AN EXPERIMENTAL STUDY ON Pt-BASED BIMETALLIC OXIDATIVE STEAM REFORMING (OSR) CATALYSTS

by
Bayram Ali Göçmen
B.S., Chemical Engineering/Chemistry, Boğaziçi University, 2004/2005

Submitted to the Institute for Graduate Studies in
Science and Engineering in partial fulfillment of
the requirements for the degree of
Master of Science

Graduate Program in Chemical Engineering
Boğaziçi University
2010

ACKNOWLEDGEMENTS

This study dedicated to some special people, whose existence provided me relief, scientific zeal and joy at times. I would like to express my sincere gratitude to my thesis supervisor, Prof. Ahmet Erhan Aksoylu, for his guidance and help throughout my thesis. He always trusted in me and was always available with their effective contributions.

Heartfelt thanks go to Feyza Gökaliler and Şeyma Özkara for their intimate friendship, support and alliance that they provided. They were ready to help me whenever I needed.

Apart from those cited above, my appreciations are for the whole CATREL team, especially to Assoc. Dr. Ahmet Kerim Avcı and Burcu Selen Çağlayan for their guidence in technical part of the study. I would like to thank İsa Rahmanlar, M. Erkan Karabekmez, Duygu Başaran, Eray Gürel, and Tuğba Davran for their intimate friendship.

I will appreciate Bilgi Dedeoğlu, Nurettin Bektaş, Belgin Balkan, Melike Gürbüz, and Fatma Odak for their significant efforts and cordial friendship during my thesis study.

I would also like to thank all my friends in Chemical Engineering Department at Boğaziçi University.

Finally, my heartfelt thanks go to my fiancé, Esma Benli, because of her encouragement to me during final preparation of the thesis.

This study is supported by State Planning Organization of Turkey, DPT, through projects DPT-07K12630, DPT-03K120250, and TUBİTAK through project 105M282.

ABSTRACT

AN EXPERIMENTAL STUDY ON Pt-BASED BIMETALLIC OXIDATIVE STEAM REFORMING CATALYSTS

In the current study, Pt-Ni/Al_2O_3 system was optimized for catalytic hydrogen production via oxidative steam reforming of propane. Oxidative steam reforming of propane was tested over four Pt-Ni/δ-Al_2O_3 bimetallic and one Pt-Au-Ni/δ-Al_2O_3 tri-metallic catalysts aiming to investigate the effect of Ni:Pt loading ratio on catalyst performance. Catalyst types and reaction conditions were firstly arranged to identify the effect of reaction temperature, carbon to oxygen ratio, residence time, and catalyst loadings on hydrogen production. The catalysts were prepared as having two different levels of Pt loadings (0.2 wt % and 0.3 wt %) and two different levels of Ni loadings (10 wt % and 15 wt %) on alumina support. Gold was added to the Pt-Ni system, aiming to see its affect both on OSR performance of the catalyst as well as its secondary WGS activity. The effect of C/O_2 ratio on the hydrogen production and H_2/CO selectivity were found dependent on the Pt and Ni loadings, and their loading ratio (Ni:Pt) as well. The highest hydrogen production and H_2/CO ratio levels were obtained for the highest C/O_2 ratio tested. Lower Pt loadings have made the catalysts more sensitive to the changes in C/O_2 ratio. An optimum Ni:Pt ratio was found around 50 by weight due to suppressed methanation and enhanced hydrogen production activities of these catalysts. The presence of gold in the trimetallic catalyst caused poor activity and selectivity in comparison to bimetallic catalysts.

ÖZET

PLATİN BAZLI ÇİFT METALLİ OKSİDATİF BUHAR DÖNÜŞÜMÜ KATALİZLERİ ÜZERİNDE DENEYSEL ÇALIŞMA

Bu çalışmada, Pt-Ni/delta-Al_2O_3 sistemi, propanın oksidatif buhar çevrimi ile katalitik hidrojen üretimi için optimize edilmiştir. Propanın oksidatif buhar dönüşümü dört Pt-Ni/delta-Al_2O_3 çift metalli ve bir Pt-Au-Ni/delta-Al_2O_3 üç metalli kataliz üzerinde, katalizdeki Ni:Pt miktarının kataliz performansı üzerindeki etkisini araştırmak amacıyla test edilmiştir. Öncelikle, kataliz tipleri ve reaksiyon şartları, reaksiyon sıcaklığı, karbon: oksijen oranı, bekleme süresi ve kataliz içeriğinin hidrojen üretimindeki etkisini belirlemek amacıyla düzenlenmiştir. Kataliz, delta alümina destek üzerinde iki farklı Pt oranı (ağırlıkça % 0,2 ve 0,3) ve iki farklı Ni oranı (ağırlıkça % 10 ve 15) olacak şekilde hazırlanmıştır. Katalizin, oksidatif buhar dönüşümü ile ikincil su-gaz dönüşüm performansını görmek için Pt-Ni/delta-Al_2O_3 katalizine altın ilave edilmiştir. Hidrojen üretimi ve H_2/CO seçiciliğinde, C/O_2 oranının etkisi, katalizdeki Pt & Ni miktarına ve Pt:Ni oranına bağlı olduğu bulunmuştur. En yüksek hidrojen üretimi ve H_2/CO oranı seviyeleri test edilen en yüksek C/O_2 oranında elde edilmiştir. Katalizdeki düşük Pt miktarı, katalizi C/O_2 oranındaki değişimlere daha duyarlı hale getirmiştir. Düşük metanasyon ve artan hidrojen üretimi aktivasyonu sebebiyle, optimum Ni:Pt oranı ağırlıkça 50 olarak bulunmuştur. Altının üç metalli kataliz içinde bulunması, iki metalli katalizlerle karşılaştırıldığında zayıf aktivite ve seçiciliğe neden olmuştur.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

The need for a sustainable energy supply is becoming more crucial considering the depletion of fossil energy resources, environmental pollution, climate change, and increasing dependency on OECD countries. Considering the enormous ecological and economic importance of the decentralized small scale energy production and transport sectors in the industrialized and developing countries, the introduction of alternative fuels and energy production systems will be a key to for sustainable energy production and development.

Among new energy production strategies, the use of hydrogen production is expected to play an important role in future energy scenarios considering the drastic increase in energy demand. Therefore, hydrogen is expected to replace the fossil fuels to some degree in the future and to become the preferred portable energy carrier especially for vehicles. Emerging new technologies will be implemented through process modifications and/or renewal of existing energy production technologies like the system utilizing internal combustion.

The transition to a hydrogen-based energy technology, where the main chemical energy carrier is hydrogen and the main non-chemical energy form is electricity, will be gradual, and is likely to continue till the end of the 21st century. Nowadays, conversion of chemical energy (occluded in hydrogen gas) to electricity, which is an easy handled form of energy, is being made through using an intelligent and unconventional system called fuel cell.

Compared with conventional technologies, fuel cells offer significant advantages like operating at zero emission level when pure hydrogen is used as a fuel. Actually, a variety of fuel cells operating with different fuels and electrolytes are under investigation, but the proton exchange membrane fuel cell (PEMFC) fuelled by hydrogen seems to be the most promising option for both vehicular and small scale combined heat and power applications due to its compactness, modularity, high power density and fast response (Ahmed and Krumpelt, 2001; Avcı, 2003).

The crucial point in energy production via fuel cells is providing high purity/CO-free hydrogen feed continuously and stably. In vehicular and small scale immobile applications, this may be accomplished by storing hydrogen or producing it on site by a catalytic system called fuel processor. Since there are technological barriers in hydrogen storage which cannot be overcome in short and midterm, the most promising way to supply hydrogen fuel to a fuel cell is to produce it on site via a fuel processor.

The fuel processors contain series of catalytic reactors which convert various hydrocarbon feeds like LPG, methane, ethanol, etc. to CO-free hydrogen. The serial catalytic reactions should run in a fuel processor are i) reforming of hydrocarbons to hydrogen via steam reforming, direct partial oxidation or oxidative reforming/ indirect partial oxidation, ii) water-gas shift reaction for decreasing the concentration of carbon monoxide and, at the same time, increasing the concentration of hydrogen; and iii) preferential carbon monoxide oxidation which eliminates carbon monoxide in the reformer product to levels less than 10 ppm. CO concentration level in the feed stream as 10 ppm guarantees the stable operation of PEMFC without any loss of activity.

Oxidative steam reforming (OSR), which has alternative names as autothermal reforming (ATR) and indirect partial oxidation (IPOX), is the combination of the total oxidation and steam reforming; since steam reforming and total/partial oxidation run simultaneously, and the heat generated by total oxidation is used for an endothermic steam reforming, the energy efficiency of the system is optimized.

Additionally, since the energy need of endothermic SR is supplied by exothermic total oxidation (TOX), the production of hydrogen from hydrocarbons by OSR is free from the disadvantages of the other reforming methods, like slow start-up, considerable heat input or output, higher catalyst loadings and larger reactors, mass transfer limitations problems, and low efficiencies. The heat exchange during the reaction on the OSR catalysts optimizes the energy efficiency of the system.

$$C_nH_m + n\ H_2O \rightarrow n\ CO + (\tfrac{1}{2}\ m + n)\ H_2 \qquad \text{SR} \qquad (1.1)$$

$$C_nH_m + (n + \tfrac{1}{4}\ m)\ O_2 \rightarrow n\ CO_2 + \tfrac{1}{2}\ m\ H_2O \qquad \text{TOX} \qquad (1.2)$$

OSR has been tested many times in literature over monometallic catalysts. At temperatures up to 827 ^oC, above which thermal sintering is significant, various Ni-based catalysts and Pt/δ-Al_2O_3 have been studied as the suitable catalysts for steam reforming and total oxidation reactions, respectively (Avcı et al., 2003). Bimetallic catalysts have been newly start to be used due to the fact that they make it possible to reach high and stable conversion levels at relatively low operation temperatures (350-450 ^oC). Pt-Ni/δ-Al_2O_3 is a bimetallic system that improves hydrogen production in oxidative steam reforming operation. In addition, this catalyst decreases the operation temperature since the Pt sites, which catalyze total oxidation, and Ni sites which catalyze steam reforming are on the same support. Thus, the catalyst particles behave as micro heat exchangers.

Previous studies on oxidative steam reforming over Pt-Ni/δ-Al_2O_3 which were conducted using propane and LPG with different compositions (i.e. C3:C4 ratio) show that the high activity and selectivity are reached at relatively low reaction temperatures. When butane ratio in LPG is increased, coking was observed even if catalyst runs with high secondary water gas shift activity. In order to eliminate the coking problem, very high steam/ carbon ratios in the feed have been used.

The aim of this work is to obtain a bimetallic OSR catalyst, which shows high activity, selectivity and stability for a wide range of “steam/carbon” and “carbon/oxygen” ratios and residence times (W/F) in OSR of propane. In this context, the bimetallic 0.2 wt% Pt-15 wt% Ni/δ-Al_2O_3, which was tested in propane (Caglayan et al., 2004) and LPG (Caglayan et al., 2005) oxidative steam reforming, has been taken as a reference catalyst, and Pt and Ni loadings of that system is changed in an experimentally designed fashion aiming to obtain a flexible catalyst with optimal Pt:Ni ratio which shows high activity, selectivity and stability for a wide range of carbon/oxygen ratios and residence times in OSR. The performance of catalysts is evaluated in terms of their hydrogen production activity and H_2/CO selectivity for a selected reaction temperature range (i.e. 350^oC-470^oC).

2. LITERATURE SURVEY

2.1. Sustainable Energy Production Systems

The energy requirement of the world has been increasing due to increasing living standards and world population, and the technological applications demanding higher energy input (Midilli et al., 2004). Sustainability is the ability of humanity meets its present needs without compromising the ability of future generations to meet their own needs. Energy is an essential commodity for increasing productivity in all sectors like agriculture, chemical industry, etc. An increase in the energy consumption of a country provides a positive impact on the economic as well as social development of the country. Moreover, the supply and utilization of low-priced clean fuel is particularly crucial for global stability and peace since energy plays a vital role in industrial and technological development around the world. Critical energy issues in the 21st century will likely to include energy security for up to 12 billion people, the expected global population by the middle of the 21st century, and global warming, mainly caused by CO_2 emissions generated from the combustion of fossil fuels.

The investigations of alternative energy strategies have recently become important, particularly for future world stability. The most important property of alternative energy sources is their environmental compatibility. In line with this characteristic, hydrogen will likely become one of the most attractive energy carriers in the near future. Moreover, sustainable systems like wind, sun, nuclear energy have been widely accepted to have an enormous importance for future energy need of the world.

The socio-economical projections and the estimated fossil fuel reserves show that a continuous reliance on fossil fuel for global energy supply will produce major climate-induced ecological changes within 2–3 generations (Tomkiewicz, 2006). Thus, there is an urgent need to expedite the process of implementing the hydrogen economy. A worldwide conversion from fossil fuels to hydrogen would eliminate many problems and their ramifications. The optimal endpoint for conversion to the hydrogen economy is the substitution of clean hydrogen in place of the present fossil fuels. The fully sustainable way of producing hydrogen, i.e. producing it from water by utilizing a fully sustainable primary energy source, like sun, wind, etc., is the ultimate goal of that conversion. By this way, the unique property of hydrogen, that it cannot be destroyed unlike hydrocarbons, and it simply changes state from water to hydrogen and back to water during consumption, can be fully utilized. However, on the other hand, the technological barriers enforce us to produce hydrogen from hydrocarbons in the short and mid-term.

2.2. Fuel Cell Technology

Fuel cell is a promising technology to be used as a source of heat and electricity for buildings and as an electrical power source for electric vehicles. Although these applications would ideally run on pure hydrogen, they are likely to be fuelled with natural gas, methanol, or even gasoline in the short term; reforming these fuels to produce hydrogen will allow the use of much of our current energy infrastructure gas stations, natural gas pipelines, etc. while fuel cells are phased in.

In future, hydrogen could also join electricity as an important energy carrier. Hydrogen is an energy carrier which can be stored, transported, and distributed in a usable form to consumers having fuel cell (FC). Renewable energy sources, like the sun, cannot be used in energy production in continuous manner considering its exposure change from day to night. But energy converted to hydrogen, on the other hand, can be used whenever it is needed and, additionally, can be transported to wherever it is needed.

A fuel cell is an electrochemical device that converts the chemical energy stored in a fuel (usually hydrogen) into electrical energy while producing only water, heat, and minimal pollutants as by-products. Depending on the fuel and electrolyte type, different reactions occur. Since this conversion takes place via an electrochemical process, not via combustion, the process is clean, quiet and highly efficient - two to three times more efficient than fuel burning.

A fuel cell consists of an anode and a cathode separated by an ion-conducting electrolyte which also is called as membrane. Hydrogen is fed the anode and oxygen from air enters through the cathode. In a fuel cell, hydrogen atoms split into protons and electrons generating some heat; protons and electrons take different paths to reach the cathode, where they reunite and create an electrical current that can be utilized. When pure hydrogen is used as the feed, the only emission from a fuel cell is water. The output from a single fuel cell membrane electrolyte assembly (MEA) is about 0.5-0.9 volts DC electricity. The cells can be stacked in a series forming a fuel cell stack to obtain the desired power output. A schematic representation of a fuel cell with the reactant and product gases and the ion conduction flow directions through the cell is shown in Figure 2.1.

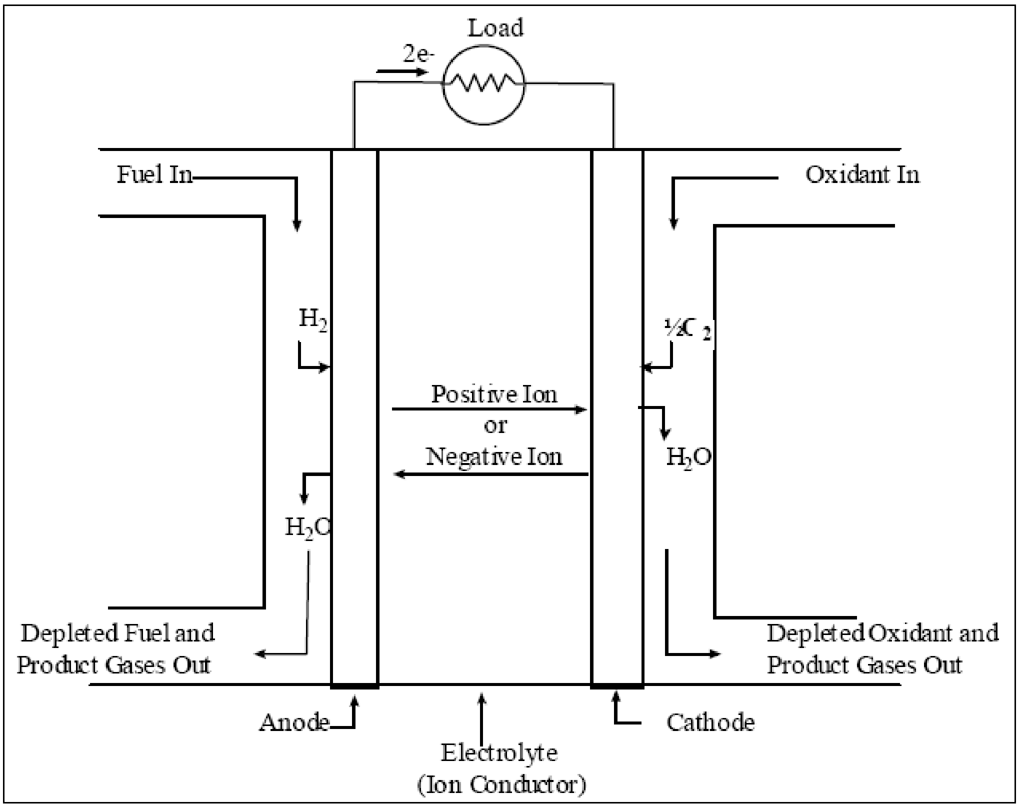


Figure 2.1. A schematic representation of a fuel cell

Fuel cell operation should be held at temperatures higher than 60°C to sustain reaction kinetics and lower than 100°C since the membrane (electrolyte) needs to be humidified to conduct protons, which migrate as hydrated species (Avcı, 2003).

