

STEAM REFORMING OF ETHANOL OVER Pt-Ni/Al₂O₃ CATALYST

by

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to my family

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ABSTRACT

STEAM REFORMING OF ETHANOL OVER Pt-Ni/Al₂O₃ CATALYST

This experimental work involves a parametric study of the bimetallic Pt-Ni/ δ -Al₂O₃ catalysts with different Pt and Ni loadings (0.2wt%Pt-10wt%Ni, 0.3wt%Pt-10wt%Ni, 0.2wt%Pt-15wt%Ni, 0.3wt%Pt-15wt%Ni) for hydrogen production by ethanol steam reforming as well as a kinetic investigation of ethanol steam reforming over 0.3wt%Pt-15wt%Ni/ δ -Al₂O₃ catalyst on the basis of power law and Langmuir-Hinshelwood-Hougen-Watson type rate equations. Experimental conditions were adjusted to eliminate coke deposition over the Ni-based catalysts by fixing the steam to carbon ratio at 3.0. The results obtained at 723 K showed that catalysts with 15wt%Ni content were more efficient and the Pt content also affected ethanol steam reforming performance. Also, above 723 K, the catalyst with 0.3wt%Pt-15wt%Ni performed better. Kinetic data were obtained at 723 K over bimetallic 0.3wt%Pt-15wt%Ni/ δ -Al₂O₃ catalyst using three different ethanol and steam compositions at six different space times each. Experimental rate data were used to estimate kinetic parameters of power law and proposed LHHW models by using the differential method of data analysis. The investigation of power law kinetics gave reaction orders of 1.01 and -0.09 with respect to ethanol and steam, respectively, and a reaction rate constant of $9.23 \text{ mol.g}_{\text{cat}}^{-1}.\text{h}^{-1}.\text{atm}^{-0.92}$. The first order dependence of the rate on ethanol concentration was also confirmed by the integral method of data analysis. Both power law and single-site LHHW models gave very good fit to the experimental data.

ÖZET

Pt-Ni/Al₂O₃ KATALİZÖRÜ ÜZERİNDE ETANOLÜN BUHARLA REFORMLANMASI

Bu deneysel çalışma, etanol buhar reformlaması kinetiğinin çift metalli 0.3wt%Pt-15wt%Ni/ δ -Al₂O₃ katalizörü üzerinde üssel ve Langmuir-Hinshelwood-Hougen-Watson tipi hız denklemleri kullanılarak incelenmesinin yanı sıra etanol buhar reformlamasıyla hidrojen üretimi için farklı miktarlarda Pt ve Ni içeren çift metalli Pt-Ni/ δ -Al₂O₃ katalizörlerinin (0.2wt%Pt-10wt%Ni, 0.3wt%Pt-10wt%Ni, 0.2wt%Pt-15wt%Ni, 0.3wt%Pt-15wt%Ni) parametrik çalışmasını içermektedir. Deneysel çalışma şartları Ni temelli katalizörler üzerinde kok oluşumunu engellemek amacıyla buhar karbon oranı 3.0' te sabit tutularak ayarlanmıştır. 723 K' de elde edilen sonuçlar ağırlıkça yüzde 15 Ni içeren katalizörlerin daha iyi sonuç verdiğini ve Pt içeriğinin de etanol buhar reformasyonunu etkilediğini göstermiştir. Ayrıca, 723 K' nin üzerindeki sıcaklıklarda 0.3wt%Pt-15wt%Ni katalizörü daha iyi sonuç vermiştir. Kinetik veriler her biri altı farklı boşluk zamanlarında olmak üzere üç farklı etanol ve buhar konsantrasyonu kullanılarak çift metalli 0.3wt%Pt-15wt%Ni/ δ -Al₂O₃ katalizörü üzerinde ve 723 K' de elde edilmiştir. Deneysel hız verileri kullanılarak üssel hız denkleminde ve önerilen LHHW modellerinde yer alan kinetik parametreler diferansiyel veri analiz yöntemi ile hesaplanmıştır. Etanol ve buharın reaksiyon mertebeleri sırasıyla 1.01 ve -0.09, reaksiyon hız sabiti ise 9.23 mol.g_{cat}⁻¹.h⁻¹.atm^{-0.92} olarak belirlenmiştir. Reaksiyon hızının etanol konsantrasyonuna birinci mertebeden bağlı olması integral veri analiz yöntemi ile de kanıtlanmıştır. Gerek üssel gerekse tek-merkezli LHHW modelleri deneysel verilerle çok uyumlu sonuçlar vermiştir.

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LIST OF SYMBOLS/ABBREVIATIONS

A	Ethanol
B	Steam
C _i	Concentration of component i
D	Internal diameter of the reactor
ΔG	Gibbs energy
D _p	Catalyst particle size
F_{EtOH}	Ethanol flow rate
k	Reaction rate constant
K_i	Adsorption constant of component i
L	Catalyst bed height
N	Number of experiments
p	Number of parameters
P_i	Pressure of component i
Q _T	Total flow rate
R	Universal gas constant
r_{EtOH}	Ethanol consumption rate
S	Active site
T	Temperature
W _{cat}	Weight of catalyst
W/F_{EtOH}	Space time
X _{EtOH}	Ethanol conversion
ΔH°	Enthalpy of the reaction at the standart conditions
α	Reaction order with respect to ethanol
β	Reaction order with respect to steam
AFC	Alkaline Fuel Cell
ATR	Autothermal Reforming
EtOH	Ethanol

GC	Gas Chromatograph
HPLC	High Performance Liquid Chromatography
ID	Inside Diameter
LHHW	Langmuir-Hinshelwood-Hougen-Watson
MCFC	Molten Carbonate Fuel Cell
NSTA	Nonstoichiometric Thermodynamic Approach
PAFC	Phosphoric Acid Fuel Cell
PEM	Polymer Electrolyte Membrane
PEMFC	Proton Exchange Membrane Fuel Cell
PO	Partial Oxidation
PROX	Preferential Oxidation
SOFC	Solid Oxide Fuel Cell
STA	Stoichiometric Thermodynamic Approach
TCD	Thermal Conductivity Detector
TOS	Time-on-stream
TPR	Temperature programmed reduction
WGS	Water-Gas Shift Reaction

1. INTRODUCTION

The environmental problems caused by the intensive use of fossil fuels—as well as their limited availability—are increasingly demanding a more rational use of our energy resources (Navarro *et al.*, 2005). Among all the different alternatives available, there is now growing interest in the use of hydrogen as an alternative fuel. Its combustion does not result in any emission other than water vapor (although under certain air/hydrogen ratios, NOX can also be produced) and hence it is the least polluting fuel that could be used in an internal combustion engine. It can also be used in a fuel cell for the production of electricity for stationary applications and mobile electric vehicle operations (Vaidya and Rodrigues, 2006). Thus, the use of hydrogen as an alternative energy source contributes toward two goals: reduction of atmospheric pollution and greenhouse gas emissions, and reduction of global dependency on fossil fuels (Fatsikostas and Verykios, 2004).

Fuel cells are electrochemical devices that convert the chemical energy of a fuel and an oxidant directly into electricity and heat on a continuous basis. Among the various types of fuel cells, the proton exchange membrane fuel cells (PEMFCs), the solid oxide fuel cells (SOFCs) and the molten carbonate fuel cells (MCFCs) have attracted considerable interest. SOFCs and MCFCs operate at high temperatures (around 973 K) and are used for stationary power generation. PEMFCs are primarily used for automotive applications. They have a low operating temperature (353 K), high current density and low CO tolerance (10 ppm). They use hydrogen as the fuel and this can be supplied as pure hydrogen. However, current hydrogen storage techniques are heavy and bulky. Also, there is no proper infrastructure for hydrogen transport and distribution. Therefore, chemical storage of hydrogen in liquid fuels is considered to be one of the most advantageous options for supplying hydrogen to the fuel cells (Vaidya and Rodrigues, 2006).

Among the various fuels which can be converted into alcohols, in particular, methanol and ethanol, are very promising candidates because they are easily decomposed in the presence of water and generate an H₂-rich mixture suitable for feeding fuel cells. When compared to methanol, ethanol seems more promising since it is much less toxic, CO₂ neutral and offers a high octane number, a high heat of vaporization, and a low

photochemical reactivity. The steam reforming, partial oxidation, and autothermal reforming or oxidative steam reforming are the major processes used to create hydrogen from hydrocarbons and alcohols (Fierro *et al.*, 2005; Perna, 2007). Currently steam reforming has the highest efficiency for hydrogen production among other alternatives, the only inconvenience being its highly endothermic nature. Further investigations of steam reforming are being performed mostly related to alternative fuel choices, new catalyst types and effects of different parameters on the process. However recent studies are deficient in kinetics of ethanol steam reforming as the process consists of various side reactions.

The objective of the present study is to conduct a complete kinetic study to obtain a Langmuir-Hinshelwood-Hougen-Watson (LHHW) type and power law type rate equations for ethanol steam reforming over the bimetallic Pt-Ni catalyst covering a wide range of feed composition and reaction temperatures. In the first part, parametric studies were conducted over bimetallic Pt-Ni/ δ -Al₂O₃ catalysts with different Pt and Ni loadings to find out how the ethanol steam reforming characteristics of Pt-Ni catalysts are affected by their Pt and Ni content and select the best catalyst among them for further investigations. In the second part, kinetic investigation of ethanol steam reforming was brought into completion including determination of the rate constant and rate parameters with respect to ethanol and steam. Section 2 composes of a literature survey related to fuel cell technology and catalytic oxidation, steam reforming and partial oxidation of hydrocarbons. The techniques, procedures, equipment and systems used in the experiments are presented in Section 3. Results of the study and their related discussions can be found in Section 4. Section 5 includes the conclusions that can be drawn from this study and the recommendations for future work.

2. LITERATURE SURVEY

2.1. Fuel Cell Technology

2.1.1. Concept of Fuel Cell

Fuel cells are electrochemical devices that convert a fuel's chemical energy directly to electrical energy with high efficiency. Fuel cells are similar to batteries because of the electrochemical principle. An important difference is that batteries store energy, while fuel cells can produce electricity continuously as long as fuel and air are supplied. Fuel cells electrochemically combine a fuel (typically hydrogen) and an oxidant without burning, thereby dispensing with the inefficiencies and pollution of traditional energy conversion systems. Since the conversion of the fuel to energy takes place via an electrochemical process, not combustion, the process is clean, quiet and highly efficient than fuel burning (Ahmed and Krumpelt, 2001; Song, 2002; Alcaide *et al.*, 2006).

A single fuel cell consists of an electrolyte sandwiched between two thin electrodes (a porous anode and cathode). Fuel cells function on the principle of electrolytic charge exchange between a positively charged anode plate and a negatively charged cathode plate. When hydrogen is used as the basic fuel, "reverse hydrolysis" occurs, yielding only water and heat as byproducts while converting chemical energy into electricity. Pollutant emissions are practically zero. Although there are different fuel cell types, all work on the same principle. Hydrogen, or a hydrogen-rich fuel, is fed to the anode where hydrogen's negatively charged electrons are separated from positively charged ions (protons) by a catalytic reaction. The free electrons, produced at the anode, are conducted in the form of a usable electric current through the external circuit while the ions move through the electrolyte toward the cathode. At the cathode, oxygen from the air, electrons from the external circuit and protons combine to form water and heat. Depending on the fuel and electrolyte, different types of chemical reactions will occur. The by-products of fuel cell operation are heat, water in the form of steam or liquid water, and carbon dioxide in the case of hydrocarbon fuel (Song, 2002; Acres, 2001).

