICP-MS

H_2 chemisorption technique was used to measure the metallic surface area and metal dispersion of the active nickel component in the final prepared monometallic catalysts; the observed results are summarized in Table 4.2. It is important to once again highlight that all of these catalysts were prepared by applying a standard wet impregnation method. The actual mass fraction of Ni present in the three catalysts was determined by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) technique. The ICP-MS analyses results are also given in table 4.2. During a chemisorption experiment, initially, the sample is dried followed by reduction with hydrogen, evacuated, then cooled

to the analysis temperature (35°C), and finally evacuated before performing actual measurements. In a volumetric H_2 chemisorption measurement, known amounts of hydrogen are dosed and then adsorbed at different partial pressures, generating a chemisorption isotherm. In order to remove weakly adsorbed species (back-sorption or a dual isotherm method), the isothermal measurement is repeated after applying an evacuation step at the analysis temperature. The chemically bonded reactive gas is represented by the difference between the two isotherms and is employed to calculate the active metal surface area. This information can be combined with information on metal loading to estimate the metal dispersion. The relative measurement of chemically bound hydrogen was used to distinguish the catalyst tested in this study (table 4.2.). Ni dispersion and Ni surface area is a strong function of the catalyst formulation. The descending order of Ni dispersion was found to be 5N/CeZrCa > 5N/CeZrY> 5N/CeZrLa > 5N/CeZrGd > 5N/CeZrMg (S/M ratio 0.5).

Table 4.2 Ni Dispersion, Ni Surface Area (sample basis), Ni Surface Area (total Ni Basis) and Ni Mass Fraction (ICP-MS) of the catalysts obtained by H_2-Chemisorption.

Catalyst (5N/CeZrM)	**Ni Surface Area (m^2/g sample)**	**Ni Surface Area (m^2/g Ni)**	**Ni Dispersion (%)**	**Ni Mass Fraction (ICP-MS Result) (%)**
5N/CeZrCa	3.18	76.28	11.46	5.5
5N/CeZrGd	1.18	23.56	3.54	7.8
5N/CeZrLa	3.19	75.86	9.57	7.3
5N/CeZrMg	1.32	8.76	0.44	NM*
5N/CeZrY	3.19	63.73	9.57	NM*

*Not Measured

4.1.3. Temperature Programmed Reduction (TPR)

TPR technique was used to study the reducibility of the catalyst (5N/CeZrGd) as well as support (CeZrGd) prepared in the current study in an ambient to 920°C temperature range using 5%H_2/balance N_2 as the reactive gas. Pristine NiO indicates a sharp reduction peak at about 455°C, which can be ascribed to the transformation of Ni^{2+} to Ni^0 species (Sengupta, 2011). In the case of pristine CeO_2, the peak at the lower temperature (T_{max}= 577°C) was attributed to the reduction of the surface oxygen species, and the other broad peak at the higher temperature (T_{max} = 754°C) was because of the reduction of bulk oxygen species (Khan and Smirniotis, 2008). During the reduction process, the removal of lattice oxygen can occur with the help of higher mobility of the surface oxygen ions. Generally, in the low temperature region, the co-ordinately unsaturated surface capping oxygen ions can be easily removed. On the other hand, bulk oxygen needs to be transported to the surface prior to its reduction. Therefore, the bulk reduction occurs at a higher temperature compared to the surface reduction. After the complete reduction of the surface sites, the bulk reduction process starts to happen (Sengupta , 2011). Based on the literature, pristine ZrO_2 does not reveal any sign of reduction below 1000°C because of its refractory nature. As observed in the figure, the TPR profile of the pure support 'CeZrGd' exhibits broad H_2 consumption peaks in the temperature range of 600°C – 700°C and two other peaks in the temperature range of 800°C – 920°C. These peaks can be referred to the reduction of both surface and bulk oxygen anions. However, the corresponding Ni impregnated '5N/CeZrGd' catalyst showed an additional sharp peak in the temperature range 400°C – 500°C because of the reduction of active metal NiO to Ni. The T_{max} values observed for the reduction of NiO to

Ni in the 5N/CeZrGd catalyst is shown in figure 4.1.The Ni reducibility is calculated by applying the equation $1/T_{max}$, and reducibility is inversely proportional to the T_{max} value.

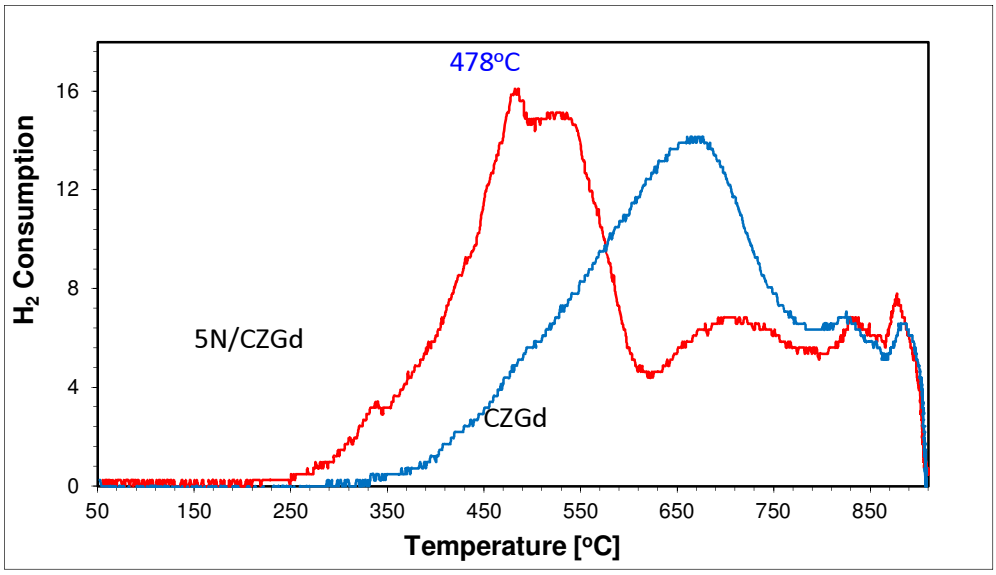

Figure 4.1 TPR peak profiling and assignment for CeZrGd support and 5N/CeZrGd catalyst.

4.1.4. UV-Vis Diffuse reflectance

UV-Vis Diffuse reflectance technique was used to study the structural features, oxygen exchange properties, and redox behaviour of CeZrGd and 5N/CeZrGd as shown in figures 4.2 and 4.3. As noted from the figure 4.2, in the case of the support, strong interaction were observed between the Zr^{4+} and Ce^{4+}/Ce^{+3} ion pairs, which increases the efficiency of redox processes at lower temperatures. ZrO_2 addition to the ceria improves the thermal stability and modifies the surface acid-base properties of exposed Ce^{4+} and Zr^{4+}. The UV-Vis reflectance spectroscopy can be applied to study all these surface properties. The DRS of CeZrGd sample shows two absorption peaks at 275 and 229 nm as expected for ZrO_2 sample. Another peak was seen at 679 nm that is attributed to the low coordination of surface charge transition between: $Ce^{3+} \rightarrow Ce^{4+}$ (Rao and Sahu

2001.From 5N/CeZrGd catalyst in figure 4.3, it is found that the observed asymmetric UV band at 240 nm and a shoulder around 310 nm indicating its origin from $O^{2-} \rightarrow Ni^{2+}$ charge transitions. The shoulder is due to $O^{2-} \rightarrow Ce^{4+/3+}/Zr^{4+}$ transitions. The weak d–d bands of octahedrally coordinated Ni^{2+} were also observed at 725, and 653 nm (Srinivas et al., 2003). All these findings imply that Ni^{2+} is well dispersed over the surface of the CeZrGd support in the final catalyst.

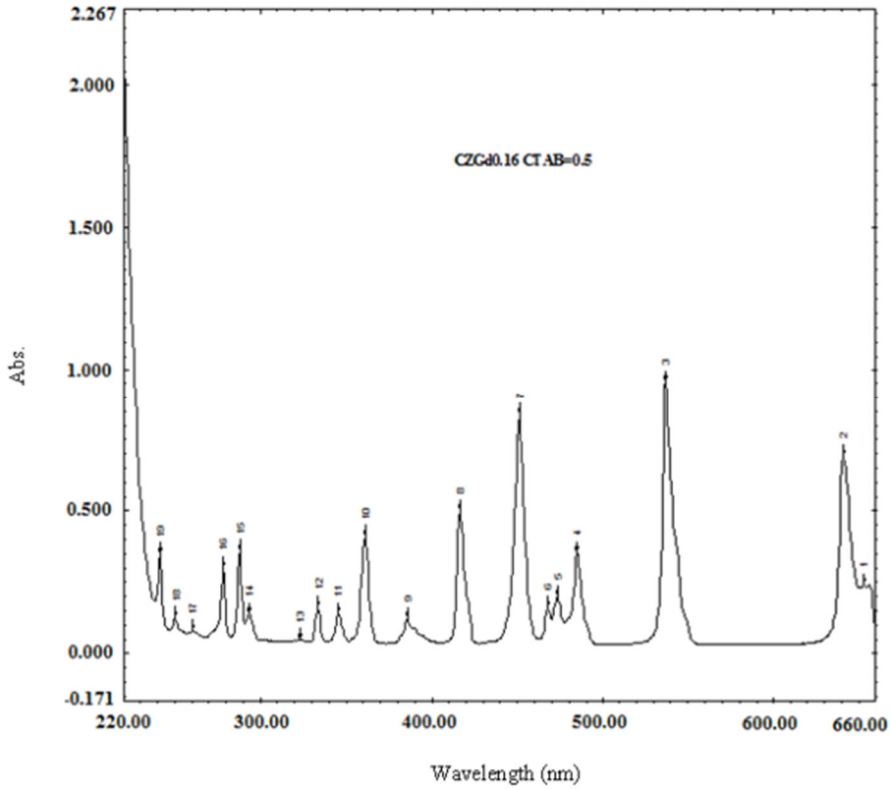

Figure 4.2 UV-diffuse reflectance spectra of CeZrGd

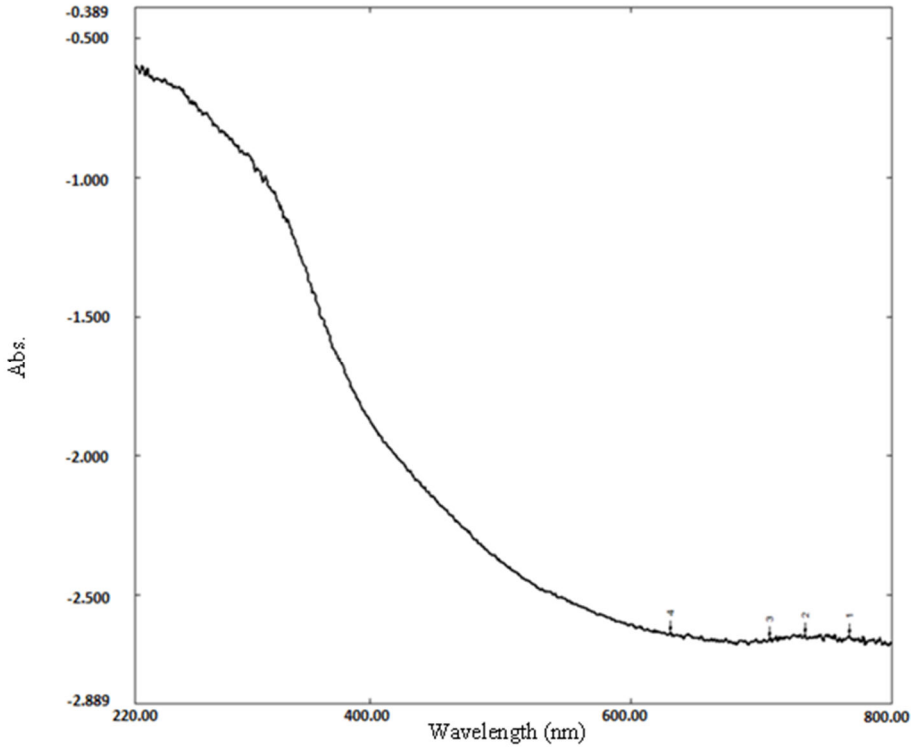

Figure 4.3 UV-diffuse reflectance spectra of 5N/CeZrGd

4.1.5. X-ray diffraction (XRD)

Powder XRD patterns were investigated on a Bruker Discover diffractometer applying nickel-filtered Cu Kα (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 1s per point. Crystalline phases were identified and confirmed by comparison with the reference data from ICDD files. The XRD patterns are shown in figures 4.4 to 4.7. The diffraction patterns of both supports and catalysts exhibit diffraction patterns exactly the same as that of pristine ceria; therefore, it confirms the existence of a single-phase cubic fluorite-type structure. The XRD profile of pristine NiO was also used to identify the existence or absence of crystalline NiO in the nickel-impregnated catalyst samples for

5N/CeZrM (where M is: Mg, Ca, Gd, La). It also confirmed the existence of crystalline NiO phase in all the samples.

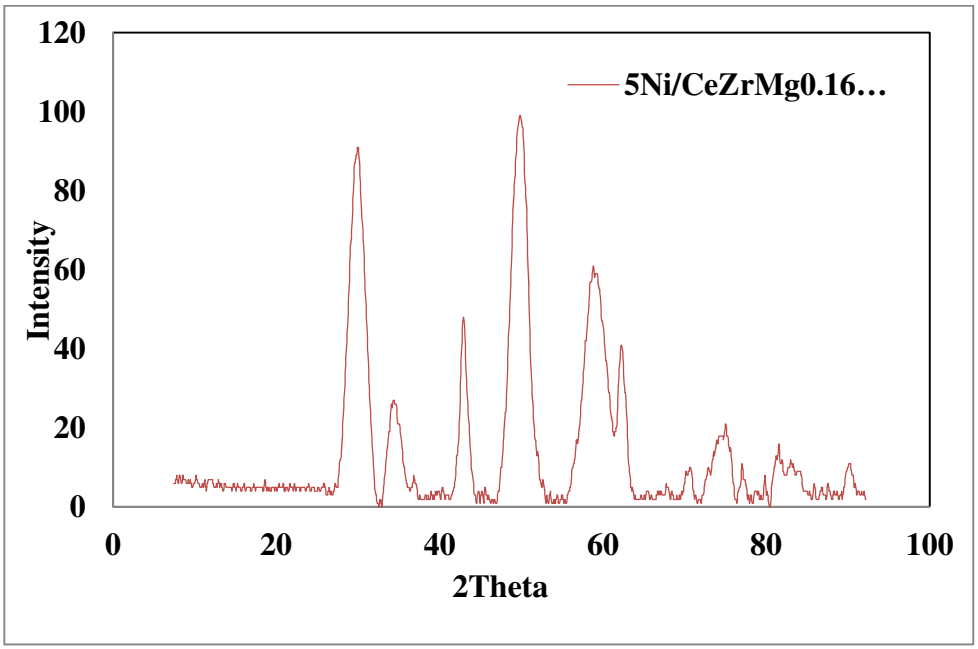

Figure 4.4 : XRD pattern of (5N/CeZrMg)

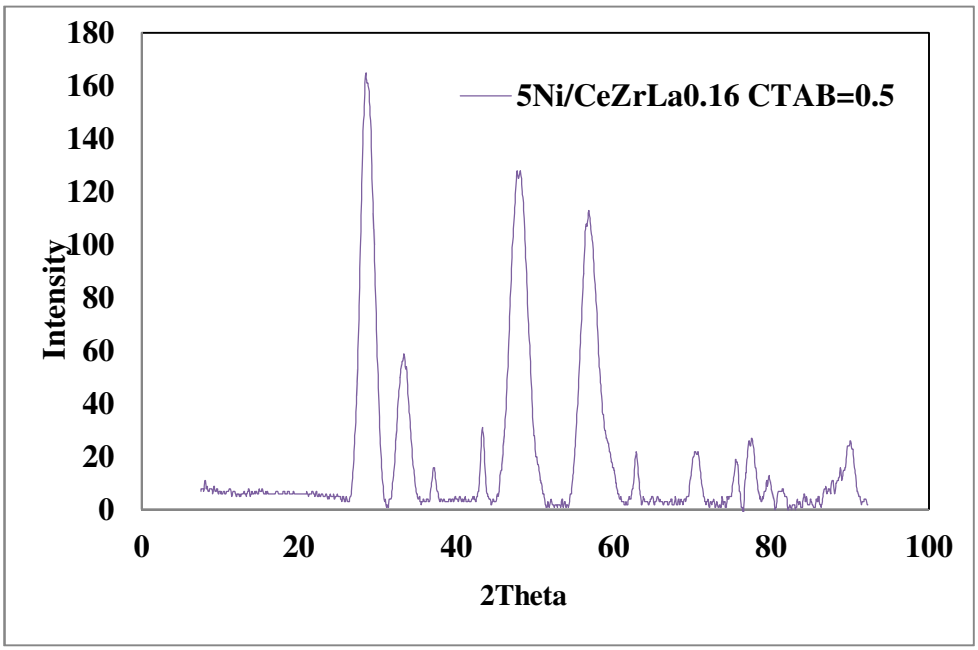

Figure 4.5 : XRD pattern of (5N/CeZrLa)

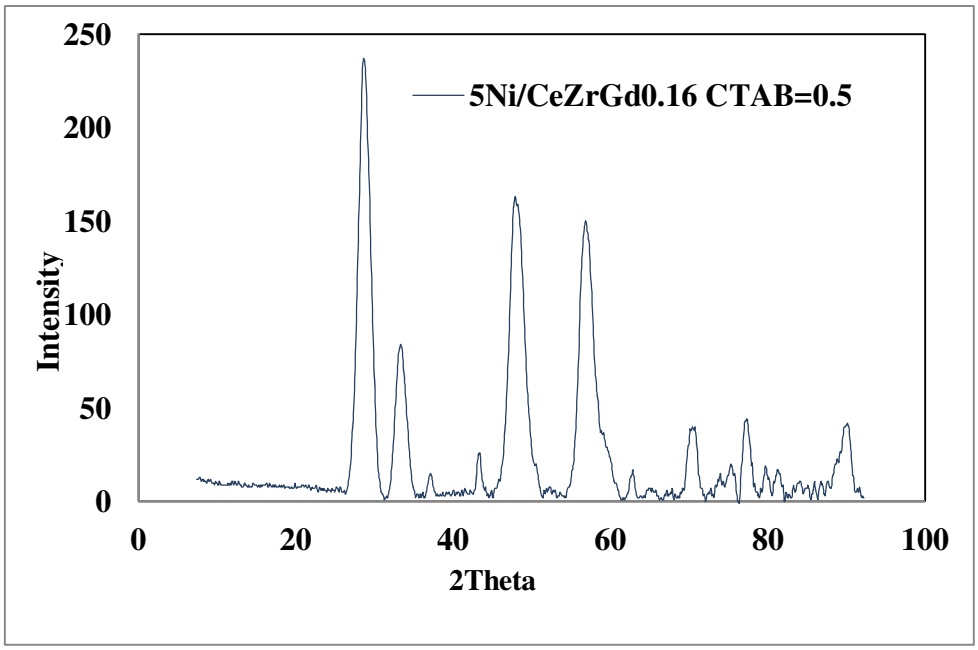

Figure 4.6 : XRD pattern of (5N/CeZrGd)

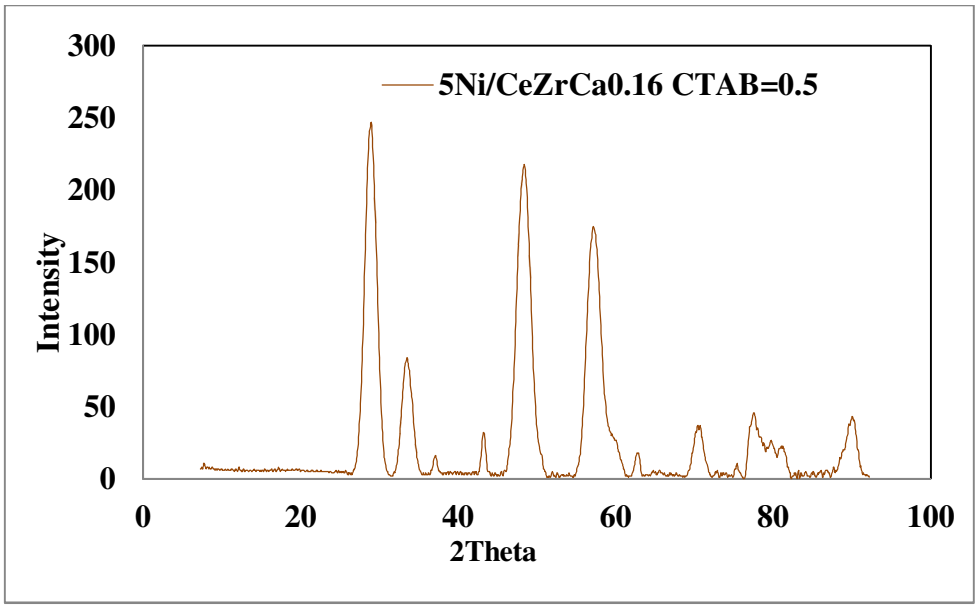

Figure 4.7 XRD pattern of (5N/CeZrCa)

4.2. CATALYTIC ACTIVITY EVALUATION

4.2.1. Catalyst Screening

The catalytic activities of the 5N/CeZrM (M = Ca, Gd, La, Mg, Y) catalysts were investigated and compared under identical operating conditions in a PBTR. Initially, the activity was evaluated at 500°C, and the corresponding results are presented in figure 4.8. As noted from figure 4.9, all the catalysts exhibit almost steady activity in terms of glycerol conversion and H_2 selectivity. Among the five catalysts tested, 5N/CeZrGd exhibits the highest value for glycerol conversion (48 mol. %) and H_2 selectivity (58 mol. %) while, 5N/CeZrMg shows the lowest (32 mol. %) conversion and H_2 selectivity (33 mol.%).

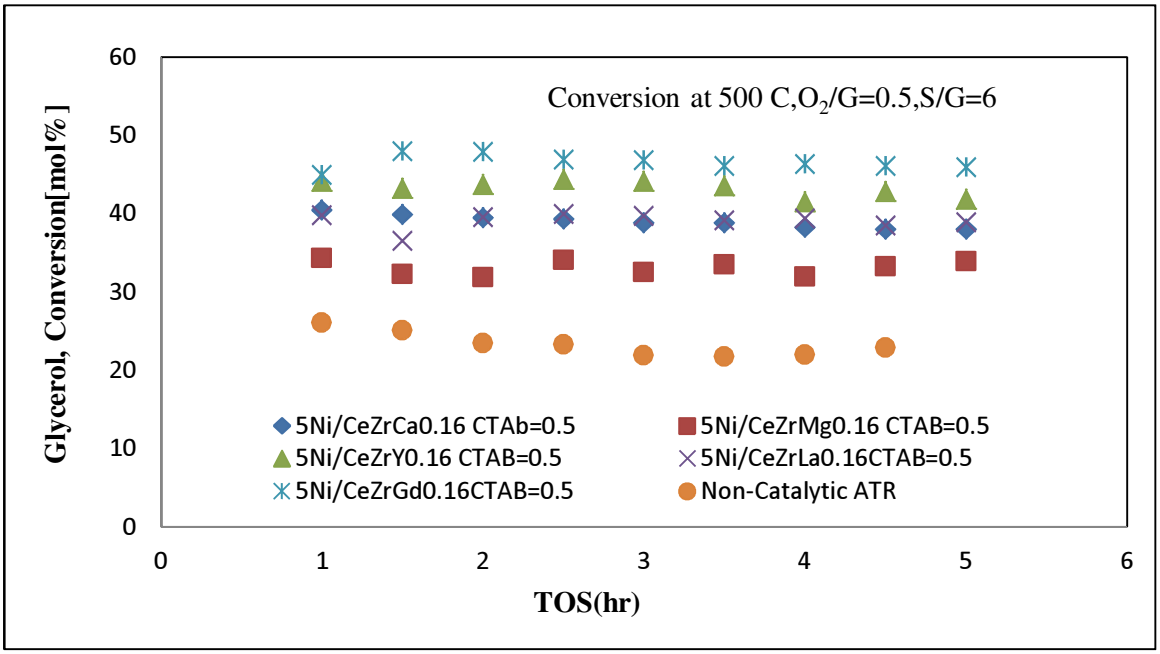

Figure 4.8 : Performance evaluation of auto-thermal reforming of glycerol over 5N/CeZrM (M = Ca, Mg, La, Gd, Y) catalysts at 500°C reaction temperature, Glycerol Conversion

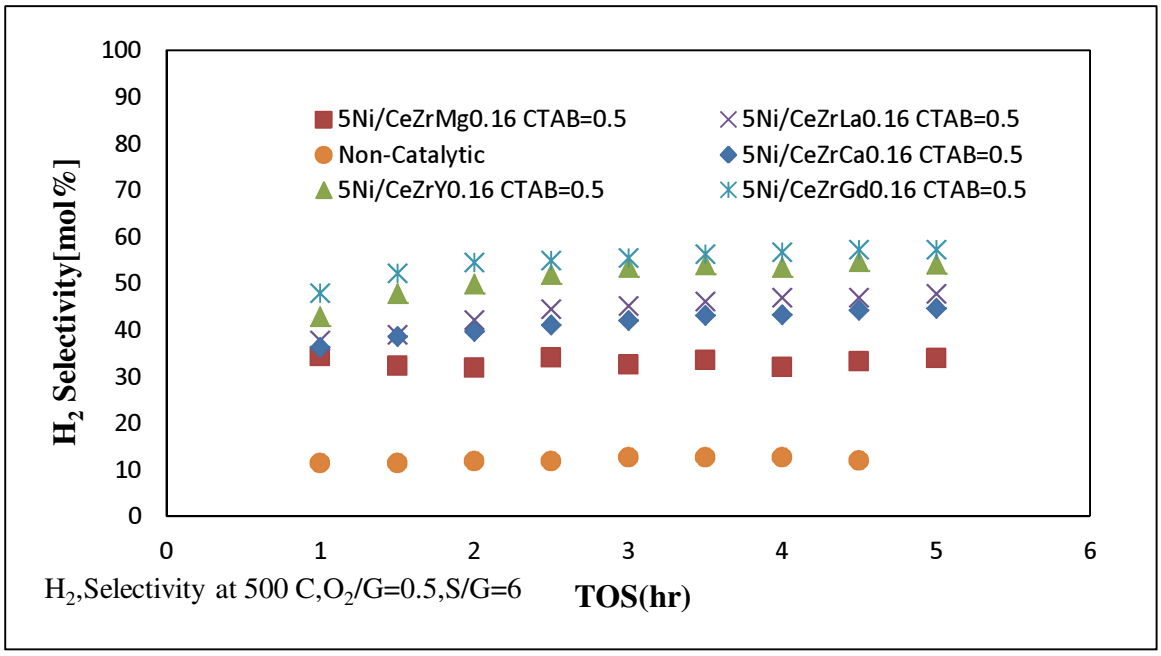

Figure 4.9 Performance evaluation of auto-thermal reforming of glycerol over 5N/CeZrM (M = Ca, Mg, La, Gd, Y) catalysts at 500°C reaction temperature, H_2 Selectivity.

4.2.2. Identification of Thermal and Catalytic Effect

In order to demonstrate the significant role played by the catalysts in the auto-thermal reforming of glycerol and to distinguish the thermal effect from the catalytic effect, a systematic study was carried out in which the auto-thermal reforming of the glycerol was conducted at different temperatures in the absence of a catalyst. The temperatures employed were 700°C, 600°C, 550°C, 500°C, and 450°C. In these set of experiments, except for the absence of catalyst, rest of the operating conditions and process parameters remained same. The results obtained are given in figures 4.10 and 4.11. The glycerol conversion increased with increasing temperature because it can generate heat for the endothermic nature of the steam reforming, which is part of auto-thermal process. However, the H_2 selectivity showed close values at different temperatures. It is important to mention, here, that, no pressure build up was noted while a catalyst was employed and the H_2 selectivity increased with temperature. Figures 4.12 to 4.15 represent the true thermal effects and true catalytic effects, separately. The results obtained for auto-thermal reforming of glycerol feed without and with catalyst 5N/CeZrGd are shown, respectively. From the figure 4.14, it is observed that at 600°C, the magnitude of catalytic effect is at maximum compared to the other temperatures (i.e., 500°C, 550°C, and 700°C). At 600°C, an average glycerol conversion of ~ 82 mol.% was recorded when employing 5N/CeZrGd catalyst; without it an average glycerol conversion of ~30 mol.% was noted, which implies that the catalyst enhanced the glycerol conversion by 2.8 fold. At 700°C, 600°C, 500°C, and 450°C, the catalyst improved the conversions by 1.6, 2.8, 2.2, and 1.8 folds, respectively. By magnitude, catalyst 5N/CeZrGd contributed to an improvement in conversion values from the corresponding

non-catalytic reactions by 15 mol.%, 25 mol.%, 55 mol.%, and 35 mol.% at 450°C, 500°C, 600°C, and 700°C, respectively. Based on the observed results, it can be concluded that 600°C operating temperature is optimal for obtaining high feed conversions and also to make maximal utilization of the catalyst's effect.