Fuel cells are characterized by their electrolytes and their temperature of operation. There are two major types of fuel cells: low temperature fuel cells and high temperature fuel cells. Three types of low temperature fuel cells are Polymer electrolyte membrane fuel cells (PEMFC), Phosphoric acid fuel cells (PAFC), and Alkaline fuel cells (AFC).

High temperature fuel cells are Molten carbonate fuel cells (MCFC) and Solid oxide fuel cells (SOFC). They are suitable for stationary rather than small scale and/or vehicular applications because of their high operating temperatures, which in turn let them operate at higher efficiencies in electrical energy generation and producing waste heat.

When the fuel cells are listed in the order of approximate operating temperature, the list starts with ~80°C for PEMFC, ~100°C for AFC, ~200°C for PAFC, ~650°C for MCFC, and goes up to ~600-1000°C for SOFC. The operating temperature and useful life of a fuel cell dictate the physicochemical and thermo-mechanical properties of materials used in the cell components. Aqueous electrolytes are limited to temperatures of about 200°C or lower because of their high water vapor pressure and rapid degradation at higher temperatures. The operating temperature also plays an important role in dictating the type of fuel that can be used in a fuel cell. The low-temperature fuel cells with aqueous electrolytes are, in most practical applications, restricted to hydrogen as a fuel. In high temperature fuel cells, CO and even CH_4 can be used because of the inherently rapid electrode kinetics and the lesser need for high catalytic activity at high temperature (Caglayan et al., 2004).

Among the fuel cells mentioned above, PEMFCs have many advantages such as a low operating temperature, sustained operation at a high current density, low weight, and compactness. PEM fuel cells use pure hydrogen as the fuel and a perflorinatedsulphonic acid (poly-perflourosulfonic acid) as the polymeric membrane. They operate at 70 - 90^{o}C temperature range. They have high power density, which is an order of magnitude higher than other fuel cell systems, they can vary their output quickly to meet shifts in power demand, and they are suited for applications, like automobiles where quick startup is required. PEM fuel cells are primarily suited for residential, small scale commercial and transportational applications. The solid organic polymer electrolyte reduces corrosion, safety and management problems. Cell outputs generally range from 50 to 250 kW. The major properties of PEMFCs are given in Table 2.1 (Avcı, 2003).

Table 2.1. Properties of PEMFCs

Operating temperature	343 -353 K
Cathode/Anode catalyst	Pt/Pt
Start up (from room temperature)	Minutes
Efficiency (5 kW size)	30-40 per cent
Efficiency (50 kW size)	35-45 per cent
Estimated cost	$200/kW
Major challenges	Membrane durability System complexity
Major advantages	High power density Quick start-up Reduced corrosion and management problems Low temperature
Major applications	Transportation Small scale CHP Portable/leisure

PEMFCs have recently passed the demonstration phase and have partly reached the commercialization stage on account of the rapid development and an impressive research effort worldwide. However, the remaining challenges that are needed to be overcome will take several years before its full commercialization. The main challenges include supply of high purity hydrogen, cost reduction and the like (Jung-Ho, 2006).

While there are several fuel cell types with features applicable to certain fields, PEMFCs are the most promising system in terms of energy efficiency and compactness. Generally, there are three main application fields for PEMFC system: transportation, small-scale stationary and portable applications. The development direction of PEMFCs in each nation is bound up with their social and industrial environment as well as their structure of energy supply and demand.

The development of a Fuel Cell Vehicle (FCV) requires the on site integration of a fuel-cell system and electric energy storage devices, with an appropriate energy management system. In order to meet the future transportation needs, most major carmakers in the world are actively engaged in developing prototype FCVs and assessing their performance. In order to evaluate the FCV on-board PEMFC, it is important that their driving test be conducted according to a standard duty (driving) cycle, which includes reiteration such as stop, acceleration, cruising, start, and brake (Jung-Ho, 2006). There are some applications of new intelligent battery systems for vehicles. Hybrid electric cars have been used for electrical energy transmission to the wheels. The engine–generator combination provides sufficient power to maintain the vehicle at a steady cruising speed. Here, the battery system may be augmented by the inclusion of a super capacitor, which provides an efficient means for the capture of energy from regenerative braking. In the final analysis, the choice of hybrid system depends on the required duty cycle of the vehicle, the degree of engineering complexity, the capital and running costs, and the emission regulations that have to be observed.

Various on-board applications about PEMFC have been carried out in the world since 2002. For example, hybrid power bus with 50 kW power output has been used in European countries. In 2005, a 300 kW PEMFC system was evaluated for liquid gas-powered operation with their main focus on leisure yachts (Beckhaus et al., 2004). In 2004, Hwang et al. published the test results of a prototype of electric bicycle powered by a PEM.

For a stationary power system, it was reported in 2005 that the development of the key components, specifications, configuration and operation characteristics of a 5kW H_2/air PEMFC system is of great importance (Wang et al., 2005). They consisted of a 5 kW stack consisting of 56 cells with an active area of 250 cm^2 per cell. In addition, it was also reported that future studies should be aimed to overcome the traditionally known problems such as developing CO tolerant anode electro catalysts with low Pt loadings, increasing the cell operation temperature and improving exhaust gas quality. Due to the feasible energy production, large scale stationary energy production systems, which are fed by hydrogen, require more efficient hydrogen supply, storage, and fuel cells with lower Pt loadings and high stability for a long life time.

When portable power systems are considered, rechargeable batteries are well-suited to portable power applications where the energy requirement between recharges is relatively small. In recent years, for example, lithium-ion batteries have proved their worth in mobile communications (cellular phones), laptop computers, and cameras. With the advent of mobile broadband computing, however, the next generation of portable electronic equipment will demand ever-greater amounts of stored energy. For this reason, attention is turning to so-called ‘micro fuel cells’ that promise an energy-storage capability of over an order of magnitude greater than that of the best batteries. Already, there has been a surge of interest in the development of units that generate just a few watts to power a wide range of consumer electronics, as well as in larger cells.

2.3. Hydrogen for Fuel Cell Applications

For fuel cell applications, especially for PEMFC applications, the most important factor is supplying pure hydrogen to fuel cell in fuel cell powered vehicles that run at zero emission levels. In order to produce pure hydrogen, there are two alternatives available: hydrogen may be stored or it may be produced on site for both stationary and mobile applications.

Hydrogen is the simplest element; an atom consisting of only one proton and one electron. Despite its simplicity and abundance, hydrogen does not occur naturally as a gas on Earth. It is always combined with other elements. Water, for example, is a combination of hydrogen and oxygen (H-O-H). Hydrogen is also found in many organic compounds, notably the “hydrocarbons” that make up many of fuels such as gasoline, natural gas, methanol and propane. Hydrogen can be made by separating it from hydrocarbons by applying heat, a process known as “reforming” hydrogen. Currently, most hydrogen is made by this way from natural gas. An electrical current can also be used to separate water into its components of oxygen and hydrogen. Some algae and bacteria, using sunlight as their energy source, even give off hydrogen under certain conditions. Hydrogen is high in energy content and perfectly clean energy source: an engine that burns pure hydrogen produces almost no pollution. NASA has used liquid hydrogen since the 1970s to propel the space shuttle and other rockets into orbit.

Some important advantages of hydrogen:

- Hydrogen is a non-toxic, clean energy carrier that has a high specific energy on a mass basis e.g., the energy content of 9.5 kg of hydrogen is equivalent to that of 25 kg of gasoline.
- Many different production processes for hydrogen exist, including processes where some of the hydrogen is contributed by fossil fuels e.g., steam reforming of natural gas or other light hydrocarbons, gasification of coal and other heavy hydrocarbons, electrolysis of water, direct and indirect thermochemical decomposition, and processes driven directly by sunlight.
- Hydrogen can be safely transported in pipelines.
- Hydrogen can be used advantageously as a chemical feedstock in the petrochemical, food, microelectronics, ferrous and non-ferrous metal, production industries in chemical and polymer synthesis, metallurgical process industries, and as an energy carrier in clean sustainable energy systems.
- When combusted, hydrogen produces non-toxic exhaust emissions.
- Compared to electricity, hydrogen can be stored over relatively long periods of time.
- Hydrogen can be utilized in all parts of the economy e.g., as an automobile fuel and to generate electricity via fuel cells.

Some disadvantages of hydrogen follow:

- When mixed with air, hydrogen can burn in lower concentrations and this can cause safety concerns.
- Storage of hydrogen in liquid form is difficult, as very low temperatures are required to liquefy hydrogen.

2.3.1. Hydrogen Storage

After hydrogen source, hydrogen storage is another crucial point for fuel cell applications. There are many methods for storing hydrogen; the three most common methods are:

Compressed gas in pressure vessels: New materials have allowed pressure vessels and storage tanks to be constructed can store hydrogen at extremely high pressures.

Hydrogen absorbing materials:

- A number of metals (pure and alloyed) can combine with hydrogen to make a metal hydride. The hydride releases hydrogen when it is heated. Hydrogen stored in hydrides under pressure has a very high energy density.
- Hydrogen molecules that have been absorbed on charcoal can approach the storage density of liquid hydrogen.
- Small glass spheres (microspheres), carbon nanotubes, and fullerenes can hold hydrogen if it is induced at high pressures and temperatures. The hydrogen is held captive in the solid matrix when the temperature lowers. Hydrogen can be released by heating the solid.

Liquid storage: Hydrogen can be converted to liquid form by reducing the temperature to -253 ^{o}C. This can save cost in transportation, but requires additional energy and cost to keep the hydrogen at low temperatures. Refrigerating hydrogen to liquid form uses the equivalent of 25 to 30 percent of its energy content. A concern of storing liquid hydrogen is minimizing loss of liquid hydrogen by boil-off.

Unless the carbon nanotube method is used, these storing methods are expensive, need excessive weight and volume and are far from satisfying the ideal vehicular performance. The recent studies on carbon nanotubes have shown that the gap between storage capacities reached, ca. 1.0 wt%, is still far less than 6.5 wt%, which is accepted as economically feasible level. Apart from these storage based problems, the problems of availability and distribution of hydrogen have led to the consideration of compact, efficient devices called fuel-processors that can convert hydrocarbon fuels into hydrogen on board the vehicle.

2.3.2. Hydrogen Production

In future world, hydrogen would be produced from renewable sources by harnessing solar, wind, or geothermal energy to power an electrolyzer that generates hydrogen from water. Currently, this environmentally benign energy cycle is not economically feasible. Renewable energy production systems and processes must continue to be improved in performance; their overall capacity must grow to support a robust infrastructure and their production must be cost effective. Electrolyzing water via electricity is another alternative. However, since the most efficient water electrolyzing system is operating at roughly 30% efficiency and dominated by coal power, that option is neither efficient nor environmentally friendly.

Presently, most of the hydrogen is produced from raw fossil materials. Any carbonaceous material can be used to produce hydrogen by steam reforming, but they are more likely to contain higher amount of contaminants than natural gas, and would require cleanup before using. The main reason why natural gas is used in hydrogen production is that it is abundant and its price still remains relatively low.

A number of hydrocarbons such as natural gas, LPG, gasoline, methanol and ethanol are considered as the fuels for on site hydrogen production. Diesel, despite the fact that it can be stored in liquid form in the vehicle, deposits coke too easily and, therefore, is not suitable for on-board conversion (Avcı, 2003).

Methanol, being a liquid fuel at ambient conditions and easy to reform at temperatures lower than those used for other fuels, is the fuel that has taken the most interest worldwide. Methanol has the advantages of low impurities in the product stream after reforming - in fact among all fuels it is the only one that carbon monoxide is not a major product when it is reformed - low cost, high energy content and ease of handling. However, methanol has availability and distribution problems; it is produced from synthesis gas via methane reforming, and current methanol production is far from meeting the demands, thus requiring extra synthesis plants and investment (Avcı, 2003). It also has severe safety problems during its distribution and usage.

Ethanol is currently used in internal combustion engines as an additive to gasoline in order to decrease the emissions. It is a renewable source since it can be produced from any starch or sugar source via fermentation. In the production regions, ethanol offers a potential as the fuel to be converted on site.

Gasoline has clear advantages of being already available and of having a widespread refueling infrastructure; it is obtained by refining crude oil, without requiring an extra synthesis step. However, gasoline has reforming temperatures up to 827 ^{o}C which leads to coke formation very easily; has high sulphur content, which leads deactivation of catalyst, and is a complex fuel that contains a lot of undesired aromatics (Avcı, 2003).

The major component of natural gas is 75 to 85 percent methane, with the remainder being composed of ethane, propane and traces of carbon dioxide. Natural gas is cleaner than any other hydrocarbon fuel, and it is available either through widespread pipeline networks in the form of gas or can be shipped in the form of liquefied natural gas (LNG). However, it requires heavy and large pressurized cylinder for on-board storage and it is very stable; thus, considerable energy input is required for its conversion. Therefore, natural gas is not suitable for on-board hydrogen production; however, it is considered to be the ultimate fuel for processing in small or large-scale stationary applications.

Liquefied petroleum gas (LPG) is a typical widespread fuel, since it can be easily transported and be stored in liquid form in pressurized vessels for mobile and portable use. LPG is an important by-product of oil exploration and of crude oil processing in refineries. It is a cheap fuel with high power density. LPG is a mixture of propane and n-butane, whose relative amounts depend on the region from which crude oil is obtained. Propane can be stored in pressurized vessels with typical contents ranging from 425 g. for very small gas canisters up to 33 kg for mobile and portable use. Commercial propane is a mixture of at least 95 mass per cent propane and propylene, the residual fraction consists of ethane, ethylene, butane and butene (Ledjeff-Hey et al., 2000). It has also high power density: Avcı (2003) has found that the maximum possible values of molar hydrogen yields are 300 percent for methanol and 1000 per cent for combined propane steam reforming and water-gas shift.

Finally, as it is known that water is the other huge storeroom of hydrogen. Breaking down water to hydrogen requires energy. Electrical, chemical, light or thermal energy can be employed. Solar systems may be used in order to get hydrogen from water. In obtaining hydrogen from water by utilizing solar energy, a sustainable energy source is converted to another useful energy carrier, to be used it in various applications.

Hydrogen production may be accomplished by several processes with the use of fuels mentioned above. Hydrogen conversion from hydrocarbons may be accomplished by thermal cracking, steam reforming, and oxidation.

The gasification of coal is the oldest means of obtaining hydrogen from fossil fuels. When heated in a restricted supply of air**,** coal is converted to mixture of hydrogen, methane and carbon monoxide, together with coal tar and coke. Alternatively, when it is heated, coal is reacted with steam and the ‘water-gas reaction’ occurs, i.e.

$$C + H_2O \rightarrow CO + H_2 \qquad (2.1)$$

The water-gas reaction is highly endothermic. Conversely, the combustion of coal or coke in air is highly exothermic. It is, therefore, usual to pair off the two reactions so as to balance the heat evolved with that is absorbed. The resulting gas is a mixture of CO, H_2, CO_2, and N_2. This may be upgraded in terms of hydrogen content by the ‘water-gas shift reaction’. The gas is reacted with steam over a catalyst that converts carbon monoxide to carbon dioxide and increases the amount of hydrogen, i.e.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{WGS} \qquad (2.2)$$

The carbon dioxide can be removed by a variety of gas scrubbing techniques. The process engineering of coal gasification is quite complex.

Steam reforming run on nickel based catalysts is the most well known and cheapest way of large-scale hydrogen production, and it gives the highest amounts of hydrogen in the product stream.

$$C_nH_m + n\ H_2O \rightarrow n\ CO + (\tfrac{1}{2}\ m + n)\ H_2 \qquad \text{SR} \qquad (2.3)$$

However, considerable heat input, higher catalyst loadings and larger reactors are required for this process; therefore, it is not suitable by itself for on-board hydrogen production for vehicular applications (Caglayan, 2003).

The energy required for endothermic steam reforming reaction can be met by oxidizing part of the fuel to supply heat to the system. Indirect partial oxidation, which is the combination of total oxidation and steam reforming reactions, is accepted to be the most promising routes to produce hydrogen from hydrocarbon fuels for mobile applications (Ahmed and Krumpelt, 2001; Ma and Trimm, 1996).

2.4. Fuel Processors

The main objective of a fuel reformer is to convert hydrocarbon fuels into a hydrogen-rich reformate gas. In general, a reformer accomplishes this task by thermo chemically processing a hydrocarbon feedstock in a high temperature reactor with steam and/or oxygen. An effective reformer must efficiently produce relatively pure hydrogen while generating minimal pollution.