The amount of power produced by a fuel cell depends upon several factors, such as fuel cell type, cell size, the temperature at which it operates, and the pressure at which the gases are supplied to the cell. A single fuel cell is only capable of producing about 1 volt, so typical fuel cell designs link together many individual cells to form a “stack” to produce a more useful voltage. Increasing the number of cells in a stack increases the voltage, while increasing the surface area of the cells increases the current. A fuel cell stack can be configured with many groups of cells in series and parallel connections to further tailor the voltage, current, and power. Still, a single fuel cell produces enough electricity for only the smallest applications. A typical fuel cell stack may consist of hundreds of fuel cells.

2.1.2. Fuel Cell Types and Applications

Fuel cells are classified according to the type of electrolyte used in the cell as well as the operating conditions of the unit. Fuel cells can also be characterized as either low or high temperature and by the types of fuel or oxidants used. Materials of construction play an important role in determining the limitations of fuel cell systems. This determines the kind of chemical reactions that take place in the cell, the kind of catalysts required, the temperature range in which the cell operates, the fuel required, and other factors. These characteristics, in turn, affect the applications for which these cells are most suitable. There are several types of fuel cells currently under development, each with its own advantages, limitations, and potential applications. In general, there are five different types of fuel cells, which include the solid oxide fuel cell (SOFC), molten carbonate fuel cell (MCFC), phosphoric acid fuel cell (PAFC), alkaline fuel cell (AFC), and polymer electrolyte fuel cell (PEFC). The different types of fuel cells together with their characteristics are summarized in Table 2.1 (Alcaide *et al.*, 2006).

Table 2.1. Summary of the major differences of the fuel cell types (Alcaide *et al.*, 2006; Kordesch and Shimader, 1996)

	PEMFC	AFC	PAFC	MCFC	SOFC
Electrolyte	Ion Exchange Membranes	Mobilized or Immobilized Potassium Hydroxide	Immobilized Liquid Phosphoric Acid	Immobilized Liquid Molten Carbonate	Ceramic
Operating Temperature	<393 K	335 K – 493K	423 K – 493 K	923 K	873 K – 1273 K
Charge Carrier	H ⁺	OH ⁻	H ⁺	CO ₃ ⁻	O ⁻
External Reformer for CH ₄ (below)	Yes	Yes	Yes	No	No
Prime Cell Components	Carbon-based	Carbon-based	Graphite-based	Stainless-based	Ceramic
Catalyst	Platinum	Platinum	Platinum	Nickel	Perovskites
Product Water Management	Evaporative	Evaporative	Evaporative	Gaseous Product	Gaseous Product
Product Heat Management	Process Gas + Independent Cooling Medium	Process Gas + Electrolyte Calculation	Process Gas + Independent Cooling Medium	Internal Reforming + Process Gas	Internal Reforming + Process Gas
Applications	Motive Small Utility Portable	Aerospace	Small utility	Utility	Utility

2.1.2.1. Proton Exchange Membrane Fuel Cell (PEMFC). PEM fuel cells, also known as polymer electrolyte fuel cells, use a solid polymer as an electrolyte and porous carbon electrodes containing a platinum catalyst. They need only hydrogen, oxygen from the air, and water to operate and do not require corrosive fluids like some fuel cells. They are typically fueled with pure hydrogen supplied from storage tanks or onboard reformers. A PEMFC requires cooling and management of the exhaust water to function properly. The fuel cell must operate under conditions where the byproduct water does not evaporate faster than it is produced because the membrane must be hydrated. PEMFCs operate at a temperature much lower than other fuel cells, because of the limitations imposed by the thermal properties of the membrane itself. They can produce high power density at temperatures below 373 K, allowing fast start-ups and immediate response to changes in

the demand for power. However, the PEMFC can be contaminated by CO (acts as a poison at low temperatures), reducing the performance and damaging catalytic materials within the cell, making it necessary to employ an additional reactor to reduce CO in the fuel gas if the hydrogen is derived from an alcohol or hydrocarbon fuel (Son, 2006; Alcaide *et al.*, 2006).

PEM fuel cells are used primarily for transportation applications and some stationary applications. Due to their fast startup time, low sensitivity to orientation, and favorable power-to-weight ratio, PEM fuel cells are particularly suitable for use in passenger vehicles, such as cars and buses.

2.1.2.2. Alkaline Fuel Cell (AFC). AFCs use a potassium hydroxide (KOH) solution as the electrolyte and operate at temperatures between 373 K and 573 K. Higher temperature AFCs use a concentrated (85wt %) KOH solution while lower temperature AFCs use a more dilute KOH solution (35-50wt %). The electrolyte is retained in a matrix (usually asbestos), and a wide range of electrocatalysts can be used such as Ni, Ag, metal oxides, spinels, and noble metals. The AFC features high specific power and energy density when used as hydrogen / oxygen fuel cell. The fuel supply is limited to non-reactive constituents except for hydrogen. Carbon monoxide (CO) poisons an AFC, and CO₂ will react with the KOH to form K₂CO₃, thus altering the electrolyte (Son, 2006; Alcaide *et al.*, 2006).

2.1.2.3. Phosphoric Acid Fuel Cell (PAFC). PAFCs use concentrated 100% phosphoric acids (H₃PO₄) electrolyte retained on a silicon carbide matrix and operate at temperatures between 423 K and 493 K. Concentrated H₃PO₄ is a relatively stable acid, which allows operation at these temperatures. At temperatures lower than 433 K, problems with CO poisoning of the anode electro-catalyst (usually platinum) and poor ionic conduction in the electrolyte becomes severe (Son, 2006; Alcaide *et al.*, 2006). The electrodes typically consist of Teflon TM-bonded platinum and carbon (PTFE-bonded Pt/C). This type of fuel cell is typically used for stationary power generation, but some PAFCs have been used to power large vehicles such as city buses.

2.1.2.4. Molten Carbonate Fuel Cell (MCFC). The electrolyte in this fuel cell is usually a combination of alkali (Na, K, Li) carbonates retained in a porous, chemically inert LiAlO₂

matrix. The fuel cell operates at relatively high temperatures (873 K – 973 K), where the alkali carbonates form a highly conductive molten salt with carbonate ions providing ionic conduction through the electrolyte matrix, allowing them to operate with unreformed fuels. Consequently, the electrode kinetics are fast and noble metals are not needed. Ni and nickel oxide catalysts are adequate to promote reaction on the anode and cathode respectively at the high operating temperatures of an MCFC. MCFCs are very efficient when the heat produced is used for co-generation. However, because MCFCs use a corrosive electrolyte, their durability is limited (Kordesch and Simader, 1996).

2.1.2.5. Solid Oxide Fuel Cell (SOFC). The electrolyte typically consists of a solid non-porous metal oxide such as Y_2O_3 stabilized ZrO_2 with conductivity based on oxygen ions. Typically the anode is Co- ZrO_2 or Ni- ZrO_2 cermets, and the cathode is Sr-doped LaMnO_3 . SOFCs operate between 873 K and 1273 K. Because of the high operating temperature, a wide range of carbonaceous fuels can be supplied to SOFC's and high-grade heat is available. Size, heat output and a long start-up time make this fuel cell more suitable for stationary applications and to be used by utilities (Song, 2002).

2.1.3. Advantages of Fuel Cells Compared to Conventional Devices

Fuel cells have several important advantages over conventional power sources, such as internal combustion engines or batteries. They convert hydrogen and oxygen directly into electricity and water, with no combustion in the process. The resulting efficiency is between 50 and 60%, about double that of an internal combustion engine. In contrast to an internal combustion engine, a fuel cell produces no emissions of sulphur dioxide, nor nitrogen oxides, their only by-product is water (or water and carbon dioxide in the case of methanol cells). Because of their modularity, fuel cells of varying sizes can be stacked together to meet a required power demand. Thus they are very attractive from both energy and environmental standpoints.

The general advantages of fuel cells are reflected by the following desirable characteristics: (1) high energy conversion efficiency; (2) extremely low emissions of pollutants; (3) extremely low noise or acoustical pollution; (4) effective reduction of greenhouse gas (CO_2) formation at the source compared to low-efficiency devices; and (5)

process simplicity for conversion of chemical energy to electrical energy. Depending on the specific types of fuel cells, other advantages may include fuel flexibility and existing infrastructure of hydrocarbon fuel supplies; co-generation capability; modular design for mass production; relatively rapid response (Song, 2002).

2.2. On-board Hydrogen Storage Challenges

Hydrogen is a potentially attractive domestic energy source that can be used for both electricity and transportation needs without significantly increasing emissions of CO₂ or greenhouse gases. In this context storage of hydrogen is one of the key challenges in developing hydrogen economy. Available technologies permit directly to store hydrogen by modifying its physical state in gaseous or liquid form in pressurized or in cryogenic tanks (David, 2005; Zhou, 2005). Alternatively, it can be chemisorbed on a metal or alloy in the form of metal hydrides or absorbed on carbon nanotubes (Avci, 2003). However, these ways of storing hydrogen are somewhat heavy and bulky, hence difficult to fit into a vehicle, and not easily refillable. Furthermore, there is no existing network for hydrogen transportation and local distribution (Br elle *et al.*, 1979).

The key challenge for on-board hydrogen storage is to find innovative solutions that can lower costs and improve the energy efficiency of on-board storage systems for hydrogen-use cars. Problems associated with the production, distribution and on-board storage of the hydrogen gas have led to the consideration of compact and efficient devices, called fuel processors, to generate hydrogen on board from a primary fuel such as a fossil fuel (gasoline or diesel) or from a chemical intermediate (ammonia, methanol or higher alcohols) (Avci *et al.*, 2001).

2.3. Hydrogen Production by On-board Fuel Conversion

Hydrogen is a clean gaseous energy carrier. Unlike hydrocarbons, it does not occur naturally in any significant quantities, but chemical storage of hydrogen in liquid fuels is considered to be one of the most advantageous options for supplying hydrogen to the fuel cells. A variety of liquid fuels, such as alcohols and hydrocarbons are suitable for this purpose (Fierro *et al.*, 2005). Various processing options exist depending on the primary

fuel considered and on the purity of gas needed (Figure 2.1). Worldwide, hydrogen as a raw material for the chemical industry is derived as follows: 77% from natural gas/petroleum, 18% from coal, 4% by water electrolysis and 1% by other means. Onboard processing of liquid fuels is regarded as the most promising method of supplying hydrogen for fuel cells mounted in a vehicle. Recent technology advances have increased attention on the use of hydrogen and fuel cells as a substitute, or complement, to oil-based fuels and internal combustion engines in transport (Prigent, 1997; Pietrogrande and Bezzeccheri, 1993).

Hydrogen from on-site or on-board fuel processing is an important part of most PEM-based fuel cell systems. Among the various fuels which can be converted into hydrogen to be used in fuel cells for automotive and stationary applications, alcohols, in particular, methanol and ethanol, are very promising candidates because they are easily decomposed in the presence of water and generate an H₂-rich mixture suitable for feeding fuel cells. There are three common methods of processing hydrocarbon fuels to create the hydrogen required by the fuel cells. They are steam reforming, partial oxidation, and autothermal reforming or oxidative steam reforming, and the fuels include alcohols and hydrocarbons (Song, 2002; Perna, 2007).

PO and ATR processes have a merit on fast start-up time because of exothermic nature of oxidation reaction. However, the PO and ATR processes provide lower efficiency and reformat quality, i.e., lower hydrogen production yield, higher rate of side reactions, and by-products. SR process gives high concentration of hydrogen ca. 70–80 per cent on a dry basis, while those for PO and ATR are estimated to be ca. 40–50 per cent on a dry basis (Faungnawakij *et al.*, 2006).

In steam-reforming water vapor reacts with the primary fuel, forming carbon monoxide, carbon dioxide, and hydrogen. The equilibrium amounts of these products depend strongly on temperature, less strongly on pressure. The higher the temperature is, the greater the amount of CO in the product. Steam-reforming is always endothermic, so energy must be supplied for this reaction (Brown, 2001; Ahmed and Krumpelt, 2001).