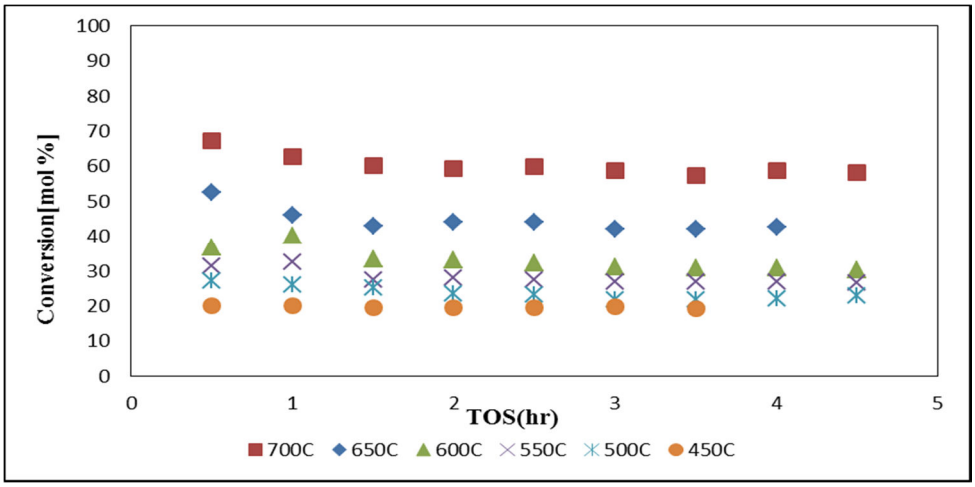

Figure 4.10 Performance evaluation of auto-thermal reforming of glycerol without catalyst at different reaction temperature Conversion

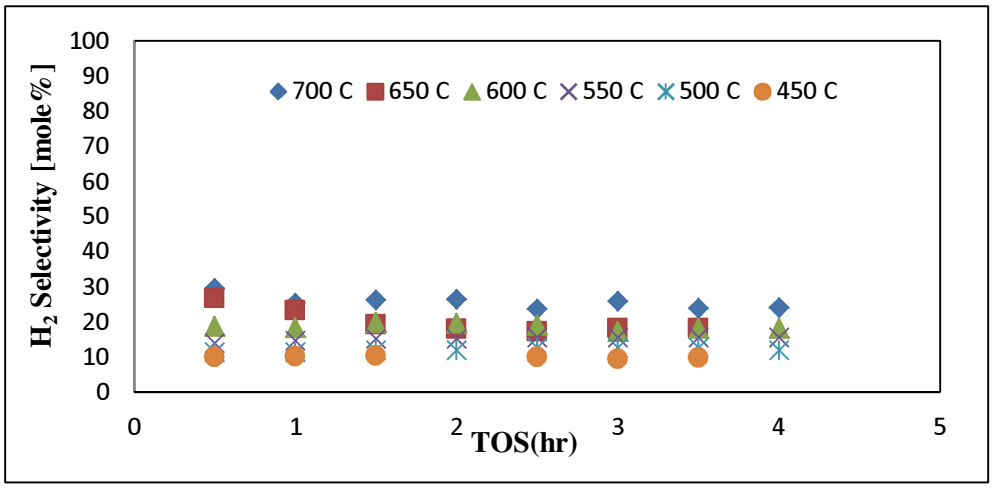

Figure 4.11 Performance evaluation of auto-thermal reforming of glycerol without catalyst at different reaction temperature H_2 Selectivity.

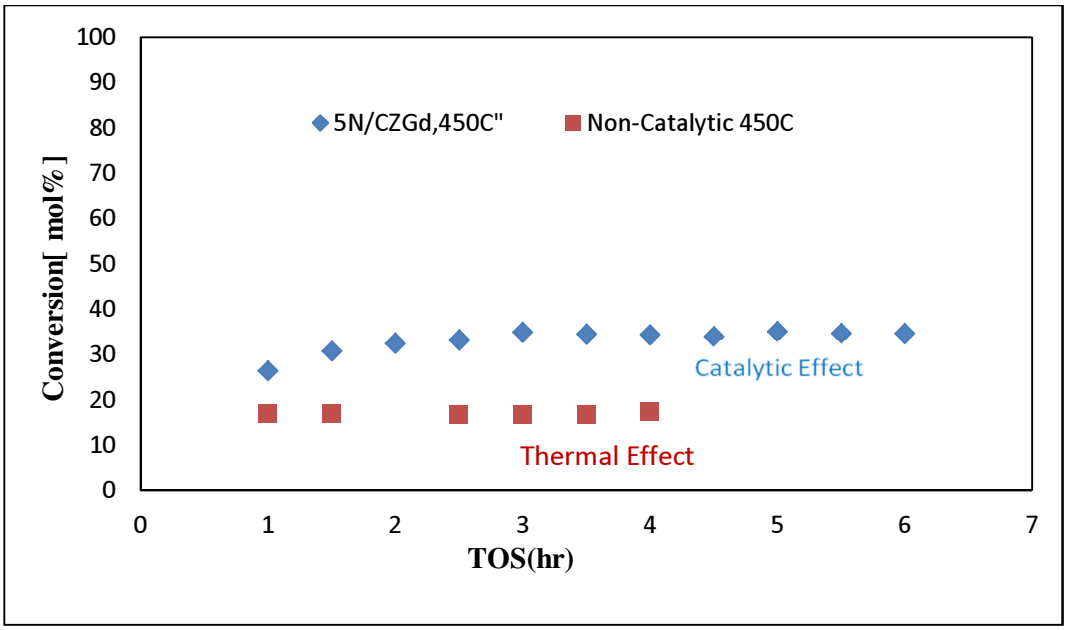

Figure 4.12 Identification of catalytic and thermal effect at different reaction temperatures for catalyst 5N/CeZrGd 450°C

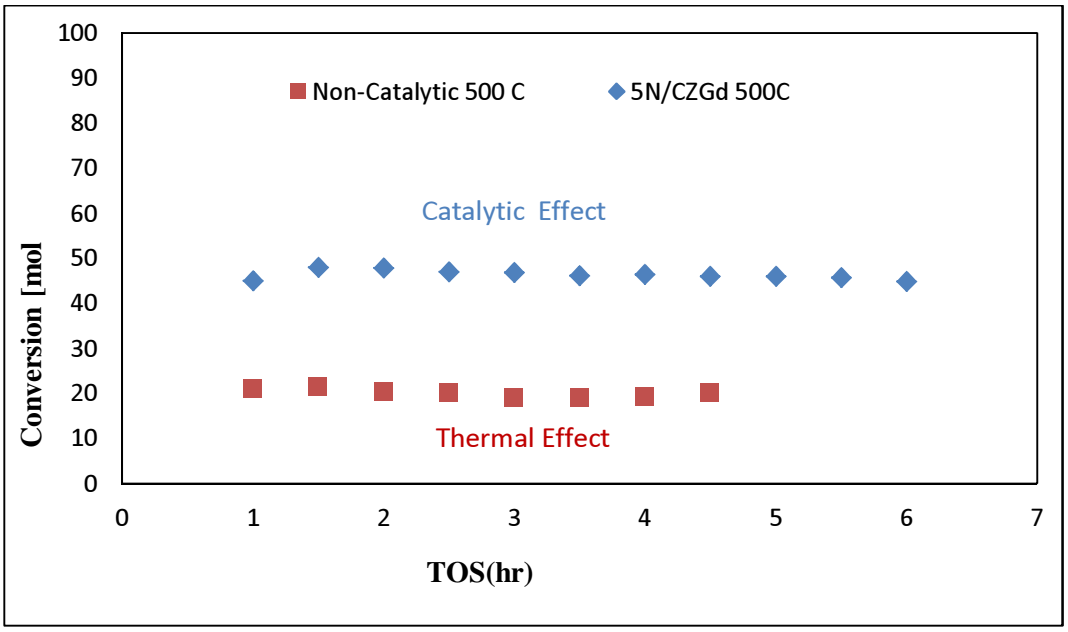

Figure 4.13 Identification of catalytic and thermal effect at different reaction temperatures for catalyst 5N/CeZrGd 500°C

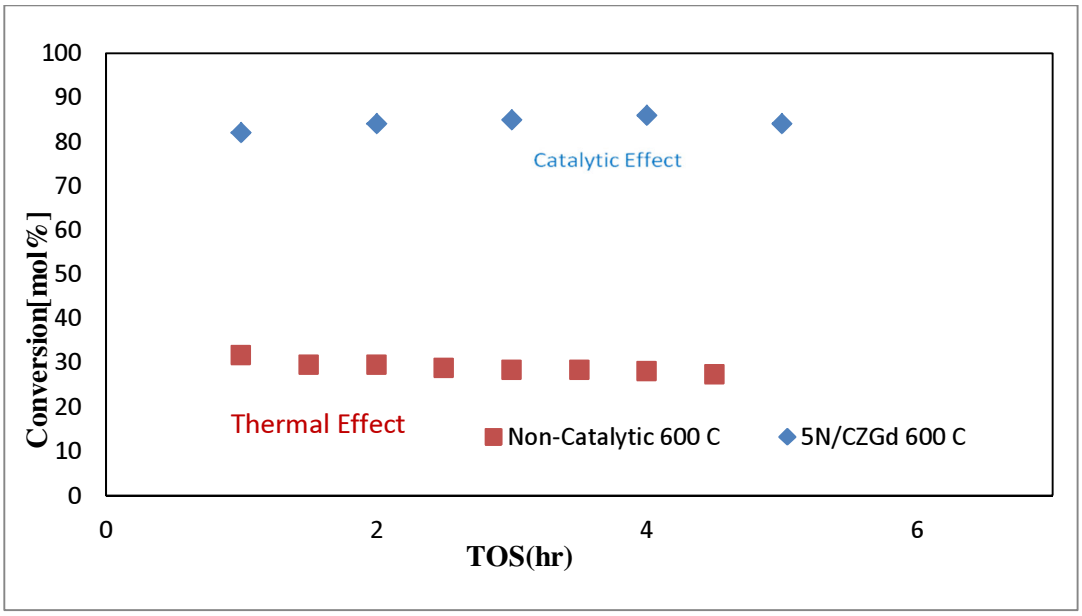

Figure 4.14 : Identification of catalytic and thermal effect at different reaction temperatures for catalyst 5N/CeZrGd 600°C

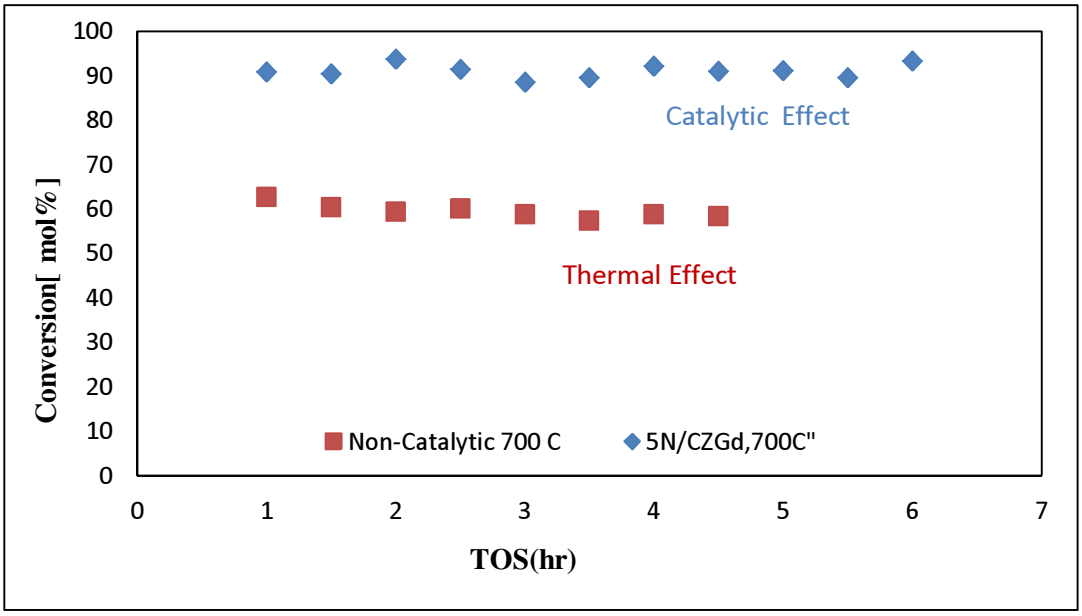

Figure 4.15 : Identification of catalytic and thermal effect at different reaction temperatures for catalyst 5N/CeZrGd 700°C.

4.2.3. Effect of Reaction Temperature on the Product Gas Distribution

4.2.3.1. Non-Catalytic Reaction

The effect of reaction temperature on the product gas composition for non-catalytic auto-thermal reaction is presented in figure 4.16. As observed from figure 4.16, the H_2 concentration of the reformate gas increased with an increase in reaction temperature from 450°C to 700°C. From the CO_2 concentration profiles at various reaction temperatures, it can be noted that the concentration of CO_2 in the reformate gas gradually decreased with an increase in the reaction temperature to reach its minimum value at 700°C. On the other hand, increasing the reaction temperature from 450°C to 500°C resulted in a decrease in the CO concentration, as shown in figure 4.5. The above variation in the relative composition of CO, CO_2, and H_2 can be explained by the occurrence of water gas shift (WGS) and reverse water gas shift (RWGS) reaction equilibria. As observed from figure 4.16, the H_2 concentration of the reformate gas increases with an increase in the reaction temperature. Most importantly, increasing the reaction temperature from 450°C to 500°C results in a 2 mol % increase in the H_2 concentration in the reformate effluent gas; however, a further increase in the operating temperature from 500°C to 700°C does enhance the hydrogen concentration form 20% mol to 32%. From the CO_2 concentration at various reaction temperatures, it can be noted that the concentration of CO_2 in the reformate gas sharply decreased with an increase of the reaction temperature. Increasing the reaction temperature from 450°C to 700°C results in a 35 mol % decrease in the CO_2 concentration; however, the CO concentrations gradually increased with the reaction temperature. At lower temperatures, CO is

converted to CO_2 by a WGS reaction ($CO + H_2O \rightarrow CO_2 + H_2$), and additional H_2 is produced.

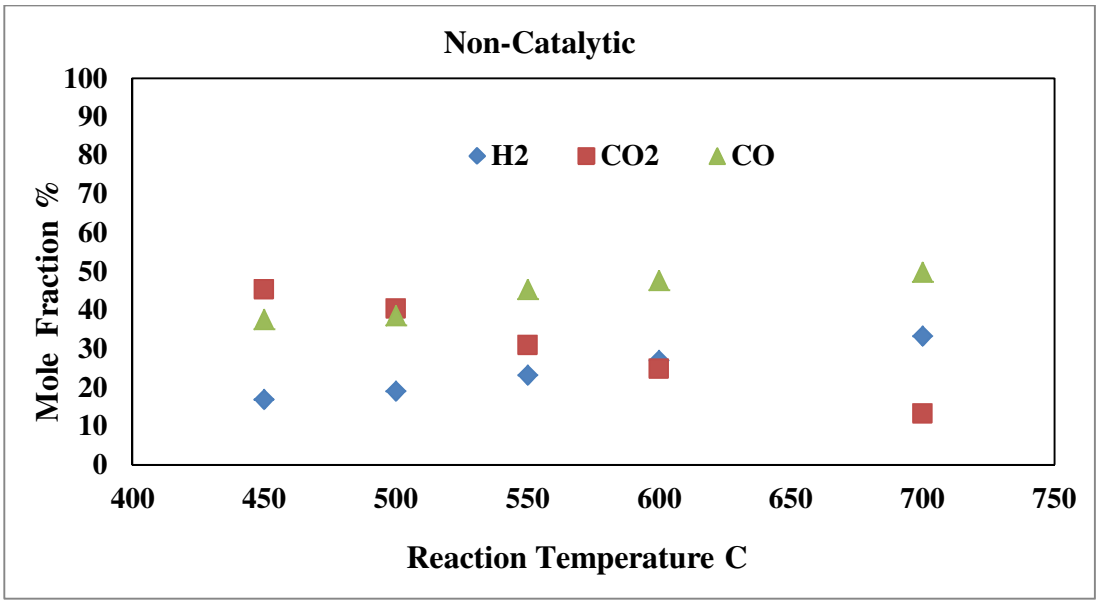

Figure 4.16 Influence of reaction temperature on reformate gas composition for non-catalytic reaction for H_2, CO_2, and CO: Product Distribution vs. Reaction Temperature plot.

However, the WGS reaction has an exothermic nature, and with the increase of the reaction temperature, the RWGS reaction occurs, resulting in a gradual increase in CO and a gradual decrease in CO_2 concentrations.

4.2.3.2. Catalytic Reaction

The effect of reaction temperature on the reformate gas composition for catalytic ATR of glycerol over 5N/CeZrGd catalyst is shown in figure 4.17. As observed from figure 4.17, the H_2 concentration of the reformate gas increases with increase in reaction temperature. From the CO_2 concentration at different reaction temperatures, it can noted that the concentration of CO_2 in the reformate gas gradually decreased, while the CO concentrations gradually increased with the reaction temperature. In the ATR reaction, at

lower temperatures, CO is converted to CO_2 by a water gas shift (WGS) reaction ($CO + H_2O \rightarrow CO_2 + H_2$) and additional H_2 is produced. However, as WGS is exothermic in nature, with the increase of reaction temperature, the reverse water gas shift reaction (RWGS) happens, causing a gradual increase in CO and a gradual decrease in CO_2. However, the increase in H_2 concentration due to the increase in reaction rate with the temperature increase and the decrease in H_2 concentration due to the RWGS reaction with the increase in reaction temperature counter-balance each other to keep the H_2 concentration almost constant from 550°C to 700°C. It is to be noted that in the case of catalytic reaction, the percentage of CO produced at higher temperature is comparatively less varied than that of the corresponding non-catalytic reaction, which implies that the 5N/CeZrGd catalyst influences the water gas shift (WGS) reaction equilibria.

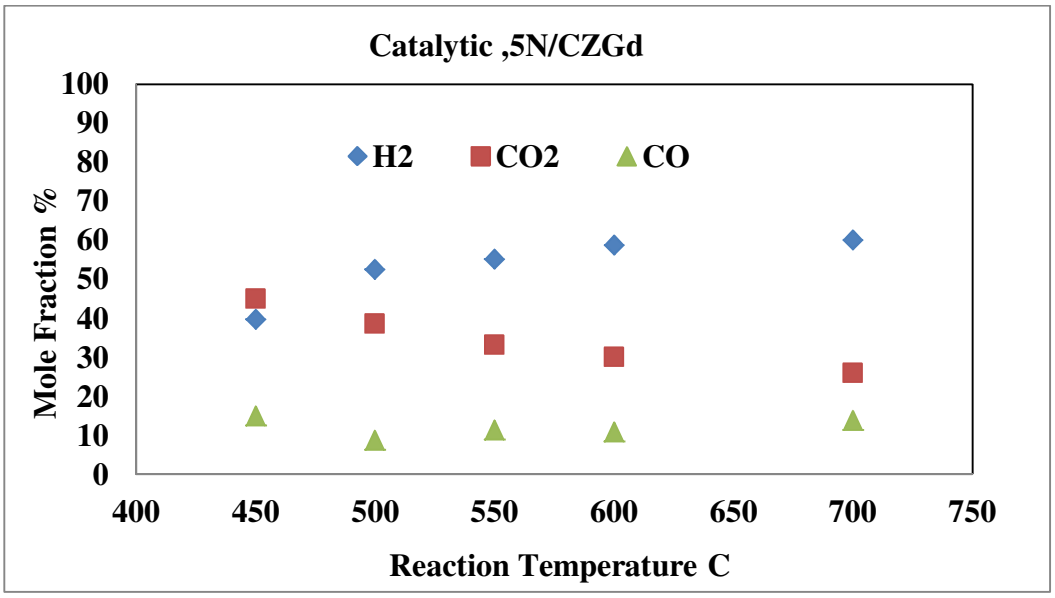

Figure 4.17 Influence of reaction temperature on reformate gas composition for catalytic reaction with 5N/CeZrGd for H_2, CO_2, and CO product distribution vs. reaction temperature

4.2.4. Effect of Reaction Temperature on Conversion and Selectivity

4.2.4.1. Non-Catalytic Reaction

The influence of operating temperature on the non-catalytic auto-thermal reforming of glycerol was investigated by varying the reaction temperature from 450°C to 700°C, and the corresponding results are compared in figures 4.18 and 4.19. The results represent the gradual increase in glycerol conversion with the increase in operating temperature, which is expected on account of the endothermic nature of the steam reforming reaction in the auto-thermal reforming process. Furthermore, the H_2 selectivity increases with the increase in reaction temperature.

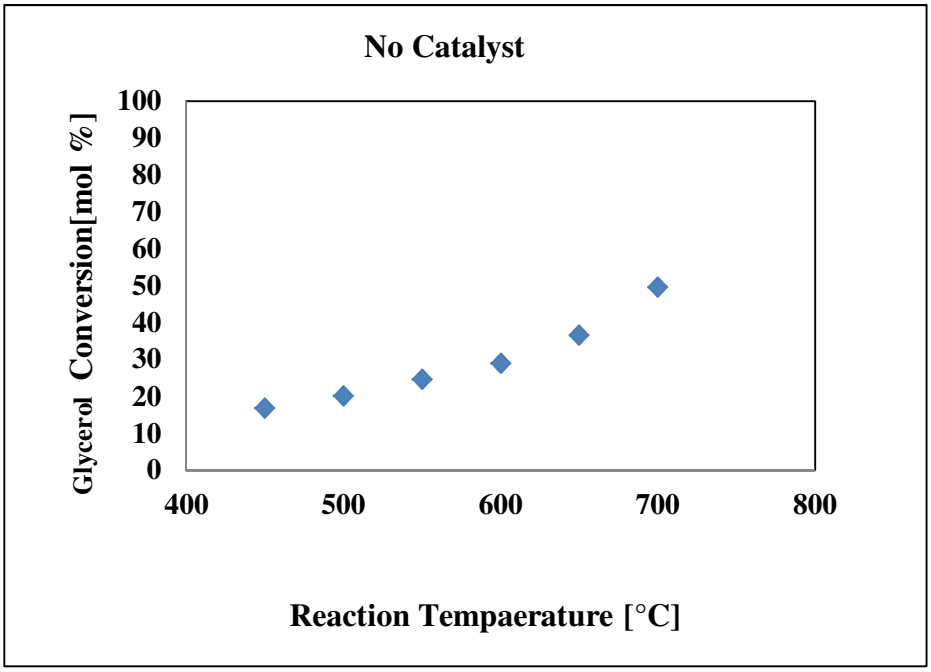

Figure 4.18 Effect of reaction temperature on glycerol conversion

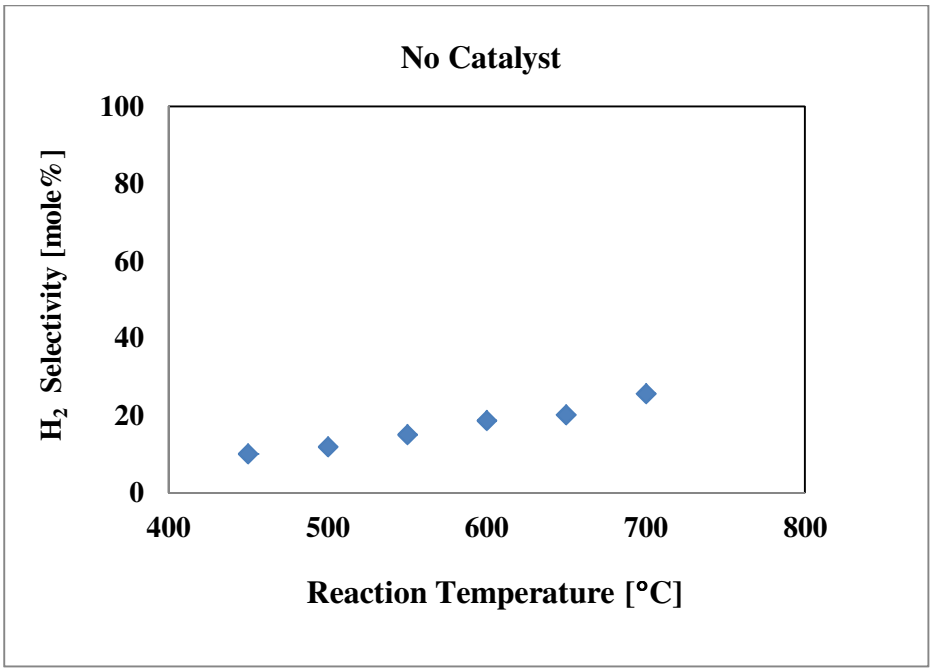

Figure 4.19 Effect of reaction temperature on H_2 selectivity for non-catalytic auto-thermal reforming of glycerol.

4.2.4.2. Catalytic Reaction

The influence of operating temperature on the catalytic performance over catalyst 5N/CeZrGd for auto-thermal reforming of glycerol was investigated by varying the temperature from 450°C to 700°C, and the corresponding results are compared in figure 4.20 and figure 4.21. The figures reveal the improvement in catalytic activity with increase in operating temperature, which is clearly expected on account of the endothermic nature of the steam reforming that, occurs in an auto-thermal reforming process. The performance of the catalyst 5N/CeZrGd was found to be stable at various temperatures applied in the current work. Moreover, similar to the non-catalytic auto-thermal reforming of glycerol, the H_2 selectivity increases with increasing temperature. The possible reason for this increase is that the water gas shift reaction is affected by

catalyst even at high temperatures, which is corroborated by the finding of Kumar and Idem (2007). Kumar and Idem employed 3%Ni.5%Cu over Ce-Zr-based mixed oxide support prepared by the same route as in this work and obtained 71% CO conversion even at 700°C and found that, CO conversion increases with an increase in temperature, and as a result, it can explain the increase in selectivity with increase in temperature. On the other hand, as the water-gas shift reaction has a slightly exothermic nature, still, there are other thermodynamic limitations in the reaction, which makes the selectivity vs. temperature curve flat at higher temperatures.

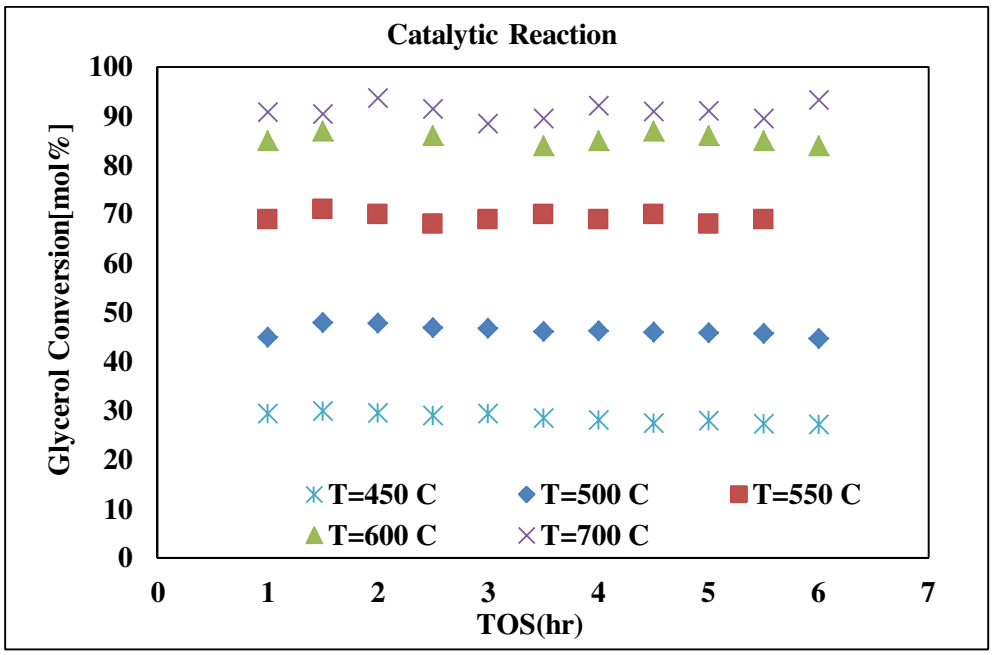

Figure 4.20 Effect of reaction temperature on glycerol conversion for catalyst 5N/CeZrGd, Conversion plots at different reaction temperature

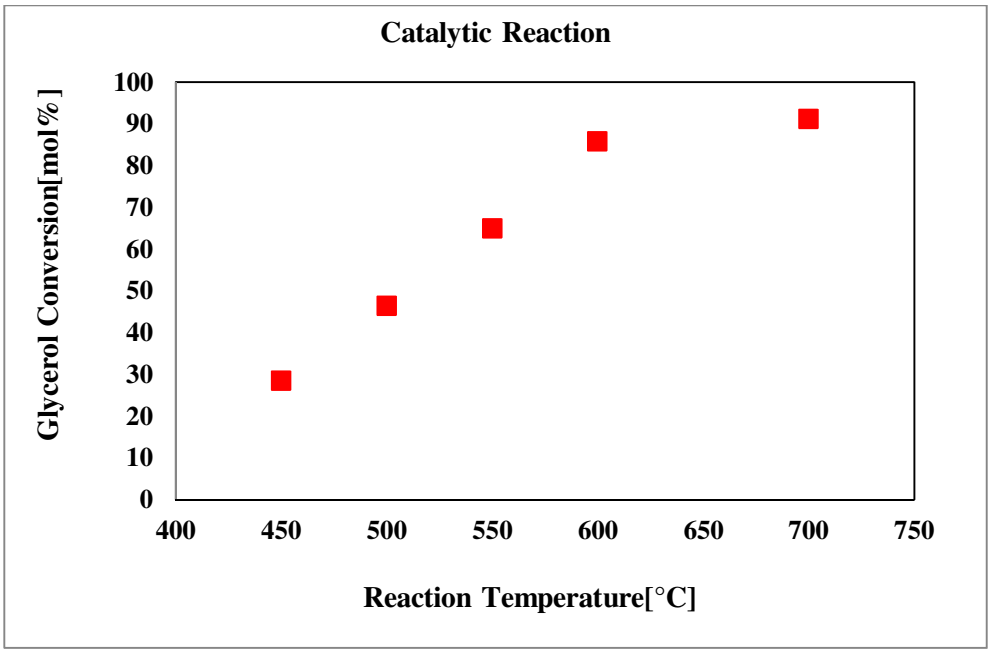

Figure 4.21 Effect of reaction temperature on glycerol conversion for catalyst 5N/CeZrGd, Conversion vs. Reaction Temperature plot.