A fuel processor integrates a reformer and peripheral subsystems for converting hydrocarbon feedstock into hydrogen and delivering it at the appropriate temperature, pressure, composition, and purity to a fuel cell or other hydrogen-consuming device. Since fuel cells require relatively pure hydrogen, about 99.5% pure for PEM fuel cells, the ability to meet purity requirements is critical for the optimal performance, reliability, and operating life of a fuel cell system.

The on site hydrogen production unit has to satisfy many requirements such as efficiency, compactness, weight and simple plant displacement. Accordingly, the hydrogen rich reformate from natural gas is suitable for residential PEMFC systems in terms of infrastructure and technical abundance. Many types of fuel processing system with different architectures are being developed to produce hydrogen having the required purity that is pure and fast enough production ability required for PEMFCs operation. General principle of designing a fuel processor is shown in Figure 2.2.

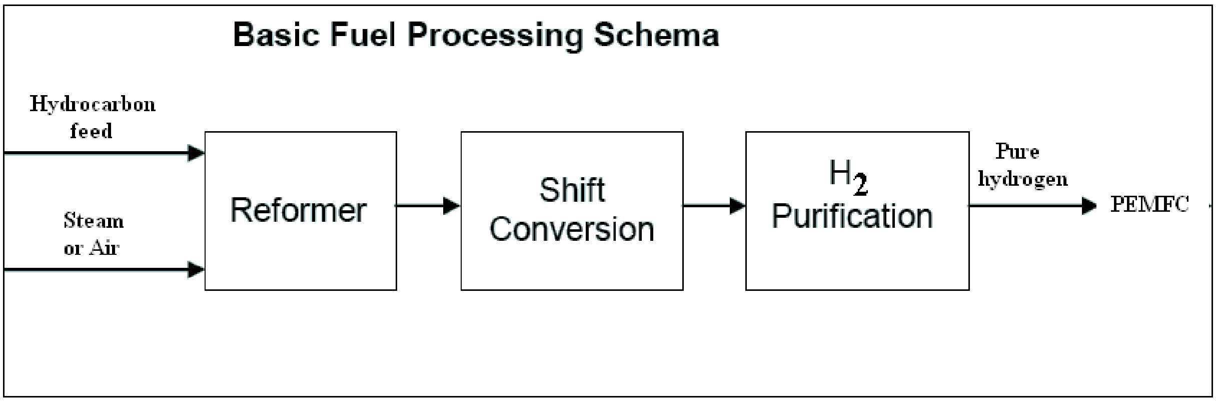


Figure 2.2. The elements of a fuel processor

Reformer contains the reactions for hydrogen production from hydrocarbons mentioned before, like thermal cracking, steam reforming, oxidation etc. Shift conversion (WGS) is required since it increases H_2 concentration while decreases CO concentration down to 1-2% levels. Hydrogen purification is the final step in order to fulfill the requirement for the fuel cell operation, i.e. 4-10 ppm as CO concentration in the final H_2-product. Reforming and shift reaction abilities of the catalysts developed are the most interested concerns in the current bi-metallic catalyst optimization study.

2.4.1. Steam Reforming

SR is an endothermic reaction that is favored at high temperatures, and involves catalytic conversion of hydrocarbons in the presence of steam to a mixture of hydrogen and carbon oxides.

$$C_nH_m + n\,H_2O \rightarrow n\,CO + (\tfrac{1}{2}\,m + n)\,H_2 \qquad (2.4)$$

Beside SR reaction, methanation reactions are also favored considerably at lower temperatures by the following reactions.

$$CO + 3\ H_2 \rightarrow CH_4 + H_2O \qquad \Delta H = -206.2\ kJ/mol \qquad (2.5)$$

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O \qquad \Delta H = -165\ kJ/mol \qquad (2.6)$$

$$C_nH_{2n+2} + ((n-1)/2)\ H_2O \rightarrow ((3n+1)/4)\ CH_4 + ((n-1)/4)\ CO_2 \qquad (2.7)$$

In addition, a very important side reaction, which eliminates CO and increases hydrogen production, exothermic Water Gas Shift (WGS) reaction occurs.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{WGS} \qquad \Delta H = -41.2\ kJ/mol \qquad (2.8)$$

Steam reforming of hydrocarbons is catalyzed by group VIII metals, with nickel being the most cost efficient (Joensen and Rostrup-Nielsen, 2001). Nickel based catalysts are usually supported on alumina or magnesia. However, for higher hydrocarbons, coke formation is a major problem on nickel. Coking may be suppressed by using precious metal catalysts (Wang and Gorte, 2002). Alkali promoters are used for activity improvement, for their ability to reduce methanation or to facilitate coke gasification; however, they suffer from the drawback of having increased volatility in high temperature steam environments (Ghenciu, 2002).

The composition of the support used for nickel-based catalysts must be adjusted to minimize coke formation. Alkaline components, such as magnesia or potassia, favor the gasification of coke. Recent studies have shown that ceria supports may also improve activity and reduce coke formation (Ghenciu, 2002). Methanol is the only fuel that does not produce carbon monoxide when it is steam reformed, however, other side reactions, such as methanol decomposition and the decomposition of the formed intermediate formaldehyde, lead to carbon monoxide formation, which increase the importance of the following water-gas shift reaction (Avcı, 2003).

Although highly active noble metal catalysts have been reported for methanol steam reforming, those based on copper are preferred for economical reasons. Iwasa et al. (2000) have studied steam reforming of methanol over Pd-Zn catalysts and concluded that the Pd-Zn alloys are highly selective for the reaction. Iwasa et al. (1998) have also investigated the same reaction on Pd-Zn, Pd-Ga, Pd-In, Pt-Zn, Pt-Ga, Pt-In alloys and observed that the catalytic functions of palladium and platinum catalysts are greatly modified in the presence of ZnO, Ga_2O_3 and In_2O_3 upon the formation of the Pd and Pt alloys.

Whittington et al. (1995a) have studied the steam reforming of propane on Pt, Pd and Rh catalysts in the absence and presence of ceria. The orders of activity have been observed to change with the presence of ceria from Pd > Rh > Pt to Rh > Pd > Pt.

Irreversible adsorption of a poison on the active sites or the deformation of active sites by reaction causes deactivation of catalysts. Competitive reversible adsorption of poison precursors with reactants is another important problem. Poison-induced restructuring of catalytic surface may also cause poisoning. Sulphur and halogens are well known poisons for steam reforming catalysts because their compounds are strongly chemisorbed on metal surfaces.

Sintering results from the loss of catalytic sites due to agglomeration of metal or support. So it will cause overall loss of area or of the active metal crystallites. Main cause of sintering in steam reforming reaction is the thermal instability of alumina support.

Fouling results from physical blockage of the active sites on surface. A typical foulant, coke, is usually observed in reactions involving hydrocarbons. At temperatures higher than 447 ^{o}C and low ratios of steam/carbon, whisker carbon may form from diffusion of carbon through nickel crystals. Formation of whisker carbon does not cause deactivation of nickel catalyst but it may result in break-down of the catalyst (Ma, 1995).

Steam reforming suffers from coke deposition. When exposed to high temperatures, hydrocarbon fuels tend to dehydrogenate to form solid species with very low H/C ratios. Those species are called as coke which may deactivate the catalyst by depositing on the active sites and leading to blockage of the catalyst pores. Coke may grow also in the interparticle spaces, increasing the pressure drop in the catalyst bed and eventually blocking the gas flow (Löffler et al., 2003).

The most widely accepted catalysts of steam reforming reaction, nickel based catalysts, are known to suffer from coke deposition at high temperatures. The simplest way of improving the quality of the nickel catalysts is the introduction of certain additives to them aiming to increase their resistance to coking. Small additions of molybdenum ($\leq$ 1.0 wt %) cause a significant increase in resistance to coking for nickel catalysts in steam reforming of hydrocarbons. Kepinski et al. (2000) have studied the effects of the introduction of small amounts of molybdenum compounds ($\leq$ 1.0 wt% of Mo) into impregnated Ni/Al_2O_3 catalysts in steam reforming of n-butane. The resistance to coking of the catalysts was observed to be greatly improved by the addition of Mo compounds. Much lower amount of Ni particles, which were active in formation of carbon filaments, were observed on $Ni\text{-}Mo/Al_2O_3$ catalysts.

Coking can be avoided by operating at relatively high temperatures and by introducing oxygen to the feed stream. For a given O_2/C ratio, it is preferable that the oxygen is fed in the form of water. In other words, the coking tendency is reduced at high O_2/C and H/C ratios. Thus, less coke is formed in the order of partial oxidation > oxidative steam reforming> steam reforming.

2.4.2. Water Gas Shift

The interest to the water-gas shift (WGS) reaction was grown significantly during the last years due to the targeted pure hydrogen production to be used in fuel-cell applications. A small amount of CO from the output of fuel reformers has to be converted, but the applied Pt catalysts are not resistant enough to the poisoning of CO at the operating temperatures. From other side, cupper based catalysts, which are traditionally used in the industry for low temperature WGS, are not suitable for automobile application due to the fact that their contact with air and/or condensed moisture during start-up and shut-down operation deactivates the catalysts. Obviously, the new catalysts are needed to eliminate these problems.

In a fuel cell, water-gas shift reaction, equation 2.9, removes the majority of carbon monoxide present in the reformer outlet. This reaction is usually classified as high temperature (350 – 400 ^{o}C) water-gas shift over mixtures of Fe/Cr oxides (Hakkarainen et al., 1994; Li et al., 1999), and low temperature (180–250 ^{o}C) water-gas shift over mixtures of Cu/Zn oxides (Karyobkina et al., 2003, Kepinski et al., 2000). Water-gas shift reaction running simultaneously with steam reforming not only produces hydrogen and reduces carbon monoxide, but it also gasifies the carbon deposited on the surface of the catalyst.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -41.2 \text{ kJ/mol} \qquad (2.9)$$

Apart from the catalysts mentioned above, gold-based catalysts, especially Au/ceria for the low-temperature WGS reaction have been investigated widely (Fu et al., 2003; Luengnaruemitchai et al., 2003). However, 1% Pt/ceria was found to be more active than Au/ceria between the temperature range of 393- 633 ^{o}K (Luengnaruemitchai et al., 2003). Reuttinger et al. (2003) have developed a new catalyst alternative to Cu/Zn-oxides, referred to as Selectra Shift, which not only has stable activity under various process conditions but is also non-pyrophoric, i.e. does not spontaneously generate heat dangerously caused extremely high temperatures when exposed to air.

According to Jacobs et all, addition of Au to ceria catalyzes the surface reduction process and reduces the peak reduction temperature from 450 ^{o}C, for the unpromoted catalyst, to 100 ^{o}C, for the 5 wt. % Au/ceria catalyst. A systematic decrease in the temperature required for ceria surface shell reduction was observed by increasing the Au promoter loading as follows: 0.1, 0.25, 0.5, 1.0, 2.5, and 5.0 wt. %. 5 wt.% Au/ ceria was found to have about 1/20th the activity of 5 wt.% Pt/ceria in the range 200–300 ^{o}C, and 5 wt.% Pt/ceria exhibited a higher steady-state activity (about double that of Au) at 175 ^{o}C. The rate of formate decomposition was approximately 20 times faster for Pt/ ceria than that observed with Au/ceria, suggesting that the metal (in addition to the rate promotion of H_2O) is also involved in promoting the formate decomposition, which is the proposed rate limiting step of the formate reaction mechanism. It is suggested that Pt accomplishes this higher turnover rate i) due to its greater dehydrogenating ability over Au, or ii) via an electronic influence, or iii) since it may possibly be involved in dissociating H_2O to promote the decomposition of formate intermediate.

2.4.3. PROX

Sufficient CO elimination to levels below 10 ppm for PEM fuel cells cannot be achieved during water-gas shift reaction. Other methods to remove CO are methanation, selective membranes and selective oxidation. Methanation and usage of Pd-based diffusion membranes result in considerable hydrogen and overall efficiency losses respectively.

For the preferential oxidation (PROX) of carbon monoxide to decrease its ratio to desirable ppm level in H_2 production, shown in reactions eq. 2.10 & eq. 2.11, a catalyst that can selectively oxidize CO in the presence of water and carbon dioxide by using stoichiometric amounts of oxygen at relatively low temperatures is needed.

$$CO + O_2 \rightarrow CO_2 \qquad (2.10)$$

$$H_2 + O_2 \rightarrow H_2O \qquad (2.11)$$

Adding Ce to Pt/g-Al_2O_3 produced higher CO conversion and selectivity at lower temperatures and lower O_2 to CO ratios because of an enhanced oxygen supply to the Pt. The CO conversion and selectivity were enhanced with an optimum loading wt% of Ce and Pt; too high a loading weight ratio of Ce to Pt yielded lower CO conversion and selectivity due to higher H_2 oxidation. With decreasing contact time, the catalyst Pt/γ-Al_2O_3 with Ce showed a higher CO selectivity at lower temperatures because of the Ce effect of supplying oxygen to Pt, which became larger (Son et al., 2002).

Ozkara, S. and A. E. Aksoylu have also studied the selective oxidation of CO in a H_2-rich gas stream over a series of Pt-Ce and Pt-Sn catalysts supported on activated carbon. Their results have showed that oxygen bearing surface groups of activated carbon led to enhanced Pt–CeO_x and Pt–SnO_x interaction besides alloy formation and Pt-Sn prepared on air-oxidized activated carbon has the highest activity and selectivity between the samples prepared in this study (Ozkara, S. and A. E. Aksoylu, 2003).

2.5. Oxidative Steam Reforming

Steam reforming is not a suitable process for fuel cell applications since it needs high energy input and the operating conditions include very high temperatures. Conversely, partial oxidation has all the properties to satisfy the needs of a fuel cell application to produce motive power: it is energetically self-sustainable once triggered, much faster than steam reforming and it needs smaller amounts of catalyst.

The partial oxidation of hydrocarbons is known to occur by direct partial oxidation, which includes a single step or oxidative steam reforming, which is the combination of total oxidation and steam reforming reactions.

In direct partial oxidation the primary fuel reacts with oxygen whose quantity is inadequate for complete combustion. The reaction (Reaction 2.12) is thermodynamically favored only at high temperatures (~1023 K) and for short residence times. It is much faster than any of the indirect reactions and response time for changes in fuel supply is shorter. The overall efficiency can suffer from the waste heat production (Ghenciu, 2002). However, partial oxidation only takes place under oxygen deficient conditions and so it produces much less heat than total oxidation (Ma, 1995). This less emission of heat compared to total oxidation contributes the consumption of fossil fuel by steam reforming reaction to produce more hydrogen.

$$C_nH_m + \frac{1}{2} m\, O_2 \rightarrow m\, CO + \frac{1}{2} n\, H_2 \qquad (2.12)$$

Catalytic partial oxidation is difficult to control. It has disadvantages of overheating and hot spots due to exothermic nature of the reaction which may lead to the coking problem (Song, 2002).

On the other hand, oxidative steam reforming combines the thermal effects of the partial oxidation and SR reactions by feeding the fuel, water and air together into the reactor. The thermal energy generated from partial oxidation is absorbed by SR and, hence, the overall temperature is lower. This is also favorable for the water-gas shift reaction which consumes carbon monoxide and produces more hydrogen. Thus, the autothermal reactor is more compact and practical to be used in mobile fuel cell applications. Nevertheless, the OSR mechanism is not straightforward, and it requires sophisticated operating techniques for a proper combination of the POX and SR.

$$C_nH_m + n\, H_2O \rightarrow n\, CO + (\frac{1}{2} m + n)\, H_2 \quad \text{(SR)} \qquad (2.13)$$

$$C_nH_m + (n + \frac{1}{4} m)\, O_2 \rightarrow n\, CO_2 + \frac{1}{2} m\, H_2O \quad \text{(POX)} \qquad (2.14)$$

Autothermal operations are stand–alone systems in which fuel is partly oxidized and partly steam reformed to produce hydrogen. The system must start to operate at low temperatures, and the balance between oxidation and steam reforming should be formed based on the heat demands for the particular fuel. Careful control must be made on the oxygen content of the entering mixture in oxidative steam reforming process for maintaining proper reaction temperatures. The side product carbon monoxide requires high- and low-temperature water-gas shifts to decrease CO concentration and provide additional hydrogen (Brown, 2001).

The oxidative steam reforming catalysts have to be active for both steam reforming and total oxidation reactions, robust at high temperatures and resistant to sulphur and coke formation, especially in the catalytic zone that runs at oxygen limited conditions. The catalysts for the indirect partial oxidation of higher hydrocarbons typically comprise of metals such as Pt, Rh and Ni deposited or incorporated into the oxide supports such as ceria-containing oxides. These can be further promoted or doped with other elements for improved thermal robustness or better activity (Guenchiu, 2002).

Ma and Trimm (1996) have parametrically investigated the autothermal conversion of methane to hydrogen in response to the configurations of an oxidation and a steam reforming catalyst. They concluded for a mixed bed system that it was necessary to pre-heat the bed to 317 ^{o}C when methane oxidation was initiated over a supported platinum catalyst (0.2 wt% $Pt/\delta\text{-}Al_2O_3$): the heat and steam produced by oxidation facilitated steam reforming of methane over a supported nickel catalyst (27 wt% Ni/MgO).

Pt-based catalysts are shown to be more active than Ni-based catalysts for indirect partial oxidation of ethane and propane for an autothermal system in which heat and steam was produced by oxidation over $Pt/\delta\text{-}Al_2O_3$ catalyst and consumed by steam reforming over $Ni/MgO\text{-}Al_2O_3$ catalyst (Ma et al., 1996).