In partial oxidation the primary fuel reacts with a substoichiometric amount of oxygen. Partial oxidation is exothermic, so does not need a supply of energy. Nevertheless, the overall efficiency can suffer because of waste heat production. To prevent excessive temperature increase, steam is usually added to the feed (Brown, 2001). The steam reacts endothermically with the primary fuel. This has some aspects of autothermal reforming, which combines steam-reforming and oxidation, and the oxidation supplies the energy required by the steam-reforming (Brown, 2001; Ahmed and Krumpelt, 2001).

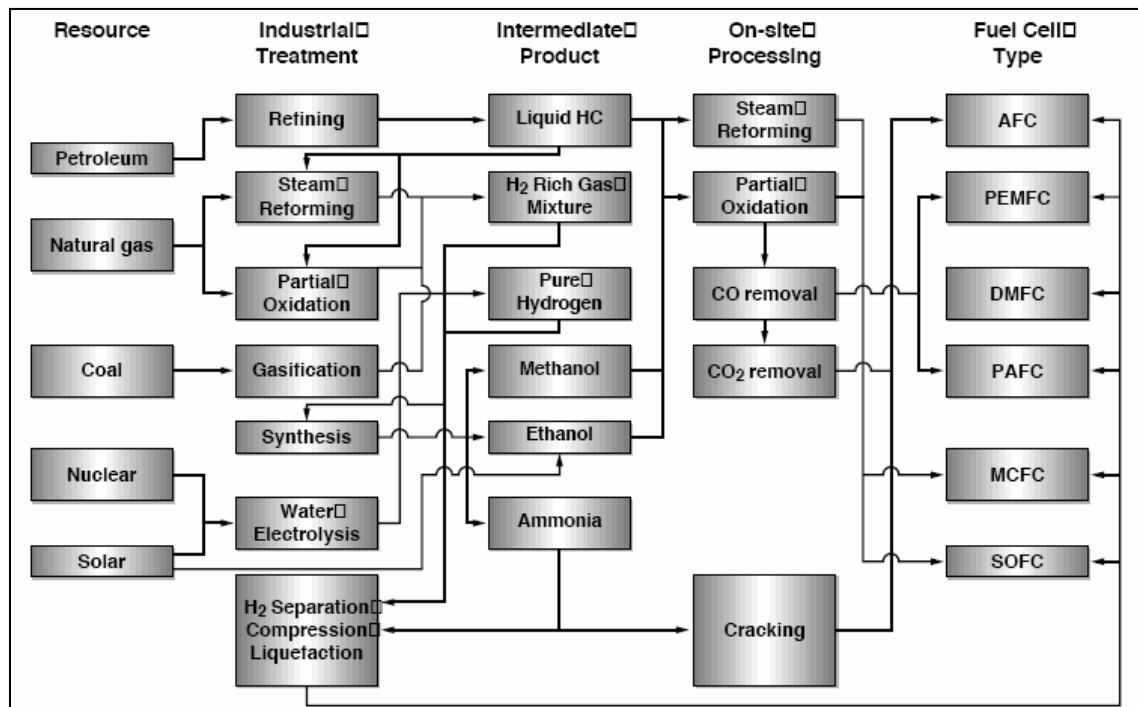
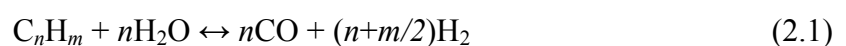


Figure 2.1. Fuel production and processing for the various fuel cell types (Prigent, 1997)

2.3.1. Hydrogen Production from Hydrocarbons

Catalytic steam reforming is a major process for the conversion of hydrocarbons into hydrogen. In this process, hydrocarbons and steam react at elevated temperatures in a first catalytic bed to form carbon monoxide and hydrogen (Ahmed and Krumpelt, 2001; Prigent, 1997):



The reformer effluent is then passed through a second catalytic bed, where carbon monoxide is converted at low temperature into hydrogen according to the water-gas shift reaction (Reaction 2.2):



Figure 2.2 shows the changes in the standard Gibbs free energy ($\Delta G^0/RT$) associated with Reaction 2.1 for a series of alkanes (CH_4 , C_2H_6 , C_3H_8 , C_6H_{14}), normalized per mole of CO produced. It can be seen that the steam reforming of alkanes is thermodynamically favorable (i.e., negative values of $\Delta G^0/RT$) only at temperatures higher than 675 K (and higher than 900 K for methane reforming) (Davda *et al.*, 2005). Steam reforming of gasoline normalized per mole of CO may be represented by the following chemical equation:



Reaction 2.3 is strongly endothermic ($\Delta H > 200 \text{ kJ.mol}^{-1}$ for CH_4) and requires external heat input. This is done in industrial units by filling the catalyst in tubes immersed inside the radiant section of a furnace where heat is exchanged directly between the flame and the tube wall. In small-sized power plants specifically designed for fuel cells, the catalyst is most frequently located inside a low thickness cylindrical annulus surrounding a burner. The amount of energy required is typically of the order of 22 per cent of the liquid fuel lower heat of combustion.

The reforming reactions are catalyzed by Group VIII-X metals with nickel as the preferred metal for industrial applications. With a steam-to-carbon ratio of 3.5, methane conversions up to 98 per cent are obtained at moderate pressure. The reforming catalysts are, however, very sensitive to poisoning by elements such as sulphur, chlorine or heavy metals. At temperatures above 873-923 K, i.e. at temperatures characteristics to steam reforming, the thermal reactions begin to compete with the catalytic processes and increasingly so as the catalyst activity decreases, e.g. due to sulphur poisoning. The feed gas must be treated before entering the reformer in order to remove these contaminants.

The thermal cracking of the higher hydrocarbons produces olefins which are precursors for coke formation. In particular, ethylene leads to rapid coke formation. One major point is the need to avoid the risk of carbon deposition on the catalyst itself and in the downstream equipment due to the Boudouard reaction (Reaction 2.4) that occurs during the effluent gas cooling (Rostrup-Nielsen, 2001; Joensen and Rostrup-Nielsen, 2002; Prigent, 1997).

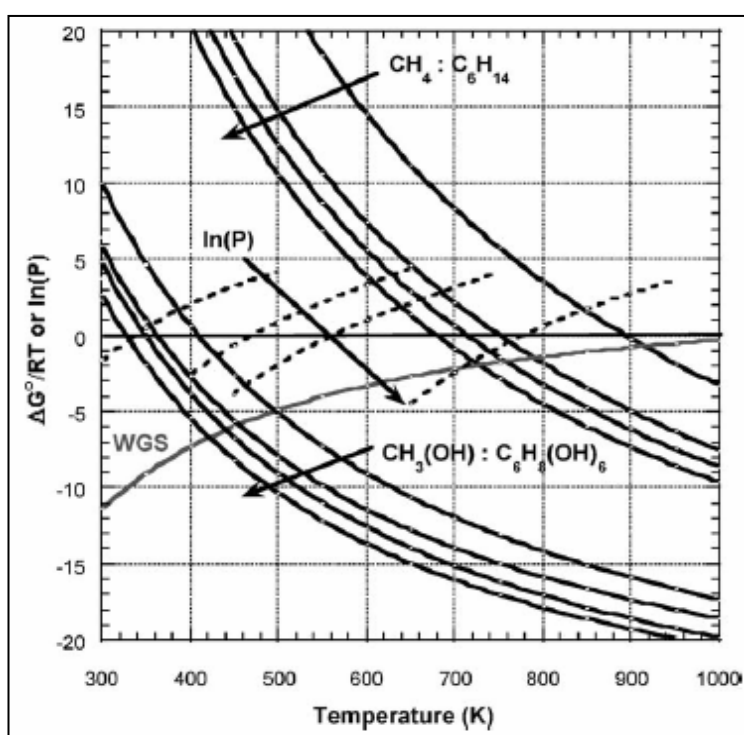


Figure 2.2. $\Delta G^\circ/RT$ vs. temperature for production of CO and H₂ from vapor phase reforming of CH₄, C₂H₆, C₃H₈, C₆H₁₄ and some oxygenated hydrocarbons (Davda *et al.*, 2004)

Another way to promote hydrocarbon steam reforming consists in the partial oxidation process. Partial oxidation, unlike the steam reforming process, provides a simplified system without the need for external water and heat supply. Furthermore, the transient response characteristics are improved since there is no heat transfer process involved. In return, the produced gas contains residual nitrogen and, moreover, since

partial oxidation is exothermic, about 17 per cent of the low heating value of the fuel is lost (Prigent, 1997).

The generation of hydrogen from gasoline via partial oxidation may be represented here by the following chemical equation:



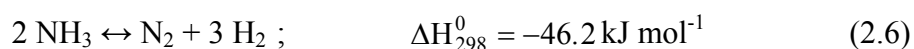
The reaction heat, rather than being supplied externally through the reactor tube walls, is produced within the reactor by adding a controlled quantity of air in the feed to promote the combustion of part of the hydrocarbons. When a catalyst is used, the operating temperature can be lower than the steam reforming temperature, i.e. between 873 and 1073 K. It is also possible to operate in a refractory-lined thermal reactor without catalyst but at temperatures in excess of 1273-1373 K (Prigent, 1997).

The catalytic conversion of hydrocarbons to synthesis gas, i.e. a mixture of hydrogen and carbon monoxide, via partial oxidation is known to occur via two major routes. When total oxidation and steam reforming reactions are combined to utilize the total oxidation heat to promote the endothermic steam reforming reaction, the process is termed as indirect partial oxidation (Avcı *et al.*, 2001; Avcı *et al.*, 2002). Since the water produced in total oxidation is not sufficient to drive the steam reforming, further water injection is necessary. Extra water addition also plays an important role in temperature control and in suppressing coke formation, which is likely to occur at steam reforming conditions (Avcı, 2003). In the second route, which is known as direct partial oxidation, hydrocarbon is converted into synthesis gas in a single step. Compared with indirect partial oxidation, the direct route has some serious operational challenges in supplying hydrogen for fuel cells in vehicles. The process requires high temperatures exceeding 1273 K, millisecond contact times and operates at nearly explosive feed conditions, all of which are significant drawbacks in applications involving frequent start-up/shut-down periods as in the case of vehicles. However, computer simulations have shown that direct partial oxidation coupled with water injection and low-temperature water-gas shift conversion gives higher hydrogen yields than the indirect route (Avcı, 2003; Avcı *et al.*, 2001; Avcı *et al.*, 2002). In addition, the rapid response and requirements of smaller reactor volumes make direct partial oxidation a process to be further considered for use in fuel cell applications.

Whatever the process used, steam reforming, direct partial oxidation or indirect partial oxidation, the gas obtained has a carbon monoxide content which is much too high for direct use in most fuel cells except for those operating at high temperature. A further steam shift-conversion of CO is necessary. It can be performed in one or two steps depending on the maximum acceptable residual CO level. To lower the concentration to about 1-2 per cent, which is acceptable for phosphoric fuel cells for example, a CO shift catalyst composed of iron and chromium mixed oxides operating at 623-673 K is in common use. When CO in the product gas has to be reduced further, a low temperature copper-zinc catalyst operating at 473-523 K must be used. CO concentration can then be brought down to a few hundred ppm (Prigent, 1997). This level is however still too high for low temperature fuel cells (AFC or PEMFC), and a third processing is needed to reduce it to a few ppm. It is possible to lower the CO concentration to trace amounts with the methods such as selective oxidation of CO to CO₂ (Özkara and Aksoylu, 2003; Dudfield *et al.*, 2000a, Dudfield *et al.*, 2000b), methanation of CO (Aksoylu *et al.*, 1996; Aksoylu *et al.*, 1998) and the use of hydrogen diffusion membranes (Larminie and Dicks, 2000), but the selective oxidation method is reported to be the optimal choice for CO removal (Avcı, 2003; Avcı *et al.*, 2003a). For this purpose, Trimm and Önsan (2001) have reviewed selective low temperature CO oxidation in hydrogen-rich streams.