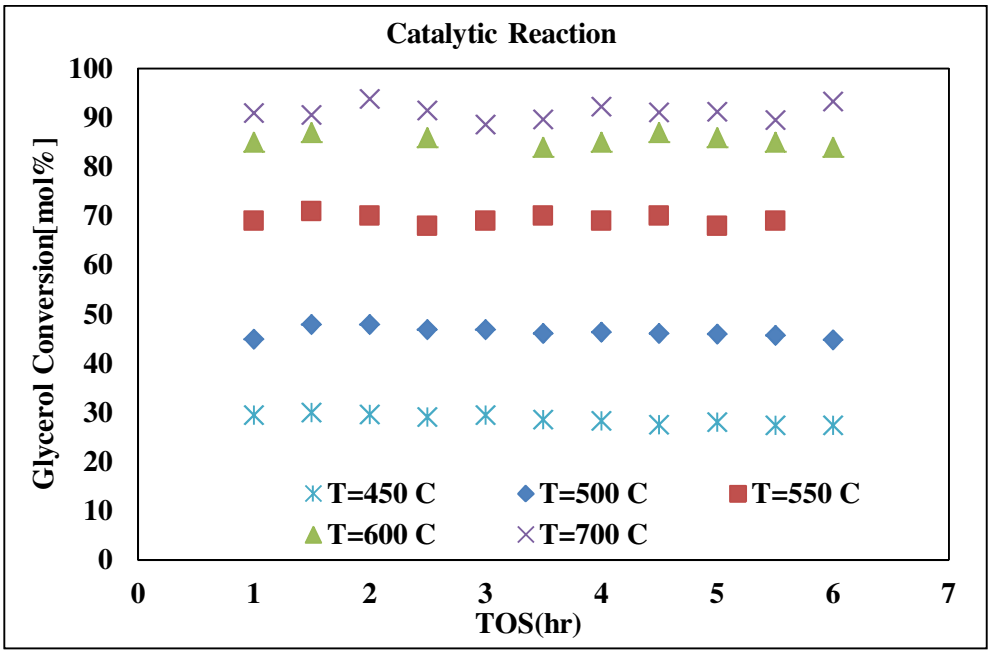

Figure 4.22 Effect of reaction temperature on glycerol conversion for catalyst 5N/CeZrGd, Conversion plots at different reaction temperature

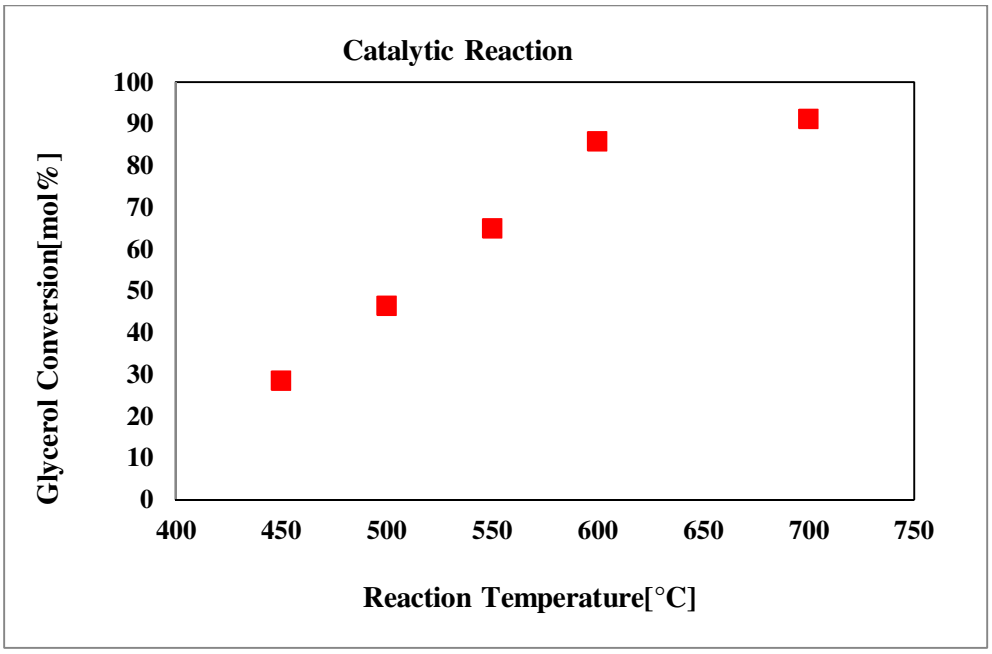

Figure 4.23 Effect of reaction temperature on glycerol conversion for catalyst 5N/CeZrGd Conversion vs. Reaction Temperature plot.

4.2.5. Effect of Promoter Element on the Gas Product Distribution

The impact of promoter elements (Ca, Gd, La, Mg, and Y) on the gas product distribution for auto-thermal reforming of glycerol was studied at 500°C as well as 600°C for three promoter elements including Ca, Y, and Gd. The corresponding results are shown in figures 4.24 and 4.25. From figure 4.24, it is clear that, at 500°C, there were noticeable differences in the reformate gas compositions for different promoter elements. At that temperature, Gd revealed the highest H_2 and CO_2 molar percentage, and CO showed the lowest value. The reverse pattern was found for Mg, which showed the lowest H_2 and CO_2 molar percentages and highest CO value. The molar percentage of the three major reformates gas components, H_2, CO_2, and CO, are almost identical for all the promoter elements at 600°C because of the high thermal and catalytic effect.

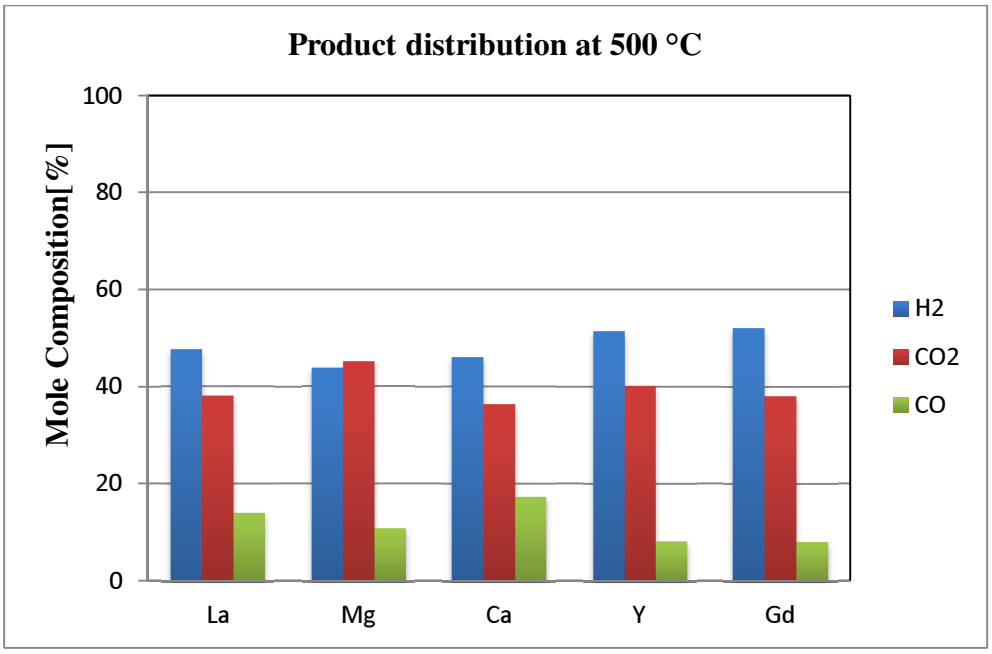

Figure 4.24 Effect of promoter element on product distribution for auto-thermal reforming of glycerol at 500°C

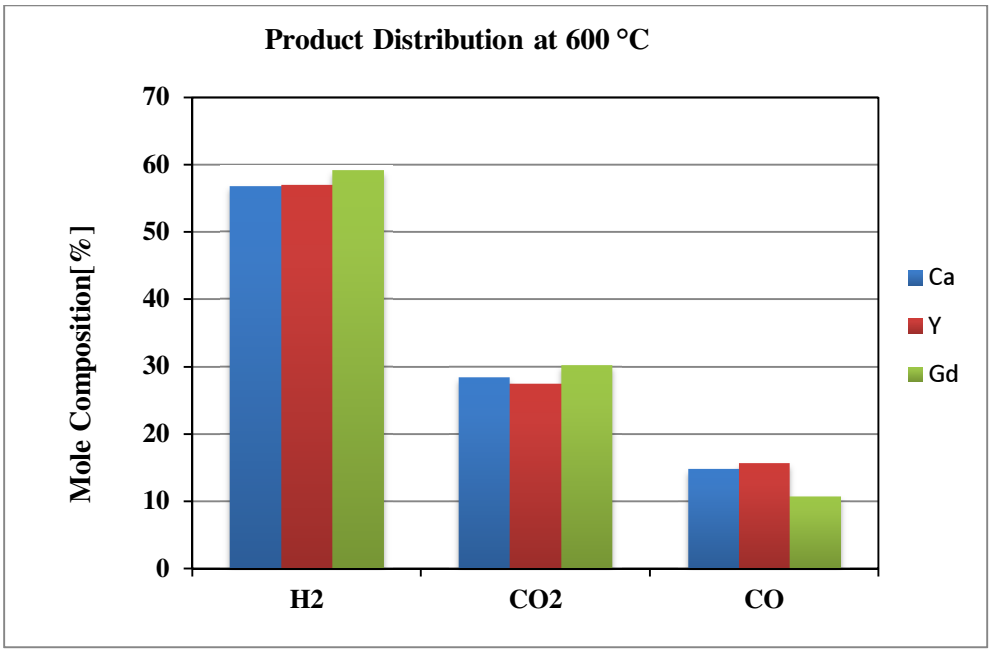

Figure 4.25 Effect of promoter element on product distribution for auto-thermal reforming of glycerol at 600°C.

4.2.6. Effect of Surfactant-to-Metal (S/M) Ratio on Catalytic Activity

Two different 5N/CeZrM (Mg, Ca) catalysts were tested to investigate the effect of surfactant-to-metal ratio at 500°C with two different S/M ratios, namely 0.5 and 1.25 for auto-thermal reforming of glycerol. All the catalysts showed steady performance with stable conversion, as seen in figure 4.26 and 4.27, and stable selectivity, as presented in figure 4.28 and 4.29. From figure 4.26, it is clear that for S/M value 0.5, the Ca catalyst shows 40% conversion, which is decreased with increase in S/M value to 32%. Also, for Mg catalyst, the increasing S/M ratio did not significantly improve the conversion. It reaches its maximum conversion value (35%) when S/M is 0.5. As a result, further increase in S/M value did not lead to any improvement in the catalytic activity for Mg, as well. Moreover, the H_2 selectivity value did not significantly change with the change in S/M value at all, which is represented in figure 4.28 and 4.29. From the figures, it can be simply concluded that for this specific application, the S/M ratio 0.5 can be optimal for catalyst preparation. This optimization makes a significant reduction in the catalyst production cost. From figure 4.28 and 4.29, it is found that for the preparation of 5N/CeZrM(Mg and Ca) catalyst, if the S/M ratio can be lowered from 1.25 to 0.5, the wastage of surfactant would be lowered by 60%. Moreover, large amounts of surfactant produce large amounts of waste while preparing the catalyst. The lowering of the surfactant decreases the waste, as well as reduces the waste disposal cost, which also leads to lower catalyst production cost.

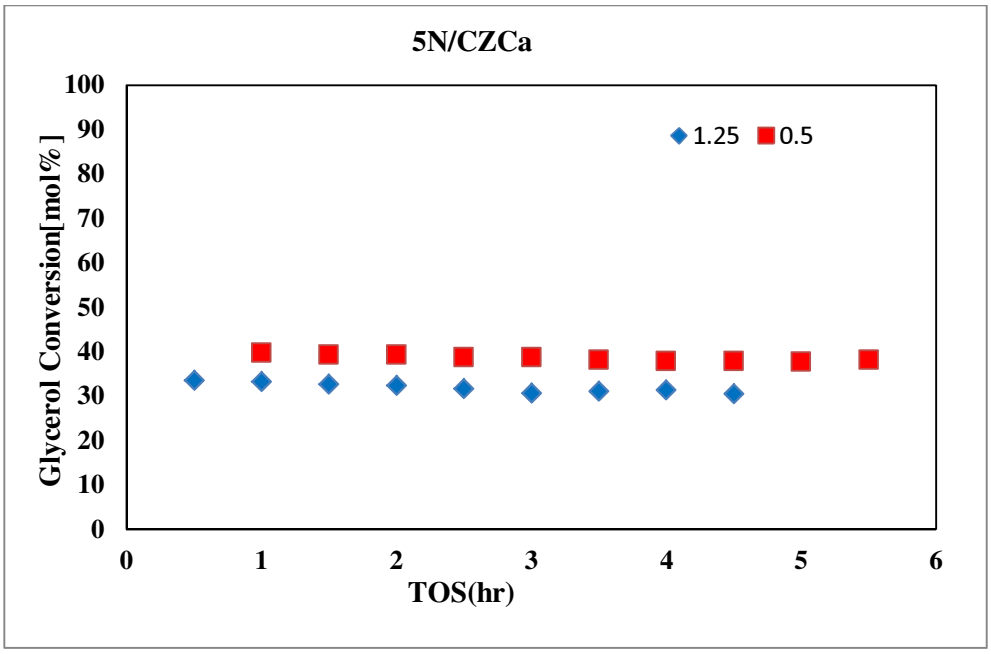

Figure 4.26 Effect of S/M ratio on catalyst activity at 500°C with respect to conversion

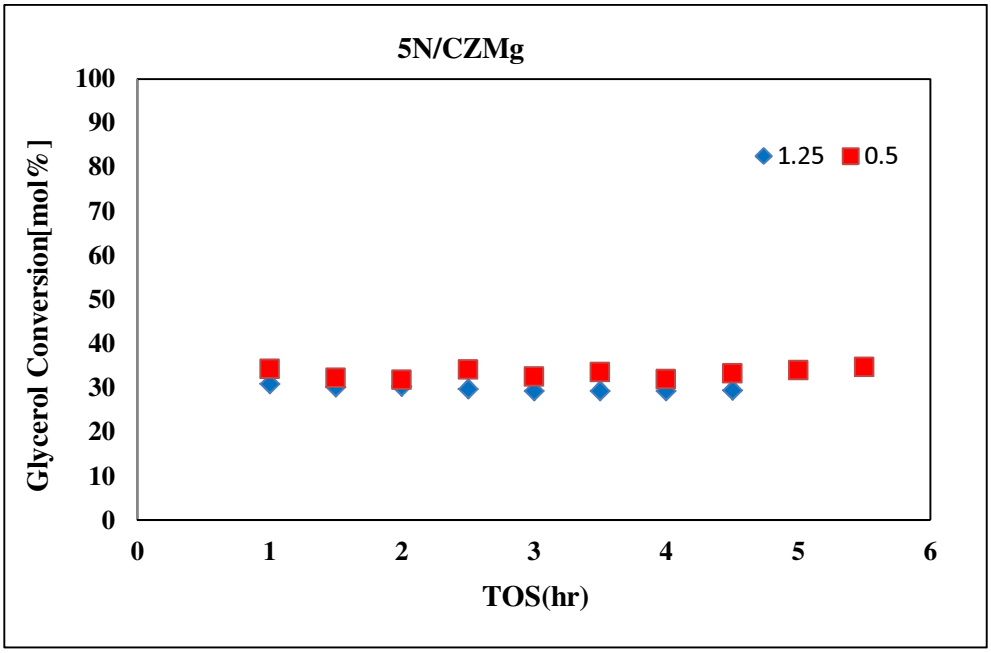

Figure 4.27 Effect of S/M ratio on catalyst activity at 500°C with respect to conversion

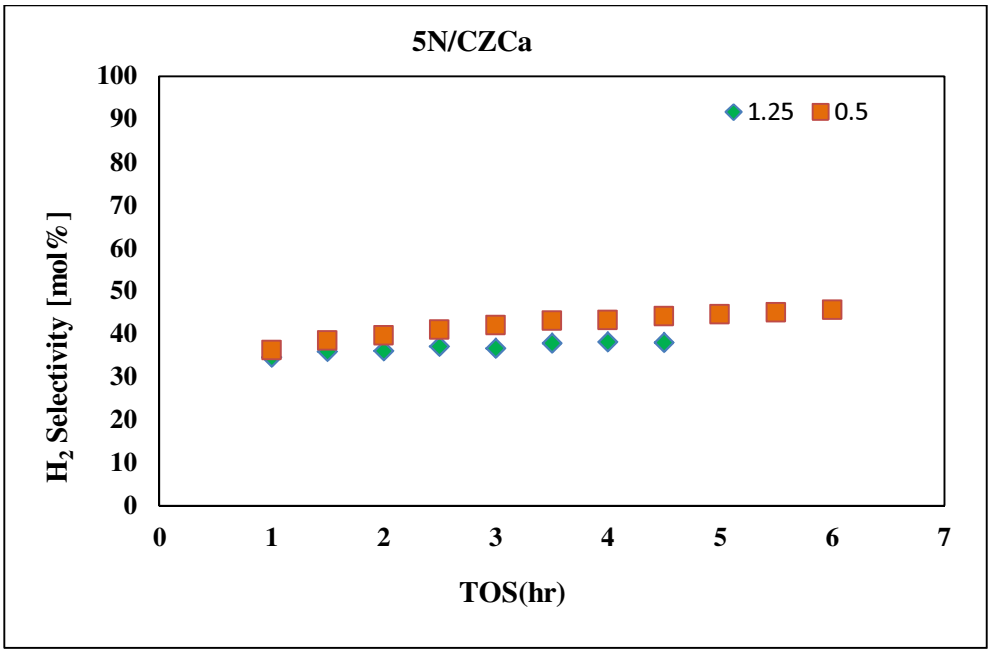

Figure 4.28 Effect of S/M ratio on catalyst activity at 500°C with respect to selectivity

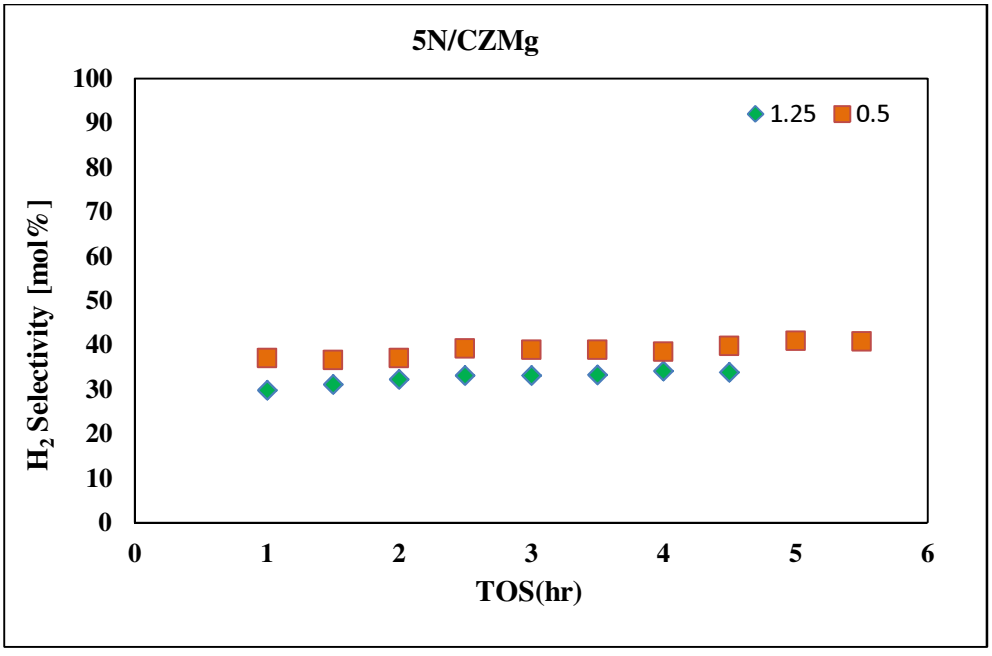

Figure 4.29 Effect of S/M ratio on catalyst activity at 500°C with respect to selectivity

4.2.7. The Comparison between Catalytic Activity for Steam Reforming and Auto-thermal Reforming of Glycerol

For comparison between conventional steam and auto-thermal reforming of glycerol processes, the 5N/CeZrCa was tested at 500°C for 6 hours; from the results, it is clear that the auto-thermal reforming process can produce higher amounts of H_2 in comparison with the previous studies. Moreover, the results demonstrate that reforming of glycerol by the auto-thermal process can produce high selectivity to synthesis of H_2 in comparison to the steam reforming process. Therefore, glycerol can be reformed to hydrogen under auto-thermal conditions on catalyst to achieve high selectivity to H_2 by adjusting the fuel/air and fuel/steam feed ratios, as well as the catalyst. Based on the results shown in figure 4.30 and 4.31, the auto-thermal reforming process of glycerol demonstrates higher conversion and selectivity in comparison to the steam reforming process. Ideally, the auto-thermal reforming process does not need any external heat to proceed forward. By optimizing a right balance between steam/glycerol and oxygen/glycerol ratios, it is possible to compensate for the heat required by the endothermic steam reforming reaction through the heat generated by the exothermic partial oxidation reaction.

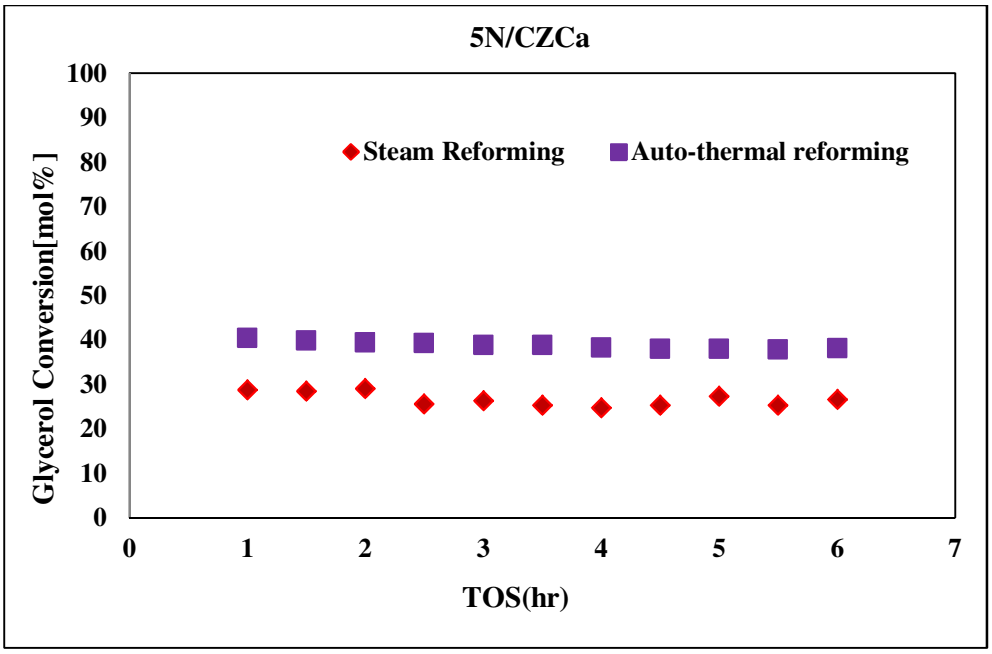

Figure 4.30 the comparison between Catalytic Activity for Steam Reforming

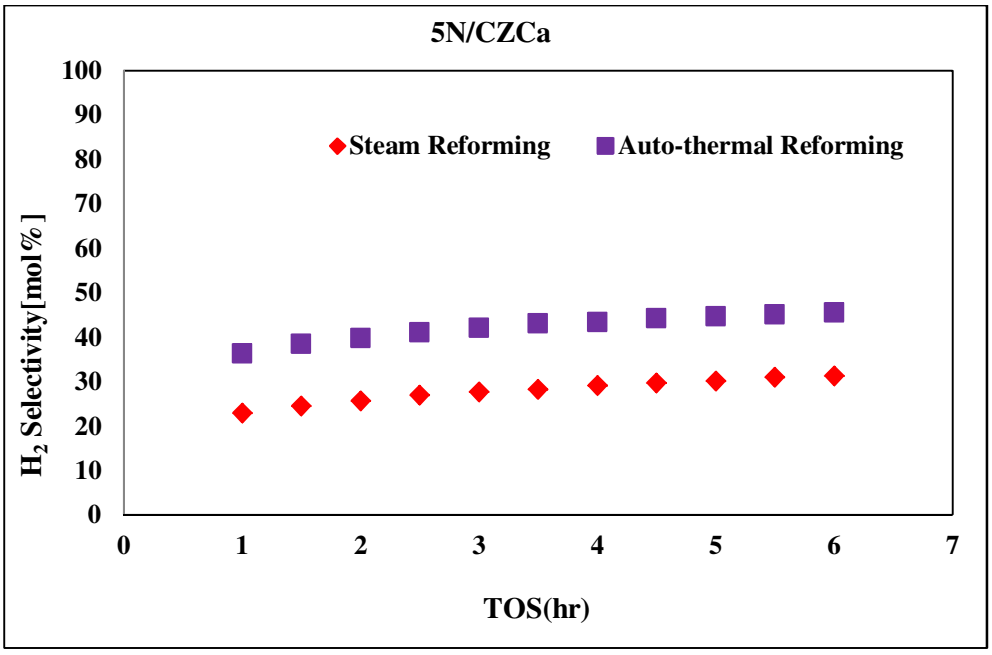

Figure 4.31 The comparison between Catalytic Activity for Auto-thermal reforming of Glycerol

4.2.8. Effect of Oxygen-to-glycerol ratio(O_2/G)

The effect of oxygen-to-glycerol ratio (O_2/G) on the auto-thermal reforming of glycerol over 5N/CeZrGd catalyst at different ratios of steam-to-glycerol, namely, 6, 9, and 12, was examined. The corresponding results are given in figure 4.32 to 4.37. Based on the results, it is noted that the conversion of glycerol increases with an increase in the O_2/G ratio, at all the steam-to-glycerol ratios investigated. It can be described as that increasing the amount of oxygen favours the partial oxidation reaction at the expense of the steam reforming reaction. Oxygen is extremely reactive species, when compared to water (steam) under any given reaction conditions. The evidence for which is obtained from the GC/TCD chromatograms, where no left over oxygen could be detected. It can postulated that initially, all the available oxygen reacts with glycerol via the partial oxidation reaction followed by the reaction of steam with the remaining glycerol via steam reforming reaction; as a result, the conversion is increased. Generally, the addition of oxygen to the reformer is a significant factor, which has a direct impact on the heat requirement to sustain the auto-thermal process. In auto-thermal reforming, the system can be operated without requiring external heat input by adjusting the ratio of oxygen-to-glycerol and steam-to-glycerol. According to the results, H_2 selectivity is not affected significantly with the increasing of oxygen-to-glycerol ratio since the increased oxidation makes more un-reacted feed steam, and, hence, the water gas shift reaction is more pronounced.