A two bed system was found to be inferior in performance to one bed containing two mixed catalysts. Optimal performance (60 – 65 per cent conversion of methane with 80 - 85 per cent selectivity to hydrogen) was obtained when both catalysts were located on the same support (0.2 wt% Pt-25 wt% Ni/δ-Al_2O_3). Improved heat transfer is responsible for better performance.

Avcı et al. (2003) have studied the total oxidation of propane and n-butane on monometallic Pt/δ-Al_2O_3, Ni/δ-Al_2O_3 and bimetallic Pt-Ni/δ-Al_2O_3 catalysts, and observed the superior performance of Pt-based catalyst over Ni-based catalyst for both hydrocarbons. It has been also observed that the bimetallic catalyst is highly active for both reactions, although the amount of platinum is kept as low as 0.2 per cent by weight. The activity order of the catalysts are Pt > Pt-Ni > Ni. Additionally, the change in conversion with temperature over Pt-Ni is greater than either monometallic catalysts in the kinetically controlled regimes.

Tomishige et al. (2003) have published the oxidative steam reforming of methane on bimetallic Pt (0.3 wt%)-Ni (10 wt %) /alumina and monometallic Ni (10 wt %) /alumina and Pt (0.3 wt %) /alumina. They observed a high temperature for Ni/alumina catalyst, indicating that methane oxidation proceeded near the catalyst bed inlet and then methane reforming proceeded. On the other hand, for the bimetallic catalyst, a flat temperature profile was observed, providing autothermicity, indicating that oxidation and steam reforming proceeded simultaneously.

Support plays a decisive role on the catalytic behavior during oxidative steam reforming of methane, in which steam reforming and partial oxidation take place simultaneously. The Pt/10% ZrO_2/Al_2O_3 catalyst showed the highest activity and stability during 70 h on stream at 800 ^oC, when compared to Pt/Al_2O_3 and Pt/ZrO_2. The composition profiles when the feed is in stoichiometric ratio showed that the reaction proceeds via a two-step mechanism with the total combustion of methane followed by reforming of unreacted methane with CO_2 and H_2O (Souza et al., 2005).

The orders of activity for the oxidative steam reforming of propane is Pt > three-way catalyst > Pd > Rh in the absence and presence of ceria. The presence of steam was reported significantly enhance the conversion of propane over both Pd and Rh while having little effect on the performance of Pt. Ceria is also seen to enhance propane conversion, particularly over Pd (Whittington et al., 1995b).

Caglayan et al. (2004) have investigated the performance of bi-metallic Pt-Ni catalyst in oxidative steam reforming of LPG and propane. Propane reforming results indicated that the superior performance of the Pt–Ni/δ-Al_2O_3 system results from the formation of distinct but very close Pt and Ni sites; there is no Pt–Ni alloy formation is detected by XRD. Bimetallic catalyst enhances energy efficiency by utilizing the catalyst particles as micro heat exchangers during oxidative steam reforming, i.e. the heat produced by total oxidation reaction on Pt sites can be readily transferred through the catalyst particles to Ni sites, which catalyze the simultaneous SR reaction. The enhanced energy efficiency of the bimetallic Pt–Ni system leads to high activities at lower temperatures as compared to monometallic Ni catalysts. Both increasing and decreasing temperature progression profiles gave very similar results for the oxidative steam reforming of propane over Pt–Ni system.

Caglayan et al. (2005) have also studied the oxidative steam reforming of LPG to compare with propane reforming for high hydrogen productivity. This oxidative steam reforming study, LPG (75% propane-25% n-butane) over the bimetallic Pt–Ni/Al_2O_3 catalyst between 623–243 ^{o}K, has shown that both the hydrogen yield (H_2 produced per mole of hydrocarbon feed) and the hydrogen selectivity (H_2/CO ratio in the product) are substantially increased as compared to pure propane. The bi-metallic Pt–Ni catalyst was found to be very stable during the 12-h time-on-stream experiments at 723 ^{o}K, for C/O_2 ratio of 2.70 and a W/F of 0.51 g cat-h/mol LPG.

Another study about oxidative steam reforming of LPG (50 wt% propane and 50 wt% butane) on 0.2% Pt- 15% Ni /δ-Al_2O_3 showed that high steam: carbon ratios resulted in greater hydrogen production rates. The decrease in residence time led to a considerable increase in the hydrogen production. Optimum conditions for oxidative steam reforming of LPG were found as steam: carbon ratio of 7, carbon: oxygen ratio of 2.7 and weight of catalyst: feed flow ratio (W/F) of 0.51. The results showed that an increase in n-butane ratio enhances the activity (hydrogen production) and the selectivity (high hydrogen to CO ratio) of the process (Caglayan et al., 2005) when coke formation is strictly controlled.

Finally, the results obtained from both studies, which are oxidative steam reforming of propane, LPG, and LPG with 50% butane, provide a strong indication for the potential use of the bimetallic Pt-Ni system in commercial fuel processors designed for fuelling PEM fuel cells. So, the next step has been thought that the composition of this bi-metallic catalyst can be optimized in order to have a catalyst with superior oxidative steam reforming performance when n-propane, which is the major component of LPG, is used as the feed. As a second aim, an additive, like a metal or alkali, can be added to enhance the secondary WGS activity of the bi-metallic system.

3. EXPERIMENTAL

3.1. Materials

3.1.1. Chemicals

All the chemicals used for catalyst preparation are presented in Table 3.1.

Table 3.1. Chemicals used for catalyst preparation

Chemicals	Specification	Source	Molecular weight
Nickel nitrate	$Ni(NO_3)_2.6H_2O$ extra pure	Merck	290.81
Tetraammineplatinum(II) nitrate	$Pt(NH_3)_4(NO_3)_2$ 50.4 % Pt	Aldrich	387.22
Gold (II) aurate	$HAuCl_4$.$3H_2O$	Aldrich	394.5
Gamma alumina	γ-Al_2O_3	Alcoa	-

3.1.2. Gases and Liquids

All of the gases used in this research were supplied by Birleşik Oksijen Sanayi (BOS) and HABAŞ Companies, Istanbul, Turkey. The specifications and uses of the liquids and gases in this study are listed in Table 3.2 and Table 3.3.

Table 3.2. Specifications and applications of the liquids used

Liquid	Specification	Application
Water	Distilled	Aqueous solutions, Reactant

Table 3.3. Specifications and applications of the gases used

Gas	Specification	Application
Hydrogen	99.99 % (BOS)	GC calibration*, Reduction
Carbon Monoxide	99.999 % (BOS)	GC calibration*
Helium	99.999 % (BOS)	GC carrier gas
Nitrogen	99.998 % (BOS)	Inert
Dry Air	78.4 % N_2 + 21.5 % O_2 (BOS)	GC calibration*, Reactant
Methane	99.9 % (BOS)	GC calibration*
Argon	99.999 % (BOS)	GC carrier gas
Propane	99.5 % (BOS)	GC calibration*, Reactant

* (Avcı, 2003)

3.2. Experimental Systems

The experimental systems used in this research can be classified into two groups:

- Catalyst Preparation Systems: The set-up used for preparing catalysts by incipient-to-wetness impregnation technique represents this group of experimental systems.

- Catalytic Reaction and Product analysis System: The continuous flow micro reactor system includes gas and liquid flow controllers, temperature controlled heated lines, gas/liquid mixer, and reaction chamber placed in a vertical oven whose temperature is made through using a programmable temperature controller, and feed and product sections. The quantitative determination of the composition of the feed and product streams is conducted by using two different gas chromatographs operating in parallel fashion one is used for analyzing fixed gasses and the other is used for hydrocarbons, which are connected to the catalytic reaction system.

3.2.1. Catalyst Preparation System

The system used for catalyst preparation by incipient-to-wetness impregnation technique includes a Retsch UR1 ultrasonic mixer, a vacuum pump, a buchner flask and a MasterFlex computerized-drive peristaltic pump.

3.2.2. Catalytic Reaction and Product Analysis System

The catalytic reaction system designed and constructed in CATREL has three sections:

- Feed section
- Reaction section
- Product analysis section

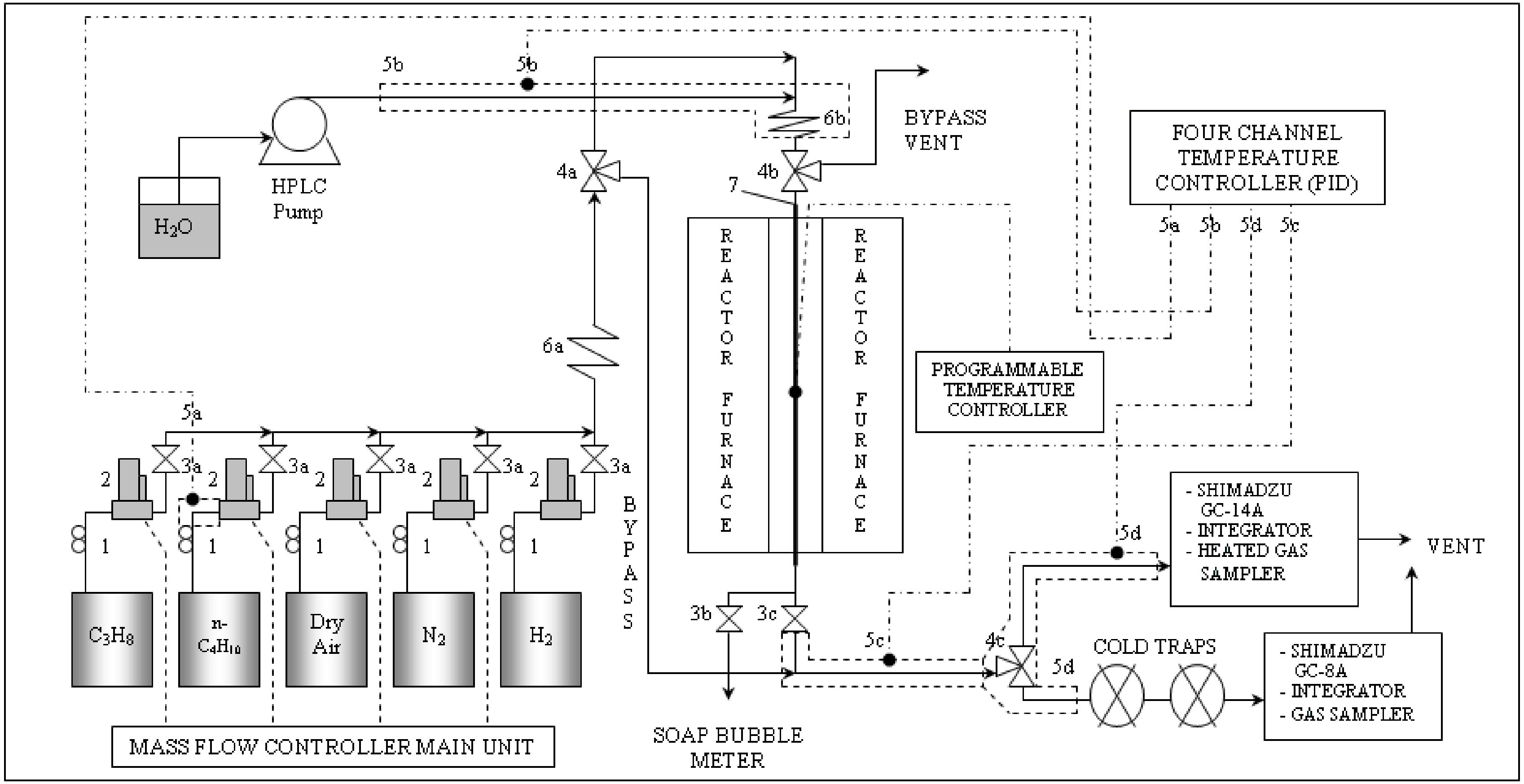


Figure 3.1. Schematic diagram of the flow microreactor system (Avcı, 2003)

1. Gas regulator, 2. Mass flow controller, 3. On/off valve, 4. Three-way valve, 5. Heated zone, 6. Mixing zone, 7. Differential reactor

The feed preparation section includes mass flow control systems, 1/4", 1/8" and 1/16" stainless steel tubes and fittings for feeding liquid water and gaseous species, i.e. propane, n-butane, dry air, nitrogen and hydrogen at desired quantities. The gases that were present kept in pressurized cylinders were passed through the gas flow regulators and the calibrated Omega Model 5878 mass flow controllers. An Aalborg GFC171S series standalone controller was used to regulate hydrogen flow. On-off valves were placed in front of the mass flow controllers to protect them from possible back-pressure fluctuations. In order to eliminate possible condensation of n-butane, the zone between the pressure regulator and the mass flow controller was kept at 348 ± 3 ^{o}K using a 0.6 m heating tape and the four channel temperature controller. All the reactants excluding water were then passed through a primary mixing zone to ensure the flow of a homogeneous gas mixture into the reactor.

Water was introduced into the reaction system at constant flow rates using a Jasco PU-1580 intelligent HPLC pump. The 1/16" tube, through which water was allowed to flow, was kept at 423 ± 3 ^{o}K by a 1.4 m heating tape whose temperature is controlled by the four channel temperature controller to generate steam and regulate its flow. Steam and the homogeneous gas mixture were mixed in a secondary mixing zone.

It was possible to divert the flowing route of the mixture using three way valves: The feed gases could be diverted to the bypass line, so that feed composition could be analyzed using gas chromatographs. Another three ways valve was used for diverting the flow to the bypass vent line for establishing steady state flow and mixing of the steam and other gaseous reactants prior to the reaction.

The reactants, upon metered and mixed in the feed section, were allowed to flow through the reaction section. This section was composed of a 40 cm x 2.4 cm ID tube furnace controlled to ± 0.5 ^{o}K by a Shimaden FP-21 programmable temperature controller and a 1/4" stainless steel fixed-bed microreactor. The reactor was also constructed in CATREL and its length was selected to be 50 cm guaranteeing the constant temperature zone and easy handling and replacement. The system guarantees 5 cm fixed temperature zone at the mid section of the reactor tube.

During the reaction tests, the catalyst bed was placed in the center of the reactor. The reaction temperature was controlled and measured by a 20-gauge wire K type sheathed thermocouple (insulation material: ceramic fiber braid) that was placed in the center of the furnace. The position of the reactor and hence catalyst bed was adjusted to coincide with the constant-temperature zone of tube furnace. Silane-treated glass wool (Alltech Associates Inc.) was used to hold the catalyst bed in a fixed position. Ceramic glass wool insulations were placed at top and bottom ends of the reactor furnace to prevent heat loss from the furnace and to provide a good temperature profile.

In order to prevent the condensation of steam in the product stream, the line from the reactor to the to both gas chromatographs were both kept heated at 398 ± 3 ^{o}K using a 1.4 m and a 2.5 m heating tape whose temperature is controlled by the four channel temperature controller. The product stream was analyzed qualitatively and quantitatively using two separate gas chromatographs operating in a parallel scheme.

The four channel temperature controller is a unit that can control the temperature of the four different heated zones transfer lines of the system independently. 16-gauge wire K type sheathed thermocouples (insulation material: Fiberglas) were placed at the middle point of each heated zone to measure and control the temperatures. The degree of power input of the heating tapes was adjusted by the controller. The heating tapes were covered with ceramic wool insulation to prevent heat losses.

The product mixture contains groups of species with different characteristics, i.e. hydrocarbons involving methane, ethane, propane, n-butane, fixed gases involving hydrogen, oxygen, nitrogen, and others involving carbon monoxide, carbon dioxide and water. Considering that all these species excluding water were needed to be analyzed quantitatively, the use of two different gas chromatographs operating in parallel fashion was essential; hydrocarbons were effectively analyzed by the first chromatograph equipped with a TCD and having a Porapak Q column with He carrier gas whereas quantitative detection of hydrogen and other fixed gases were made by a second chromatograph equipped with a TCD and having a Molecular Sieve column with Ar carrier.

A Shimadzu GC-14A gas chromatograph, equipped with a Thermal Conductivity Detector (TCD) connected to a Propak Q column and a Shimadzu CR-4A Chromatopac data processor, was used interactively to analyze hydrocarbons and carbon dioxide. In order to analyze fixed gases, carbon monoxide and methane, a Shimadzu GC-8A gas chromatograph, equipped with a Thermal Conductivity Detector (TCD) connected to a Molecular Sieve column and a Shimadzu CR-1B Chromatopac data processor, was employed. Since the analysis column can easily be deactivated if it is contacted with a stream containing water vapour, steam present in the product stream was removed by placing two salt-ice cold traps held in Dewar flasks at 273 ^{o}K before GC-8A inlet. The parallel operation of these gas chromatographs was achieved by diverting the product flow by a three-way valve. The analysis conditions are presented in Table 3.4. For both chromotographs, the previously optimized conditions by Avcı (2003) were used whereas analysis reports provided by the manufacturer were employed to finalize the operating conditions used in GC-8A. The calibration curves may be found elsewhere (Avcı, 2003).