2.3.2. Hydrogen Production from Ammonia

Ammonia has low cost and is relatively easy to transport and store, compared to hydrogen. This makes it a potential candidate for use as a hydrogen carrier for fuel cell applications. Ammonia, when heated in the presence of a suitable catalyst, dissociates into nitrogen and hydrogen via the reaction (Prigent, 1997):



From the thermodynamics standpoint, since Reaction (2.6) is endothermic and includes an increase in the total number of molecules, increasing the temperature and lowering the pressure is in favor of ammonia decomposition. Nickel, iron or ruthenium supported on alumina can be used as catalysts. The minimum temperature required to

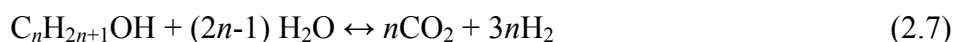
achieve a high conversion rate is about 723 K. Industrial crackers, however, generally operate at temperatures up to 1173 K to lower the residual amount of ammonia to about 500 ppm. Pressure, in spite of its negative action on equilibrium, has a favorable effect on reaction kinetics and, consequently, on reactor size and weight. Industrial units operate at pressures between 2 to 10 bar (Ross, 1981).

The dissociation product consists of around 25 per cent nitrogen plus 75 per cent hydrogen and some unconverted ammonia. It can be used directly in alkaline fuel cells but needs further purification to remove the residual ammonia for fuel cells with acid electrolytes (Metkemeijer and Achard, 1994).

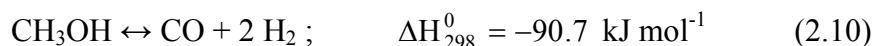
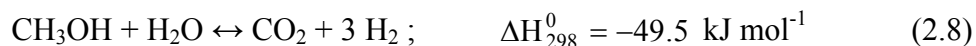
Using ammonia as a primary fuel in fuel cell has been considered for more than 30 years. The main problems with ammonia reside in the need for pressurized tanks (it is stored in liquid form under 8.7 bar at 293 K), its toxicity in case of leakage and the disposal of unconverted ammonia residues. If sent to a catalytic burner, a high proportion of the unconverted ammonia will actually be converted to into nitrogen oxide, but the problem of air pollution by nitrogen oxides would be then comparable to that raised by the internal combustion engines (Prigent, 1997).

2.3.3. Hydrogen Production from Methanol

In context of on-board hydrogen production, methanol, in particular, has received much attention since it can be stored in liquid form and it can easily be reformed into a hydrogen rich stream, both of which are highly desired for vehicular applications. The general equations for steam reforming of alcohols and methanol are as follows:



Methanol conversion can be achieved either by a combination of oxidation and steam reforming (Reaction 2.8) (indirect partial oxidation):



or by direct partial oxidation (Avcı *et al.*, 2003a):



From the thermodynamics standpoint, methanol steam reforming can be considered as the combination of endothermic methanol decomposition (Reaction 2.10), followed by the exothermic water-gas shift (WGS) reaction (Reaction 2.2).

Although steam reforming (Reaction 2.8) produces more hydrogen than direct partial oxidation, steam reforming is endothermic. As a result, methanol must be oxidized to provide the necessary heat (Reaction 2.9) and the overall yield of hydrogen is reduced (Avcı *et al.*, 2003a).

The steam reforming of methanol is much less endothermic than that of hydrocarbons. Thus, more than 99 per cent conversion is readily achieved at low temperatures, 473-573 K, with a steam:methanol ratio of 1.5 using copper-based catalysts (Joensen and Rostrup-Nielsen, 2002; Rostrup-Nielsen, 2001). Recent reports involving methanol steam reforming over Pd/ZnO claimed to lower selectivity to CO and to exhibit high activity (Chin *et al.*, 2002).

Methanol has taken a great interest considering the low impurities in the product stream after reforming, its low cost, high energy content and ease of handling. However, there are some serious issues concerning the practical use of methanol. The most important problem is that methanol is highly toxic which may result in death in case of inhalation of even a minute quantity. Besides, its production is essentially based on reforming of nonrenewable fossil fuels (mostly natural gas), and therefore its use as a feedstock for

electrical vehicle will release fossil carbon into the atmosphere. In addition, it has an availability problem since it is produced from synthesis gas via methane reforming, and current methanol production is far from meeting the demands. Methanol does not also have a widespread distribution network which will be a problem in case of commercialization of methanol fuel cell technology (Fierro *et al.*, 2005).

2.3.4. Hydrogen Production from Ethanol

Ethanol is a promising source of hydrogen for fuel cells due to its crucial advantage of producibility from renewable sources. In contrast to ethanol, for hydrogen production the most commonly mentioned sources such as natural gas, gasoline and methanol are based on the fossil fuels, and therefore suffer from the same disadvantage that they do not reduce reliance on fossil fuels or emissions of pollutants and greenhouse gases (Haryanto *et al.*, 2005).

Among the various feed stocks ethanol is very attractive because of its relatively high hydrogen content, availability, biodegradability, low toxicity and storage and handling safety. More importantly, it can be produced renewably from several biomass sources, including energy plants, waste materials from agro industries or forestry residue materials and even from the organic fraction of municipal solid wastes (Fatsikostas *et al.*, 2002). The bio-ethanol thus produced is free from sulphur, which is crucial for processes involving metal-based catalysts. Similarly, it is free from metals as well. Bio-ethanol, which is a dilute aqueous solution containing around 12 weight per cent ethanol, could be directly subjected to steam reforming thereby eliminating one unit operation of distillation required to produce pure ethanol. The entire process could therefore be economically attractive (Vaidya and Rodrigues, 2006; Liguras *et al.*, 2003, Mariño *et al.*, 2004). Also, it could be easily decomposed in the presence of water to generate a hydrogen-rich mixture. Above all, ethanol is CO₂ neutral since the amount of CO₂ produced in the process is consumed by the biomass growth offering a nearly closed carbon loop (Biswas and Kunzru, 2007). In addition, the steam reforming of ethanol to produce H₂ is thermodynamically feasible (Vaidya and Rodrigues, 2006).

Ethanol has more qualified advantages over methanol for transportation applications since it is much less toxic and offers a high octane number, a high heat of vaporization, and a low photochemical reactivity (Fierro *et al.*, 2005). Also ethanol can be produced in large quantities as renewable fuel while the current production of methanol is not enough to meet the demands. Despite these advantages, the higher steam reforming temperature of ethanol due to its C-C bond remains as the only disadvantage that has to be challenged.

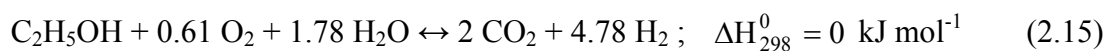
Ethanol is most commonly converted directly to hydrogen through two main reactions, steam reforming (Reaction 2.12) and partial oxidation (Reaction 2.13). The two reforming techniques are described by the respective reactions:



As steam reforming of ethanol is an endothermic process, heat must be supplied to the system in order to maintain the system at a steady reaction temperature. Heat can either be supplied internally by co-feeding oxygen or air and burning a portion of the ethanol at the expense of hydrogen production (partial oxidation, Reaction 2.13), or externally by burning some type of fuel (total oxidation, Reaction 2.14) (Liguras *et al.*, 2004; Salge *et al.*, 2005).



In one embodiment of this process, combustion occurs in the gas phase before the catalyst bed. This process is termed auto-thermal. When combustion takes place on the same catalyst as the reforming reaction, the process is usually termed catalytic partial oxidation. Due to the nature of the process, combinations of the above can easily be created (Liguras *et al.*, 2004, Salge *et al.*, 2005). By feeding ethanol, water, and oxygen in a molar ratio of 1/1.8/0.6, the overall reaction can be thermally neutral and the hydrogen concentration could approach to about 70 per cent in the outlet stream (Cai *et al.*, 2007):



The steam reforming of ethanol produces only hydrogen and CO₂ if ethanol reacts in a most desirable way. Thermodynamic studies has shown that the steam reforming of ethanol is feasible for temperature higher than 500 K, being methane, carbon oxides and H₂ the main products (Aupretre *et al.*, 2005, Llorca *et al.*, 2002). However, due to the thermodynamic equilibrium limitations, the high-temperature reforming produces a large amount of CO. This poses a problem for fuel cells because the catalysts used in the fuel cell anodes are very sensitive to CO, which chemisorbs to the active sites of the catalyst. If the feed stream of fuel cell contains more than 10 ppm carbon monoxide it will be chemisorbed deactivating the catalysts, reducing the number of active sites for H₂ and which, in turn, will decrease the energy efficiency of the fuel cell. To effectively integrate the ethanol reformer with PEM fuel cells, the reformer temperature should be as low as possible (Kugai *et al.*, 2006). However, low temperature ethanol steam reforming favors the formation of undesirable reaction byproducts such as carbon, methane, acetaldehyde, acetic acid, and diethyl ether (Table 2.2), which compete with H₂ for the hydrogen atoms as shown on Figure 2.3, leading to reduced H₂ selectivity and poor catalyst life. Thus, kinetic rather than thermodynamic control of the reaction is required (Roh *et al.*, 2006; Mariño *et al.*, 2003; Vizcaíno *et al.*, 2007).

One additional limiting factor influencing the steam reforming is the coke formation, mainly caused by hydrocarbon decomposition (Barroso *et al.*, 2006). Reactions to avoid are those that lead to C₄ species and C₂H₄. The presence of C₂H₄ especially hinders the overall H₂ production reaction by inducing the pathways toward carbon production and thus causing “coking” of the catalysts (Haryanto *et al.*, 2005). To investigate the catalytic steam reforming of ethanol and these challenges, ethanol has been considered by many researchers in a number of countries for hydrogen production. Both the thermodynamic and the experimental catalytic steam reforming studies for fuel cell applications are summarized in the next section. In these researches, the advantages of ethanol in ease of steam reforming to hydrogen, vis-à-vis methane, are stressed, as is the storage aspect of liquids for vehicle and fuel cell application.