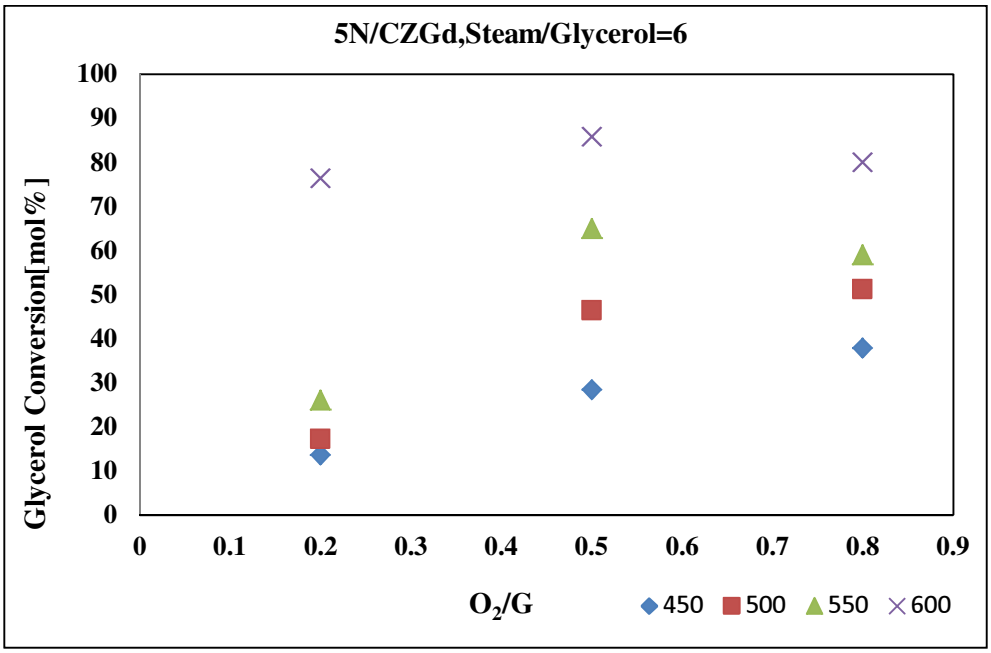

Figure 4.32 The effect of Oxygen-to-glycerol ratio on Glycerol Conversion via auto-thermal reforming at Steam to Glycerol ratio=6

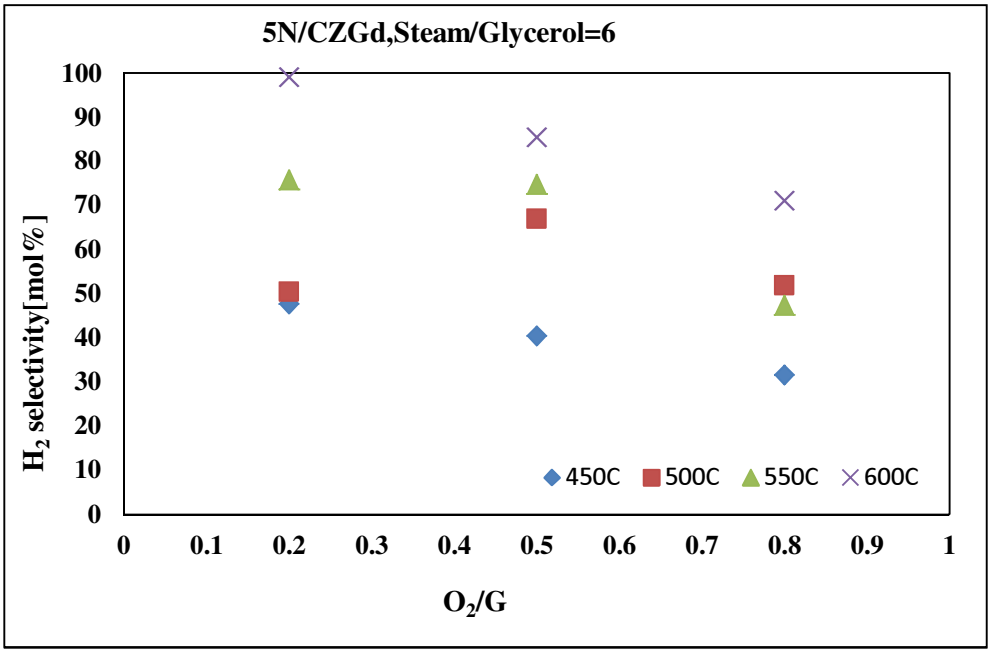

Figure 4.33 The effect of Oxygen-to-glycerol ratio on H_2 selectivity via auto-thermal reforming at Steam to Glycerol ratio=6

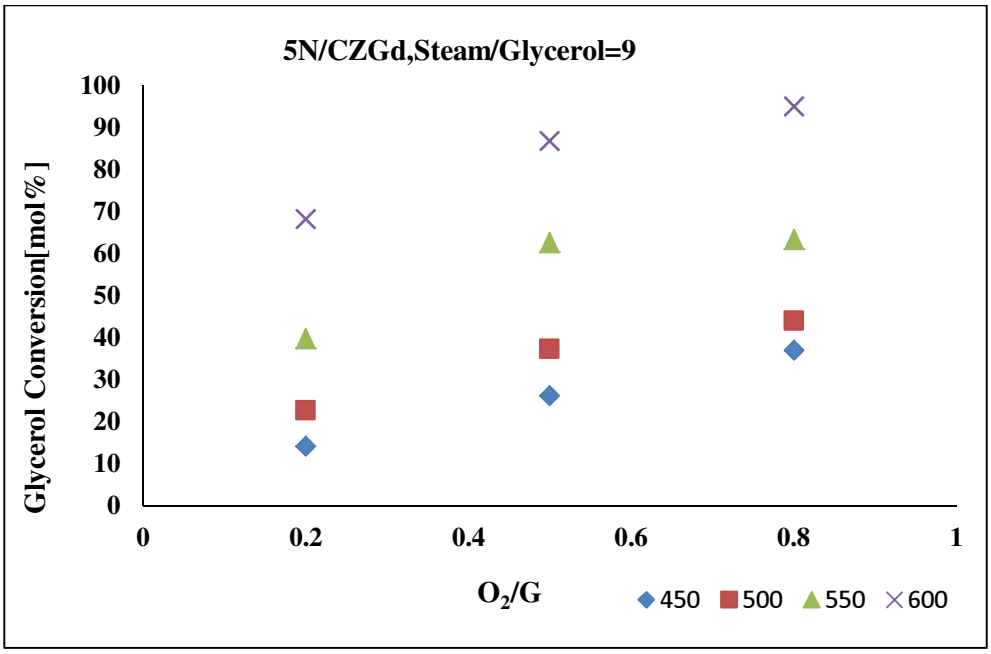

Figure 4.34 The effect of Oxygen-to-glycerol ratio on Glycerol Conversion via auto-thermal reforming at Steam to Glycerol ratio =9

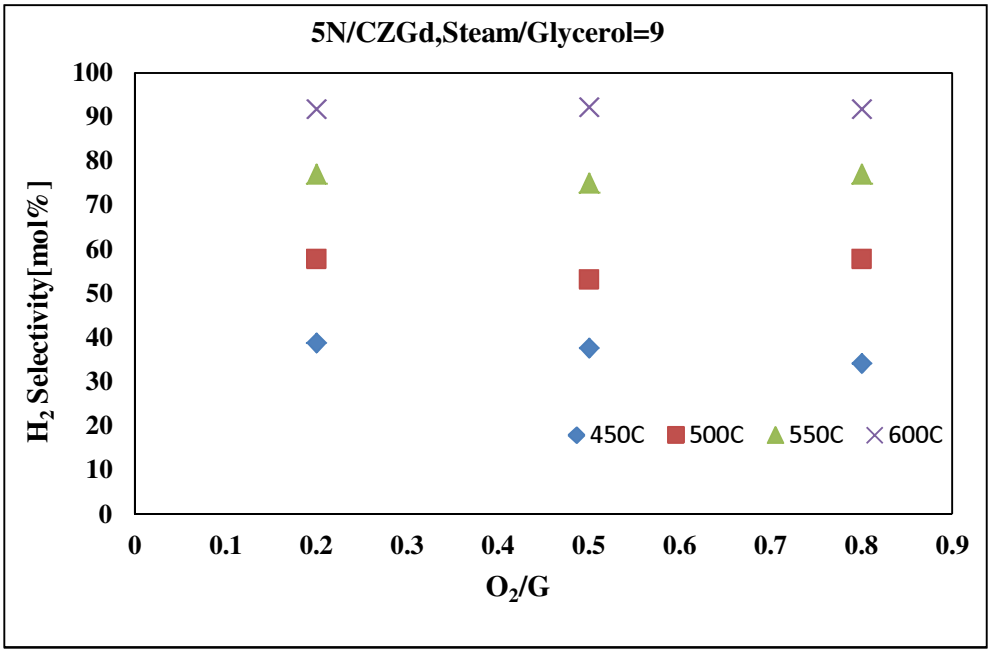

Figure 4.35 The effect of Oxygen-to-glycerol ratio on H_2 selectivity via auto-thermal reforming at Steam to Glycerol ratio=9

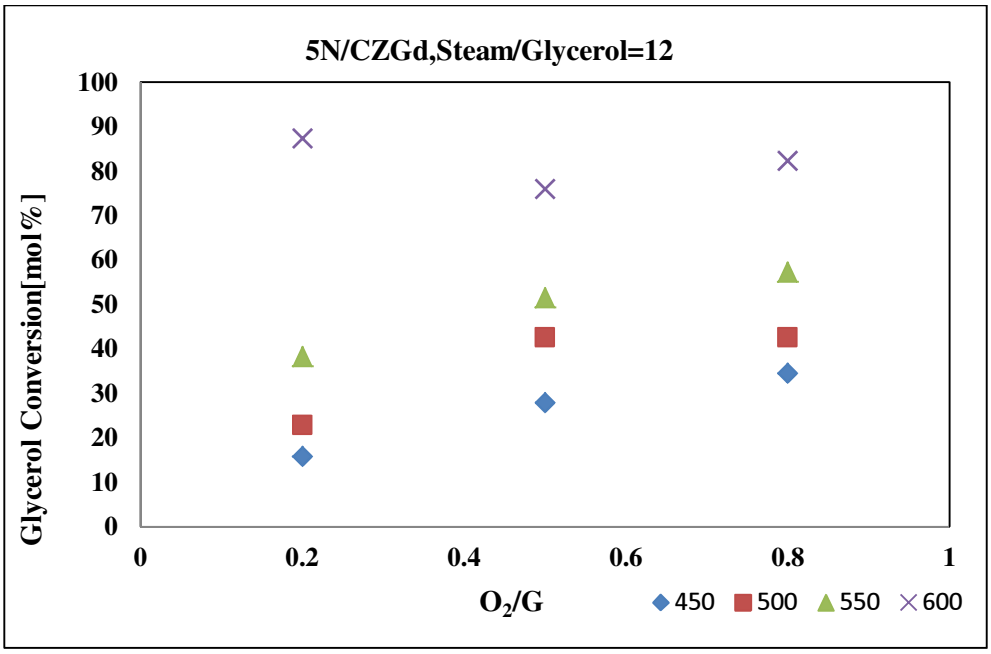

Figure 4.36 The effect of Oxygen-to-glycerol ratio on Glycerol Conversion via auto-thermal reforming at Steam to Glycerol ratio =12

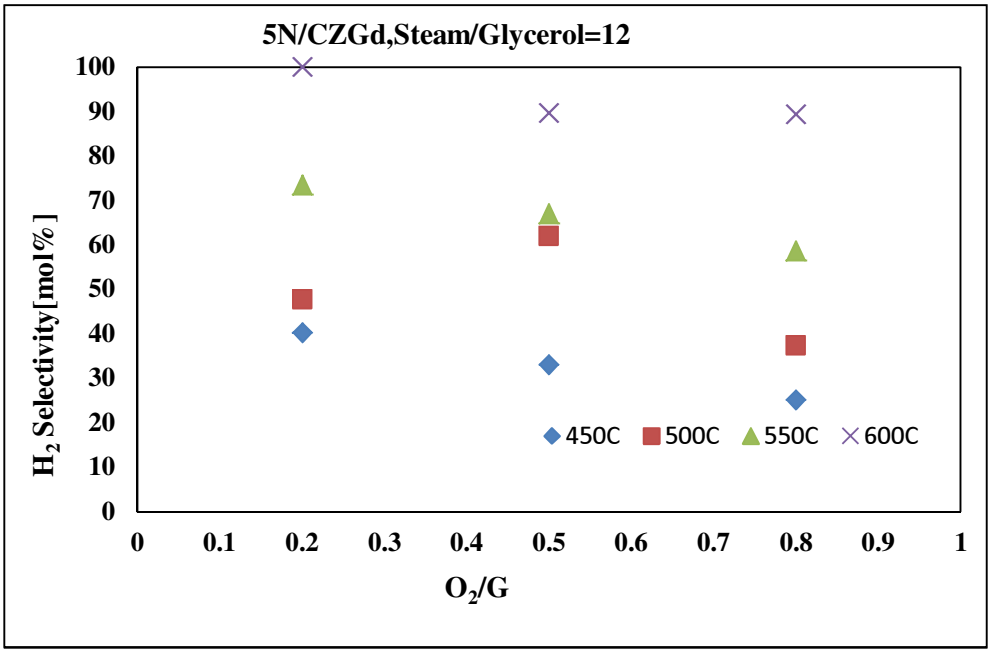

Figure 4.37 The effect of Oxygen-to-glycerol ratio on H_2 selectivity via auto-thermal reforming at Steam to Glycerol ratio=12

4.2.9. Effect of Steam-to-glycerol ratio(S/G)

According to literature the steam-to-glycerol ratio is a critical parameter that can affect the conversion and H_2 selectivity for the auto-thermal reforming process (Authayanun et al., 2010). Typically, excess steam can be applied to overcome the equilibrium limitations of the steam reforming reaction, enhancing the extent of hydrogen produced (Ashrafi et al., 2008). From the current results, as presented in figure 4.38 to 4.43, the glycerol conversion remains constant while H_2 selectivity is decreased by increasing steam-to-glycerol ratio. It can be described as un-reacted steam dilutes the hydrogen product. For oxygen-to-glycerol ratio of 0.2, there is no significant increase in CO and CO_2 concentration in reformate gas products, as shown in Table 4.3. As seen, the increase of steam-to-glycerol ratio does not increase the conversion significantly in all operating temperatures. Finally, H_2 selectivity, here, is also decreased by increasing steam-to-glycerol ratio due to dilution of hydrogen in gas products by steam.

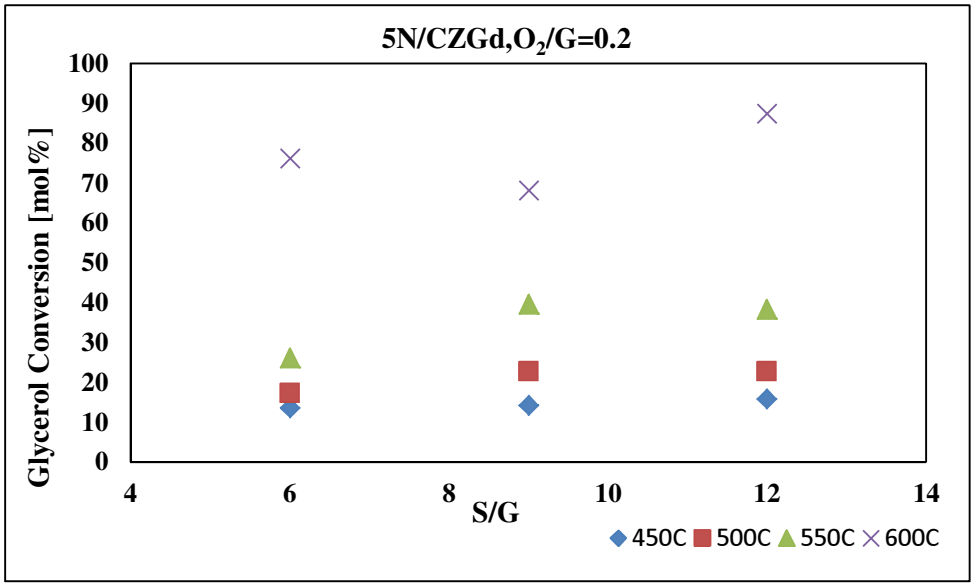

Figure 4.38 The effect of Steam-to-glycerol ratio on Glycerol Conversion at Oxygen-to-glycerol=0.2

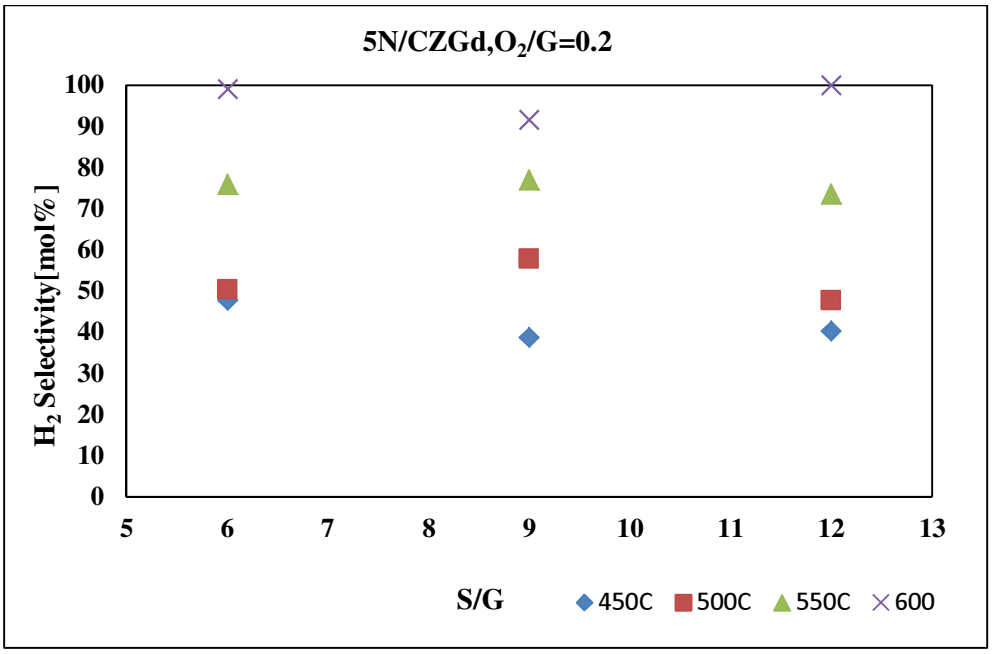

Figure 4.39 The effect of Steam-to-glycerol ratio on H_2 selectivity via auto-thermal reforming at Oxygen-to-glycerol=0.2

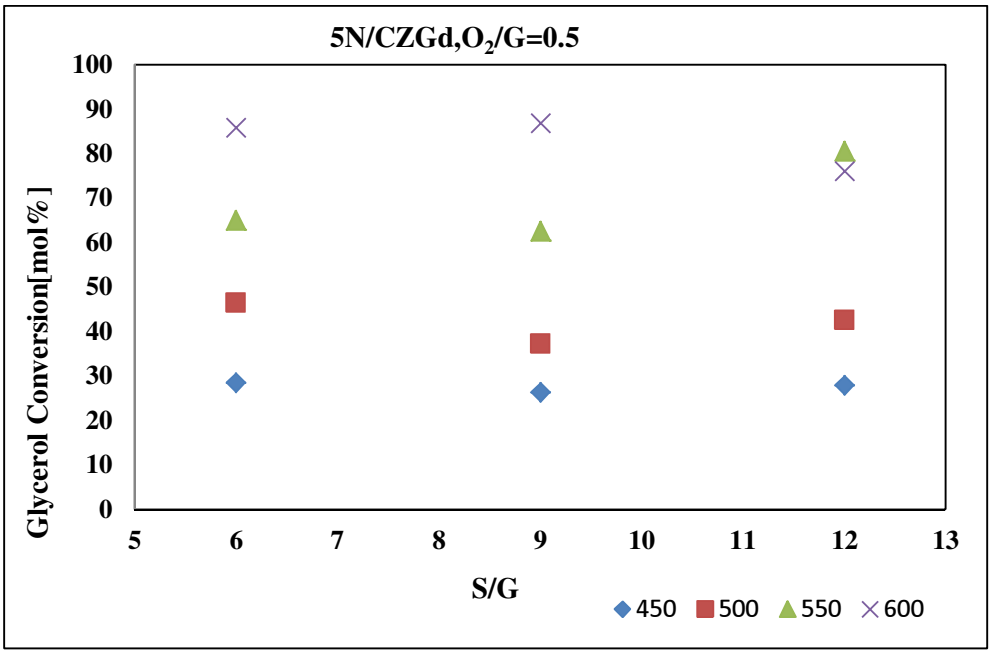

Figure 4.40 The effect of Steam-to-glycerol ratio on Glycerol Conversion at Oxygen-to-glycerol=0.5

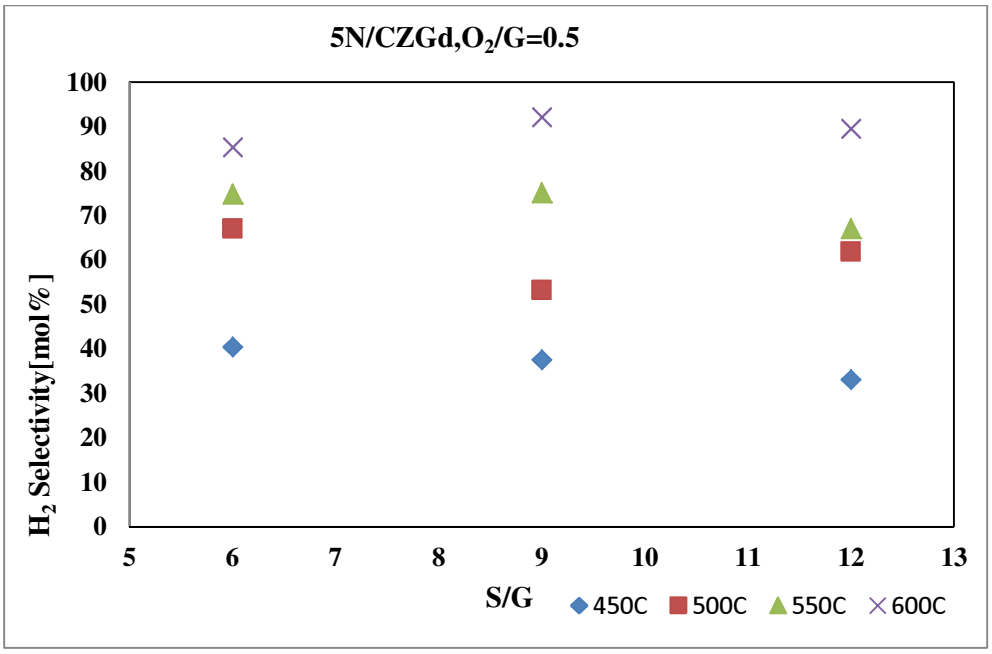

Figure 4.41 The effect of Steam-to-glycerol ratio on H_2 selectivity via auto-thermal reforming at Oxygen-to-glycerol=0.5

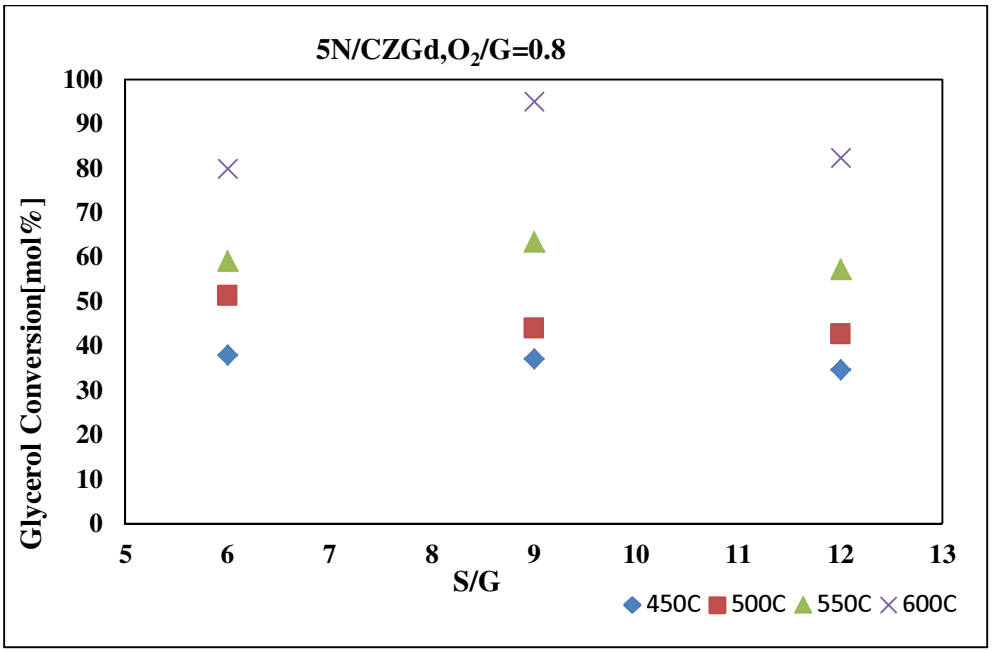

Figure 4.42 The effect of Steam-to-glycerol ratio on Glycerol Conversion at Oxygen-to-glycerol=0.8

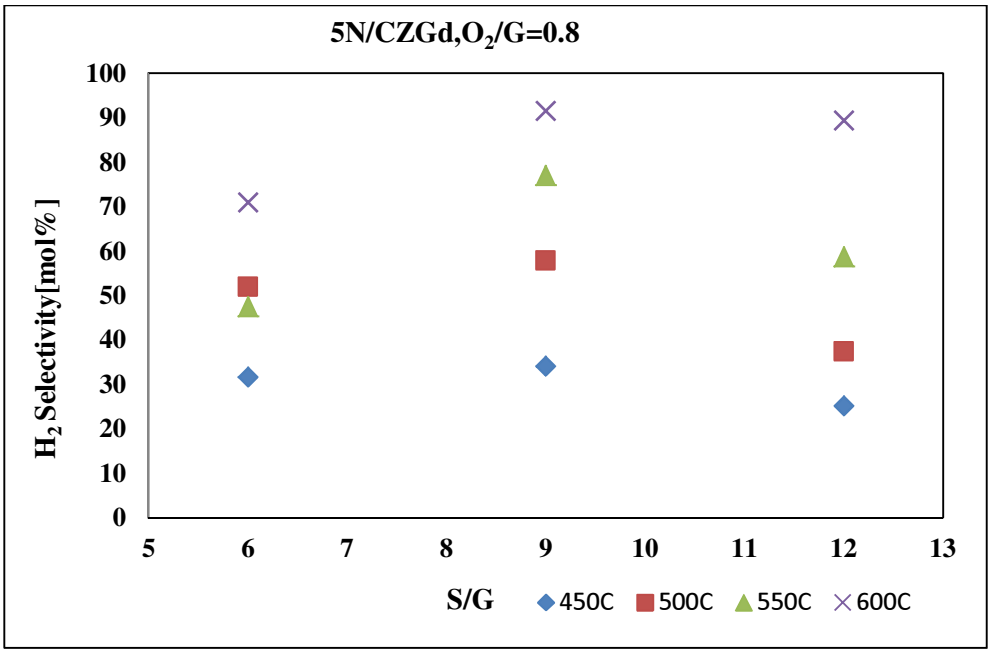

Figure 4.43 The effect of Steam-to-glycerol ratio on H_2 selectivity via auto-thermal reforming at Oxygen-to-glycerol=0.8

Table 4.3 Product distributions at different conditions

O_2/G=0.2,S/G=9	**H_2 (%) Molar flow**	**$CO_{(\%)}$ Molar flow**	**$CO_{2(\%)}$ Molar flow**
T=450°C	41.99	33.34	24.40
500°C	51.91	32.91	14.95
550°C	58.98	26.33	14.55
600°C	63.19	24.9	11.85
O_2/G=0.5,S/G=9	**H_2 (%) Molar flow**	**$CO_{(\%)}$ Molar flow**	**$CO_{2(\%)}$ Molar flow**
T=450°C	38.58	48.66	12.57
500°C	47.03	39.22	13.54
550°C	55.60	30.37	13.88
600°C	60.64	30.59	8.75
O_2/G=0.8,S/G=9	**H_2 (%) Molar flow**	**$CO_{(\%)}$ Molar flow**	**$CO_{2(\%)}$ Molar flow**
T=450°C	33.44	51.75	14.66
500°C	37.92	47.88	14.14
550°C	49.13	36.86	13.83
600°C	57.88	30.65	11.12
O_2/G=0.2,S/G=12	**H_2 (%) Molar flow**	**$CO_{(\%)}$ Molar flow**	**$CO_{2(\%)}$ Molar flow**
T=450°C	42.9	33.03	23.75
500°C	41.12	28.81	23.73
550°C	57.74	27.06	15
600°C	65.37	27.85	6.77
O_2/G=0.5,S/G=12	**H_2 (%) Molar flow**	**$CO_{(\%)}$ Molar flow**	**$CO_{2(\%)}$ Molar flow**
T=450°C	35.58	41.7	22.49
500°C	50.87	39.08	10.07
550°C	52.91	33.48	13.66
600°C	59.53	33.11	7.44
O_2/G=0.8,S/G=12	**H_2 (%) Molar flow**	**$CO_{(\%)}$ Molar flow**	**$CO_{2(\%)}$ Molar flow**

T=450°C	27	52.21	20.58
500°C	35.49	48.78	11.06
550°C	56.79	36.82	6.38
600°C	60	33.10	6.9
O_2/G=0.2,S/G=6	**H_2 (%) Molar flow**	**CO(%) Molar flow**	**CO_2(%) Molar flow**
T=450°C	28.58	41.38	22.28
500°C	43.05	30.77	25.75
550°C	52.78	27.63	19.34
600°C	61.07	26.63	12.53
O_2/G=0.5,S/G=6	**H_2 (%) Molar flow**	**CO(%) Molar flow**	**CO_2(%) Molar flow**
T=450°C	39.88	44.95	14.99
500°C	52.5	38.65	8.73
550°C	55.19	33.29	11.41
600°C	58.84	30.16	10.96
O_2/G=0.8,S/G=6	**H_2 (%) Molar flow**	**CO(%) Molar flow**	**CO_2(%) Molar flow**
T=450°C	31.05	46.07	23.13
500°C	42.64	41.4	15.6
550°C	40.58	31.00	28.06
600°C	51.07	31.9	16.49

4.2.10. Effect of Operating temperature

Overall, as shown in figures 4.15 and 4.16, for all different ratios of Oxygen-to-glycerol, as well as different ratios of steam-to-glycerol, with the increase of temperature, both conversion and H_2 selectivity increase significantly, while the decrease in CO_2 production is accompanied by a consequent increase in CO. This results from the reverse water-gas shift reaction, which has an endothermic nature and is favoured at high

temperatures. It can be concluded that an increase in reforming temperature up to 600 °C, will help achieve high glycerol conversion and high H_2 selectivity.