Table 3.4. Product analysis conditions

GC Parameter	GC 1 – Shimadzu GC-14A	GC 1 – Shimadzu GC-8A
Detector type	TCD	TCD
Column temperature, K	363	333
Injector temperature, K	423	363
Detector temperature, K	423	363
TCD temperature, K	423	363
TCD current, μA	120	60
Carrier Gas (CG)	He	Ar
CG flow rate, ml min^{-1}	25	50
Column packing material	Porapak Q, 80-100 mesh	MS 5A, 60-80 mesh
Column tubing material	Stainless steel	Stainless steel
Column length & ID	3 m x 3mm	2 m x 3mm
Sample loop	1 ml kept at 398 K	1 ml kept at 298 K

3.3. Catalyst Preparation and Pre-treatment

3.3.1. Support Preparation

The catalytic oxidation and steam reforming of hydrocarbons are known to be high-temperature reactions. Therefore, the catalyst supports should not only have high surface areas but also possess high thermal stabilities. γ-Al_2O_3 is a commonly used support material due to its high surface area. However it is reported to have low stabilities at temperatures greater than 873 ^{o}K and tends to facilitate carbon formation in the presence of steam due to its high acidity (Ma, 1995). The most thermally stable version of alumina is obtained when γ-phase is transformed into α-phase at temperatures greater than 1400 ^{o}K. However, its low surface area, which is less than 5 m^2 g^{-1}, is likely to end up with poor catalytic activities due to the low dispersion of active metals. Hence using a support such as δ-alumina – an intermediate phase between γ and α - having relatively high thermal stability and an acceptable surface area can be the optimum support providing relatively high surface area for metal dispersion without sacrificing from thermal stability (Ma, 1995).

The support preparation procedure used in this study was involved drying of γ-Al_2O_3 at 423 ^{o}K for 2h followed by calcinations at 1173 ^{o}K for 4h in a muffle furnace. BET surface area of the δ-Al_2O_3 support obtained was found as 81.6 m^2 g^{-1} (Avcı, 2003).

3.3.2. Preparation of Pt-Ni or Pt-Au-Ni/δ-Al_2O_3

The bimetallic Pt-Ni/δ-Al_2O_3 catalysts having Pt and Ni metal loadings in 0.2-0.3 wt% and 10-15 wt% ranges, for Pt and Ni, respectively, were prepared through a sequential route, in which Pt solution was impregnated over initially prepared and calcined Ni/δ-Al_2O_3 catalyst. Ni/δ-Al_2O_3 catalysts were prepared by the incipient-to-wetness impregnation technique using aqueous solution of $Ni(NO_3)_2.6H_2O$. The aqueous solutions were prepared by dissolving the calculated amount of the precursor salt in definite amounts of distilled water (ca. 1 ml solution/g support). The support, δ-Al_2O_3, was placed in a Buchner erlen and mixed ultrasonically for 25 min. under vacuum. The aqueous solution was then impregnated on the support via a peristaltic pump. The resulting slurries, which were formed after ultrasonic mixing of the aqueous solutions and the support under vacuum for 1.5 h, were then dried overnight at 393 ^{o}K and calcined at 873 ^{o}K for 4 h to obtain ($NiO/\delta\text{-}Al_2O_3$). The aqueous Pt solution was then added to $NiO/\delta\text{-}Al_2O_3$ and mixed ultrasonically under vacuum for 1.5 h. The resulting slurry involving two metals was dried overnight at 393 ^{o}K and finally calcined at 773 ^{o}K for 4 h. In the case of tri-metallic catalyst with Au promoter for enhancing secondary WGS activity, an $Au\text{-}Pt\text{-}Ni/\delta\text{-}Al_2O_3$ catalyst was prepared. For the Au-Pt-Ni system, gold impregnation has the same drying and calcination steps as in Pt impregnation, however, the order of the impregnation followed was changed such that firstly Au was impregnated on $Ni/\delta\text{-}Al_2O_3$ support and then Pt was introduced to have $Pt\text{-}Au\text{-}Ni/\delta\text{-}Al_2O_3$ catalyst.

3.3.3. Catalyst Performance Analysis Path to Observe Catalysis Improvement in Hydrogen Production

In this study, a bimetallic catalyst, which is 0.2 wt% Pt and 15 % Ni catalyst on $\delta\text{-}Al_2O_3$, has been used as the reference OSR. This reference catalyst had been tested in propane and LPG (Caglayan et al., 2004) oxidative steam reforming. On the basis of those findings, optimizing the Pt and Ni loadings were performed in an experimentally designed fashion through taking the previously tested catalyst and reaction conditions as the reference bases. In the new set of Pt-Ni catalysts, two Pt-loading levels (0.2 and 0.3 wt%) and two Ni- loading levels (10 and 15 wt%) were used, and bimetallic catalysts having those loadings in combinations were prepared. The details of the prepared catalysts in the experiment were explained in discussion section on Table 4.2. The 5th catalyst has gold for enhancing secondary water gas shift activity of Pt-Ni system in ATR. The loadings of this new catalyst were used as 0.3 wt % Pt- 0.3 % Au- 15 wt % Ni.

3.3.4. Pretreatment

In order to obtain high catalytic activities, a pre-treatment involving the reduction of the active metals from their oxide state –which is formed during calcination- to their metallic state is required prior to the reaction due to the fact that the catalysts in their oxide forms are usually inactive for the reactions.

TPR studies have shown that reduction using pure hydrogen flow at 773 °K for 4 h is a suitable procedure for pre-treatment of the bimetallic catalyst (Ma, 1995). Ma (1995) has also reported that during reduction, the water in the catalysts may cause premature sintering, which may lead to deactivation before the reaction. Considering these issues, the following stepwise reduction procedure was used for the catalyst used in all of the experiments;

After placing the catalyst into the constant temperature zone of the microreactor, N_2 was allowed to flow at 50 ml min^{-1} for 10 min. to remove oxygen from the system. The gas flow was switched from N_2 to H_2 and the latter was set to flow at 20 ml min^{-1}. Reduction was started by heating the catalyst from room temperature to 423 °K at rate of 10 °K min^{-1}. The temperature was kept constant at 423 °K for 30 min. for the removal of adsorbed water. Third step was involved heating the sample from 423 °K to 573 °K at a rate of 5 °K per min, and followed by a 30 minutes isothermal segment at 573 °K for the removal of crystalline water. The temperature was then increased from 573 °K to 773 °K at a rate of 2 °K min^{-1} and finally kept constant at 773 °K for 4 h. After reduction, the system was allowed to cool down to ca. 423 °K under H_2 flow. Below this temperature, the gas flow was switched from H_2 to N_2 and the latter was allowed to flow at a small flow rate, e.g. 3 ml min^{-1} overnight to sweep H_2 from the system.

3.4. Reaction Tests

3.4.1. Blank Tests

Blank tests were conducted to ensure that the material of construction, glass-wool and δ-alumina (used as inert material within the catalyst bed) did not interfere with the reaction test outputs. The results indicated that these items above were inactive under the conditions used in the reaction experiments.

3.4.2. Oxidative steam reforming of Propane over Pt-Ni/ δ-Al_2O_3 and Pt-Au-Ni/ δ-Al_2O_3 Catalysts

Reaction tests were conducted using stainless steel tubular down-flow microreactors. In all experiments, 150 mg of fresh catalyst was used without any dilution of the bed. The temperature of the catalyst bed was controlled by a programmable temperature controller with ±0.1 ^oK sensitivity. The catalysts were pretreated through reduction by 20 ml min^{-1} pure hydrogen flow at 773 ^oK for 4 h. Only the increasing temperature progression (ITP) was employed due to relatively low conversions observed at DTP in the preliminary experiments (Caglayan et al., 2004). In increasing temperature progression, the catalyst bed temperature was first brought to 623 ^oK under inert nitrogen flow and nitrogen was trapped in the reactor and the reactants were allowed to reach steady-state for 2 h in by-pass condition. Then, the reactants were allowed to pass through the reactor at 623 ^oK at first, and after the analyses of the products upon reacting steady state via using the two chromatographs in parallel, the temperature was increased to 643 ^oK at a rate of 2 ^oK/min. Same procedure was repeated for the 663, 683, 703, 723, and 743 ^oK reaction temperature levels. It is worth noting that 743 ^oK was not exceeded in the temperature programs due to the possibility of coke formation via thermal cracking of the hydrocarbons. For all temperature levels, propane, dry air and water flows were adjusted according to the assigned carbon:oxygen, steam:carbon and W/F ratios which are kept inside in the following limits: $1.50 < C:O_2 < 2.70$; S:C= 3; $0.51 < W/F < 1.12$. Steam to carbon ratio was fixed at 3 considering that this ratio guarantees coke formation free performance of Pt-Ni system in OSR of propane under the reaction conditions applied. Under the light of Caglayan et al.’s findings, the optimum S: C ratio was used as 3. High flow rates were preferred to eliminate temperature rises and hot-spots that may occur due to the exothermicity of the oxidation reaction. For having direct comparison with the previous results obtained from the reference Pt-Ni catalyst (Caglayan et al., 2004), same reaction conditions were applied in during reaction tests of the present study. The tabulated details of experimental conditions are shown in next session on Table 4.2.

4. RESULTS AND DISCUSSION

A bimetallic Pt-Ni/δ-alumina catalyst, 0.2 wt% Pt-15 wt% Ni/Al_2O_3, which was used in the previous studies, has been used as the reference catalyst in the current study (Avcı, 2003; Caglayan et al., 2004). In the previous studies, the optimum reaction conditions, such as temperature, feed composition, etc, for oxidative steam reforming over 0.2 wt% Pt-15 wt% Ni/Al_2O_3 catalyst were determined. In the current study, a set of Pt – Ni/ δ-Al_2O_3 catalysts -along with a Pt–Au–Ni/δ-Al_2O_3 catalyst- having experimentally designed Pt and Ni loading combinations (Table 4.1) were prepared and tested in oxidative steam reforming (OSR) of propane in order to determine optimal metal loadings, Pt:Ni metal loading ratio and reaction conditions in combined fashion for high hydrogen production activity and enhanced H_2/CO selectivity.

In catalyst preparation, two levels of Pt, and two levels of Ni loadings were used in combined fashion. The details of the Pt-Ni loadings combinations of the catalysts used are shown in Table 4.1.

Table 4.1. Pt and Ni loadings (in weight %) on δ-Al_2O_3 support

Cat A	0.2 % Pt-15 % Ni
Cat B	0.2 % Pt-10 % Ni
Cat C	0.3 % Pt-15 % Ni
Cat D	0.3 % Pt-10 % Ni
Cat E	0.3 % Pt-0.3 % Au-15 % Ni

The 5th catalyst, Pt-Au-Ni system, which contains gold as a promoter for water gas shift reaction in OSR was designed to enhance the secondary WGS activity of the Pt-Ni system without sacrificing from OSR activity. The loadings of this catalyst were designed as 0.3 wt % Pt- 0.3 % Au- 15 wt % Ni.

Experimental conditions were determined in accordance with the previous studies conducted on oxidative steam reforming of LPG and propane (Caglayan et al., 2004 and

2005). The important parameters in OSR tests are catalyst weight, temperature, steam to carbon ratio, carbon to oxygen ratio, weight of catalyst/ weight of feed ratio.

According to Caglayan et al.'s previous preliminary tests (Caglayan et al., 2004 & 2005), S/C ratio was chosen as 3 considering the fact that coke formation occurs at steam to carbon ratios lower than 3. Caglayan et al. (2004) has conducted oxidative steam reforming experiments between 350^{o}C to 470^{o}C in an increasing and temperature progression fashion. Since the decreasing temperature progression, which started from 470^{o}C, led to coke deposition on the catalyst surface at various combinations of W/F and carbon/oxygen ratios in ATR of propane - n-butane mixture (Caglayan et al., 2004 & 2005), propane OSR tests in the current study was conducted only with the increasing temperature progression.

The first four set of reaction conditions shown in Table 4.2, which were used previously by Caglayan et al. (2004) as nearly optimum values reaction are kept unchanged. The fifth set, on the other hand, was introduced aiming to get a clear trend. The details of the experimental sets are given in Table 4.2. A 100% propane conversion level was observed for the given experimental conditions even at the lowest reaction temperature, i.e. 623 K.

Table 4.2. The experimental conditions for OSR of propane

Set #	Feed composition*	Reactant/Inert flowrates** (ml s^{-1})	C/O$_2$	S/C	W/F (mg cats ml^{-1})
1	1.0:5.3:1.4:9.0	11.2:59.6:15.9:100.8	2.12	3	0.80
2	1.0:5.3:1.4:9.0	8.0:42.6:11.3:72.0	2.12	3	1.12
3	1.0:7.5:2.0:9.0	15.1:113.4:30.1:135.6	1.50	3	0.51
4	1.0:4.2:1.1:9.0	19.2:80.4:21.4:173.1	2.70	3	0.51
5	1.0:5.3:1.4:9.0	17.6:93.5:24.8:158.1	2.12	3	0.51

* Molar ratios of the reactant gases and inert (propane: nitrogen: oxygen:steam)

** Inlet flowrates (propane:nitrogen:oxygen:steam)

The reactions which were referred to during the discussion of experimental results are given in Table 4.3. OSR conversion and selectivity values obtained from the experimental sets are discussed on the basis of catalyst compositions, reaction conditions and the possible extents of listed reactions.

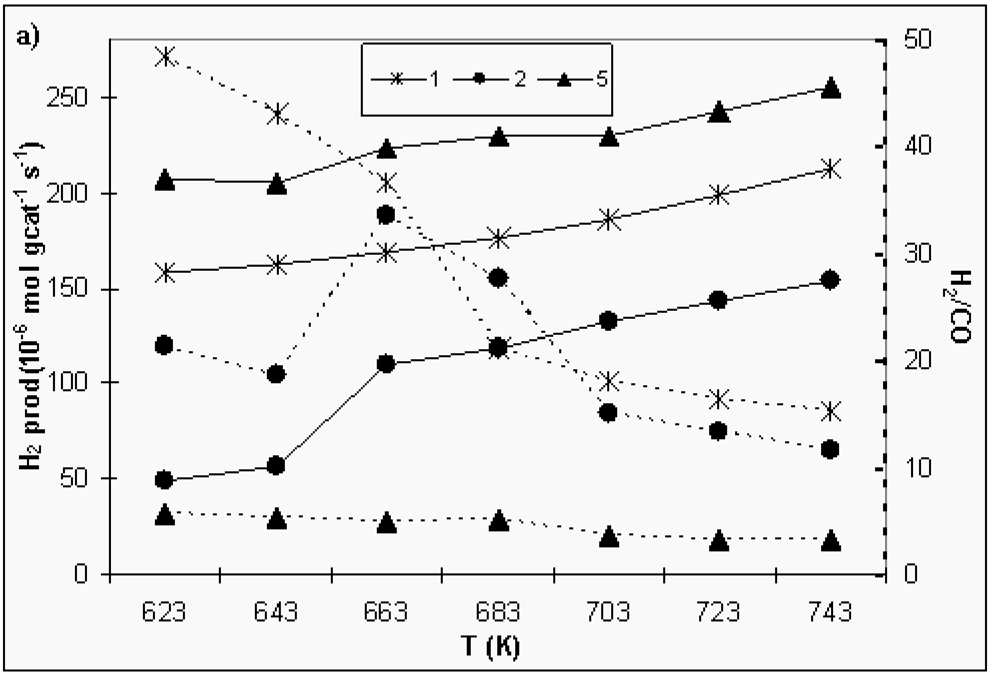
Table 4.3. Reactions occurred during OSR of propane on Pt-Ni/δ-Al_2O_3 catalyst

$C_3H_8 + 3H_2O \rightarrow 3CO + 7H_2$	CO-Producing SR	Reaction 1
$C_3H_8 + 6H_2O \rightarrow 3CO_2 + 10H_2$	CO_2-Producing SR	Reaction 2
$CO + 3H_2 \rightarrow CH_4 + H_2O$	Methanation	Reaction 3
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	Methanation	Reaction 4
$CO + H_2O \rightarrow CO_2 + H_2$	Water Gas Shift	Reaction 5
$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$	Total Oxidation	Reaction 6

The detailed micro-structural characterization of Pt-Ni system was made previously (Caglayan et al., 2005). As the BET surface area of the δ-alumina support is ca. 80 m^2/g (Avcı, 2003), the support surface was almost fully covered by Ni layer, which was introduced first in the sequential impregnation procedure. The SEM micrograph of the reduced Pt-Ni catalyst indicates that platinum agglomerates are settled on reduced nickel, which covers the alumina surface almost completely. However, Pt-Ni alloy formation was not detected by XRD; the Pt and Ni metallic sites are distinct but very close to each other on the catalyst surface, allowing heat flow from Pt sites –which mostly catalyze exothermic TOX- to Ni sites –where endothermic SR mostly occur (Caglayan et al., 2005).