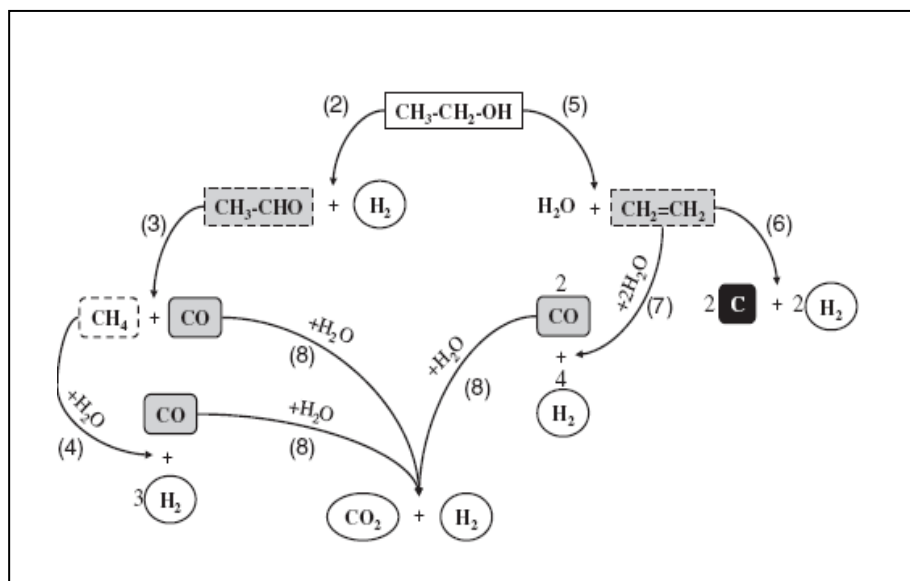


Figure 2.3. Basic reactions in the steam reforming of ethanol (Vizcaíno *et al.*, 2007)

Table 2.2. Main reactions involved in the catalytic steam reforming of ethanol
(Torres *et al.*, 2007)

	Decomposition Reactions	
Ethanol	$\text{C}_2\text{H}_5\text{OH} \leftrightarrow \text{CH}_3\text{CHO} + \text{H}_2$ $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$ $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{CO} + \text{H}_2 + \text{CH}_4$ $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 2 \text{H}_2$	Dehydrogenation Dehydration Cracking Oxidation
Acetaldehyde	$2 \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{COCH}_3 + \text{CO} + \text{H}_2$ $\text{CH}_3\text{CHO} \rightarrow \text{CO} + \text{CH}_4$	Acetone formation Decarbonilation
Acetic acid	$\text{CH}_3\text{COOH} \rightarrow \text{CO}_2 + \text{CH}_4$	Decarboxilation
Ethylene	$\text{C}_2\text{H}_4 \rightarrow 2 \text{C} + 2 \text{H}_2$	Carbon Deposition
Methane	$\text{CH}_4 \rightarrow \text{C} + 2 \text{H}_2$	Carbon Deposition
Carbon monoxide	$2 \text{CO} \leftrightarrow \text{C} + \text{CO}_2$	Carbon Deposition
	Steam Reforming Reactions	
Ethanol	$\text{C}_2\text{H}_5\text{OH} + 3 \text{H}_2\text{O} \leftrightarrow 2 \text{CO}_2 + 6 \text{H}_2$ $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \leftrightarrow 2 \text{CO} + 4 \text{H}_2$	$\Delta H^\circ = 173.5 \text{ kJ mol}^{-1}$ $\Delta H^\circ = 255 \text{ kJ mol}^{-1}$
Acetaldehyde	$\text{CH}_3\text{CHO} + \text{H}_2\text{O} \rightarrow 2 \text{CO} + 3 \text{H}_2$	
Acetic acid	$\text{CH}_3\text{COOH} + 2\text{H}_2\text{O} \rightarrow 2 \text{CO}_2 + 4 \text{H}_2$	
Acetone	$\text{CH}_3\text{COCH}_3 + 2 \text{H}_2\text{O} \rightarrow 3 \text{CO} + 5 \text{H}_2$	
Ethylene	$\text{C}_2\text{H}_4 + 2 \text{H}_2\text{O} \rightarrow 2 \text{CO} + 4 \text{H}_2$	
Methane	$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3 \text{H}_2$	
Carbon monoxide	$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$	Water gas shift
Carbon	$\text{C} + \text{H}_2\text{O} \leftrightarrow \text{CO} + \text{H}_2$	Carbon gasification

2.4. Thermodynamic and Experimental Studies on Ethanol Steam Reforming

Thermodynamic feasibility of ethanol steam reforming has received a fair amount of attention in the published literature. Effects of operational parameters on equilibrium composition can be identified either by stoichiometric thermodynamic approach (STA) or by nonstoichiometric thermodynamic approach (NSTA) (Fishtik *et al.*, 2000). In NSTA, the equilibrium composition of the system is found by direct minimization of the Gibbs free energy for a given set of species without specifying any possible reactions. In STA, on the other hand, the system is described by a set of stoichiometrically independent reactions. Major drawback of STA is that such *arbitrarily* chosen chemical reactions may lead to erroneous results. To eliminate the potential of arriving at such flawed conclusions, Fishtik *et al.* (2000) have introduced the concept of what they call as response reactions. In their study, they have transformed their arbitrary set of stoichiometrically independent reactions to be used in STA into response reactions which are unique, and thus, independent of the initial choice of that set of reactions.

Fishtik *et al.* (2000) also made use of NSTA and obtained a distribution of species based on seven species (ethanol, acetaldehyde, methane, carbon monoxide, carbon dioxide, hydrogen and water) as a function of temperature at 1 atm for an equimolar ethanol:water feed. According to their analysis, methane is the dominant species at low temperatures whereas it is hydrogen at high temperatures. As mentioned above, they have also used STA for their analysis. They have predicted the behavior of the system by selecting a particular limited set of reactions whose contribution to the system's response is the most significant. As this is the case, here it should be noted that this analysis is limited to equilibrium systems, and hence, the reactions derived only describes the system's response at equilibrium upon changing the operational parameters. Fishtik *et al.* (2000) finally concluded that at low water concentrations (water-to-ethanol ratio of 1), ethanol decomposes to produce CH_4 , while for temperatures at or above 700–800 K and for high water-to-ethanol ratios, the desired reaction of ethanol steam reforming is predominant and the formation of CO and CH_4 is minimized. At high temperatures (>1073 K), the equilibrium H_2 selectivity is nearly 100% (Goula *et al.*, 2004). However, the use of a water-to-ethanol ratio higher than stoichiometry results in increased enthalpy needs for water evaporation.

Aupretre *et al.* (2001) have performed a thermodynamic analysis of the system. They have shown that an increase in the total pressure leads to a decrease in the H₂ and CO yields while the equilibrium composition in CH₄ increases (Aupretre *et al.*, 2001). However, the entire system of H₂ production and its purification has to be operated under pressure when the CO level is reduced to traces from the H₂-rich gas by using a metallic membrane, for instance, Pd-based membrane. The theoretical production of CH₄ however decreases with a decrease in the water-to-ethanol ratio (Prigent, 1997).

Garcia and Laborde (1991) and Vasudeva *et al.* (1996) have earlier shown that an increase in temperature leads to an increase in the H₂ and CO concentration and a decrease in CH₄ concentration at equilibrium. Garcia and Laborde (1991) carried out calculations considering six chemical species (ethanol, water, carbon monoxide, methane, carbon dioxide, hydrogen and exclude carbon), pressures of 1-9 atm, temperatures of 400-600 K and water-to-ethanol feed ranges of 0.1 to 10.0. Garcia and Laborde (1991) also found that when compared to methanol steam reforming, higher temperatures and higher water-to-ethanol ratios are needed to obtain the best H₂ production from ethanol. They examined the thermodynamic equilibrium of this system and suggested operation at $T > 650$ K, atmospheric pressure and a water-to-ethanol molar ratio of up to 10 in the feed to maximize H₂ production, minimize the formation of CO and CH₄ and avoid carbon deposition on the catalyst.

Vasudeva *et al.* (1996) carried out another equilibrium study of ethanol steam reforming under conditions conducive to carbon formation. The calculations are based on the minimization of the total Gibbs free energy considering nine species in the system: methane, carbon monoxide, carbon dioxide, hydrogen, carbon, ethylene, acetaldehyde, ethanol and water. In the thermodynamic analyses, operating conditions of the system include temperatures of 800-1200 K, pressures of 1, 2 and 5 atm. and water-to-ethanol in feed (mol/mol) of 0 to 80. They found that H₂ yields as high as 5.5 mol/mol of ethanol in the feed can be obtained at equilibrium at temperatures around 773–873 K with water-to-ethanol molar ratios of above 20. They suggested that carbon formation occurs only at low water-to-ethanol ratios (<2) and low temperatures (883 K). The results differ from Garcia and Laborde (1991) under conditions conducive to carbon formation.

Ioannides (2001) has carried out thermodynamic analysis of hydrogen production from ethanol in order to feed a solid polymer fuel cell. Both steam reforming and partial oxidation (POX) reactors connected to water-gas-shift and CO-oxidation reactors were considered to assess the effect of operating parameters on hydrogen yields. The effects of reformer temperature, water-gas-shift reactor temperature, oxidation selectivity of CO in the selective oxidation reactor and pressure on hydrogen yield were investigated. Based on the thermodynamic analysis of the work, it was claimed that maximum hydrogen yields in the range of 4.43-4.50 mol per mol of ethanol may be obtained using feeds with water-to-ethanol ratio of 0.1-2.5 and exit POX temperatures in the range of 970-1050 K. Employment of feeds with water-to-ethanol ratio higher than 3.0 does not offer any significant advantage.

Tsiakaras and Demin (2001) have studied the thermodynamic analysis of a solid oxide fuel cell system (SOFC) fuelled by ethanol. They fed SOFC with the products of ethanol steam reforming, ethanol reforming with CO₂ and ethanol partial oxidation with air, being in thermodynamic equilibrium. At $T < 950$ K and $T > 1100$ K products of steam reforming gave the maximum efficiency, and reforming with CO₂ led to maximum at intermediate temperatures. Efficiency obtained by ethanol partial oxidation was, on the other hand, about 20% lower than the maximum.

Freni *et al.* (1996) carried out a thermodynamic analysis of the ethanol–water system as applied to an MCFC and suggested that a high water-to-ethanol ratio in the feed reduced the yield of undesirable products such as CO, CH₄ and carbon. In another study, Ioannides (2001) reported a H₂ yield of nearly 100% at 1000 K, atmospheric pressure and a water-to-ethanol molar ratio of 5.

In a more recent study, Mas *et al.* (2006) suggested that while high temperatures and high water-to-ethanol ratios favor H₂ production, low temperatures and high water-to-ethanol ratios are suitable to minimize CO formation. At a water-to-ethanol molar ratio of 3, temperatures higher than 500 K are required to avoid coke formation.

Besides these thermodynamics studies, a number of experimental catalytic studies have been reported by researchers around the world. Luengo *et al.* (1992) used Ni-Cu-Cr

on α - Al_2O_3 in a fixed-bed reactor to steam reform ethanol. Operating temperatures ranged from 573-823 K, steam-ethanol mole ratios varied from 0.4 to 2.0 and space velocities from 2.5 to 15 h^{-1} . The catalyst showed high activity for ethanol gasification. Comparison with thermodynamic predictions showed that catalyst activity is more pronounced at lower temperature. The 4.0 per cent Ni/O, 79 per cent Cu/O and 25 per cent Cr supported on α - Al_2O_3 gave a catalyst both active and selective for ethanol.

Catalyst coking and production of by-products like methane, acetaldehyde and diethyl ether, arise as the major problems faced in the studies of ethanol steam reforming. Formation of ethylene during steam reforming leads to catalyst coking. Starting from this, Freni *et al.* (2000) have proposed a two-layer fixed bed catalytic reactor for ethanol steam reforming reaction. They first converted ethanol into acetaldehyde over Cu/ SiO_2 catalyst under low temperature, and then converted acetaldehyde into syngas over Ni/MgO catalyst. They carried out the tests with a total gas flow rate of 218 cm^3/min at GHSV of 109000 h^{-1} , and using a feed of 8.2:1 water to ethanol ratio. Individual runs either with Cu/ SiO_2 or with Ni/MgO catalyst only were also performed. The former one resulted in the formation of only acetaldehyde and hydrogen with 100 per cent ethanol conversion up to 773 K. Above this temperature, ethylene formation and catalyst coking, and hence, catalyst deactivation were observed. The latter one, on the other hand, showed a low coking resistance, yet gave high acetaldehyde selectivity.

Mitra (1994) has carried out a kinetic study of the water to ethanol system without a catalyst. In that work, hydrogen selectivity and the presence of CH_4 , CO, CO_2 , acetaldehyde and ethylene were reported.

Marino *et al.* (2001) looked at the effect of nickel loading and calcination temperature on the structure and performance of Cu/Ni/K/ γ - Al_2O_3 catalysts for ethanol steam reforming. It was found that Ni addition to Cu/Ni/K/ γ - Al_2O_3 catalysts favored ethanol gasification, increased the gas yield and reduced acetaldehyde and acetic acid production.

Highfield *et al.* (1994) presented a scheme for hydrogen energy storage in the form of biomass-derived alcohols in which the hydrogen release step is by steam reforming.