4.2.11. Relationship between Carbon Propensity Factor (CPF) and Promoter Element by TGA

The term Carbon Propensity Factor (CPF) is used here to measure the rate of coke formation on all given catalyst formulations with different promoter elements 500°C.The common units employed to gauge CPF are amount of carbon produced (mg)/amount of catalyst (g)/time (h). The values are tabulated in table 4.4 and figure 4.44. As can be seen in the results, it is noted that carbon propensity factor is almost related to the type of promoter element employed. The descending order of CPF as a function of the promoter element M is as follows: La>Y>Mg>Gd>Ca. From the results it can be concluded that Ca and Gd are the most coke tolerant promoter among the other promoter elements employed in the current study.

Table 4.4 The CPFs of 5N/CeZrM with different promoter elements at 500°C.

Catalyst 5N/CeZrM	**CPF from(TGA)[mg of carbon(g of catalyst $^{-1}$) h^{-1}]**
5Ni/CeZrCa	44.48
5Ni/CeZrGd	47.25
5Ni/CeZrMg	52.06
5Ni/CeZrY	57.60
5Ni/CeZrLa	64.61

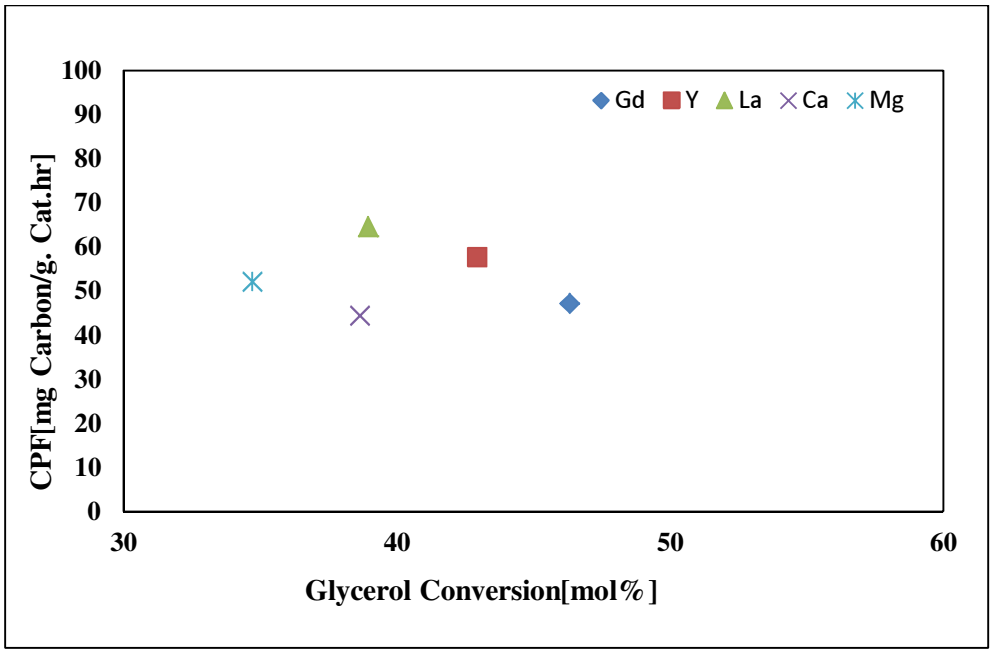

Figure 4.44 Relationship between CPF and short term stability with different promoter elements

Chapter 5 Conclusions and Recommendations

5.1. CONCLUSIONS

Among the portfolio of ceria-based ternary oxide 5N/CeZrM (M = Ca, Mg, Gd, La, Y) catalysts that were screened for auto-thermal reforming of glycerol, employing a steam/glycerol ratio of 6 and oxygen/glycerol ratio of 0.5 at 500°C and 600°C, high activity with stable performance was noted for formulations with M = Ca, Mg, and Gd at all the reaction temperatures tested in this study. Among all the tested catalysts, 5N/CeZrGd indicated the best performance at all the tested temperatures. However, from the temperature vs. conversion plot for 5N/CeZrGd, it was found that, until 600°C, conversion increased rapidly with the increase in temperature to reach 82 mol.% glycerol conversion and > 70 mol.% H_2 selectivity, which is optimal for industrial applications. Above this, the increase in temperature did not make a significant increase in glycerol conversion. In comparison with non-catalytic reactions, 5N/CeZrGd increased the conversion 2.8 fold at 600°C to show the maximum catalytic effect.In addition,it was not observed any dropping in conversion for all catalysts screenings.Another important result from the current study is that the increase of the surfactant/metal (S/M) ratio from 0.5 to 1.25 does not improve the catalyst performance and activity; hence, by choosing a S/M ratio of 0.5, we can minimize catalyst production expenses. In addition, the results obtained from the comparison between steam reforming and auto-thermal reforming processes demonstrate that auto-thermal reforming of glycerol can produce high selectivity towards H_2 in comparison to the steam reforming process, as well as higher conversions.

Finally, it was found that an increase in operating temperature enhances the H_2 selectivity, as well as glycerol conversion. Furthermore, the impact of oxygen-to-glycerol ratio shows a similar trend. Although adding more steam-to-glycerol in feed does not increase the glycerol conversion; it causes decreasing the hydrogen product, the fraction of hydrogen depletes due to the dilution effect of steam. The results also indicate that CO formation, which can cause a poisoning problem in low-temperature fuel cells, increases with increasing the reformer temperature but decreases with increasing the steam-to-glycerol ratio. Based on these results, the appropriate oxygen-to-glycerol ratio can be 0.5 irrespective of the glycerol concentration.

5.2. RECOMMENDATIONS

In this current work, the catalyst formulation, the surfactant/metal (S/M) ratio, oxygen/glycerol (O_2/G) ratio, steam /glycerol(S/G) ratio, and the reaction temperature have been optimized. In addition to all these optimizations,the nickel reduction temperature as well as calcination temperature of support can be studied to achieve the optimum temperatures . In order to optimize the overall process for an industrial application, a kinetic study over the optimized 5N/CeZrGd catalyst is highly desirable with an additional process variable W/F_{Go} (Catalyst Weight/Glycerol Molar Flow) at different temperatures, S/G and O_2/G ratios. To ensure long-term stability, the catalyst needs to be examined for at least 400 hours under the optimized operating conditions. A reactor modelling and simulation study using highly developed simulation software such as COMSOL could be a powerful simulation to be applied for industrial design prior to industrial applications. Furthermore, as discussed in the introductory sections, the real

industrial by-products, such as crude glycerol, should be tested to ensure the feedstock-flexibility of the resultant catalyst.

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APPENDICES

Appendix A: Carbon Balance

Catalyst: 5NCZGd(S/M=0.5)

Conditions: 450°C,O_2/G=0.5,S/G=6

mol. C (in) = mol. C $_g$ (out) + mol. C $_l$ (out) +Coking (from TGA)

0.89208=0.315+0.4017+0.00095

0.89208=0.7176

%difference = $\frac{0.89208-0.7167}{0.89208}\times 100\% = 11.73\%$

Catalyst: 5NCZGd(S/M=0.5)

Conditions: 500°C,O_2/G=0.5,S/G=6

mol. C (in) = mol. C $_g$ (out) + mol. C $_l$ (out) +Coking (from TGA)

0.89208=0.523747+0.3502+0.000767

0.89208=0.874714

%difference = $\frac{0.89208-0.874714}{0.89208}\times 100\% = 1.95\ \%$

Appendix B: Calculation of Heat of Reaction

The heat of reaction (25°C, 1 atm) has been calculated from the heat of formation data obtained from Albright (2009). The heat of formation values for the gaseous components employed in the current work, are given below.

Heat of formation of H_2O, $\Delta H_{f,H2O}$ (25°C, 1 atm) = - 241.8 kJ/mol

Heat of formation of CO, $\Delta H_{f,CO}$ (25°C, 1 atm) = - 110.5 kJ/mol

Heat of formation of CO_2, $\Delta H_{f,CO2}$ (25°C, 1 atm) = - 393.5 kJ/mol

Heat of formation of C_3H_8O, $\Delta H_{f,C3H8O3}$ (25°C, 1 atm) = - 577.9 kJ/mol

Sample Calculation:

$C_3H_8O_3 + 6H_2O + 0.5O_2 = 2CO_2 + CO + 5H_2 + 5H_2O$

Heat of Reaction, $\Delta H_r = (2 \times \Delta H_{f,CO2} + 5 \times \Delta H_{f,H2} + 5 \times \Delta H_{f,H2O} + 1 \times \Delta H_{f,CO}) - (\Delta H_{f,C3H8O3} + 6\ \Delta H_{f,H2O} + 0 \times \Delta H_{f,O2})$

$= \{2 \times (-393.5) + (5 \times 0) + (5 \times -241.8) + (1 \times -110.5)\} - \{(-577.9) + (6 \times -241.8) + (0.5 \times 0)\}$

So, ΔH_r (25°C, 1 atm) = -77.8 kJ/mol

Appendix C: Lab Safety Measures/Protocols

Work with chemicals should be performed in a safe and healthy research environment. To ensure regulatory fulfillment for all use of laboratory equipment and hazardous chemicals and avoid any accident or chemical spills in the lab the following safety protocols are strongly recommended:

1. A lab coat, goggles and gloves should be worn during all experiments.
2. The catalyst and support preparations should be conducted under the fume hood.
3. All chemicals waste should be properly disposed after experiments.
4. The chemical safety manual is also provided in the lab.
5. Materail safety data sheet's (MSDS) is also available online at:

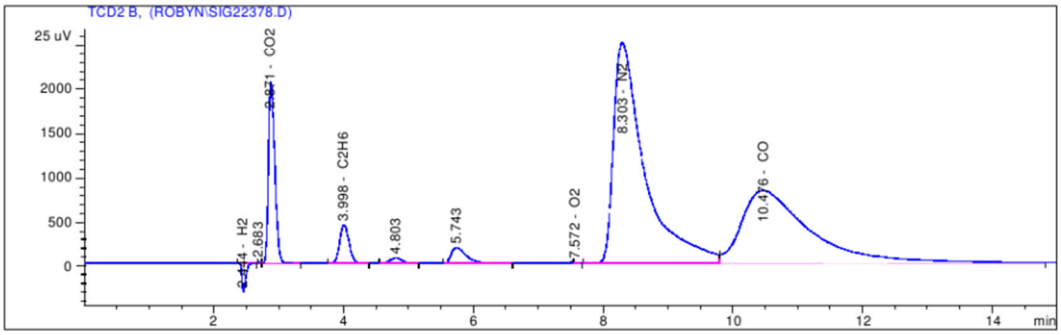
http://jr.chemwatch.net/chemffx/?X

6. The eye wash and firs aid are also provided in lab.
7. WHIMS training are also provided online at University of Regina.
8. Carbon Monoxide (CO) detector is also applied in the lab for safety issues.

Appendix D: Data Sheet of Each Experiment

```
=====================================================================
Acq. Operator    : Faezeh
Acq. Instrument  : Instrument 1
Injection Date   : 08-Sep-11, 16:45:22
```

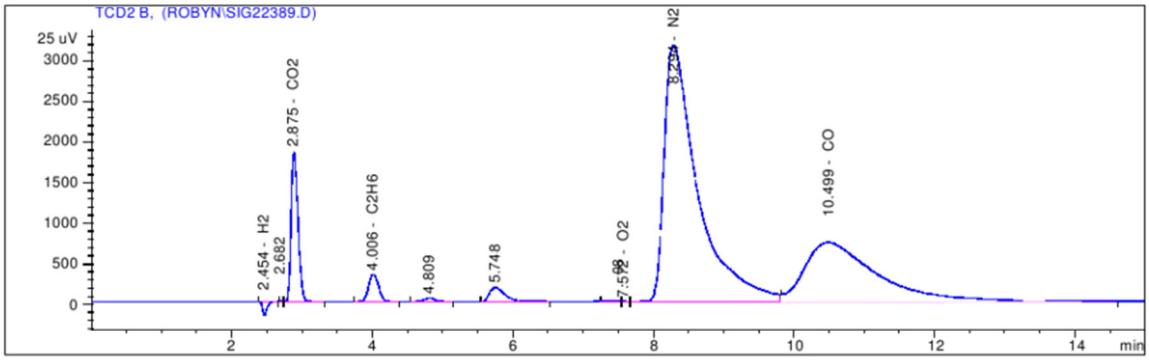
Run#1:700°C,O_2/G=0.5,S/G=6,No Catalyst




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      21/11/2012 10:14:01 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|-------------------
  2.444 BP N   1326.25195 1.40692e-2  19.421671    H2
  2.871 VB     1.39378e4  4.86207e-4   7.053563    CO2
  3.998 BB     4351.59082 4.52021e-4   2.047384    C2H6
  7.572 VB       15.54369 5.37947e-4   0.008703    O2
  8.303 BV     8.34651e4  4.82267e-4  41.897218    N2
  9.700            -          -          -        CH4
 10.476 VB     5.95117e4  4.77395e-4  29.571460    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator    : Faezeh
 Acq. Instrument : Instrument 1
 Injection Date  : 12-Sep-11, 23:21:24
```

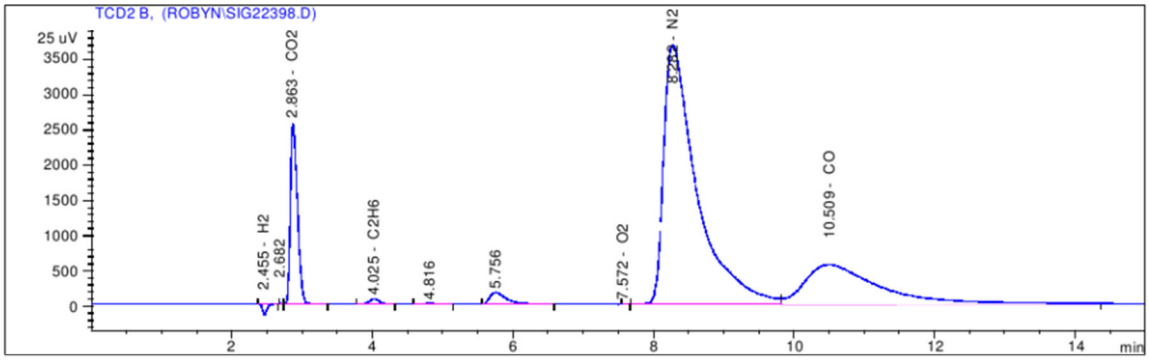
Run#2: 650°C,O2/G=0.5,S/G=6,No Catalyst




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      21/11/2012 10:14:01 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.454 BP N     695.56671 1.62411e-2  11.931238    H2
  2.875 VB      1.24163e4  4.85652e-4   6.368675    CO2
  4.006 BB      3418.32227 4.52021e-4   1.631933    C2H6
  7.572 VV        15.96494 5.37947e-4   0.009071    O2
  8.294 VV      1.05014e5  4.82191e-4  53.480691    N2
  9.700             -          -          -        CH4
 10.499 VB      5.27133e4  4.77395e-4  26.578392    CO

Totals :                               100.000000
```

```
=====================================================================
Acq. Operator    : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 14-Sep-11, 17:26:19
```

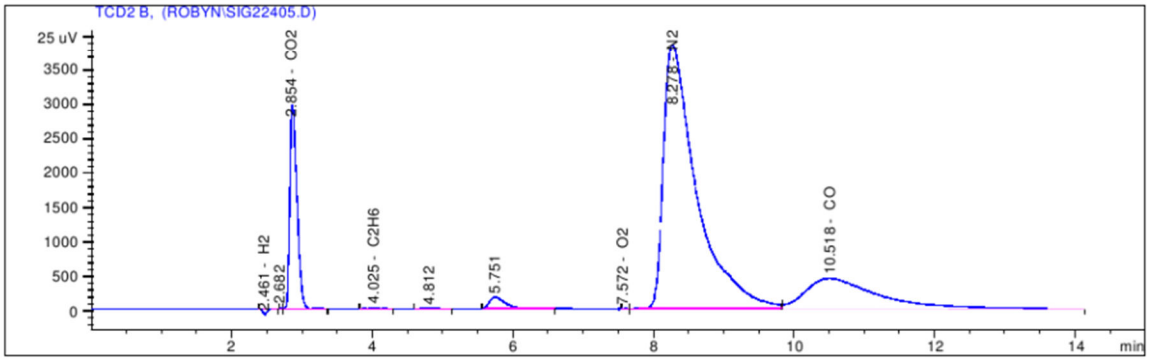
Run#3:600°C,O_2/G=0.5,S/G=6,No Catalyst




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type      Area      Amt/Area      Norm     Grp   Name
 [min]          [25 uV*s]                   %
-------|------|----------|----------|----------|--|------------------
  2.455 BP N     646.79352 1.65855e-2  11.071074    H2
  2.863 VB      1.77515e4  4.87180e-4   8.925224    CO2
  4.025 BB       723.94666 4.52021e-4   0.337722    C2H6
  7.572 BB        15.89409 5.37947e-4   0.008824    O2
  8.282 BV      1.20444e5  4.82154e-4  59.932635    N2
  9.700             -          -          -        CH4
 10.509 VB      4.00345e4  4.77395e-4  19.724522    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator    : Faezeh
Acq. Instrument : Instrument 1
Injection Date   : 15-Sep-11, 20:41:49
```

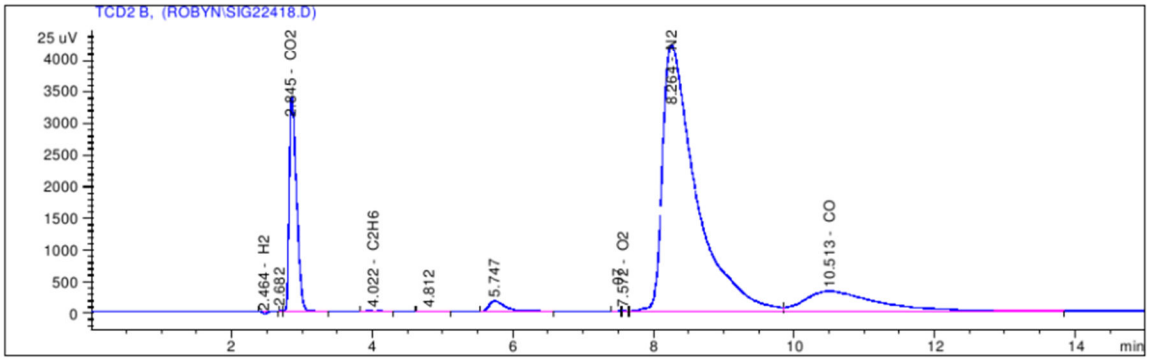
Run#4:550°C,O_2/G=0.5,S/G=6,No Catalyst




```
=====================================================================
                        Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.461 BV N     357.06738 2.05710e-2   7.893745    H2
  2.854 VB      2.07829e4  4.87699e-4  10.892707    CO2
  4.025 BB       224.37720 4.52021e-4   0.108997    C2H6
  7.572 BV        15.77357 5.37947e-4   0.009119    O2
  8.278 VV      1.25634e5  4.82143e-4  65.096927    N2
  9.700             -          -          -        CH4
 10.518 VB      3.11834e4  4.77395e-4  15.998504    CO

Totals :                               100.000000
```

```
=====================================================================
Acq. Operator    : Faezeh
Acq. Instrument : Instrument 1
Injection Date   : 26-Sep-11, 20:30:35
```

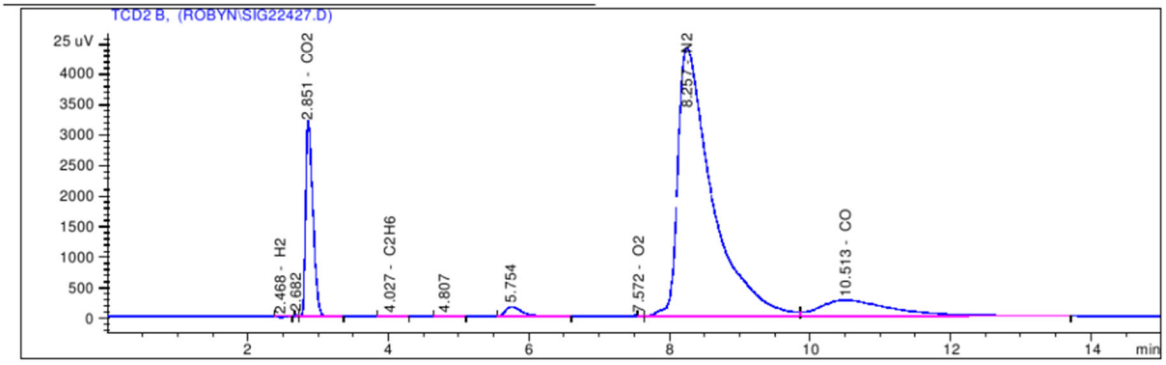
Run#5:500°C,O_2/G=0.5,S/G=6,No Catalyst




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.464 BP N    196.99312 2.78008e-2   5.720243     H2
  2.845 VB     2.42928e4  4.88138e-4  12.385870     CO2
  4.022 BB      123.29254 4.52021e-4   0.058210     C2H6
  7.572 VV       15.26695 5.37947e-4   0.008578     O2
  8.264 VV     1.40056e5  4.82118e-4  70.527726     N2
  9.700           -          -          -          CH4
 10.513 VB     2.26606e4  4.77395e-4  11.299373     CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator    : Faezeh
Acq. Instrument : Instrument 1
Injection Date   : 28-Sep-11, 14:59:49
```

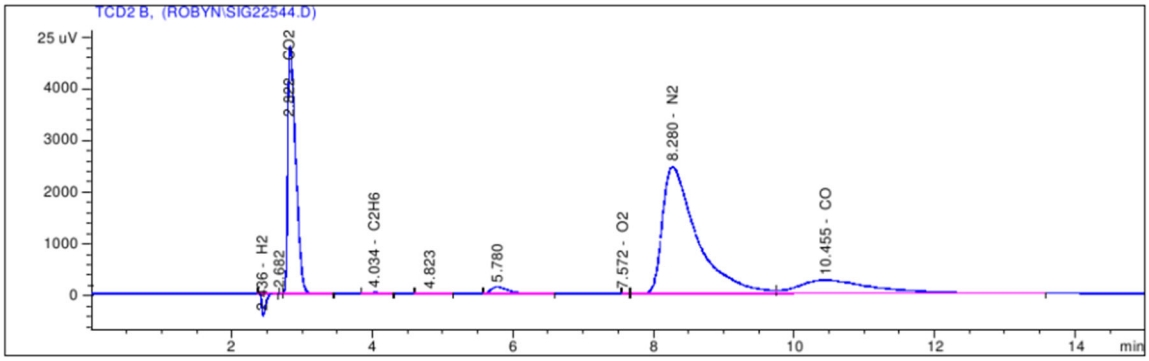
Run#6:450°C,O_2/G=0.5,S/G=6,No Catalyst




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.468 BB N     79.80161 5.14840e-2   4.266229    H2
  2.851 VB     2.27497e4  4.87962e-4  11.527129    CO2
  4.027 BB       90.40681 4.52021e-4   0.042435    C2H6
  7.572 VV       16.14577 5.37947e-4   0.009019    O2
  8.257 VV     1.49158e5  4.82105e-4  74.670159    N2
  9.700            -          -         -         CH4
 10.513 VB     1.91338e4  4.77395e-4   9.485030    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 12-Dec-11, 16:39:25
```

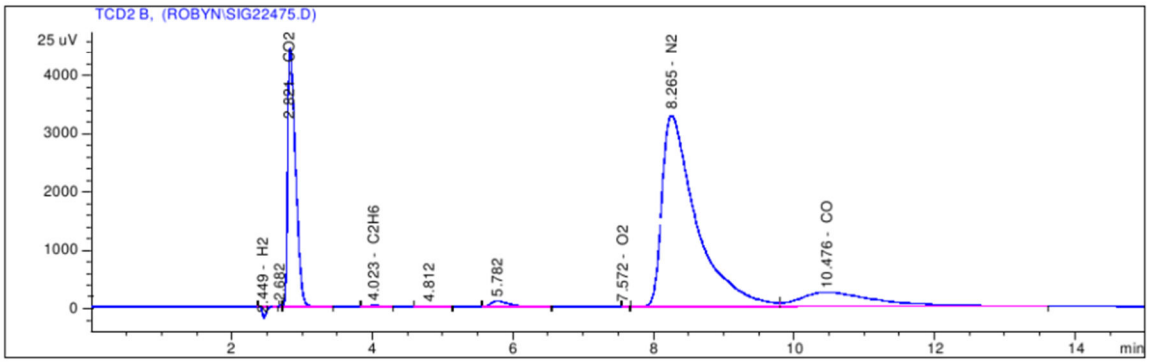
Run#7:500°C,O_2/G=0.5,S/G=6,5Ni/CeZrCa




```
=====================================================================
                      Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm    Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.436 BV N   1717.29700 1.35237e-2  25.367420    H2
  2.822 VB     3.72298e4  4.89041e-4  19.887119    CO2
  4.034 BB      226.17307 4.52021e-4   0.111670    C2H6
  7.572 VV       15.88842 5.37947e-4   0.009336    O2
  8.280 VV     8.44460e4  4.82263e-4  44.483443    N2
  9.700            -          -          -        CH4
 10.455 VB     1.94477e4  4.77395e-4  10.141013    CO

Totals :                              100.000000
```

```
============================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 07-Nov-11, 21:42:33
```

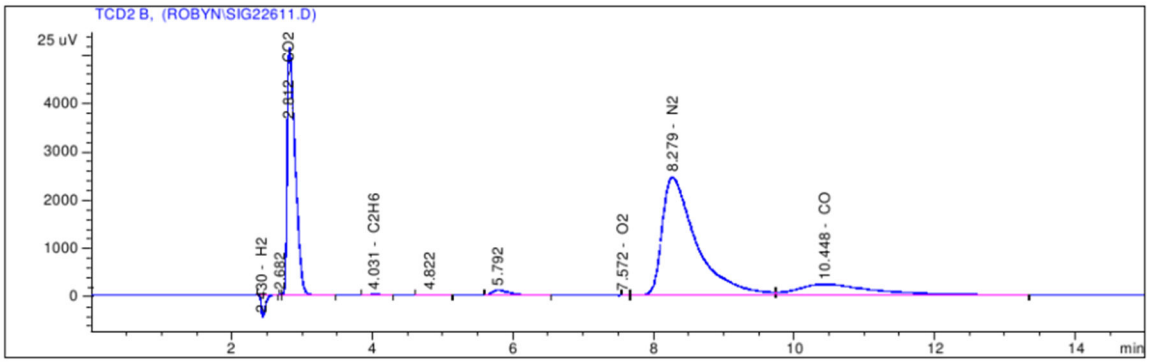
Run#8:500°C,O_2/G=0.5,S/G=6,5Ni/CeZrMg




```
====================================================================
                      Normalized Percent Report
====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.449 BV N     779.04297 1.57517e-2  13.401553    H2
  2.821 VB      3.43257e4  4.88898e-4  18.327470    CO2
  4.023 BB       178.70177 4.52021e-4   0.088217    C2H6
  7.572 VB        15.09682 5.37947e-4   0.008869    O2
  8.265 BV      1.11894e5  4.82173e-4  58.921621    N2
  9.700             -          -          -        CH4
 10.476 VB      1.77462e4  4.77395e-4   9.252270    CO

Totals :                               100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 16-Jan-12, 20:14:28
```

Run#9:500°C,O_2/G=0.5,S/G=6,5Ni/CeZrLa

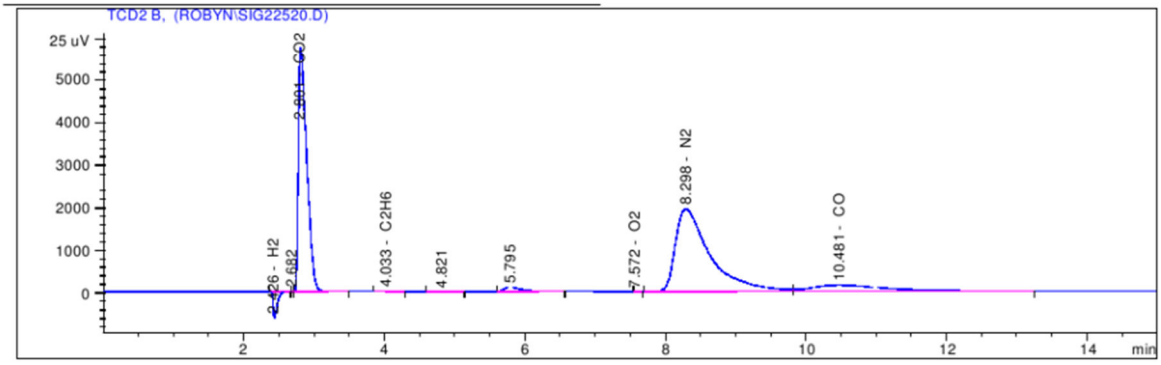