4.1. Effect of W/F

A comparison among Sets 1, 2 and 5 clearly shows that the lower the residence time, the higher the H_2 production rate. Activity and selectivity trends are the same for all bimetallic catalysts; a demonstration is given in Figure 4.1a for the performance test results of Cat B. The results clearly show that for fixed catalyst weight, the H_2 production rate increases with an increase in fresh hydrocarbon flow rate; the highest H_2 production rate belongs to tests in Set5 (W/F=0.51). Other than high H_2 production rate, low residence time in Set5 led to much higher CO and CH_4 production levels as well (Figure 4.1b). A relatively lower CO_2/CO ratio for that set indicates a lower extent of WGS at short contact times. The high CH_4 production rate is unexpected for Set5 as methanation is known to be hindered at low residence times. As a matter of fact, high CO and CO_2 concentrations in the product stream - which are the two reactants of Rxn 3 and 4 - point out that only a small fraction of CO and CO_2 was consumed in methanation due to the short contact time. At that point, the facts about the present and previous test results can be given as follows: (i) at low residence time, there is a significant CH_4 production in OSR of propane under the experimental conditions tested for all bimetallic catalysts; (ii) CH_4 production activity in OSR over Cat A had been also reported in paper (Caglayan et al., 2005) and it was mentioned there as an “unexpected result”. Thus, methanation through CO_x hydrogenation cannot be the only reason for methane formation. One can speculate that there would be another route for methane formation through surface carbon and steam; this speculation is supported by the fact that there is no coke deposition on the catalyst surface at low W/F ratio despite 100% propane conversion and very high levels of hydrogen production. It should be also noted that catalyst deactivation caused by coke deposition was not observed over the catalyst used in the previous study (Caglayan et al., 2005). Thus, it can be thought that higher flow rates of steam for the short-residence-time sets clean the catalyst surface from coke through CH_4 formation. The results hint that at higher contact times, there is a relatively higher tendency for methanation (Rxn 3 and 4) rather than coke gasification. In this section, low residence time and high residence time will be mentioned alot. Reaction sets have three different sets of W/F. Catalyst weight (W) is constant, so each time feed rate was increased. Therefore, high residence time (W/F=2.12) means contact time is almost four times greater than low residence time (W/F=0.51).



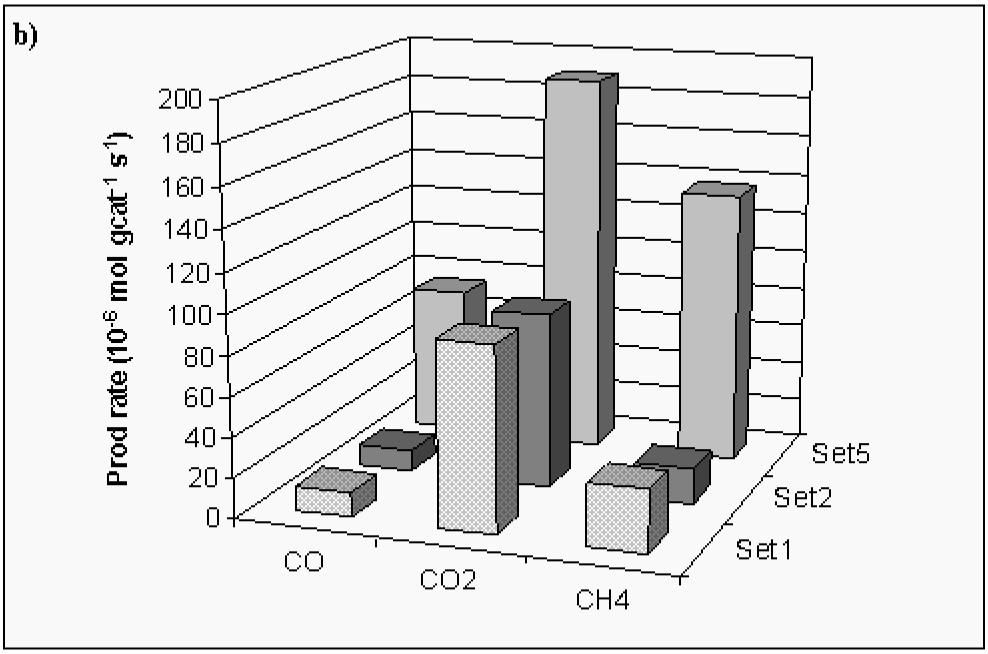


Figure 4.1. Response of Cat B to changes in residence time (dotted lines belong to right-y-axis). (a) in terms of H_2 production rate and H_2/CO selectivity ratio (b) in terms of CO, CO_2 and CH_4 production rates [Set1: W/F=0.8, Set2: W/F=1.12, Set5: W/F=0.51]

As the residence time has increased further (Set1 and 2), H_2 production was decreased in response to a decrease in fresh hydrocarbon feed rate (Table 4.2). Relatively higher CO_2/CO production ratio for Set1 and 2 indicate the facilitated WGS reaction at higher residence times. The results indicate that when the highest H_2/CO selectivity is desired, mid-level residence time values are optimum as high residence times enhance both CO and H_2 production rates simultaneously. The experimental trends for selectivity (H_2/CO) are also shown on the right y-axis of Figure 4.1a with dotted lines.

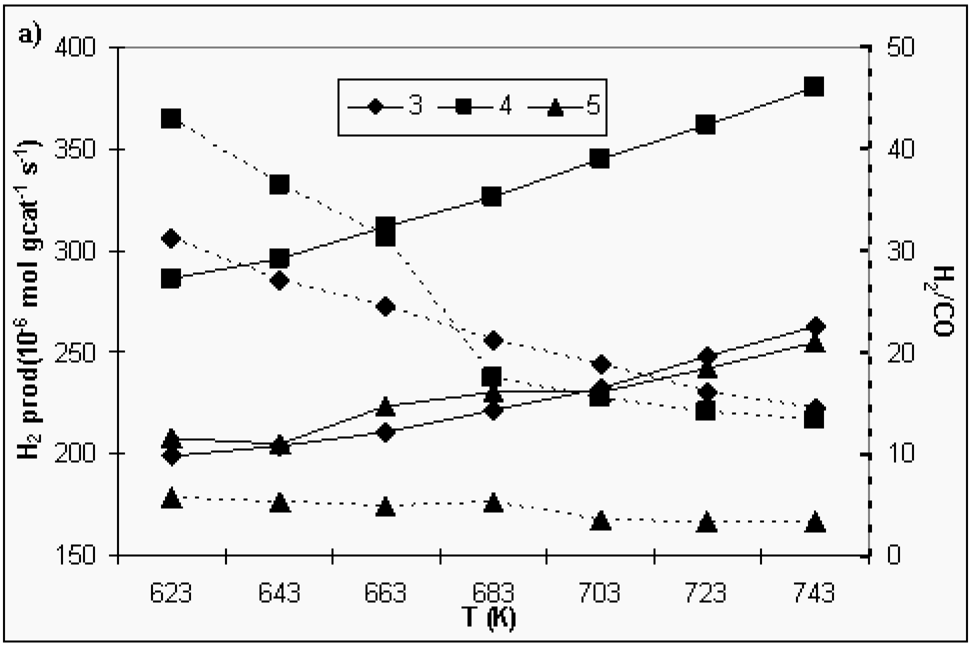
To sum up, Set5 was found to represent the best conditions in terms of H_2 production. Low residence time hinders both WGS and methanation reaction; however, CH_4 formation through an alternative route is thought to be present in Set5. The higher extent of WGS in Set1 and 2 has carried these sets to far better H_2/CO selectivity levels despite their relatively low H_2 production rates. The same trends for H_2 production rate and H_2/CO selectivity were obtained in our previous studies for pure propane (Caglayan et al., 2005) and LPG (3:1 propane: *n*-butane mixture) (Gokaliler et al., 2008).

4.2. Effect of C/O_2

The effect of C/O_2 ratio on the catalyst activity was investigated among Sets 3, 4 and 5 for a W/F level of 0.51. The OSR behaviors of Cat B (which is parallel to that of Cat A) and Cat C (which is parallel to that of Cat D) are given as examples in Figures 4.2a and 4.2b, respectively.

For all bimetallic catalysts tested, the highest H_2 production rate was obtained for C/O_2=2.7 (Set4), which is the highest C/O_2 level tested in the current study. The parallel results were also obtained previously (Caglayan et al., 2005; Gokaliler et al., 2008). As long as the S/C and W/F ratios are constant, a higher C/O_2 ratio also indicates a higher flow rate of steam in the reactant mixture (Table 4.2). As it is known that heat transfer is favored by the increased steam content (Ma et al., 1996); the higher H_2 production rate in Set4 can also be attributed to this facilitated heat exchange. However, the dependence of H_2 production rate on C/O_2 ratio is non-monotonic; therefore, H_2 production level and H_2/CO selectivity for C/O_2=2.12 (Set5) were not higher than that for C/O_2=1.5 (Set3).

The H_2 production of Set3 was far better than that of Set5 for catalysts C and D (Figure 4.2b), and the H_2 production levels of Sets 3 and 5 are nearly the same for catalysts A and B (Figure 4.2a). The results underline the importance of C/O_2 ratio as an optimization parameter for product distribution which was also mentioned previously by other researchers (Pino et al., 2006; Laosiripojana et al., 2006; Pennemann et al., 2007). No clear H_2 production and H_2/CO selectivity trend had been obtained from our previous studies, except highest production and selectivity levels at highest C/O_2 ratio tested as long as there was no coke deposition (Caglayan et al., 2005; Gokaliler et al., 2008).



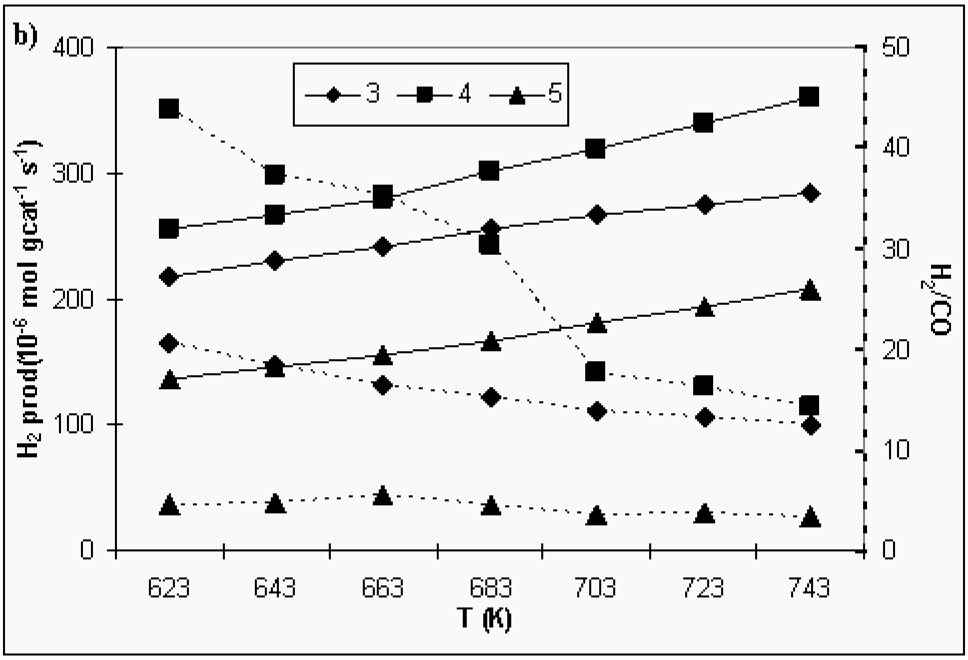
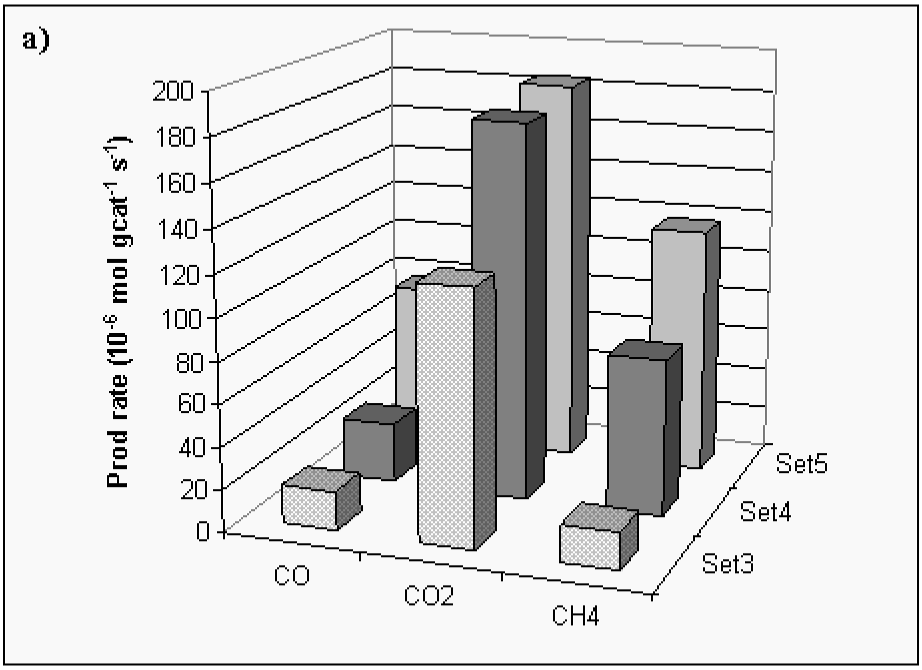


Figure 4.2. Effect of C/O_2 on H_2 production rate and H_2/CO ratio (dotted lines belong to right-y-axis) (a) for Cat B (b) for Cat C [Set3: C/O_2 =1.5, Set4: C/O_2 =2.70, Set5: C/O_2 =2.12]

The explanation of higher hydrogen production rate of Set3 in comparison to Set5 for Cat C can be understood by scrutinizing Figures 4.3a and 4.3b. Figures 4.3a and 4.3b compare CO, CO_2, and CH_4 distributions of Sets 3, 4 and 5 at 743 K over Cat B and Cat C, respectively. Production trends of CO, CO_2, and CH_4 are same for Set 4 over the two bimetallic catalysts. Careful examination reveals that the remarkable difference between Figures 4.3a and 4.3b is the CO_2 production data. Cat C's CO_2 production rate at both Set 3 and Set 5 are higher than those of Cat B for the whole temperature range. This behavior can be attributed to the higher Pt loading of Cat C. As it was explained in the previous section (see Figure 4.1b), the hydrogen production rate at Set 5 has suffered from methanation activity.

For that reason Cat B's hydrogen production rates at Set 5 and Set 3 have come close to each other. Cat C's high Pt loading, however, has led to a sufficient supply of heat to SR sites, even for low C/O_2 levels (i.e. Set 3), via promoting TOX reaction and thereby producing high amounts of CO_2. This heat supply has carried hydrogen production rate of Set 3 to a better position than Set 5.



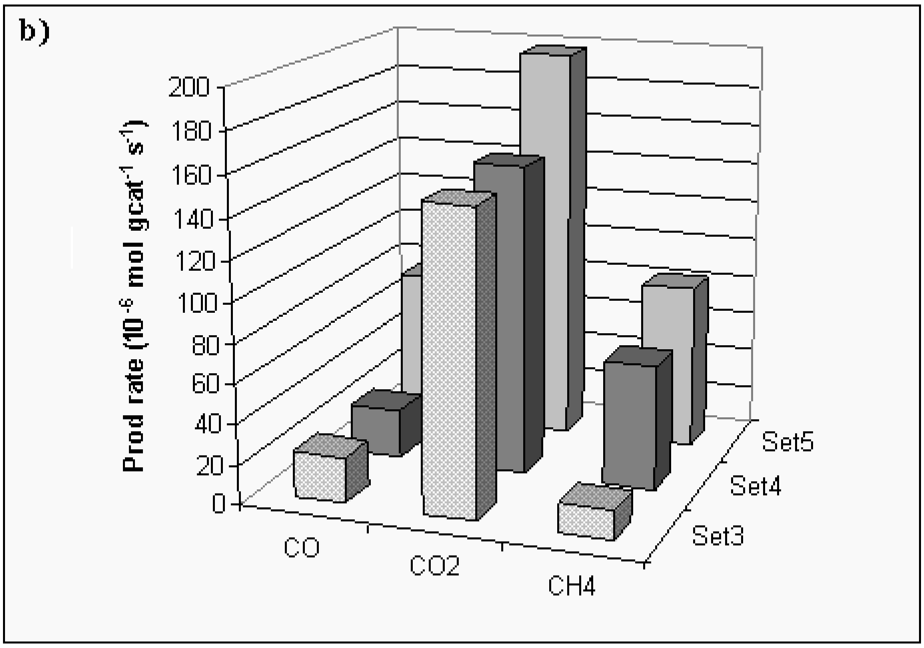


Figure 4.3. CO, CO_2 and CH_4 production levels (a) for Cat B (b) for Cat C at 743 K. [Set3: C/O_2=1.5, Set4: C/O_2 =2.70, Set5: C/O_2 =2.12]

4.3. Effect of the Pt and Ni Loading

The H_2 production rates and H_2/CO selectivity ratios of the catalysts for Sets 1-4 are given in Figures 4.4 and 4.5, respectively. The relative H_2, CO, CO_2 and CH_4 production rates of the catalysts are tabulated along with their H_2/CO selectivities (Table 4.4).

(i) Catalyst A: Ni:Pt = 75

The behavior of the catalyst in Sets 1-3 will be investigated apart from Set4 as the performance of the catalyst is quite similar for the first three sets. In Sets 1-3, the H_2 production level of Cat A was found to be average when compared to other catalysts. In these sets - since the C/O_2 ratios were not high - the flowrate of steam was not sufficient (Table 4.2). Because of the limited water vapor, the CO-producing SR (Rxn 1) was enhanced. High amount of CH_4 in the product stream is another explanation for the relatively low H_2 production rate.

In Set4, however, higher amount of steam present in the reactant mixture created a positive effect on the activity and selectivity of this high-Ni/Pt ratio catalyst. CO production rate was low especially above ca. 650 K indicating promotion of Rxn2 instead of Rxn1. Despite significant CH_4 production, H_2 production is sufficient indicating satisfactory level of WGS reaction; the high WGS activity in Set4 compared to previous sets is most probably a result of the high water flow rate in this set.