Promising catalysts consisted of Cu, Co and Ni, acting on basic, high-area supports like magnesium oxide. Preparation, characterization and testing were described. Acetic acid, originating from acetaldehyde disproportionation, was identified as a key intermediate. Beneficial effects of promotion with alkali-metal ions on coking control and selection were reported.

Ethanol steam reforming in the context of a molten carbonate fuel cell was studied kinetically with a $\text{CuO/ZnO/Al}_2\text{O}_3$ catalyst (Cavallaro and Freni, 1996; Cavallaro and Freni, 1998). The process appeared feasible between temperatures of 800 and 1000 K and pressures up to 100 bars, based on predictions from a kinetic model. At temperatures above 630 K, equilibrium was approached for $\text{CuO/ZnO/Al}_2\text{O}_3$ and NiO/CuO/SiO_2 catalysts and no appreciable quantities of coke or unexpected oxygenates were formed even with $\text{H}_2\text{O/C}_2\text{H}_5\text{OH}$ ratios lower than 3 mol/mol.

Cavallaro and Freni (1996) studying ethanol steam reforming over $\text{Cu/ZnO/Al}_2\text{O}_3$ and NiO/CuO/SiO_2 catalysts have concluded that lower pressures and higher temperatures increase ethanol gasification. Complete ethanol gasification is fundamental if the H_2 -rich mixture obtained is intended to be used to feed a fuel cell.

In later work, ethanol steam reforming on $\text{Rh/Al}_2\text{O}_3$ catalyst was explored by Cavallaro (2000). $\text{H}_2\text{O/C}_2\text{H}_5\text{OH}$ ratios of 8.4 (mol/mol) were used to simulate the composition of the ecological fuel product from vegetable biomass fermentation. Studies were conducted between from 323-923 K since the molten carbonate fuel cell standard temperature is 923 K. The acid support (Al_2O_3) promoted the dehydration of the alcohol while all other reactions were catalyzed by the rhodium. At 923 K, coking did not occur and the catalyst maintained its activity for several hours.

Freni *et al.*, (2000) investigated steam reforming of ethanol in simulated MCFC using MgO supported Ni and Co catalysts. It was concluded that Ni/MgO catalysts exhibit higher activity and selectivity to hydrogen than Co/MgO catalysts because of the lower tendency of Ni to oxidize during reaction and to promote carbon monoxide methanation and ethanol decompositions reactions.

In another research, Srinivas *et al.* (2003) conducted structural studies on NiO-CeO₂-ZrO₂ catalysts for steam reforming of ethanol. NiO-CeO₂-ZrO₂ catalysts, with varying NiO content (1-40 wt. per cent) and CeO₂/ZrO₂ ratios of 1:10, 1:1 and 100:0 were tested. The catalysts were claimed to exhibit good catalytic activity and stability. The Ni content, Ce/Zr ratio and specific surface area influenced the catalytic activity. Catalysts with Ce/Zr ratio of 1 were superior to the other compositions. A catalyst with a composition of 40wt.%NiO-30wt.%CeO₂-30wt.%ZrO₂ was stable for more than 500 h in the steam reforming of bio-ethanol.

Sun *et al.* (2004) tested the structural properties of Ni/Y₂O₃ catalyst for steam reforming of ethanol in low and middle temperature range. The catalyst exhibited long-term stability and high activity for ethanol steam reforming with an ethanol conversion of 98 per cent and hydrogen selectivity of 38 per cent at 573 K, ethanol conversion of 98 per cent and hydrogen selectivity of 55 per cent at 653 K. Increasing the temperature to or above 773 K, the conversion of ethanol increased to 100 per cent, but the selectivity to hydrogen did not increase much since it was reported to be 58 per cent at 873 K.

In one of the most recent studies, Yang *et al.* (2006), investigated Ni/ZnO catalyst for the steam reforming of ethanol by a comparison with Ni catalysts supported on La₂O₃, MgO and γ -Al₂O₃. Experimental results showed that Ni/ZnO is superior among the catalysts, especially in terms of selectivity and distribution of byproducts. They also investigated temperature, water to ethanol molar ratio, liquid hourly space velocity (LHSV) and Ni loading using a Ni/ZnO catalyst and obtained complete conversion at temperatures above 600 K, regardless of the changes in the reaction conditions. Hydrogen selectivity increased with the increase in temperature, water to ethanol ratio and Ni loading.

Comas *et al.* (2004) studied ethanol steam reforming on Ni/ γ -Al₂O₃ catalyst at temperatures between 573 and 773K and proposed an overall reaction scheme as a function of temperature. They concluded that higher water/ethanol ratio (6:1) and higher temperature (773 K) promote hydrogen production (91% selectivity).

The thermodynamic analysis of the water ethanol reaction shows that at high water concentration, steam reforming of ethanol is favored. An increase in the amount of water also has the effect of increasing the extent of the WGS and methane steam reforming reactions, which reduces the amount of the undesired products, CO and CH₄ (Fishtik *et al.*, 2000) A water to ethanol feed ratio greater than 3 is necessary in order to obtain hydrogen and prevent carbon formation (Garcia and Laborde, 1991; Mas *et al.*, 2006) Too high water to ethanol ratio increases the energy required for vaporization of water.

2.5. Catalysts and Supports for Steam Reforming of Ethanol

The steam reforming of ethanol has been extensively studied over several catalyst systems using Ni, Co, Ni/Cu and noble metals (Pd, Pt, Rh) as active phases deposited on oxide supports promoted with alkali or alkali-earth compounds to improve both thermal stability and the resistance to coke formation. Ethanol reforming reactions include several steps that involve the need for catalytic surfaces able to: (i) dehydrogenate ethanol; (ii) break the carbon–carbon bonds of surface intermediates to produce CO and CH₄ and (iii) water reforms these C1 products to generate hydrogen and finally, it must not be active for the oxidation of H₂. Additionally, catalytic systems must possess high thermal stability due to the relative high temperature range (823–1073 K) at which reforming reactions take place. On the basis of the influence of the nature of both the metal and support on the catalytic characteristics of supported metals, choice of these elements is a key factor in developing supported catalysts that fulfill the above requirements (Navarro *et al.*, 2005; Vaidya and Rodrigues, 2006; Sheng *et al.*, 2002).

An ideal support should avoid any dehydration reaction in order to reduce carbon deposition over the catalyst, and should have no capability for other C–C bond formation reactions (Sun *et al.*, 2004). γ -Al₂O₃ may be a suitable support due to its chemical and physical stability as well as its high mechanical resistance (Pompeo *et al.*, 2005). SiO₂ possesses both high thermal resistance and high surface area, which makes it suitable as support in high temperature reactions. Zeolites are effective microporous catalysts because of their morphological and particular properties such as their well-defined crystalline structure, high internal surface areas, uniform pores, good thermal stability (Vizcaíno *et*

al., 2007). Better catalytic performance with high selectivity of H_2 and low selectivity of undesirable byproducts can be expected over redox supports such as CeO_2 and ZrO_2 (Kugai *et al.*, 2005). As discussed in previous sections, the coke formation and catalyst deactivation by production of ethylene, which generally is favored over acidic supports such as Al_2O_3 , may be avoided by neutralization of the acidic sites of Al_2O_3 e.g. by addition of potassium or by using basic supports, such as La_2O_3 or MgO (Liguras *et al.*, 2003).

2.5.1. Oxide Catalysts

Al_2O_3 and V_2O_5 exhibited high activity in which they were able to convert 100 % ethanol at a temperature of 623 K. However, these two catalysts produced only small amounts of H_2 , as well as high amounts of C_2H_4 or C_2H_4O . The activity of the Al_2O_3 catalyst was attributed to its large adsorption capacity toward C_2H_5OH , whereas the low H_2 yield was attributed to C_2H_5OH dehydration to C_2H_4 that dominates the reaction pathway. (Fatsikostas and Verykios, 2004; Llorca *et al.*, 2001). Among the oxide catalysts, ZnO exhibited the best performance for the steam reforming of ethanol. This catalyst not only completely converted ethanol but also produced considerable amounts of H_2 and small amounts of C_2H_4 , C_2H_4O , or CH_3COCH_3 . Under the reaction conditions of 723 K, atmospheric pressure, a steam to ethanol molar ratio of 13:1, and a gas hourly space velocity (GHSV) of $22\,000\ h^{-1}$, the ZnO catalyst produced 97.7 % H_2 and CO_2 , together with molar values of 5.1 for H_2 and 1.7 for CO_2 , representing 85 % of the stoichiometrical coefficients (Llorca *et al.*, 2001). This implies that the ZnO catalyst is extremely selective to the overall steam reforming reaction of C_2H_5OH . However, no information was available that was associated with the durability of this catalyst.

2.5.2. Supported Cobalt Catalysts

Among the reported catalysts, the cobalt-based systems seem to be the most promising. However, they are usually affected by deactivation mainly because of metal sintering and surface Co oxidation (Freni *et al.*, 2003). It is also known that supports with acid properties such as Al_2O_3 and with low Co loadings promote the dehydration of ethanol to produce a significant amount of C_2H_4 (Fierro *et al.*, 2005). However, increasing

the cobalt content by >8 % prevented the formation of C_2H_4 (Batista *et al.*, 2005). In addition, Co/SiO₂ catalysts prevent the formation of C_2H_4 , but the product distribution (H_2 , CO, CO₂ and CH₄) depends on the reaction conditions (Haga *et al.*, 1997).

Besides, Co/Al₂O₃ was reported to be a promising catalyst for ethanol steam reforming (Haga *et al.*, 1997). Co/Al₂O₃ was very selective toward the overall reaction by suppression of methanation of CO and C₂H₅OH decomposition. This catalyst was able to convert 100 % of the C₂H₅OH with a H_2 selectivity of 70 per cent (Haga *et al.*, 1997; Batista *et al.*, 2003).

Haga *et al.* (1998) studied the catalytic properties of Co among other metals and found that selectivity to H_2 was in the order Co > Ni > Rh > Pt, Ru, Cu. In another study, they found that the supports vastly influenced the properties of Co catalysts (Haga *et al.*, 1997). The formation of H_2 decreased in the order: Co/Al₂O₃ > Co/ZrO₂ > Co/MgO > Co/SiO₂ > Co/C. The Co/Al₂O₃ catalyst exhibited the highest selectivity to H_2 (67% at 673 K) by suppressing methanation of CO and decomposition of ethanol. Similarly, Cavallaro *et al.* (2001) found that Co/MgO is more resistant to coke formation because of its lower acidity compared to Co/Al₂O₃ at 923 K.

Also, the H_2 selectivity and product compositions are dependent on the preparation method and the precursor of support that was used. With the impregnation method, the H_2 selectivity over Co/Al₂O₃ was 67.3%, whereas with the sol-gel method, the yield selectivity was just 50.7 % under the same reaction conditions (Kaddouri and Mazzocchia, 2004).

Llorca *et al.* (2002; 2003a) proposed the use of ZnO-supported Co catalysts in steam reforming of ethanol. The use of Co(CO)₈ as precursor produced a highly stable catalyst that enabled the production of CO-free H_2 at low temperatures (623 K). They concluded that the method of catalyst preparation affected its performance and structural characteristics. In another study, Llorca *et al.* (2003b) characterized and evaluated several supported cobalt catalysts (Co/MgO, Co/Al₂O₃, Co/SiO₂, Co/TiO₂, Co/V₂O₅, Co/ZnO, Co/La₂O₃, Co/CeO₂ and Co/Sm₂O₃) under ethanol steam reforming conditions. It was shown that the catalysis involved both metallic and oxidised cobalt species. These species

were in equilibrium in reaction conditions, and they contributed, in addition to the support contribution, to the global performance of the catalyst.