```
=====================================================================
                      Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,
```

RetTime [min]	Type	Area [25 uV*s]	Amt/Area	Norm %	Grp	Name
2.430	BV N	1876.36743	1.33669e-2	27.047196		H2
2.812	VB	4.05014e4	4.89178e-4	21.365465		CO2
4.031	BB	168.46051	4.52021e-4	0.082117		C2H6
7.572	VV	15.67835	5.37947e-4	0.009095		O2
8.279	VV	8.28600e4	4.82270e-4	43.093269		N2
9.700		-	-	-		CH4
10.448	VB	1.63220e4	4.77395e-4	8.402858		CO
Totals :				100.000000		

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 05-Dec-11, 16:51:38
```

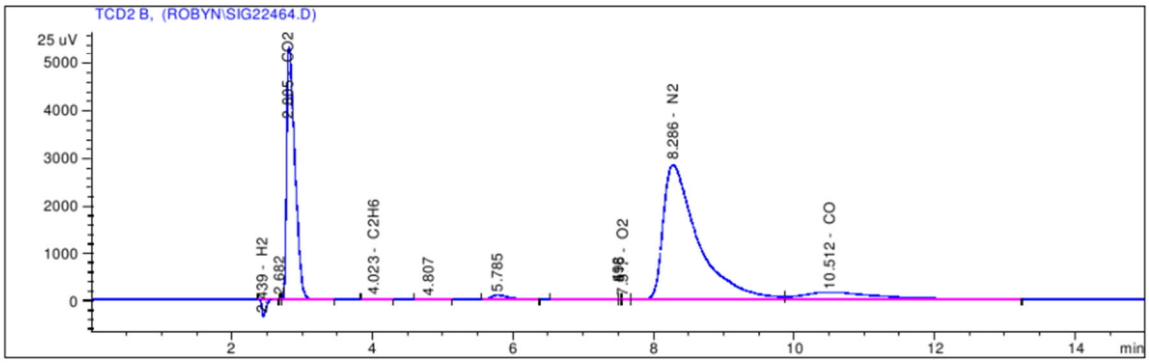
Run#10:500°C,O_2/G=0.5,S/G=6,5Ni/CeZrY




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.426 BP N   2470.41626 1.29597e-2  34.503681    H2
  2.801 VB S   4.70379e4  4.89395e-4  24.808840    CO2
  4.033 BB      151.46506 4.52021e-4   0.073785    C2H6
  7.572 VB       18.61741 5.37947e-4   0.010793    O2
  8.298 BV     6.69577e4  4.82358e-4  34.807188    N2
  9.700            -          -         -         CH4
 10.481 VB     1.12649e4  4.77395e-4   5.795712    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 02-Nov-11, 17:53:50
```

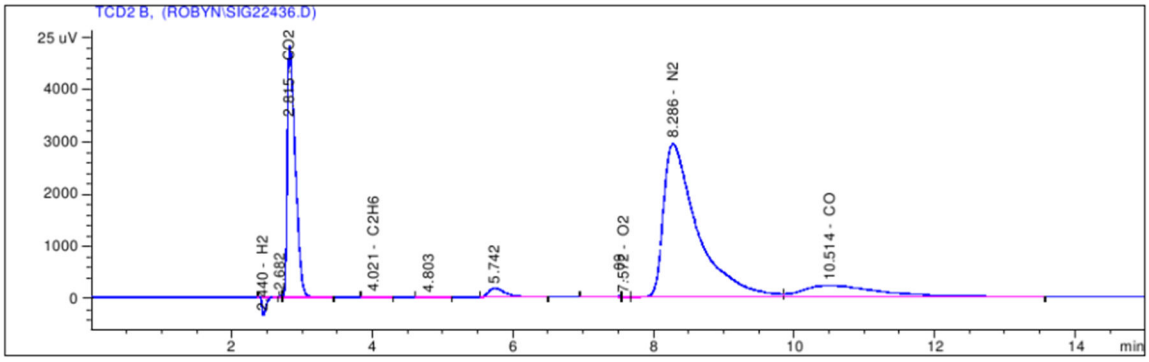
Run#11:500°C,O_2/G=0.5,S/G=6,5Ni/CeZrMg,S/M=1.25




```
=====================================================================
                      Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm    Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.439 BP N   1469.49146 1.38357e-2  21.792464    H2
  2.805 VB     4.28770e4  4.89265e-4  22.485742    CO2
  4.023 BB      131.09015 4.52021e-4   0.063514    C2H6
  7.572 VV       16.71753 5.37947e-4   0.009639    O2
  8.286 VV     9.72961e4  4.82215e-4  50.289237    N2
  9.700            -          -          -        CH4
 10.512 VB     1.04737e4  4.77395e-4   5.359404    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 04-Oct-11, 16:12:40
```

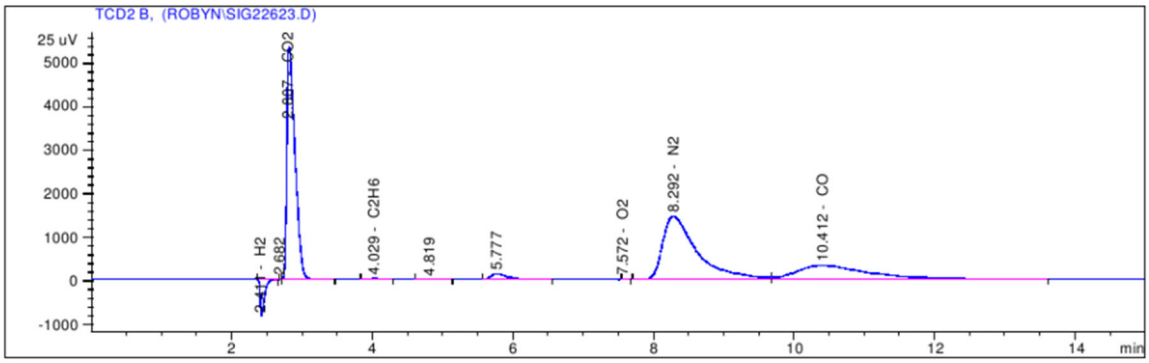
Run#12:500°C,O_2/G=0.5,S/G=6,5Ni/CeZrCa,S/M=1.25




```
=====================================================================
                      Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.440 BP N   1458.13647 1.38525e-2  21.441527    H2
  2.815 VB     3.76440e4  4.89060e-4  19.542843    CO2
  4.021 BB      115.82309 4.52021e-4   0.055576    C2H6
  7.572 VV       15.11158 5.37947e-4   0.008629    O2
  8.286 VV     9.89412e4  4.82209e-4  50.645658    N2
  9.700            -          -          -        CH4
 10.514 VB     1.63897e4  4.77395e-4   8.305767    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator    : Faezeh
Acq. Instrument : Instrument 1
Injection Date   : 18-Jan-12, 18:08:19
```

Run#13:600°C,O_2/G=0.5,S/G=6,5Ni/CeZrY

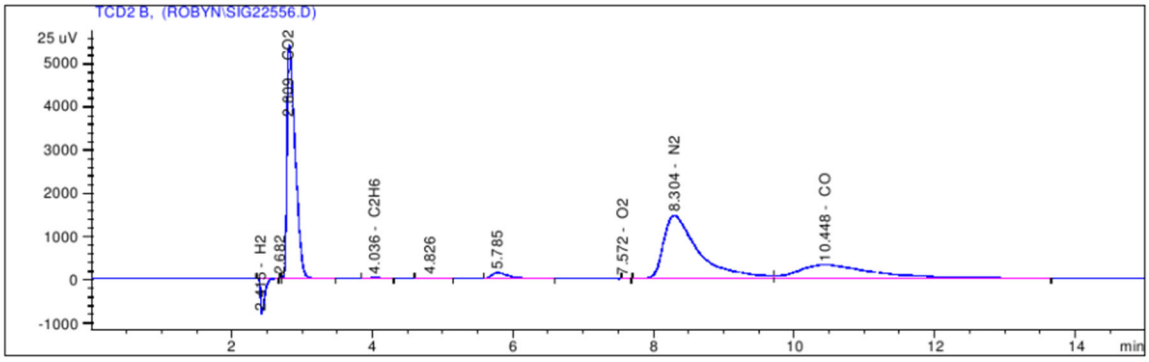



```
=====================================================================
                      Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,
```

RetTime [min]	Type	Area [25 uV*s]	Amt/Area	Norm %	Grp	Name
2.411	BV N	3406.43921	1.26064e-2	43.373750		H2
2.807	VB	4.26143e4	4.89256e-4	21.058516		CO2
4.029	BB	213.97649	4.52021e-4	0.097693		C2H6
7.572	VB	15.30496	5.37947e-4	0.008316		O2
8.292	BV	4.96261e4	4.82518e-4	24.185810		N2
9.700		-	-	-		CH4
10.412	VB	2.33850e4	4.77395e-4	11.275916		CO
Totals :				100.000000		

```
=========================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 16-Dec-11, 16:19:38
```

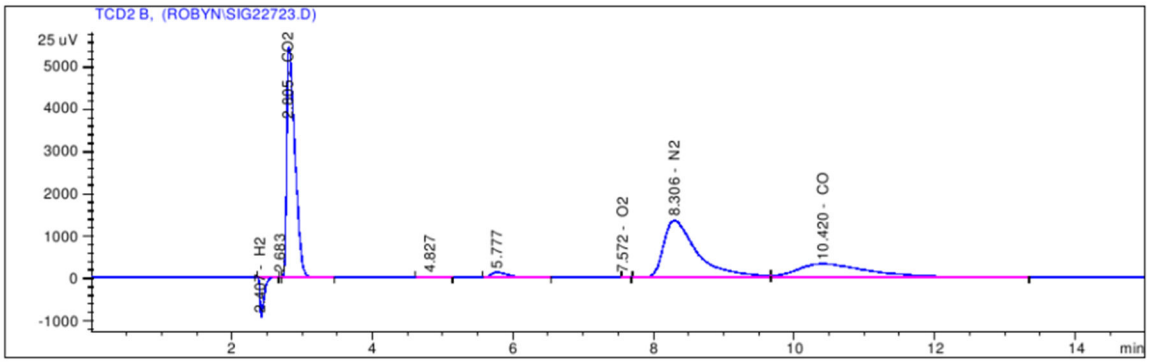
Run#14:600°C,O_2/G=0.5,S/G=6,5Ni/CeZrCa




```
=====================================================================
                      Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm    Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.415 BP N   3355.84717 1.26204e-2  42.818487    H2
  2.809 VB     4.34333e4  4.89283e-4  21.485156    CO2
  4.036 BB      186.80864 4.52021e-4   0.085371    C2H6
  7.572 VB       15.65909 5.37947e-4   0.008517    O2
  8.304 BV     5.02983e4  4.82510e-4  24.536601    N2
  9.700           -          -          -         CH4
 10.448 VB     2.29273e4  4.77395e-4  11.065867    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 27-Apr-12, 16:10:09
```

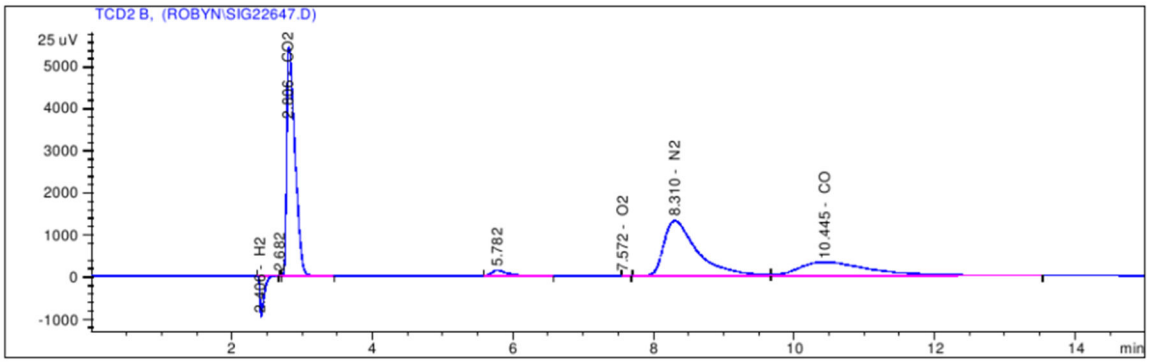
Run#15:600°C,O_2/G=0.5,S/G=6,5Ni/CeZrGd




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.407 BP N   3744.66626 1.25221e-2  46.789056     H2
  2.805 VB S   4.37148e4  4.89293e-4  21.342770     CO2
  4.027           -           -           -         C2H6
  7.572 VB       15.72546 5.37947e-4   0.008441     O2
  8.306 BV     4.43761e4  4.82591e-4  21.368872     N2
  9.700           -           -           -         CH4
 10.420 VB     2.20232e4  4.77395e-4  10.490861     CO

Totals :                             100.000000
```

```
======================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 05-Feb-12, 15:34:27
```

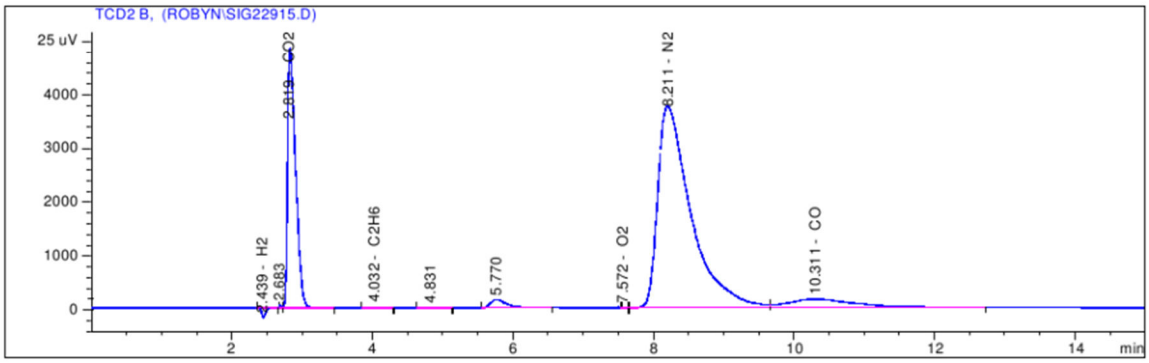
Run#16:700°C,O_2/G=0.5,S/G=6,5Ni/CeZrGd




```
======================================================================
                      Normalized Percent Report
======================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm    Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.406 BP N   3896.43579 1.24891e-2  47.765574    H2
  2.806 VB S   4.37195e4  4.89293e-4  20.997182    CO2
  4.027           -           -           -        C2H6
  7.572 BB      15.59715 5.37947e-4   0.008236    O2
  8.310 BV     4.34015e4  4.82607e-4  20.559621    N2
  9.700           -           -           -        CH4
 10.445 VB     2.27690e4  4.77395e-4  10.669388    CO

Totals :                             100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 27-Sep-12, 21:53:20
```

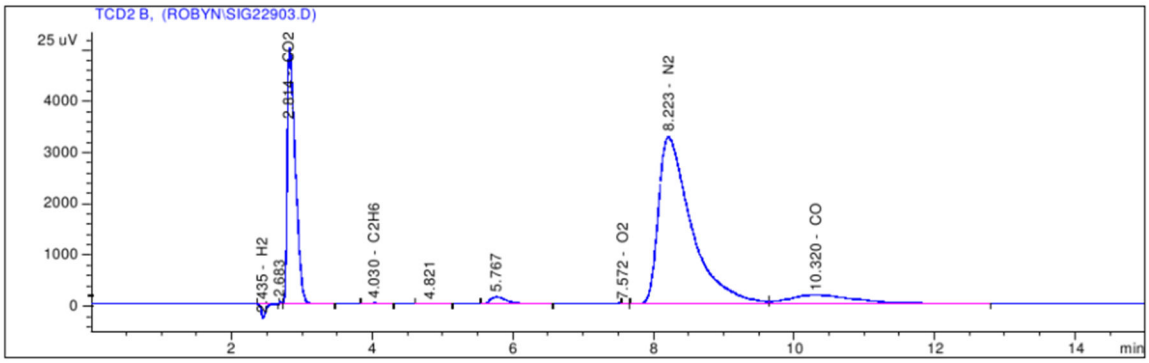
Run#17:450°C,O_2/G=0.8,S/G=9,5Ni/CeZrGd




```
=====================================================================
                      Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.439 BP N     743.45148 1.59470e-2  12.424695    H2
  2.819 VB      3.80750e4  4.89079e-4  19.515255    CO2
  4.032 BB       103.40968 4.52021e-4   0.048986    C2H6
  7.572 VV        15.41231 5.37947e-4   0.008689    O2
  8.211 VV      1.24212e5  4.82146e-4  62.762129    N2
  9.700            -          -          -         CH4
 10.311 VB      1.04741e4  4.77395e-4   5.240246    CO

Totals :                               100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 18-Sep-12, 19:24:20
```

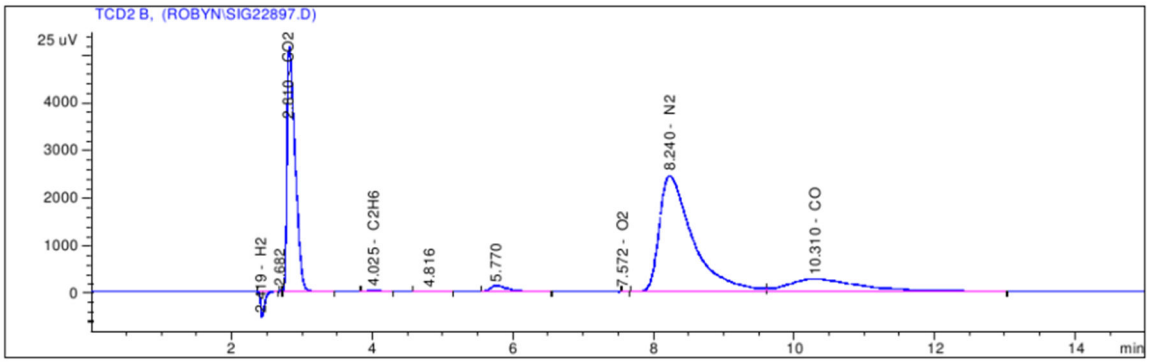
Run#18:500°C,O_2/G=0.8,S/G=9,5Ni/CeZrGd




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.435 BP N   1065.95605 1.46541e-2  16.759113    H2
  2.814 VB     3.99546e4  4.89157e-4  20.968496    CO2
  4.030 BB      178.36287 4.52021e-4   0.086500    C2H6
  7.572 VB       14.96255 5.37947e-4   0.008636    O2
  8.223 BV     1.08303e5  4.82183e-4  56.028118    N2
  9.700            -          -          -        CH4
 10.320 VB     1.20056e4  4.77395e-4   6.149138    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 11-Sep-12, 19:46:21
```

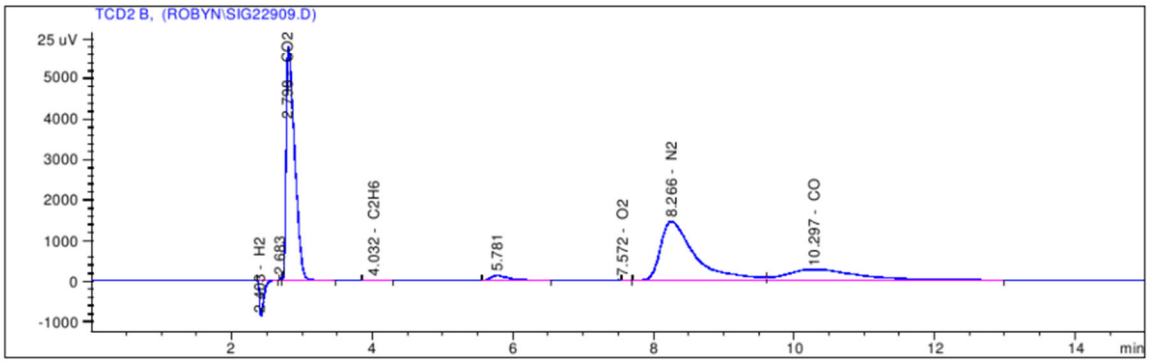
Run#19:550°C,O_2/G=0.8,S/G=9,5Ni/CeZrGd




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.419 BV N   2106.96313 1.31816e-2  29.077031    H2
  2.810 VB     4.10589e4  4.89199e-4  21.029034    CO2
  4.025 BB      280.48032 4.52021e-4   0.132736    C2H6
  7.572 VB       14.85443 5.37947e-4   0.008366    O2
  8.240 BV     8.06816e4  4.82280e-4  40.737984    N2
  9.700            -          -          -        CH4
 10.310 VB     1.80366e4  4.77395e-4   9.014849    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 25-Sep-12, 18:45:25
```

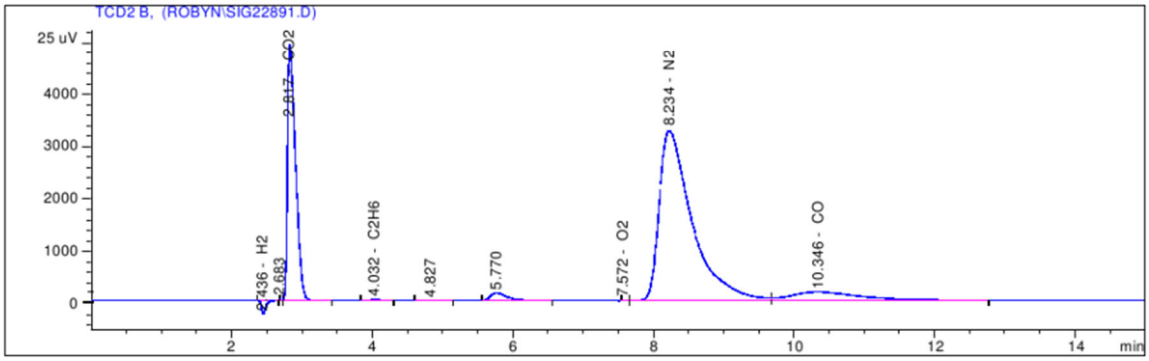
Run#20:600°C,O_2/G=0.8,S/G=9,5Ni/CeZrGd




```
=====================================================================
                      Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm    Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.403 BP N   3594.76221 1.25575e-2  44.904414    H2
  2.798 VB S   4.76906e4  4.89413e-4  23.217939    CO2
  4.032 BB       30.90405 4.52021e-4   0.013896    C2H6
  7.572 VB       14.64895 5.37947e-4   0.007839    O2
  8.266 BV     4.86334e4  4.82531e-4  23.344005    N2
  9.700            -          -          -        CH4
 10.297 VB     1.79239e4  4.77395e-4   8.511906    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 10-Sep-12, 19:11:25
```

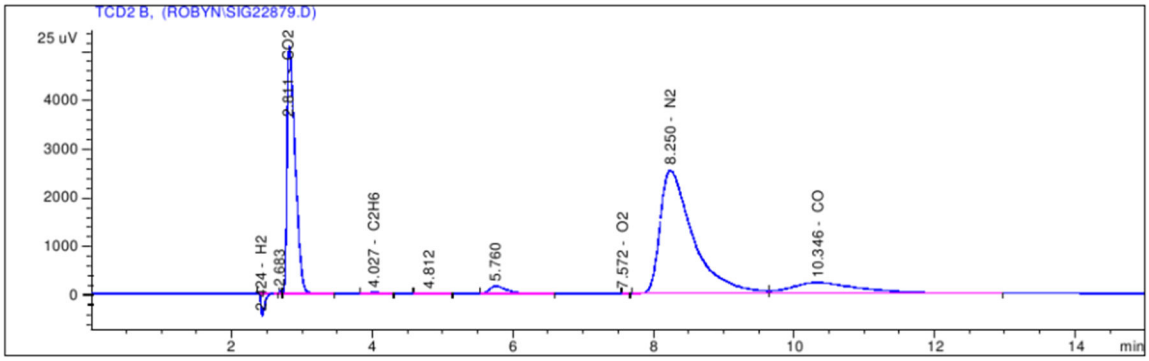
Run#21:450°C,O_2/G=0.5,S/G=9,5Ni/CeZrGd




```
=====================================================================
                      Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm    Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|-----------------
  2.436 BP N   1087.91003 1.45940e-2  17.323132    H2
  2.817 VB     3.88450e4  4.89112e-4  20.730225    CO2
  4.032 BB      164.89024 4.52021e-4   0.081323    C2H6
  7.572 VV       14.81952 5.37947e-4   0.008698    O2
  8.234 VV     1.06583e5  4.82187e-4  56.074523    N2
  9.700            -          -          -        CH4
 10.346 VB     1.11006e4  4.77395e-4   5.782099    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 25-Aug-12, 19:28:06
```

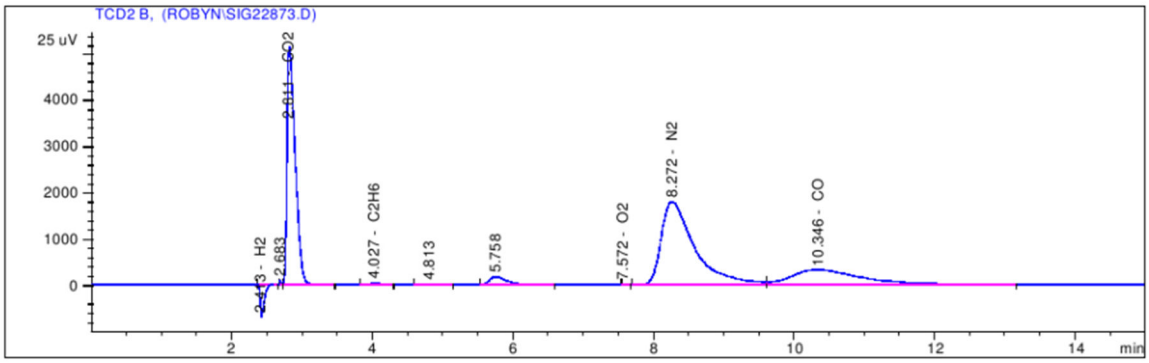
Run#22:500°C,O_2/G=0.5,S/G=9,5Ni/CeZrGd




```
=====================================================================
                      Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm    Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.424 BV N   1822.66724 1.34167e-2  26.586574    H2
  2.811 VB     4.08794e4  4.89193e-4  21.741647    CO2
  4.027 BB      250.24556 4.52021e-4   0.122980    C2H6
  7.572 BB       14.79029 5.37947e-4   0.008650    O2
  8.250 BV     8.32240e4  4.82268e-4  43.635977    N2
  9.700            -          -          -        CH4
 10.346 VB     1.52290e4  4.77395e-4   7.904173    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 24-Aug-12, 18:54:24
```

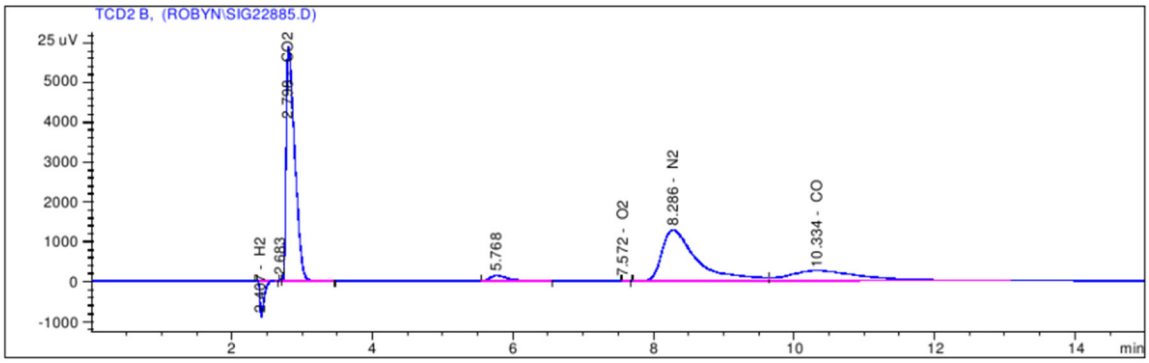
Run#23:550°C,O_2/G=0.5,S/G=9,5Ni/CeZrGd




```
=====================================================================
                      Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.413 BV N   2801.34131 1.28078e-2  38.119838    H2
  2.811 VB     4.08094e4  4.89190e-4  21.210373    CO2
  4.027 BB      288.87186 4.52021e-4   0.138731    C2H6
  7.572 VB       17.92080 5.37947e-4   0.010243    O2
  8.272 BV     5.82057e4  4.82427e-4  29.833688    N2
  9.700            -          -          -        CH4
 10.346 VB     2.10704e4  4.77395e-4  10.687128    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 09-Sep-12, 17:32:24
```