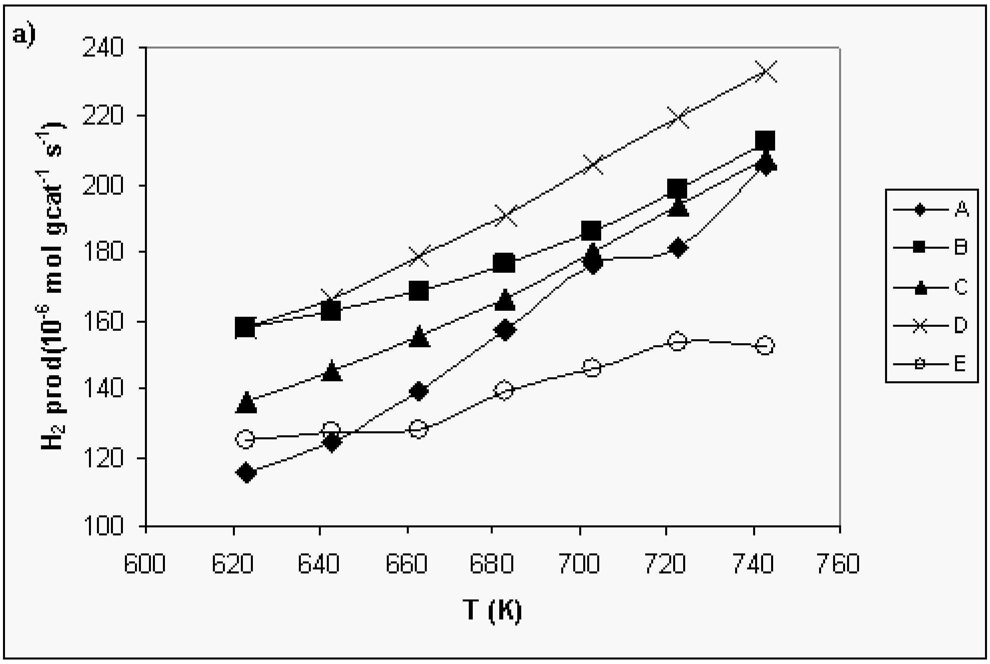
(ii) Catalyst B : Ni:Pt = 50

In Set1 and 2, H_2 production rate of Cat B was one of the highest compared to other catalysts. For these medium and high contact times sets; the catalyst was able to limit methanation, and the low CO production rate along with high H_2 concentration in the product stream indicated ample WGS activity.

The H_2 production rate of Cat B in Set3 was a little bit lower than that of other catalysts most probably due to the low C/O_2 ratio. In this set, Cat B’s low Pt loading has led to limited TOX activity which results in insufficient level of heat flow to SR sites compared to the other sets with higher C/O_2 ratios. Low methanation activity makes H_2/CO

high even though the catalyst has modest WGS activity indicated by limited CO production.

At the high C/O_2 level (Set4), Cat B's H_2 production rate was the highest. High H_2 production can be explained by the combined effects of i) very limited methanation due to which H_2 produced remains in the product stream, and ii) WGS activity indicated by high CO_2/CO ratio (Figure 4.3a).



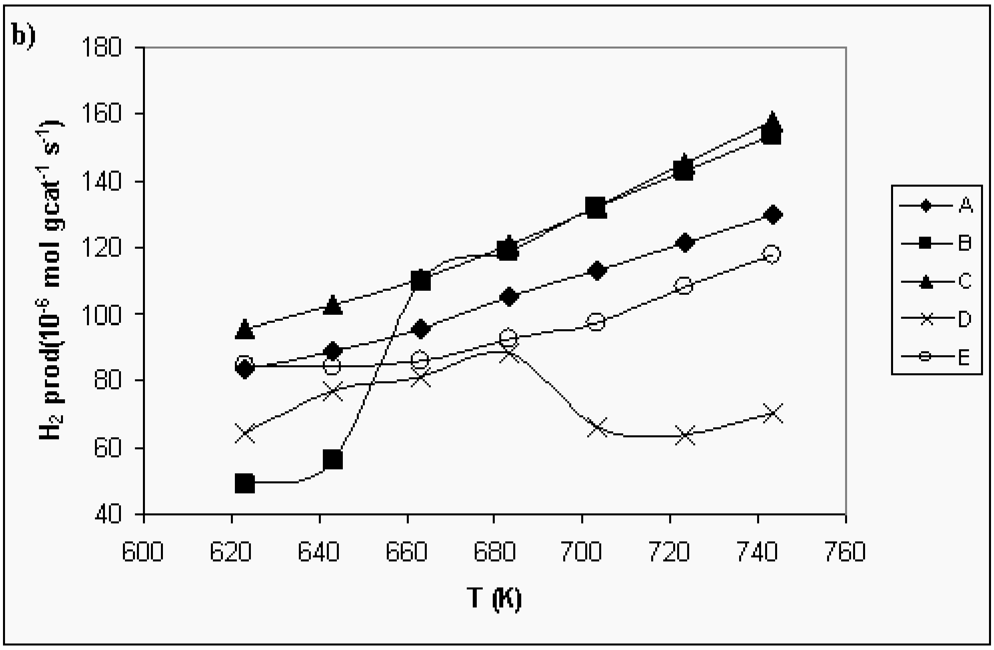
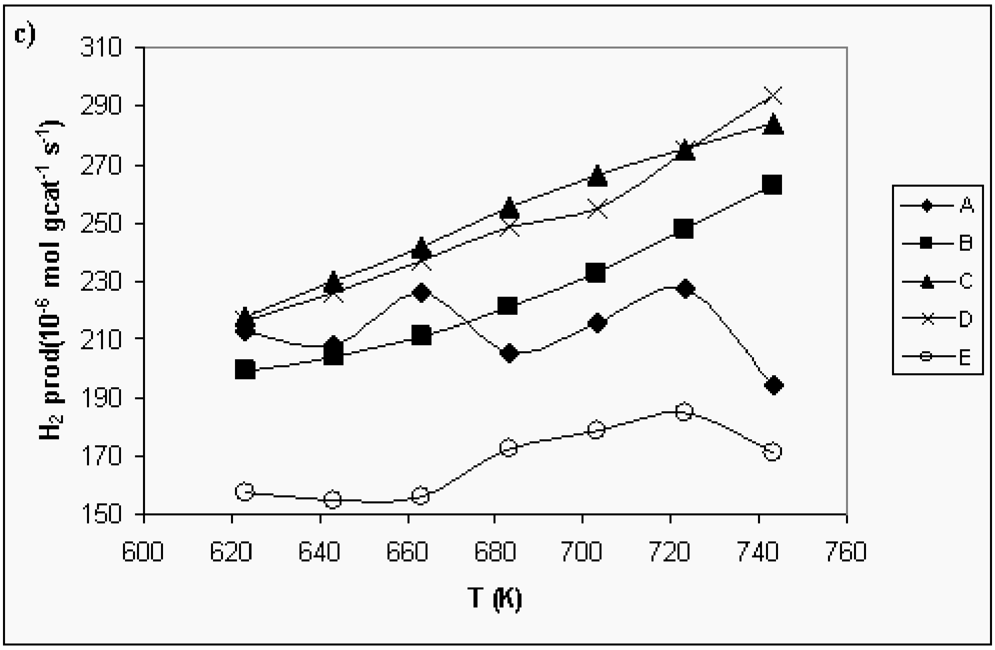


Figure 4.4. H_2 production rates for Catalysts A, B, C, D, and E (a) Set1; $C/O_2=2.12$, W/F=0.8 (b) Set2; $C/O_2=2.12$, W/F=1.12.



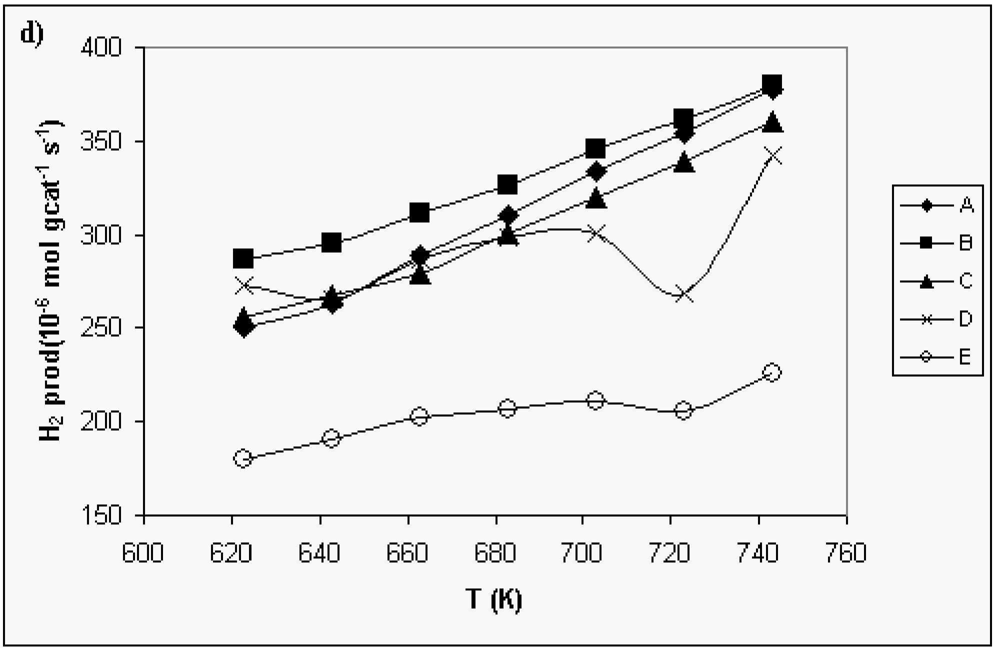


Figure 4.4.(continued) H_2 production rates for Catalysts A, B, C, D, and E (c) Set3; C/O_2=1.5, W/F=0.51, (d) Set4; C/O_2=2.7, W/F=0.51.

(iii) Catalyst C : Ni:Pt = 50

Even though Cat C showed a medium level H_2 production rate in Set1, its H_2/CO selectivity was high, indicating a great extent of WGS reaction. The catalyst has greatly suppressed methanation on its surface, like Cat B.

Unlike to Set1, H_2 production was enhanced In Set2. CO and CH_4 production levels were low. Based on these results, Cat C was the optimum catalyst for Set2. A comparison between Set1 and 2 reveals that as the residence time of the reactants on the catalyst surface increases both the H_2 production rate and WGS activity increases provided that the catalyst is able to prevent methanation.

In Set3, though H_2 production rate was the highest among the catalysts, high production rate of CO has lowered the selectivity. In this set, steam flowrate was low due to the low C/O_2 ratio. As steam is one of the reactants of WGS reaction, its limited flow rate might be the reason for relatively lower WGS activity. In the same set, Cat B had shown a slightly better WGS performance (Figures 4.3a and 4.3b). Even though the Ni/Pt ratios of the two catalysts are the same, higher Ni loading - which mainly promotes SR reactions - of Cat C has made the catalyst more sensitive to steam limitations.

Cat C’s performance in Set4 was similar to that in Set1; taking the medium level production of H_2 into consideration, the methanation was limited and the selectivity ratio was high. High selectivity level is a result of good WGS activity indicating the enhanced WGS performance of the catalyst when there is no scarcity of steam. For this low residence time set, WGS reaction has occurred to a larger extent than methanation mainly because of highly exothermic nature of methanation.

(iv) Catalyst D : Ni:Pt = 33

In Sets 1 and 3, the H_2 production levels of the catalyst were the highest; however the selectivity ratios were far from the desired ratio, indicating poor WGS activity. This catalyst has suppressed methanation to some extent at low residence times.

H_2 production rate has decreased in Set2 mainly because of the high methanation rate at this high W/F ratio.

Cat D could not show enough activity in Set 4 when C/O_2 level was high (Set4). Even though there were sufficient amount of hydrocarbon available, the limited Ni loading of Cat D led the use of hydrocarbon mostly in TOX resulting in suppressed SR activity. Therefore, both the H_2 and CO production levels were low, which inevitably increased the H_2/CO ratio.

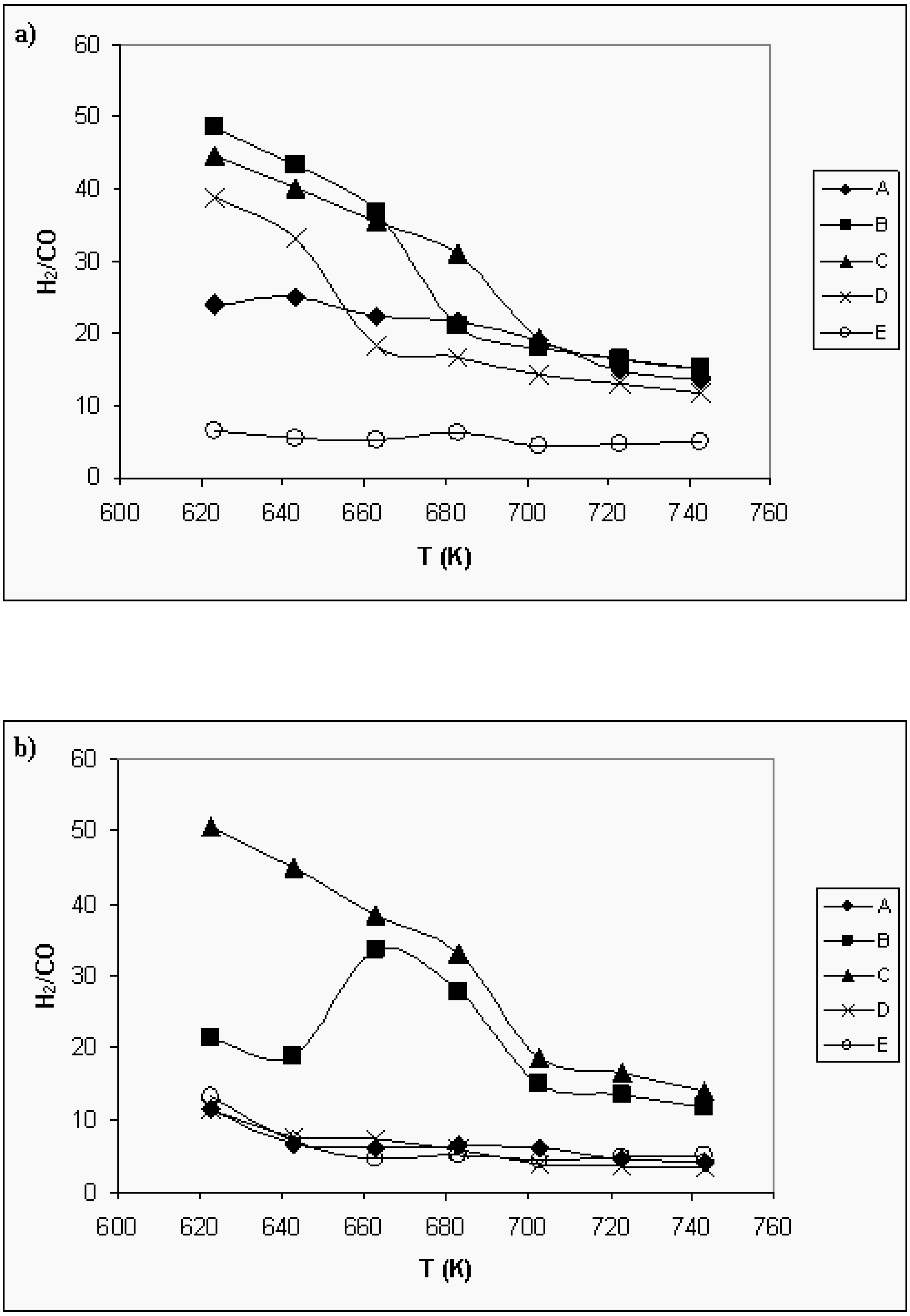
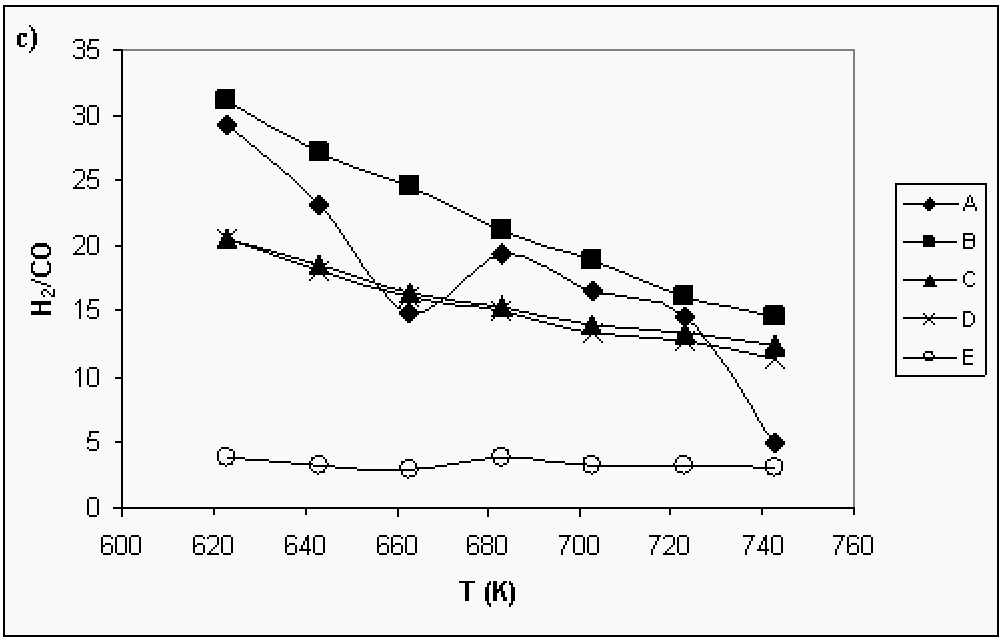


Figure 4.5. H_2/CO selectivities for Catalysts A, B, C, D, and E. (a) Set1; C/O_2=2.12, W/F=0.8 (b) Set2; C/O_2=2.12, W/F=1.12.