Kaddouri and Mazzocchia (2004) reported high catalytic activity of Co/SiO₂ and Co/Al₂O₃ for steam reforming of ethanol and concluded that the product distribution was dependent on both the nature of the support and the method of catalyst preparation, thereby suggesting metal–support interaction.

Batista *et al.* (2004) studied ethanol steam reforming over Co/Al₂O₃ and Co/SiO₂. The catalysts showed average conversion higher than 70% at 673 K. The metal loading influenced ethanol conversion and product distribution.

2.5.3. Noble Metal Catalysts

Among noble metal based catalysts Rh is significantly more active and selective as compared to Pt, Pd, and Ru catalysts of comparable metal loading (Liguras *et al.*, 2003; Auprêtre *et al.*, 2002); however the high cost of Rh represents a considerable handicap in large scale application (Frusteri *et al.*, 2004). At 673 K, Rh/Al₂O₃ catalyst has been reported to be more active and selective than Ru, Pd and Pt supported on Al₂O₃ (Auprêtre *et al.*, 2002; Cavallaro *et al.*, 2003a) and, due to its ability to form less amounts of carbon at the surface, had the longest catalytic life (Kaddouri and Mazzocchia, 2004).

Frusteri *et al.* (2004) investigated the performance of MgO-supported metal catalysts and reported that H₂ could be efficiently produced from ethanol over Rh/MgO at 923 K. However, it was also noticed that Rh/MgO produced significant amounts of CH₄ (10%). This implies that this catalyst is active in C₂H₄O decomposition and WGS reactions or CO_x methanation and is not active in the C₂H₅OH steam reforming reaction. Another drawback of Rh/MgO is coke formation, although at a low rate (<1 mg C/g_{cat}.h). The activity of the catalysts reduced in the order Rh > Co > Ni > Pd. Rh/MgO was most resistant to coke formation (Vaidya and Rodrigues, 2006; Haryanto *et al.*, 2005).

Rhodium supported on alumina (Rh/Al₂O₃) also showed good performance for ethanol steam reforming. Cavallaro *et al.* (2003a; 2003b) studied ethanol reforming over

Rh/Al₂O₃ at 923 K and found that the addition of a small amount of O₂ (0.4 vol %) in the feed gas significantly decreased the catalyst deactivation but promoted metal sintering. In another study Cavallaro (2000) offered a reaction pattern over Rh/Al₂O₃ and found that coke formation could be prevented at high temperatures by sufficiently large amounts of Rh and strong excess of water. At 973 K, only C1 products were present in the exit stream. The C₂H₄O was decarbonylated by the rhodium to form CH₄ and CO, whereas C₂H₄ was converted to C1 species by steam reforming. Fierro *et al.* (2003) reported high activity and selectivity to H₂ production of Rh/Al₂O₃ catalyst in bio-ethanol oxidative steam reforming. In addition, the catalyst was highly stable.

Aupretre *et al.* (2002) noted that Rh/Al₂O₃ was better than other M/Al₂O₃ catalysts, where M is Pt, Pd, Ru, Cu, Zn, and Fe). It was also found that Rh/Al₂O₃ showed the highest activity among Rh/oxides catalysts, in which oxides are CeO₂, TiO₂, ZrO₂, MgO, and SiO₂ (Haryanto *et al.*, 2005). In another study, Aupretre *et al.* (2004) studied ethanol steam reforming over Rh/Al₂O₃ under pressure (1.1MPa). They reported that the nature of the metal precursor salt, metal loading and the reaction conditions influenced the performance of the catalyst.

Another Rh-based catalyst that showed potential for ethanol steam reforming is Rh/CeO₂. Although it was reported as the activity of Rh/CeO₂ was lower than that of Rh/Al₂O₃, Aupretre *et al.* (2002) reported that the H₂ yield on Rh/CeO₂ was higher than that on Rh/Al₂O₃ at 873 K. Deluga *et al.* (2004) reported that Rh/CeO₂ was more stable and showed greater WGS activity than the noble metal alone. Furthermore, Rh/CeO₂ was good for oxidative reforming and converted >95% of ethanol for all C/O compositions with no significant deactivation. However, this catalyst produced significant amounts of CO.

Navarro *et al.* (2005) studied oxidative reforming of ethanol over a Pt/Al₂O₃ catalyst modified by Ce and La. The presence of Ce as an additive was found to be beneficial for hydrogen production. The presence of La however did not promote ethanol conversion. When both Ce and La were present on the support, poorer catalyst behavior was observed due to lower Pt–Ce interaction with respect to La-free ceria–alumina support.

Few studies on Pd catalyzed steam reforming of ethanol have also been reported earlier. Goula *et al.* (2004) studied steam reforming of bio-ethanol over a commercial Pd/Al₂O₃ catalyst and reported 95% selectivity to hydrogen at 923 K. Ethanol conversion was 100% even at low temperatures (573–623 K). In another such study on Pd/Al₂O₃, these researchers reported that CO concentration was minimum at 723 K and the amount of coke formed was negligible even at stoichiometric water-to-ethanol ratios (Goula *et al.*, 2003). Galvita *et al.* (2002) studied ethanol decomposition over a Pd catalyst supported on a porous carbonaceous material in presence of steam in the range of temperatures 603–633 K. The catalyst was found to have high activity and stability. Frusteri *et al.* (2004a) however observed that a Pd/MgO catalyst drastically deactivated during reaction due to metal sintering at 923 K. Coke formation on Pd/MgO occurred at a higher rate than on MgO supported Rh, Ni and Co catalysts.

Liguras *et al.* (2003) studied Ru-catalyzed steam reforming of ethanol in the range of temperatures 873–1123 K. There was a marked increase in conversion of ethanol and selectivity to H₂ over Ru/Al₂O₃ with an increase in the Ru content. At a high Ru loading (5 wt.%), the performance of Ru was comparable to Rh. The catalyst was stable and had activity and selectivity higher than Ru/MgO and Ru/TiO₂. Fierro *et al.* (2003) showed that the order of performance of alumina-supported noble metal catalysts (5% metal loading) for bio-ethanol oxidative steam reforming at 973 K was Pt < Pd << Ru < Rh.

Breen *et al.* (2002) studied a range of oxide-supported metal catalysts for reforming of ethanol–water mixtures. They found that Al₂O₃-supported catalysts promote dehydration of ethanol to ethylene and the order of activity of metals for such catalysts is Rh > Pd > Ni = Pt. However, with CeO₂/ZrO₂-supported catalysts, ethylene is not formed and the order of activity at higher temperatures is Pt ≥ Rh > Pd. They showed that by using a combination of CeO₂/ZrO₂ supported metal catalysts with alumina support ethylene formation does not inhibit steam reforming at high temperatures.

2.5.4. Ni-Supported Catalysts

Among transition metals, the high C–C bond-breaking activity and the relatively low cost of Ni make it a suitable active phase for ethanol-reforming reactions. Among oxide

supports, using Al_2O_3 as support promotes catalysts deactivation by deposition of carbon from the ethylene intermediate produced via dehydration reactions of ethanol on acid sites of the support. Thus, basic additives or promoters that favor water adsorption and OH surface mobility are usual in Al_2O_3 supports to lower the rate of coke deposition on catalyst surfaces (Sánchez-Sánchez *et al.*, 2007).

Comas *et al.* (2004) studied steam reforming of ethanol over $\text{Ni}/\text{Al}_2\text{O}_3$ in the range of temperatures 573–773 K and did not find any evidence of the water gas shift reaction occurring over Ni.

Frusteri *et al.* (2004a) reported high H_2 selectivity (>95%) at a space velocity $4 \times 10^4 \text{ h}^{-1}$ over Ni/MgO at MCFC operating conditions (923 K). The performance of alkali-doped Ni/MgO catalysts on bio-ethanol steam reforming was also studied (Frusteri *et al.*, 2004). The addition of Li and K enhanced the catalyst stability mainly by depressing Ni sintering. Freni *et al.* (2003) found that Ni/MgO exhibited high activity and selectivity to H_2 than Co/MgO due to the lower tendency of Ni to oxidize during reaction and to promote methanation of CO and decomposition of ethanol.

Fatsikostas *et al.* (2001; 2002) showed that $\text{Ni}/\text{La}_2\text{O}_3$ exhibited high activity and stability in steam reforming of ethanol to hydrogen. This was attributed to the formation of lanthanum oxycarbonate species ($\text{La}_2\text{O}_2\text{CO}_3$), which reacts with the surface carbon deposited during reaction and prevents deactivation. In another study, Fatsikostas and Verykios (2004) studied ethanol reforming over Ni catalysts supported on $\gamma\text{-Al}_2\text{O}_3$, La_2O_3 and $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$. The impregnation of Al_2O_3 with La_2O_3 reduced carbon deposition. The presence of La_2O_3 on the catalyst, high water-to-ethanol ratios and high temperatures offered high resistance to carbon deposition.

Sun *et al.* (2005) studied steam reforming of ethanol over Ni supported catalysts at lower temperatures (523–623 K). The catalytic activity, stability and selectivity of H_2 formation reduced in the order $\text{Ni}/\text{La}_2\text{O}_3 > \text{Ni}/\text{Y}_2\text{O}_3 > \text{Ni}/\text{Al}_2\text{O}_3$. A kinetic study revealed that the reaction was first order with respect to ethanol. Akande *et al.* (2005) studied reforming of crude ethanol over $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts and suggested a power law model for crude ethanol reforming in the range of temperatures 593–793 K. Aboudheir *et al.* (2006)

also reported an Eley Rideal type kinetic model for catalytic reforming of crude ethanol over Ni/Al₂O₃ for temperatures in the range 593–793 K, assuming dissociation of adsorbed crude ethanol as the rate-determining step.

Yang *et al.* (2006) studied steam reforming of ethanol over a Ni/ZnO catalyst and found that the catalyst was more selective to H₂ than Ni/La₂O₃, Ni/MgO and Ni/Al₂O₃. Selectivity to hydrogen was occurred in the following order: Ni/ZnO $\approx$ Ni/La₂O₃ > Ni/MgO > Ni/ γ -Al₂O₃. Ethanol was completely converted at temperatures above 603 K and the selectivity to H₂ was around 95% at 923K at a space velocity of 5 h⁻¹.

Fierro *et al.* (2003) found that a Ni–Cu/SiO₂ catalyst is more active and selective towards H₂ production in bio-ethanol oxidative steam reforming than Ni/SiO₂ which rapidly deactivates due to coke formation.

Marino *et al.* (2004) reported that Cu/Ni/K/-Al₂O₃ catalyst exhibited acceptable activity, stability and selectivity to hydrogen at 573 K. In this system, Cu is the active agent and promotes fast ethanol dehydrogenation to acetaldehyde, Ni promotes C-C bond rupture of acetaldehyde to produce CH₄ and CO and increases hydrogen selectivity while K neutralizes acidic sites of γ -Al₂O₃, avoids formation of products such as ethylene and diethyl ether and improves the general performance of the catalyst. In another study, Marino *et al.* (2003) have reported the formation of CuNiAl hydrotalcite type compounds during catalyst preparation. The addition of Ni favored the formation of these compounds thereby suggesting metal–support interaction.

Velu *et al.* (2002; 2005) have used Cu–Ni–Zn–Al mixed metal oxide catalysts in oxidative steam reforming of bio-ethanol. They found that the dehydrogenation of ethanol to acetaldehyde is favored by Cu-rich catalysts while the introduction of Ni leads to C-C bond rupture producing CO, CO₂ and CH₄. Luengo *et al.* (1992) reported ethanol reforming over Ni/Cu/Cr/Al₂O₃ catalyst at 573–823K and suggested that the catalytic effect was more pronounced at lower temperatures.

Morgenstern and Fornango (2005) showed that Cu-plated Raney nickel is an active and stable catalyst for low temperature steam reforming of ethanol (523–573 K).