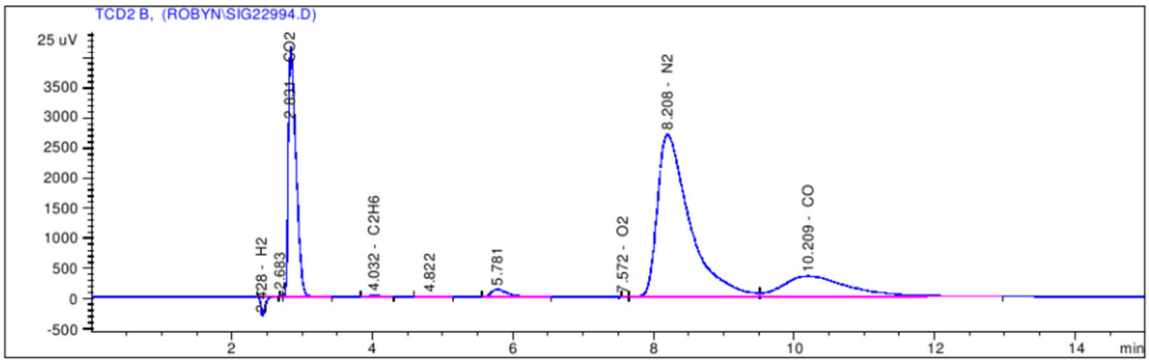
Run#24:600°C,O_2/G=0.5,S/G=9,5Ni/CeZrGd




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm    Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.407 BV N   3636.39917 1.25474e-2  46.278069    H2
  2.798 VB S   4.88787e4  4.89445e-4  24.264646    CO2
  4.027           -           -           -        C2H6
  7.572 BB       14.73872 5.37947e-4   0.008042    O2
  8.286 BV     4.33542e4  4.82608e-4  21.221486    N2
  9.700           -           -           -        CH4
 10.334 VB     1.69923e4  4.77395e-4   8.227757    CO

Totals :                              100.000000
```

```
======================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 16-Oct-12, 19:12:35
```

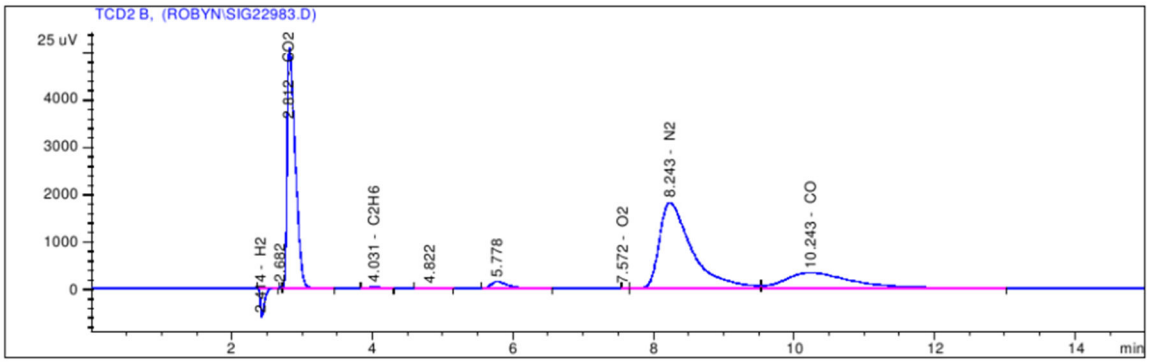
Run#25:450°C,O_2/G=0.2,S/G=9,5Ni/CeZrGd




```
======================================================================
                      Normalized Percent Report
======================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm    Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.428 BP N   1347.46326 1.40314e-2  21.840955    H2
  2.831 VB     3.12332e4  4.88716e-4  17.632963    CO2
  4.032 BB      261.53177 4.52021e-4   0.136564    C2H6
  7.572 VV       14.26361 5.37947e-4   0.008864    O2
  8.208 VV     8.63352e4  4.82255e-4  48.096824    N2
  9.700           -          -          -         CH4
 10.209 VB     2.22743e4  4.77395e-4  12.283830    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 11-Oct-12, 19:10:24
```

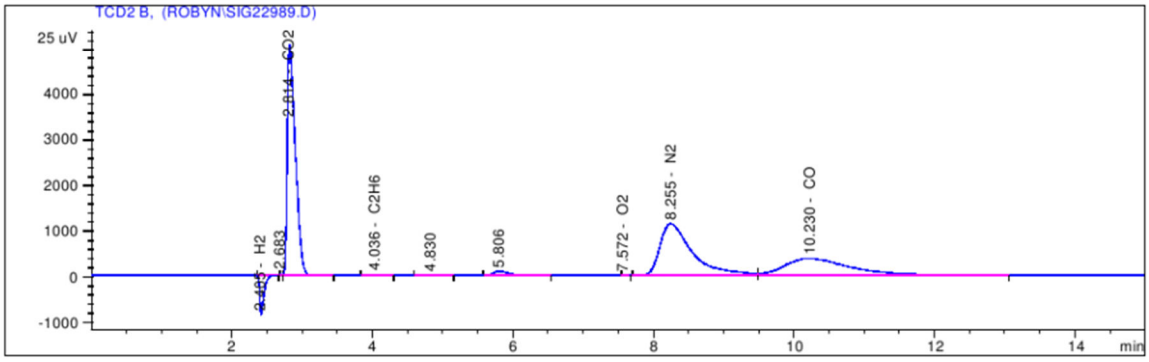
Run#26:500°C,O_2/G=0.2,S/G=9,5Ni/CeZrGd




```
=====================================================================
                      Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.414 BV N   2467.73267 1.29611e-2  35.714521    H2
  2.812 VB     4.02513e4  4.89169e-4  21.985814    CO2
  4.031 BB      330.07080 4.52021e-4   0.166598    C2H6
  7.572 BV       14.96881 5.37947e-4   0.008991    O2
  8.243 VV     5.75770e4  4.82433e-4  31.016277    N2
  9.700           -          -          -         CH4
 10.243 VB     2.08375e4  4.77395e-4  11.107799    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 15-Oct-12, 18:51:16
```

Run#27:550°C,O_2/G=0.2,S/G=9,5Ni/CeZrGd

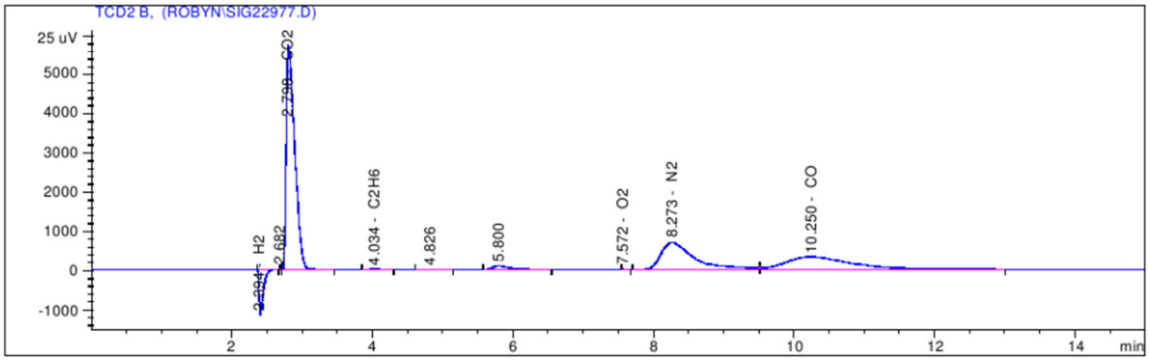



```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,
```

RetTime [min]	Type	Area [25 uV*s]	Amt/Area	Norm %	Grp	Name
2.405	BP N	3485.26147	1.25853e-2	47.162008		H2
2.814	VB	4.01807e4	4.89166e-4	21.133332		CO2
4.036	BB	259.37445	4.52021e-4	0.126061		C2H6
7.572	VB	14.88827	5.37947e-4	0.008611		O2
8.255	BV	3.67663e4	4.82735e-4	19.083262		N2
9.700		-	-	-		CH4
10.230	VB	2.43263e4	4.77395e-4	12.486726		CO
Totals :				100.000000		

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 09-Oct-12, 19:18:07
```

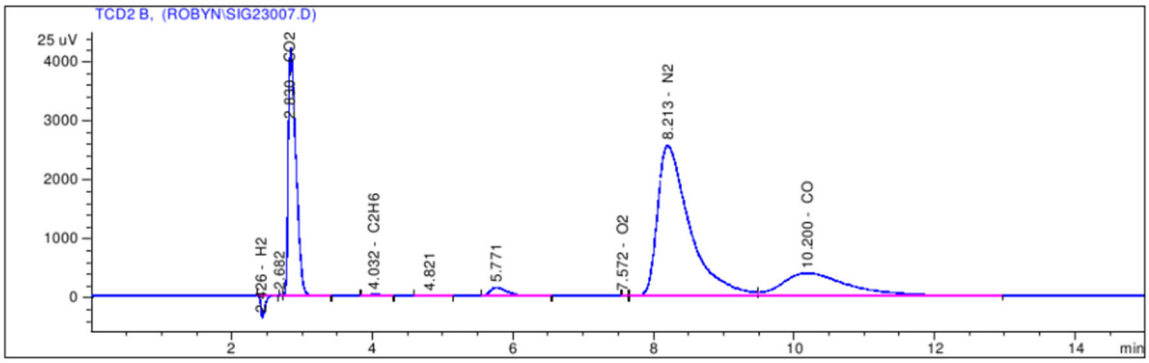
Run#28:600°C,O_2/G=0.2,S/G=9,5Ni/CeZrGd




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm    Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.394 BP N    4707.66455 1.23486e-2  56.871341    H2
  2.798 VB S    4.73422e4  4.89404e-4  22.666617    CO2
  4.034 BB        86.76270 4.52021e-4   0.038367    C2H6
  7.572 BB        14.79066 5.37947e-4   0.007784    O2
  8.273 BV      2.27088e4  4.83252e-4  10.735927    N2
  9.700             -          -          -        CH4
 10.250 VB      2.07264e4  4.77395e-4   9.679963    CO

Totals :                               100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 19-Oct-12, 20:17:18
```

Run#29:450°C,O_2/G=0.2,S/G=12,5Ni/CeZrGd

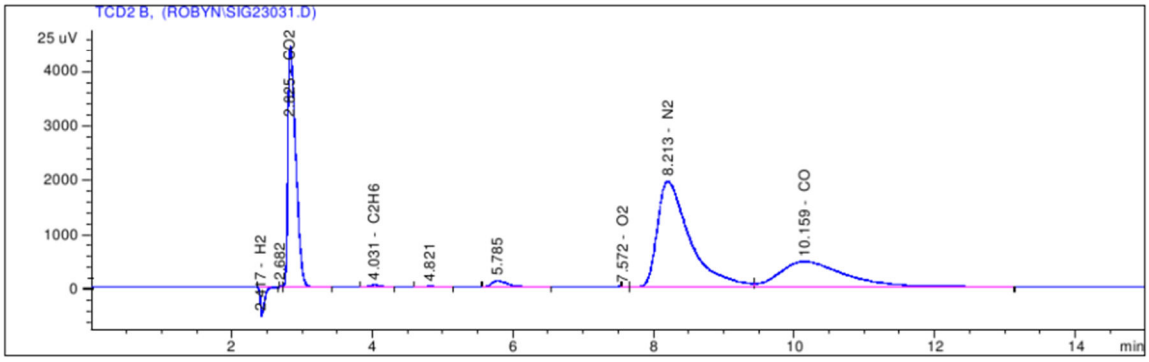



```
=====================================================================
                      Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,
```

RetTime [min]	Type	Area [25 uV*s]	Amt/Area	Norm %	Grp	Name
2.426	BV N	1500.92310	1.37904e-2	23.562552		H2
2.830	VB	3.19208e4	4.88759e-4	17.760536		CO2
4.032	BB	327.66696	4.52021e-4	0.168608		C2H6
7.572	BV	14.20804	5.37947e-4	0.008701		O2
8.213	VV	8.17511e4	4.82275e-4	44.882360		N2
9.700		-	-	-		CH4
10.200	VB	2.50567e4	4.77395e-4	13.617244		CO
Totals :				100.000000		

```
======================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 27-Oct-12, 21:42:07
```

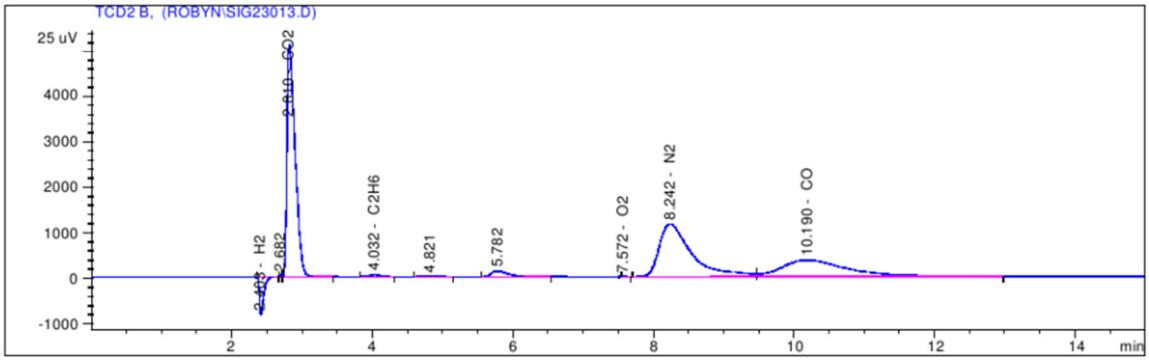
Run#30:500°C,O_2/G=0.2,S/G=12,5Ni/CeZrGd




```
======================================================================
                    Normalized Percent Report
======================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.417 BP N   2121.02905 1.31716e-2  31.004977    H2
  2.825 VB     3.42663e4  4.88895e-4  18.592185    CO2
  4.031 BB      463.34683 4.52021e-4   0.232441    C2H6
  7.572 VV       15.47658 5.37947e-4   0.009240    O2
  8.213 VV     6.31445e4  4.82386e-4  33.804725    N2
  9.700            -          -          -        CH4
 10.159 VB     3.08719e4  4.77395e-4  16.356432    CO

Totals :                              100.000000
```

```
======================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 21-Oct-12, 20:40:32
```

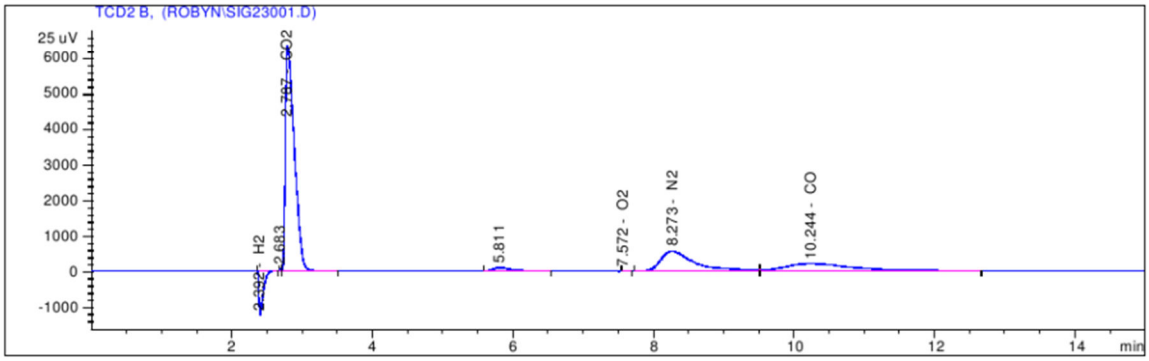
Run#31:550°C,O_2/G=0.2,S/G=12,5Ni/CeZrGd




```
======================================================================
                    Normalized Percent Report
======================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.403 BP N   3347.07373 1.26229e-2  45.837069    H2
  2.810 VB     4.06340e4  4.89183e-4  21.565196    CO2
  4.032 BB      434.18259 4.52021e-4   0.212923    C2H6
  7.572 VB       15.07736 5.37947e-4   0.008799    O2
  8.242 BV     3.78061e4  4.82712e-4  19.798923    N2
  9.700           -          -          -         CH4
 10.190 VB     2.42834e4  4.77395e-4  12.577089    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator    : Faezeh
Acq. Instrument : Instrument 1
Injection Date   : 18-Oct-12, 23:11:25
```

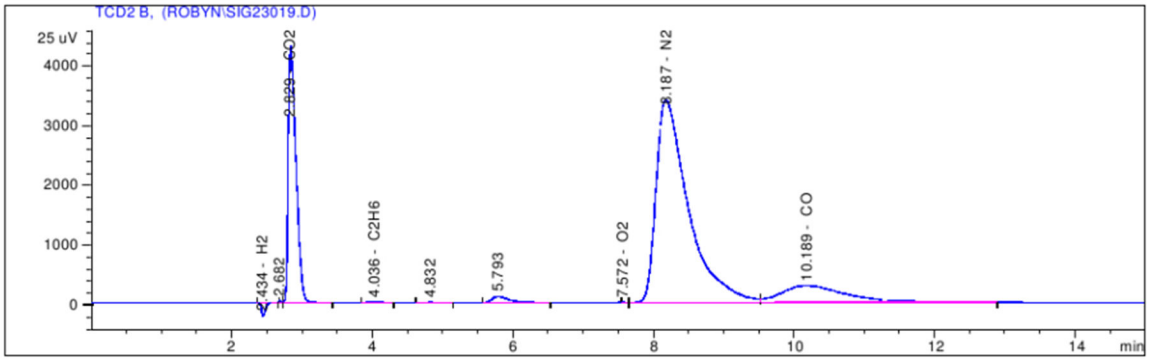
Run#32:600°C,O_2/G=0.2,S/G=12,5Ni/CeZrGd




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.392 BV N   5077.25635 1.22995e-2  59.898050    H2
  2.787 VB S   5.47459e4  4.89584e-4  25.708495    CO2
  4.027           -           -           -        C2H6
  7.572 BB       14.52180 5.37947e-4   0.007493    O2
  8.273 BV     1.82125e4  4.83586e-4   8.447740    N2
  9.700           -           -           -        CH4
 10.244 VB     1.29682e4  4.77395e-4   5.938223    CO

Totals :                             100.000000
```

```
=====================================================================
Acq. Operator    : Faezeh
Acq. Instrument : Instrument 1
Injection Date   : 22-Oct-12, 21:51:15
```

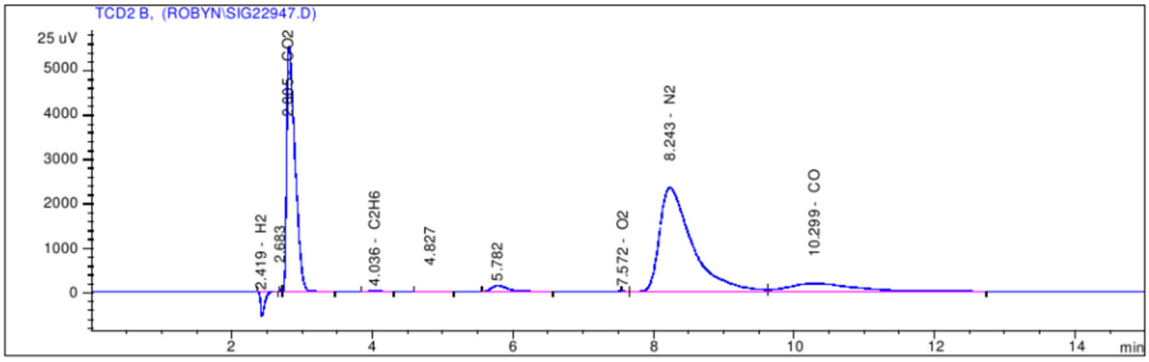
Run#33:450°C,O_2/G=0.5,S/G=12,5Ni/CeZrGd




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.434 BP N    890.28021 1.52422e-2  14.757109    H2
  2.829 VB     3.29924e4  4.88823e-4  17.538494    CO2
  4.036 BB      182.82004 4.52021e-4   0.089869    C2H6
  7.572 VV       16.07007 5.37947e-4   0.009401    O2
  8.187 VV     1.10097e5  4.82178e-4  57.730906    N2
  9.700            -          -          -        CH4
 10.189 VB     1.90194e4  4.77395e-4   9.874221    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator    : Faezeh
Acq. Instrument : Instrument 1
Injection Date   : 02-Oct-12, 17:54:23
```

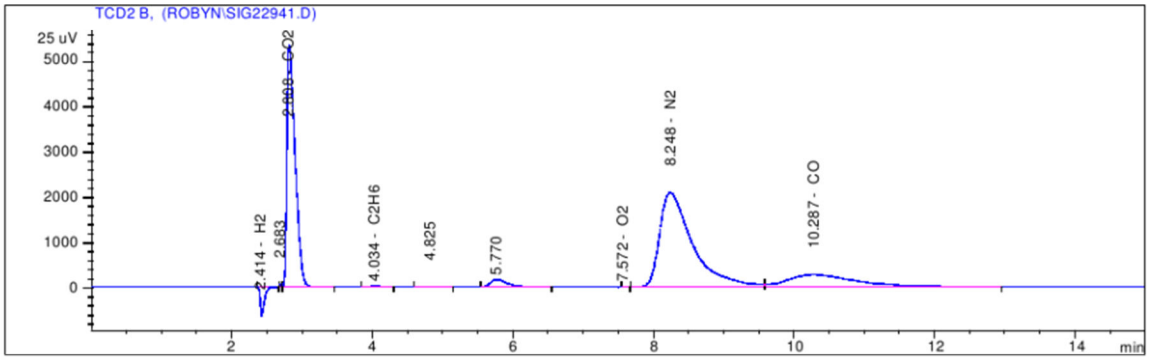
Run#34:500°C,O_2/G=0.5,S/G=12,5Ni/CeZrGd




```
=====================================================================
                        Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type      Area      Amt/Area      Norm     Grp    Name
 [min]          [25 uV*s]                   %
-------|------|----------|----------|----------|--|------------------
  2.419 BP N   2221.77832 1.31036e-2  31.198785    H2
  2.805 VB S   4.50146e4  4.89335e-4  23.604989    CO2
  4.036 BB      139.83600 4.52021e-4   0.067736    C2H6
  7.572 VV       15.10268 5.37947e-4   0.008706    O2
  8.243 VV     7.54665e4  4.82306e-4  39.005164    N2
  9.700            -          -          -        CH4
 10.299 VB     1.19522e4  4.77395e-4   6.114619    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 30-Sep-12, 18:42:22
```

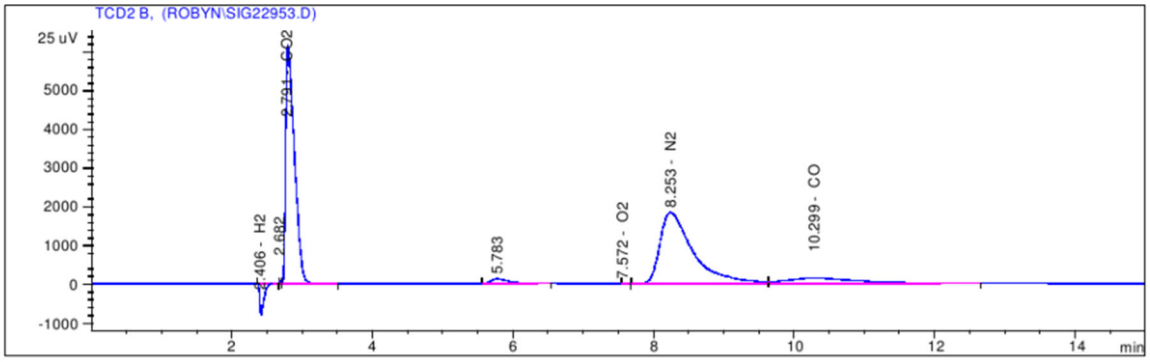
Run#35:550°C,O_2/G=0.5,S/G=12,5Ni/CeZrGd




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm    Grp   Name
 [min]          [25 uV*s]                  %
-------|------|----------|----------|----------|--|------------------
  2.414 BP N   2564.72168 1.29124e-2  34.827250    H2
  2.808 VB     4.27659e4  4.89261e-4  22.004361    CO2
  4.034 BB      209.42950 4.52021e-4   0.099556    C2H6
  7.572 VB       15.16295 5.37947e-4   0.008578    O2
  8.248 BV     6.73802e4  4.82355e-4  34.179797    N2
  9.700            -          -          -        CH4
 10.287 VB     1.76883e4  4.77395e-4   8.880458    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator    : Faezeh
Acq. Instrument : Instrument 1
 Injection Date  : 05-Oct-12, 20:15:20
```

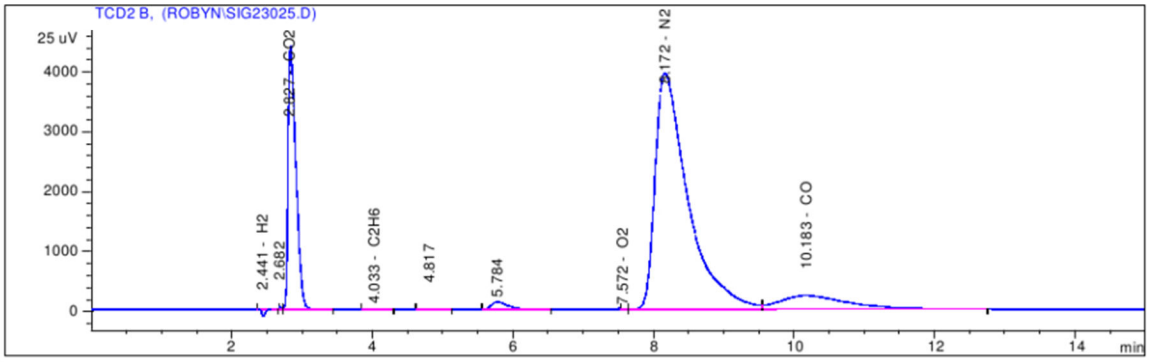
Run#36:600°C,O_2/G=0.5,S/G=12,5Ni/CeZrGd




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type      Area      Amt/Area      Norm     Grp   Name
 [min]          [25 uV*s]                  %
-------|------|----------|----------|----------|--|------------------
  2.406 BP N   3321.10815 1.26303e-2  41.731149    H2
  2.791 VB S   5.21031e4  4.89525e-4  25.374738    CO2
  4.027            -          -          -        C2H6
  7.572 BB       15.19471 5.37947e-4   0.008132    O2
  8.253 BV     5.95624e4  4.82415e-4  28.586151    N2
  9.700            -          -          -        CH4
 10.299 VB     9053.37207 4.77395e-4   4.299831    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 26-Oct-12, 21:05:06
```

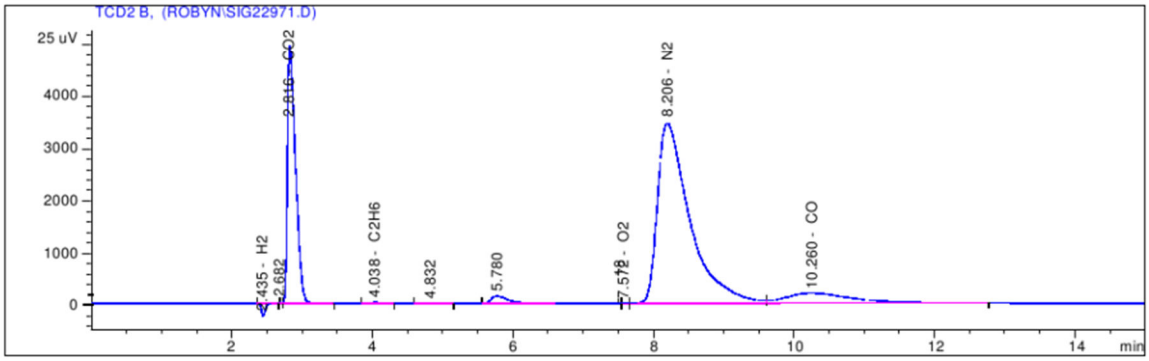
Run#37:450°C,O_2/G=0.8,S/G=12,5Ni/CeZrGd




```
=====================================================================
                        Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type      Area      Amt/Area      Norm     Grp    Name
 [min]          [25 uV*s]                   %
-------|------|----------|----------|----------|--|------------------
  2.441 BP N     482.84012 1.82534e-2   9.275720    H2
  2.827 VB      3.38474e4  4.88872e-4  17.414884    CO2
  4.033 BB       145.64850 4.52021e-4   0.069289    C2H6
  7.572 VV        16.64435 5.37947e-4   0.009423    O2
  8.172 VV      1.29412e5  4.82136e-4  65.666398    N2
  9.700             -          -          -        CH4
 10.183 VB      1.50553e4  4.77395e-4   7.564286    CO

Totals :                               100.000000
```

```
======================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 08-Oct-12, 20:00:04
```

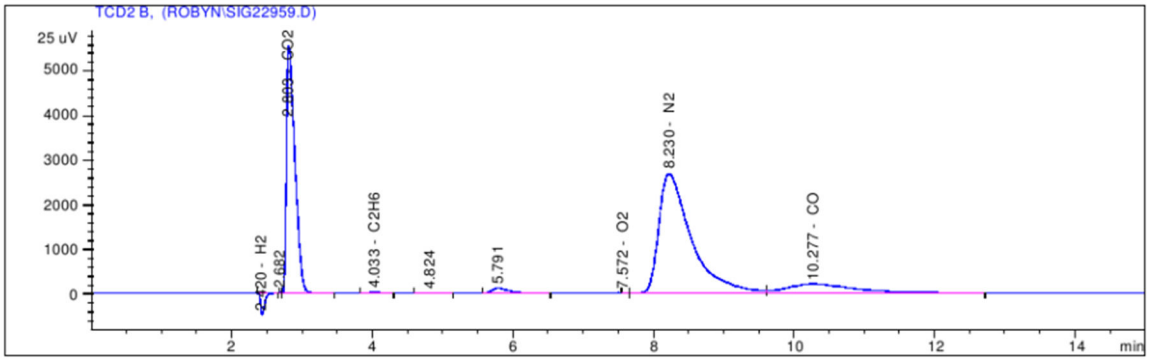
Run#38:500°C,O_2/G=0.8,S/G=12,5Ni/CeZrGd