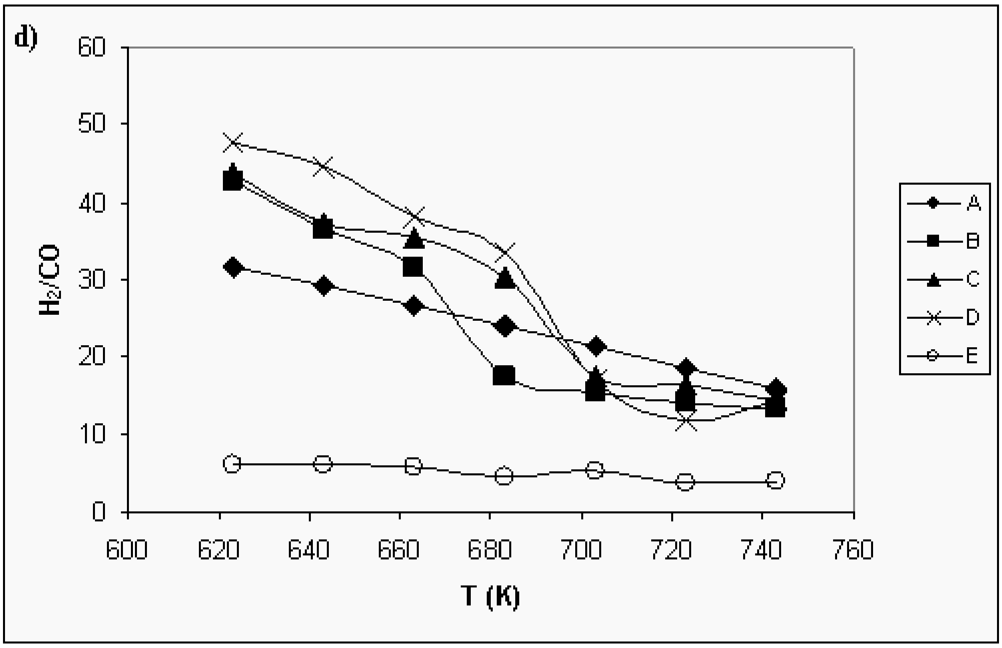


Figure 4.5. (Continued) H_2/CO selectivities for Catalysts A, B, C, D, and E. (c) Set3; C/O_2=1.5, W/F=0.51, (d) Set4; C/O_2=2.7, W/F=0.51.

(v) Catalyst E : Pt-Au-Ni

Promoting the bimetallic Pt-Ni catalyst with Au was thought to increase the WGS activity. However, addition of Au has decreased H_2 production rate of the bimetallic catalyst in addition to increasing the production rate of undesired products, i.e. CO and CH_4, in all of the experimental sets.

Table 4.4. Relative production rates of H_2, CO, CH_4 and H_2/CO ratio of five catalysts

Set #	C/O_2	W/F	H_2 production	H_2/CO	CO production	CH_4 production
1	2.12	0.80	D>B>C>A>E	C~B>A>D>E	E>>D>A~B>C	A>E>C~B~D
2	2.12	1.12	C>B>A>E>D	C>B>A~D>E	A~E>D>B~C	D>E>A>B>C
3	1.50	0.51	C~D>B~A>E	B>A>C~D>E	E>>D~C>A>B	A>B>C~D~E
4	2.70	0.51	B>A>C>D>E	D>C>B>A>E	E>>B>A~C~D	A>E>D>C>B

5. CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

Experiments conducted in OSR of propane over the five catalysts supported on δ-Al_2O_3 have shown that;

i) Lower residence times promote H_2 production rate mainly because of the higher flow rate of fresh hydrocarbons. On the other hand, if one seeks high H_2/CO ratio, medium level W/F ratios -which enhance WGS reaction- should be preferred.

ii) Among all of the bimetallic catalysts tested, the highest H_2 production rate and H_2/CO selectivity was obtained for the highest C/O_2 level. However, while decreasing C/O_2 from 2.7 down to 2.12 and then to 1.5, a clear trend in H_2 production decrease was not experienced.

iii) The previously tested Cat A produced high amount of H_2 only if there was enough steam in the medium. Its WGS activity performance was also found to depend on the concentration of steam present. Methanation reaction had occurred extensively on Cat A’s surface.

Cat B not only hindered methanation but also facilitated WGS reaction in all experimental sets. When compared to Cat A, it can be said that a decrease in Ni/Pt ratio has prevented methanation, made the catalyst more robust to the water vapor level in the reactant mixture, and increased the WGS performance.

Cat C had also suppressed methanation, like Cat B. It is the optimum catalyst at low residence times as it produces more H_2 and thereby prevents methanation on the catalyst surface. Comparing the performance of Cat A with that of Cat C, the results indicate the increase in Pt loading and the decrease in Ni/Pt ratio enhances H_2 production -especially at low C/O_2 level sets-, augments WGS reaction, and significantly decreases methanation level.

Cat D was prone to methanation particularly at high residence times. Moreover, its WGS activity was far below sufficient.

Addition of Au to bimetallic Pt:Ni system have led to a poor performance in both H_2 production activity and H_2/CO selectivity.

The results obtained in this study clearly show that when a bimetallic catalyst, like Pt-Ni, is used in OSR of hydrocarbons; a combined optimization involving reaction parameters, metal contents of the catalysts as well as metal loading ratio should be performed to benefit from the superior performance specs of the bimetallic system.

5.2. Recommendation

As mentioned before, promoting the bimetallic Pt-Ni catalyst with Au was thought to increase the WGS activity. However, addition of Au has decreased H_2 production rate of the bimetallic catalyst in addition to increasing the production rate of undesired products, i.e. CO and CH_4, in all of the experimental sets. Three-metallic catalyst with gold is thought to have dominant TOX activity because of total Pt-Au loading (0.6 %w). TOX consumes hydrocarbon feed and steam reforming on Ni sites may not have enough time or feed. Therefore, next study may be on new gold ratio in the catalyst. It should be 0.1 wt% Au and 0.2 wt% Pt with same Ni content.

Another gold promotion activity search may be on the catalyst preparation types. We prepared all catalysts by impregnating one by one and calcined he catalyst. Next study may be on different catalyst preparation techniques.

REFERENCES

Andreeva, D., V. Idakiev, T. Tabakova, L. Ilieva, P. Falaras, A. Bourlinos, and A. Travlos, 2002, “Low-Temperature Water-Gas Shift Reaction over Au/CeO_2 Catalysts”, *Catalysis Today,* Vol. 72, pp. 51-57.

Avcı, A. K., 2003, C*omputational and Experimental Investigation of Catalytic Hydrocarbon Fuel Processing for Autothermal Hydrogen Production*, Ph.D. Dissertation, Boğaziçi University.

Avcı, A. K., D. L. Trimm, A. E. Aksoylu, and Z. I. Önsan, 2003, “Ignition Characteristics of Propane and n-Butane over Supported Pt, Ni, Pt-Ni Catalysts”, *Catalysis Letters*, Vol. 88, pp. 17-22.

Beckhaus P., M. Dokupil, A. Heinzel, S. Souzani, and C. Spitta, 2004, “On-board Fuel Cell Power Supply for Sailing Yachts”, *Journal of Power Sources*, Vol. 145, pp.639-643.

Brown, L.F., 2001, “A Comparetive Study of Fuels for On-board Hydrogen Production for Fuel-Cell-Powered Automobiles”, *International Journal of Hydrogen Energy,* Vol. 26, pp. 382-397.

Caglayan, B. S., A. K. Avcı, Z. I. Önsan, and A. E. Aksoylu, 2004, “Production of Hydrogen over Bimetallic Pt-Ni/δ-Al_2O_3: I. Indirect partial oxidation of Propane", *Applied Catalysis A: General*, Vol. 280, pp.181-188.

Caglayan, B. S., Z. I. Önsan, and A. E. Aksoylu, 2005, “Production of Hydrogen over Bimetallic Pt-Ni/δ-Al_2O_3: II. Indirect partial oxidation of LPG”, *Catalysis Letters*, Vol. 102, pp.63-67.

Fu, Q., S. Kudriavtseva, H. Saltsburg, and M. Flytzani-Staphanopoulos, 2003, “Gold-Ceria Catalysts for Low-Temperature Water-Gas Shift Reaction”, *Chemical Engineering Journal*, Vol. 93, pp. 41-53.

Ghenciu, A. F., 2002, “Review of Fuel Processing Catalysts for Hydrogen Production in PEM Fuel Cell Systems”, *Current Opinion in Solid State & Materials Science*, Vol. 6, pp. 389-399.

Gokaliler, F., B. Caglayan, Z. Önsan, and A. E. Aksoylu, 2008, “Hydrogen Production by Autothermal Reforming of LPG for PEM Fuel Cell Applications”, *Hydrogen Energy*, Vol. 33, pp. 1383-1391.

Hakkarainen, R., T. Salmi, and R. L. Keiski, 1994, “Comparison of the Dynamics of the High-Temperature Water-Gas Shift Reaction on the Oxide Catalysts”, *Catalysis Today*, Vol. 20, pp. 395-408.

Hwang, J. J., D. Y. Wang, N. C. Shih, D. Y. Lai, and C. K. Chen, 2004, “Development of Fuel-Cell-Powered Electric Bicycle”, *Journal of Power Sources*, Vol. 133, pp.223-228.

Iwasa N., T. Mayanagi, S. Masuda, and N. Takezawa, 2000, “Steam Reforming of Methanol over Pd-Zn Catalysts”, *Reaction Kinetics Catalysis Letters*, Vol. 69, pp. 355-360.

Iwasa, N., T. Mayanagi, N. Ogawa, K. Sakata, and N. Takezawa, 1998, “New Catalytic Functions of Pd-Zn, Pd-Ga, Pd-In, Pt-Zn, Pt-Ga and Pt-In Alloys in the Conversion of Methanol”, *Catalysis Letters*, Vol. 54, pp. 119-123.

Jacobs, G., S. Ricote, P. M. Patterson, U. M. Graham, S. Khalid, E. Rhodus, and B. H. Davis, 2005, Low Temperature Water-Gas Shift: Examining the Efficiency of Au as a Promoter for Ceria-based Catalysts Prepared by CVD of a Au Precursor, *Applied Catalysis A: General*, Vol. 292, pp. 229-243.

Joensen, F. and J. R. Rostrup-Nielsen, 2001, “Conversion of Hydrocarbons and Alcohols for Fuel Cells”, *Journal of Power Sources*, Vol. 4566, pp. 1-7.

Jung-Ho, W., 2006, “Applications of Proton Exchange Membrane Fuel Cell Systems”, *Reneawable and Sustainable Energy Reviews*, Vol. 26, pp.291-301.

Karyobkina, N. A., A. A. Phatak, W. F. Ruettinger, R. J. Farrauto, and F. H. Ribeiro, 2003, “Determination of Kinetic Parameters for Water-Gas Shift Reaction on Copper Catalysts under Realistic Conditions for Fuel Cell Applications”, *Journal of Catalysis*, Vol. 217, pp. 233-239.

Kepinski, L., B. Statinska, and T. Borowiecki, 2000, “Carbon Deposition on Ni/γ-Al_2O_3 Catalysts Doped with Small Amounts of Molybdenum", *Carbon*, Vol. 38, pp. 1845-1856.

Krumpelt, M. and S. Ahmed, 2001, “Hydrogen from Hydrocarbon Fuels for Fuel Cells”, *International Journal of Hydrogen Energy*, Vol. 26, pp.291-301.

Laosiripojana, N. and S. Assabumrungrat, 2006, “Hydrogen Production from Steam and Autothermal Reforming of LPG over High Surface Ceria”, *Journal of Power Sources*, Vol. 158, pp. 1348-1357.

Ledjeff-Hey, K., V. Formanski, T. Kalk, and K. J. Roes, 1998, “Compact Hydrogen Production Systems for Solid Polymer Fuel Cells”, *Journal of Power Sources,* Vol. 71, pp. 199-207.

Li, Y., X. Li, L. Chang, D. Wu, Z. Fang, and Y. Shi, 1999, “Understandings on the Scattering Property of the Mechanical Strength Data of Solid Catalysts: A Statistical Analysis of Iron-based High-Temperature Water-Gas Shift Catalysts”, *Catalysis Today*, Vol. 51, pp. 73-84.

Löfler, D. G., K. Taylor, and D. Mason, 2003, “A Light Hydrocarbon Fuel Processor Producing High-Purity Hydrogen”, *Journal of Power Sources*, Vol. 117, pp. 84-91.

Luengnaruemitchai, A., S. Osuwan, and E. Gulari, 2003, “Comparative Studies of Low-Temperature Water-Gas Shift Reaction over Pt/CeO_2, Au/CeO_2, and Au/Fe_2O_3 Catalysts”, *Catalysis Communications*, Vol. 4, pp. 215-221.

Ma, L., 1995, *Hydrogen Production from Steam Reforming of Light Hydrocarbons in an Autothermic System*, Ph.D. Dissertation, University of New South Wales.

Ma, L. and D. L. Trimm, 1996, “Alternative Catalyst Bed Configurations for the Autothermic Conversion of Methane to Hydrogen”, *Applied Catalysis A: General*, Vol. 138, pp. 265-273.

Midilli, A., M. Ay, I. Dincer, and M. A. Rosen, 2004, “On Hydrogen and Hydrogen Energy Strategies I: Current Status and Needs”, *Reneawable and Sustainable Energy Reviews*, Vol. 9, pp. 255-271.

Pennemann, H., V. Hessel, G. Kolb, H. Löwe, and R. Zapf, 2007, “Partial Oxidation of Propane Using Micro Structured Reactors”, *International Journal of Chemical Engineering*, Vol. 135, pp. 66-73.

Pino, L., A. Vita, F. Cipiti, M. Lagana, and V. Recupero, 2003, “Performance of Pt/CeO_2 Catalyst for Propane Oxidative Steam Reforming”, *Applied Catalysis A: General*, Vol. 306, pp. 68-76.

Ruettinger, W., O. Ilinich, and R. J. Farrauto, 2003, “A New Generation of Water Gas Shift Catalysts for Fuel Cell Applications”, *Journal of Power Sources*, Vol. 118, pp. 61-65.

Son, I.H., M. Shamsuzzoha, and A. M. Lane, 2002, “Promotion of Pt/δ-Al_2O_3 by New Pretreatment for Low-Temperature Preferential Oxidation of CO in H_2 for PEM Fuel Cells”, *Journal of Catalysis*, Vol. 210, pp. 460-465.

Song, C., 2002, “Fuel Processing for Low-Temperature and High-Temperature Fuel Cells: Challenges, and Opportunities for Sustainable Development in the 21st Century”, *Catalysis Today*, Vol. 77, pp.17-49.

Souza, M. M. V. M. and M. Schmal, 2005, “Oxidative steam reforming of Methane over Pt/ZrO_2/Al_2O_3 Catalysts”, *Applied Catalysis A: General*, Vol. 281, pp. 19-24.

Ozkara, S. and A. E. Aksoylu, 2003, “Selective Low Temperature Carbon Monoxide Oxidation in H_2-rich Gas Streams over Activated Carbon Supported Catalysts”, *Applied Catalysis A: General*, Vol. 251, pp. 75-83.

Tomishige, K., S. Kanazawa, S. Ito, and K. Kunimori, 2003, “Catalyst Development for Direct Heat Supply in Methane Reforming with CO_2 and O_2”, *Applied Catalysis A: General*, Vol. 244, pp. 71-82.

Tomkiewicz M., 2006, “Global Warming: Science, Money and Self-preservation”, *Comptes Rendus Chimie*, Vol. 9, pp. 172-179.

Wang, C., Z. Mao, F. Bao, X. Li, and X. Xie, 2005, “Development and Performance of 5 kW Proton Exchange Membrane Fuel Cell Stationary Power System”, *International Journal of Hydrogen Energy*, Vol. 30, pp.1031-1034.

Wang, X. and R. J. Gorte, 2002, “A Study of Steam Reforming of Hydrocarbon Fuels on Pd/Ceria”, *Applied Catalysis A: General*, Vol. 224, pp. 209-218.

Whittington, B. I., C. J. Jiang, and D. L. Trimm, 1995a, “Vehicle Exhaust Catalysis: I. The Relative Importance of Catalytic Oxidation, Steam Reforming and Water-Gas Shift Reactions”, *Catalysis Today*, Vol. 26, pp. 41-45.

Whittington, B. I., C. J. Jiang, and D. L. Trimm, 1995b, “Vehicle Exhaust Catalysis: II. The effect of Sulphur Dioxide on the Performance of Three-Way Vehicle Exhaust Catalysts”, *Catalysis Today*, Vol. 26, pp. 47-54.