```
======================================================================
                    Normalized Percent Report
======================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|-----------------
  2.435 BP N     959.91821 1.49833e-2  15.196403    H2
  2.816 VB      3.91644e4  4.89125e-4  20.239959    CO2
  4.038 BB       170.89366 4.52021e-4   0.081618    C2H6
  7.572 VV        77.41605 5.37947e-4   0.044002    O2
  8.206 VV      1.12794e5  4.82171e-4  57.462496    N2
  9.700             -          -          -        CH4
 10.260 VB      1.38293e4  4.77395e-4   6.975523    CO

Totals :                               100.000000
```

```
=====================================================================
Acq. Operator    : Faezeh
Acq. Instrument : Instrument 1
Injection Date   : 06-Oct-12, 18:42:07
```

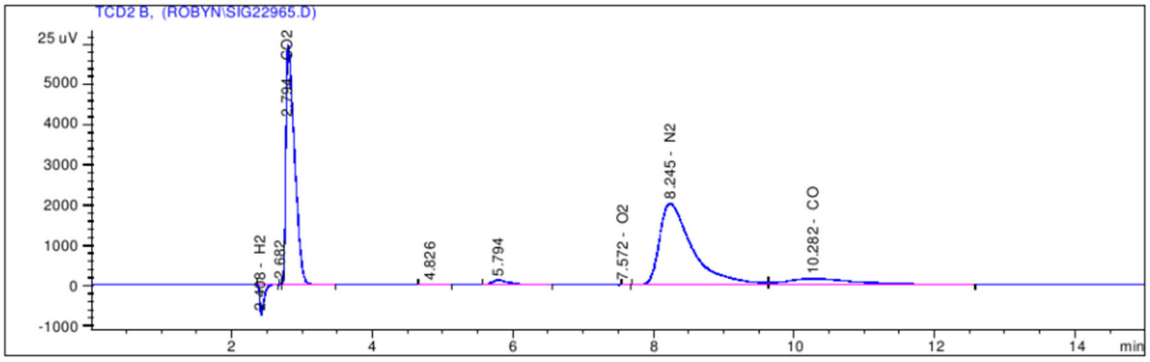
Run#39:550°C,O_2/G=0.8,S/G=12,5Ni/CeZrGd




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm    Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.420 BP N   1954.09070 1.32995e-2  27.089439    H2
  2.803 VB S   4.54351e4  4.89348e-4  23.175457    CO2
  4.033 BB      217.55353 4.52021e-4   0.102505    C2H6
  7.572 VV       15.19055 5.37947e-4   0.008518    O2
  8.230 VV     8.57611e4  4.82257e-4  43.110998    N2
  9.700            -          -          -        CH4
 10.277 VB     1.30885e4  4.77395e-4   6.513084    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 07-Oct-12, 19:40:37
```

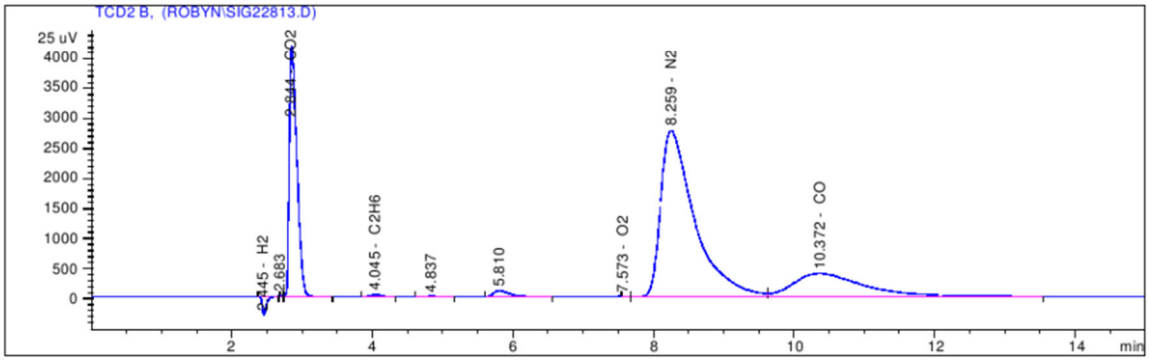
Run#40:600°C,O_2/G=0.8,S/G=12,5Ni/CeZrGd




```
=====================================================================
                      Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm    Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.408 BV N   3029.90771 1.27223e-2  39.034884    H2
  2.794 VB S   5.00484e4  4.89476e-4  24.807370    CO2
  4.027           -           -           -        C2H6
  7.572 VB       14.55324 5.37947e-4   0.007928    O2
  8.245 BV     6.47756e4  4.82373e-4  31.641249    N2
  9.700           -           -           -        CH4
 10.282 VB     9326.12793 4.77395e-4   4.508569    CO

Totals :                             100.000000
```

```
======================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 12-Jul-12, 18:36:16
```

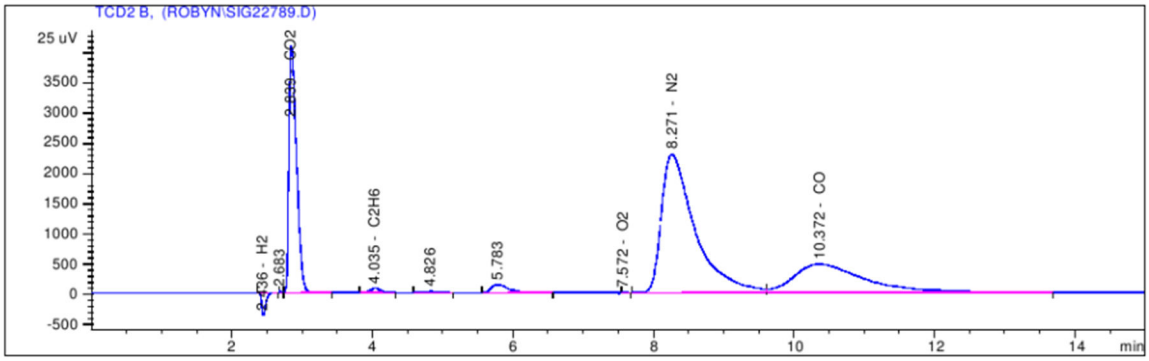
Run#41:450°C,O_2/G=0.2,S/G=6,5Ni/CeZrGd




```
======================================================================
                    Normalized Percent Report
======================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.445 BP N   1233.68774 1.42489e-2  19.321613    H2
  2.844 VB     3.11630e4  4.88711e-4  16.739737    CO2
  4.045 BB      376.46030 4.52021e-4   0.187040    C2H6
  7.573 BB       15.32118 5.37947e-4   0.009059    O2
  8.259 BV     9.30884e4  4.82229e-4  49.340794    N2
  9.700            -          -          -        CH4
 10.372 VB     2.74461e4  4.77395e-4  14.401756    CO

Totals :                              100.000000
```

```
======================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 09-Jul-12, 18:37:08
```

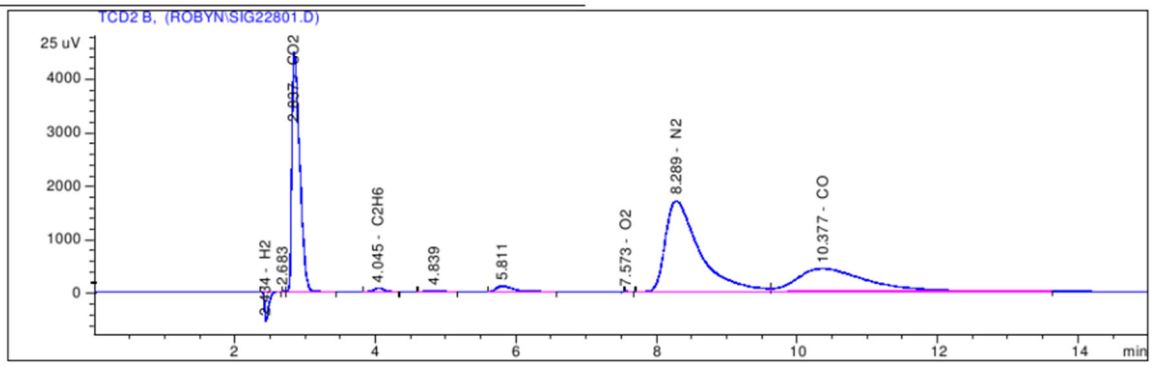
Run#42:500°C,O_2/G=0.2,S/G=6,5Ni/CeZrGd




```
======================================================================
                      Normalized Percent Report
======================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|-----------------
  2.436 BV N   1524.62183 1.37575e-2  23.701754    H2
  2.839 VB     3.02774e4  4.88652e-4  16.718522    CO2
  4.035 BB      684.88446 4.52021e-4   0.349829    C2H6
  7.572 BB       15.22051 5.37947e-4   0.009252    O2
  8.271 BV     7.61136e4  4.82303e-4  41.482115    N2
  9.700            -          -          -        CH4
 10.372 VB     3.28821e4  4.77395e-4  17.738529    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 10-Jul-12, 19:07:21
```

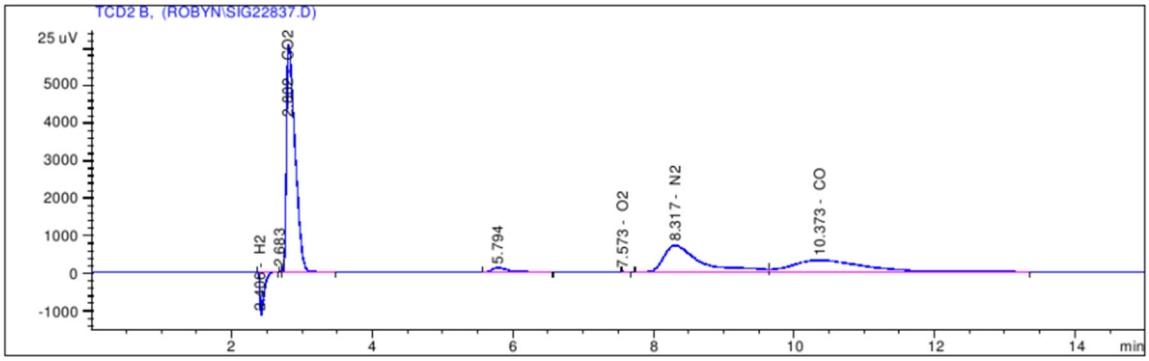
Run#43:550°C,O_2/G=0.2,S/G=6,5Ni/CeZrGd




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm     Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.434 BV N   2231.13916 1.30976e-2  32.908747    H2
  2.837 VB     3.44488e4  4.88904e-4  18.966575    CO2
  4.045 BB      680.51715 4.52021e-4   0.346409    C2H6
  7.573 BB       15.22530 5.37947e-4   0.009224    O2
  8.289 BV     5.77581e4  4.82431e-4  31.379057    N2
  9.700            -          -          -        CH4
 10.377 VB     3.04866e4  4.77395e-4  16.389987    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 23-Jul-12, 18:15:41
```

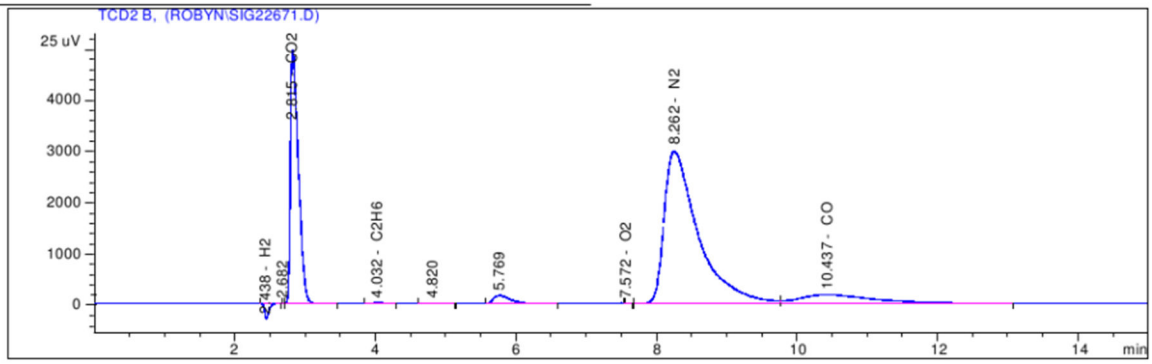
Run#44:600°C,O_2/G=0.2,S/G=6,5Ni/CeZrGd




```
=====================================================================
                      Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm    Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.406 BV N   4610.50732 1.23628e-2  54.158764    H2
  2.802 VB S   5.05900e4  4.89489e-4  23.529419    CO2
  4.027           -           -          -        C2H6
  7.573 BB       15.41749 5.37947e-4   0.007881    O2
  8.317 BV     2.59865e4  4.83081e-4  11.928079    N2
  9.700           -           -          -        CH4
 10.373 VB     2.28740e4  4.77395e-4  10.375858    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 08-Feb-12, 20:29:07
```

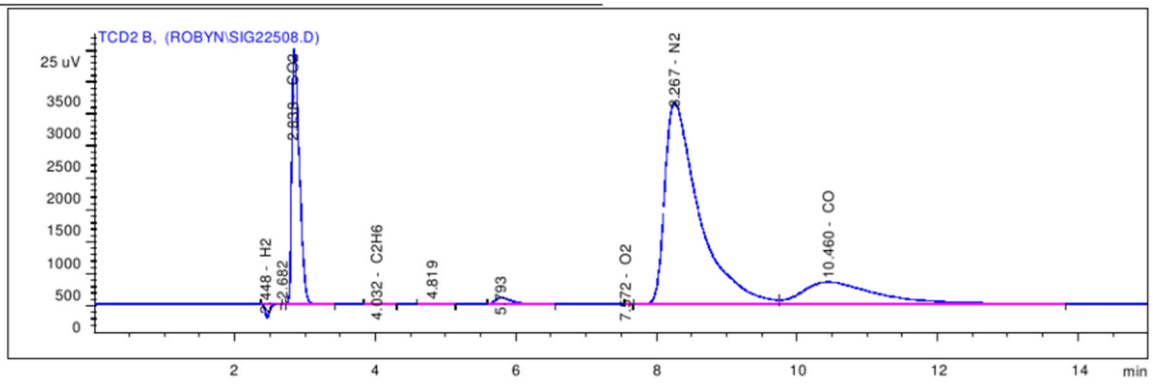
Run#45:450°C,O_2/G=0.5,S/G=6,5Ni/CeZrGd




```
=====================================================================
                      Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm    Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|------------------
  2.438 BP N   1225.36816 1.42664e-2  19.179056    H2
  2.815 VB     3.89590e4  4.89117e-4  20.905818    CO2
  4.032 BB      198.38039 4.52021e-4   0.098380    C2H6
  7.572 VB       14.99272 5.37947e-4   0.008848    O2
  8.262 BV     1.00897e5  4.82203e-4  53.377079    N2
  9.700            -          -          -        CH4
 10.437 VB     1.22784e4  4.77395e-4   6.430819    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 30-Nov-11, 20:05:15
```

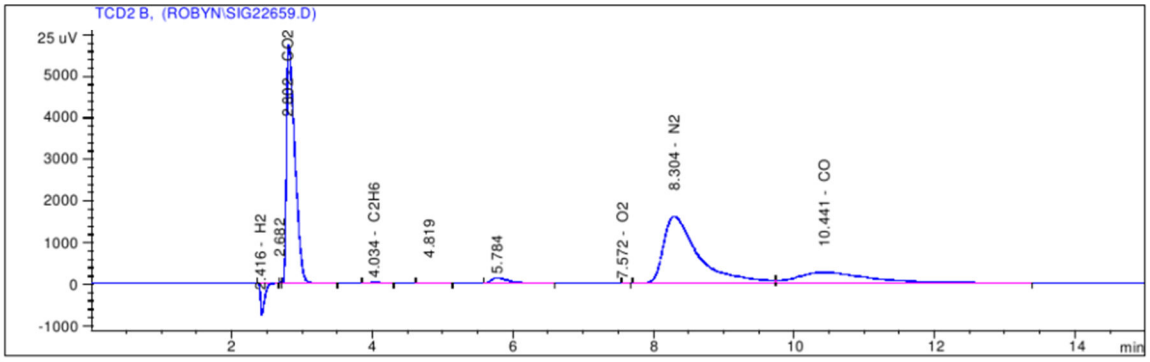
Run#46:500°C,O_2/G=0.5,S/G=6,5Ni/CeZrGd




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type      Area      Amt/Area      Norm     Grp   Name
 [min]          [25 uV*s]                   %
-------|------|----------|----------|----------|--|------------------
  2.448 BV N     901.03253 1.51996e-2  14.911660    H2
  2.838 VB      2.95333e4  4.88599e-4  15.711530    CO2
  4.032 BB       182.90668 4.52021e-4   0.090020    C2H6
  7.572 VB        15.53429 5.37947e-4   0.009099    O2
  8.267 BV      1.07111e5  4.82186e-4  56.234571    N2
  9.700             -          -          -        CH4
 10.460 VB      2.50929e4  4.77395e-4  13.043120    CO

Totals :                               100.000000
```

```
=====================================================================
Acq. Operator    : Faezeh
Acq. Instrument : Instrument 1
Injection Date   : 06-Feb-12, 18:00:35
```

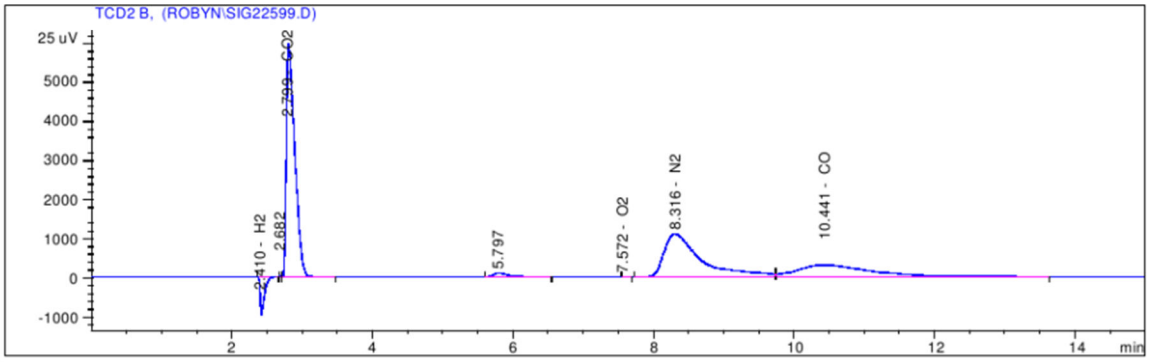
Run#47:550°C,O_2/G=0.5,S/G=6,5Ni/CeZrGd




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm    Grp   Name
 [min]          [25 uV*s]                  %
-------|------|----------|----------|----------|--|------------------
  2.416 BP N   3104.71460 1.26970e-2  40.530711    H2
  2.802 VB S   4.66227e4  4.89383e-4  23.458889    CO2
  4.034 BB      181.23787 4.52021e-4   0.084230    C2H6
  7.572 VB       15.67644 5.37947e-4   0.008671    O2
  8.304 BV     5.46595e4  4.82461e-4  27.113757    N2
  9.700            -          -          -        CH4
 10.441 VB     1.79361e4  4.77395e-4   8.803741    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator    : Faezeh
Acq. Instrument : Instrument 1
 Injection Date  : 11-Jan-12, 17:23:51
```

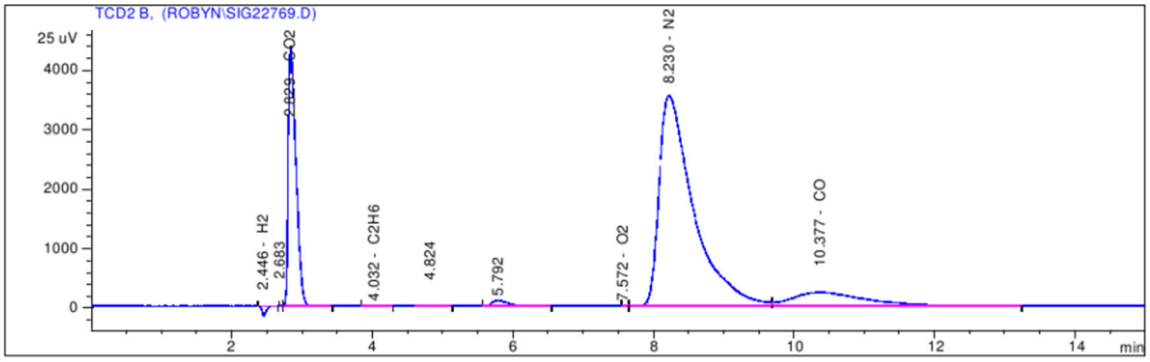
Run#48:600°C,O_2/G=0.5,S/G=6,5Ni/CeZrGd




```
=====================================================================
                        Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type      Area      Amt/Area      Norm     Grp    Name
 [min]          [25 uV*s]                  %
-------|------|----------|----------|----------|--|------------------
  2.410 BP N   3968.74536 1.24742e-2  47.952942    H2
  2.799 VB S   4.88768e4  4.89445e-4  23.171587    CO2
  4.027            -          -          -        C2H6
  7.572 BB       16.15941 5.37947e-4   0.008420    O2
  8.316 BV     3.99067e4  4.82669e-4  18.657064    N2
  9.700            -          -          -        CH4
 10.441 VB     2.20800e4  4.77395e-4  10.209987    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator    : Faezeh
Acq. Instrument : Instrument 1
Injection Date   : 24-May-12, 15:30:21
```

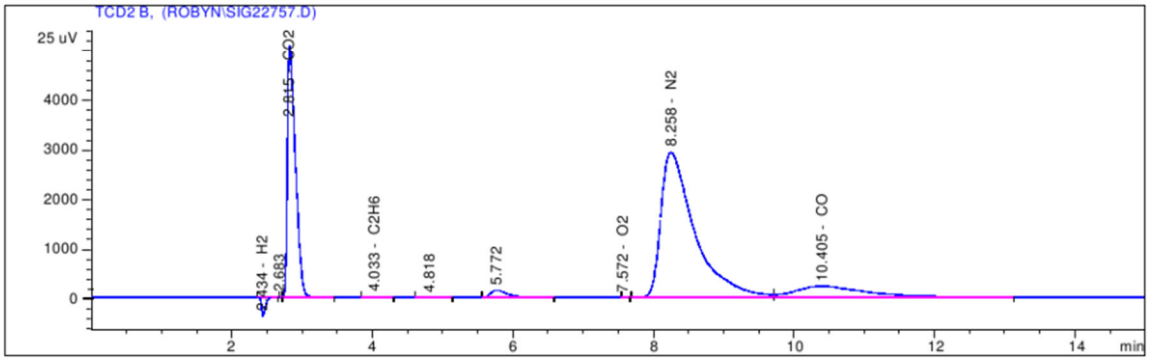
Run#49:450°C,O_2/G=0.8,S/G=6,5Ni/CeZrGd




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type      Area      Amt/Area      Norm     Grp   Name
 [min]          [25 uV*s]                   %
-------|------|----------|----------|----------|--|------------------
  2.446 BV N     696.13922 1.62374e-2  12.015322    H2
  2.829 VB      3.32292e4  4.88837e-4  17.266643    CO2
  4.032 BB       122.35688 4.52021e-4   0.058791    C2H6
  7.572 VV        14.70548 5.37947e-4   0.008409    O2
  8.230 VV      1.21298e5  4.82152e-4  62.166974    N2
  9.700             -          -          -        CH4
 10.377 VB      1.67183e4  4.77395e-4   8.483860    CO

Totals :                               100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 15-May-12, 16:18:07
```

Run#50:500°C,O_2/G=0.8,S/G=6,5Ni/CeZrGd

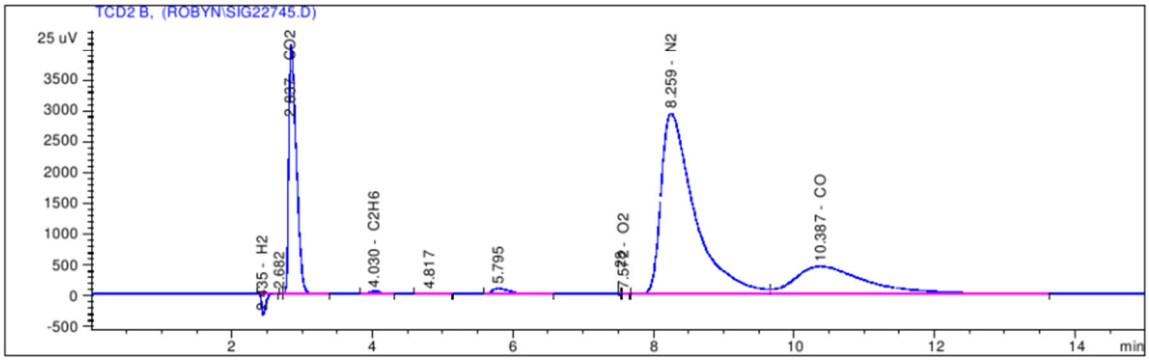



```
=====================================================================
                        Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,
```

RetTime [min]	Type	Area [25 uV*s]	Amt/Area	Norm %	Grp	Name
2.434	BV N	1506.04773	1.37832e-2	21.878176		H2
2.815	VB	3.99908e4	4.89158e-4	20.617319		CO2
4.033	BB	148.96051	4.52021e-4	0.070966		C2H6
7.572	VB	14.98337	5.37947e-4	0.008495		O2
8.258	BV	9.78993e4	4.82213e-4	49.755481		N2
9.700		-	-	-		CH4
10.405	VB	1.52430e4	4.77395e-4	7.669562		CO
Totals :				100.000000		

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 08-May-12, 18:50:06
```

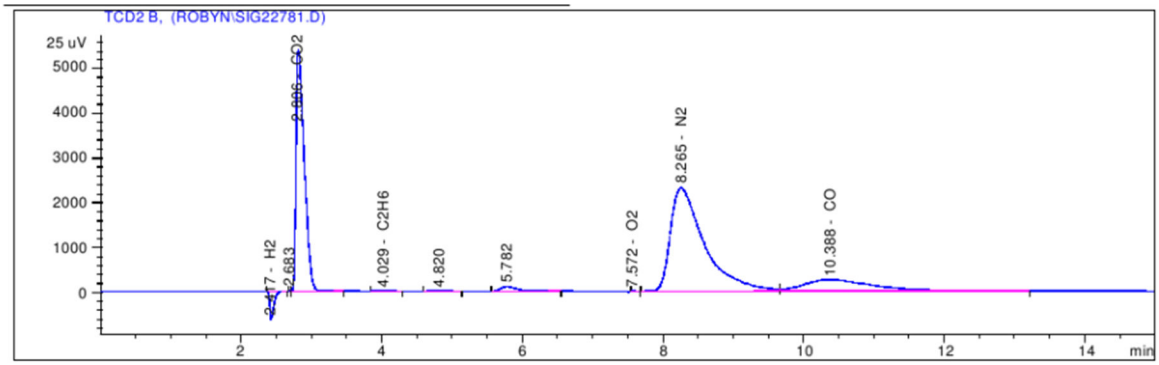
Run#51:550°C,O_2/G=0.8,S/G=6,5Ni/CeZrGd




```
=====================================================================
                      Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm    Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|-----------------
  2.435 BV N   1373.31067 1.39871e-2  20.057777    H2
  2.837 VB     2.97972e4  4.88618e-4  15.203116    CO2
  4.030 BB      393.16888 4.52021e-4   0.185577    C2H6
  7.572 VB       34.74377 5.37947e-4   0.019517    O2
  8.259 BV     9.71959e4  4.82215e-4  48.941345    N2
  9.700            -          -          -        CH4
 10.387 VB     3.12792e4  4.77395e-4  15.592667    CO

Totals :                              100.000000
```

```
=====================================================================
Acq. Operator   : Faezeh
Acq. Instrument : Instrument 1
Injection Date  : 06-Jul-12, 20:02:06
```

Run#52:600°C,O_2/G=0.8,S/G=6,5Ni/CeZrGd




```
=====================================================================
                    Normalized Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      02/10/2012 3:12:21 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD2 B,

RetTime  Type     Area      Amt/Area     Norm    Grp   Name
 [min]          [25 uV*s]                 %
-------|------|----------|----------|----------|--|-----------------
  2.417 BV N   2502.84204 1.29431e-2  32.546667    H2
  2.806 VB     4.30813e4  4.89272e-4  21.177517    CO2
  4.029 BB       99.37104 4.52021e-4   0.045129    C2H6
  7.572 VB       15.49632 5.37947e-4   0.008375    O2
  8.265 BV     7.77600e4  4.82294e-4  37.679398    N2
  9.700            -          -          -        CH4
 10.388 VB     1.78112e4  4.77395e-4   8.542915    CO

Totals :                              100.000000
```