Methanation was not observed but WGS activity was very poor. The kinetics were modeled by a sequence of two first order reactions: dehydrogenation of ethanol to acetaldehyde ($E_{act} = 149 \text{ kJ mol}^{-1}$) and decarbonylation of acetaldehyde. Kugai *et al.* (2005) studied oxidative steam reforming of ethanol over a bimetallic Rh–Ni/CeO₂ catalyst at low temperatures (<723 K) to produce a H₂-rich gas. The presence of O₂ enabled complete conversion of ethanol even at low temperatures (648 K) and reduced the selectivity to CO.

2.5.5. Cu-Based Catalysts

Cu-based catalysts have received particular attention and Cu is known as a strong inhibitor of coke formation. The methanol reforming system for industrial H₂ production uses Cu/ZnO/Al₂O₃ catalyst. Cavallaro and Freni (1996) investigated steam reforming of ethanol over CuO/ZnO/Al₂O₃ and found that the catalyst exhibited good activity with CO, CO₂ and H₂ as the main products above 630 K.

Nishiguchi *et al.*, (2005) studied steam reforming of ethanol over CuO/CeO₂ and found that, acetaldehyde and hydrogen were mainly produced at 533 K and at 653 K acetone was the main product. Ceria played an important role as an oxygen supplier. The addition of MgO to CuO/CeO₂ resulted in the production of hydrogen at lower temperatures by accelerating aldol condensation.

3. EXPERIMENTAL WORK

3.1. Materials

3.1.1. Chemicals

The chemicals used for catalyst preparation are listed in Table 3.1.

Table 3.1. Chemicals used for catalyst preparation

Chemicals	Specification	Source	Molecular weight
Nickel nitrate	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ extra pure	Merck	290.81
Tetraammineplatinum(II) nitrate	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ 50.4 % Pt	Aldrich	387.22
Gamma alumina	$\gamma\text{-Al}_2\text{O}_3$	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. Table 3.2 and Table 3.3 list the specifications and applications of the liquids and gases used in this study.

Table 3.2. Specifications and applications of the liquids used

Liquid	Specification	Application
Water	Distilled	Aqueous solutions, Reactant
Ethanol	99.8 vol. %(Riedel-deHaën)	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
Methane	99.9 % (BOS)	GC calibration*
Argon	99.999 % (BOS)	GC carrier gas

* (Avcı, 2003)

3.2. Experimental Systems

The experimental systems used in this research can be classified into three 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 System:** This continuous flow microreactor system includes gas and liquid flow controllers, temperature controlled heated lines, gas/liquid mixer, reaction chamber placed in a vertical oven whose temperature is controlled by a programmable temperature controller, and feed and product sampling sections. This system is used for assessing catalytic activity and for measuring reaction kinetics.
- **Product Analysis Systems:** The quantitative determination of the composition of the feed and product streams is conducted by using two different gas chromatographs operating in parallel.

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 (Avcı, 2003).

3.2.2. Catalytic Reaction System

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

- Feed section
- Reaction section
- Product analysis section

The feed section includes mass flow control systems, 1/4", 1/8" and 1/16" stainless steel tubes and fittings for feeding liquid water, ethanol and gaseous species, i.e. nitrogen and hydrogen at desired quantities. Nitrogen present in pressurized cylinders was passed through the gas flow regulators and calibrated Omega Model 5878 mass flow controllers. Hydrogen flow was regulated by using an Aalborg GFC171S series standalone controller. In order to protect the mass flow controllers from possible back-pressure fluctuations on-off valves were placed in front of them. The gases were then passed through a primary mixing zone to ensure a homogeneous gas mixture flow into the reactor.

The liquid feed, consisting of an ethanol-water mixture was introduced into the reaction system at constant flow rates at a desired ratio using a Jasco PU-1580 intelligent HPLC pump. The 1/16" tube through which the reactants were allowed to flow was kept at 448 ± 3 K by a 1.4 m heating tape whose temperature is controlled by the temperature controller to feed the liquid reactants in the form of a vapor mixture. The water-ethanol vapor mixture and the homogeneous gas mixture were mixed in a secondary mixing zone.

It was possible to divert the flow direction using three way valves for establishing steady state flow and mixing of the water-ethanol vapor mixture and nitrogen prior to the reaction.

The reactants, 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 K by a Shimaden FP-21 programmable temperature controller and a

1/4" stainless steel fixed-bed downflow microreactor. The reactor was also constructed in CATREL and its length was selected to be 50 cm so that it was longer than the furnace.

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 around the microreactor. 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 in 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 vapor in the product stream, the line from the reactor to the to both gas chromatographs were both kept heated at 448 ± 3 K using a 1.4 m and a 2.5 m heating tape whose temperatures were controlled by temperature controller. The product stream was analyzed qualitatively and quantitatively using two separate gas chromatographs operating in a parallel scheme. Four different temperature controllers were employed to control the temperature of the four different zones independently. 16-gauge wire K type sheathed thermocouples (insulation material: fiberglass) 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.

3.2.3. Product Analysis Systems

The product mixture contains groups of species with different characteristics, i.e. hydrocarbons involving ethanol, methane, ethane, acetone, acetaldehyde, 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, use of two different gas chromatographs was essential; hydrocarbons were effectively analyzed using a Porapak Q column with He carrier gas whereas quantitative detection of hydrogen and other fixed gases were analyzed using a Molecular Sieve column with Ar carrier.

A Shimadzu GC-14A gas chromatograph equipped with a Thermal Conductivity Detector (TCD) 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) and a Shimadzu CR-1B Chromatopac data processor involving a Molecular Sieve column was employed. Since the analysis column can easily be deactivated when contacted with a stream containing water, ethanol and other liquid products existing in the product stream were removed by placing two salt-ice cold traps held in Dewar flasks at 273 K before the 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 chromatographs, the previously optimized conditions by Aksoylu (1999) and 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, °C	90	60
Injector temperature, °C	150	90
Detector temperature, °C	150	90
TCD temperature, °C	150	90
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 125°C	1 ml kept at 25°C

3.3. Catalyst Preparation and Pretreatment

3.3.1. Support Preparation

The catalytic steam reforming of hydrocarbons is known to be a high-temperature reaction. 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 higher than 873 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 higher than 1400 K. However, its low surface area, which is less than $5 \text{ m}^2 \text{ g}^{-1}$, 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 optimum in terms of obtaining an efficient catalytic performance (Ma, 1995).

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

3.3.2. Preparation of Pt-Ni/ δ - Al_2O_3 Catalyst

The bimetallic Pt-Ni/ δ - Al_2O_3 catalyst (metal loadings were 0.3 and 0.2 weight per cent for Pt while 10 and 15 weight per cent for Ni) was 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 $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. 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 flask and mixed ultrasonically for 25 min under vacuum. The aqueous solution was then impregnated on the support via a peristaltic pump. The resulting slurries that were formed after ultrasonic mixing of the aqueous solutions and the support under

vacuum for 1.5 h were then dried overnight at 393 K and calcined at 873 K for 4 h to obtain (NiO/ δ -Al₂O₃). The aqueous Pt solution was then added to NiO/ δ -Al₂O₃ and mixed ultrasonically under vacuum for 1.5 h. The resulting slurry involving two metals was dried overnight at 393 K and finally calcined at 773 K for 4 h.

3.3.3. Pretreatment

In order to obtain high catalytic activities, a pretreatment involving the reduction of the active metals from the oxide state –which is formed while calcinations- to the metallic state is required prior to the reaction, since 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 pretreating the bimetallic catalyst Pt-Ni (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 (Avci, 2003).

After placing the catalyst into the constant temperature zone of the microreactor, N₂ was allowed to flow at 50 ml/min for 10 minutes to remove oxygen from the system. The gas flow was switched from N₂ to H₂ and the latter was set to flow at 20 ml/min. Reduction was started by heating the catalyst from room temperature to 423 K at a rate of 10 K/min. 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/min, followed by a 30 min 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 and finally kept constant at 773 K for 4 h. After reduction, the system was allowed to cool down to ca. 423 K under H₂ flow. Below this temperature, the gas flow was switched from H₂ to N₂ and the latter was allowed to flow at a small flow rate, e.g. 3 ml/min overnight to sweep H₂ 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. Steam Reforming of Ethanol over Pt-Ni/ δ -Al₂O₃ Catalysts

Reaction experiments were conducted at atmospheric pressure and 673-823 K in 4 mm-ID stainless steel fixed-bed down-flow microreactors placed inside a tube furnace controlled to ± 0.5 K. Before reaction experiments catalysts were reduced under 20 ml/min pure hydrogen flow at 773 K for 4 h. After reduction, the temperature of the reactor was raised to the reaction temperature (673 K, 723 K, 773 K, or 823 K) under inert nitrogen flow, and nitrogen was trapped within the reactor. Liquid water-ethanol feed mixtures were evaporated into a preheated diluent nitrogen stream using an HPLC pump and mixed to ensure homogeneity prior to microreactor inlet. In all experiments, 250-450 μ m fresh catalyst particles were diluted with inert δ -Al₂O₃ to a total bed weight of 250 mg.

For parametric studies, in each experiment, 20 mg of fresh catalyst was used. The parameters investigated were feed composition, space time, time-on-stream and temperature. The microreactor was operated in the integral mode; the steam-to-carbon ratio and the space time were fixed at 3.0 and 80 mg.s/ml in order to compare the performances of different catalyst at 723 K. In all experiments both ethanol conversion and hydrogen yield were measured at various intervals up to 6 h time-on-stream.

Table 3.5. Conditions for parametric studies of ethanol steam reforming

Set #	T (K)	Catalyst	C ₂ H ₅ OH (ml.min ⁻¹)	H ₂ O (ml.min ⁻¹)	N ₂ (ml.min ⁻¹)	S/C
1	673	0.2wt.%Pt-15wt.%Ni	15	90	135	3.0
2	673	0.3wt.%Pt-15wt.%Ni	15	90	135	3.0
3	723	0.2wt.%Pt-10wt.%Ni	15	90	135	3.0
4	723	0.3wt.%Pt-10wt.%Ni	15	90	135	3.0
5	723	0.2wt.%Pt-15wt.%Ni	15	90	135	3.0
6	723	0.3wt.%Pt-15wt.%Ni	15	90	135	3.0
7	773	0.2wt.%Pt-15wt.%Ni	15	90	135	3.0
8	773	0.3wt.%Pt-15wt.%Ni	15	90	135	3.0
9	823	0.2wt.%Pt-15wt.%Ni	15	90	135	3.0
10	823	0.3wt.%Pt-15wt.%Ni	15	90	135	3.0

3.4.3. Kinetic Study of Ethanol Steam Reforming

To investigate the effects of ethanol and water on intrinsic reaction rates, the flow rates of the reactants and inert nitrogen were adjusted so that external and internal heat/mass transfer resistances could be minimized. Details of experimental conditions are presented in Table 3.6. The total inlet flow was changed between 133 ml.min⁻¹ and 240 ml.min⁻¹ and a 45-60 mesh (250-425 μ m) particle size was selected. In this work, the ratio of catalyst bed height to catalyst particle size (L/D_p) of 68 and the ratio of internal diameter of the reactor to the catalyst particle size (D/D_p) of 12 used in all kinetic experiments in order to ensure plug flow behavior in the reactor, where the values L and D_p are 2.3x10⁻² m and 3.4x10⁻⁴ m, respectively.

Based on the results of the steam reforming experiments described in Section 3.4.2, the catalyst 0.3wt.%Pt-15wt.%Ni/ δ -Al₂O₃ was selected in the kinetic investigations. Also, the temperature used to measure reaction rates at different initial concentrations and space times was selected to be 723 K.

Table 3.6. Conditions for the kinetic study of steam reforming of ethanol

Set #	W (mg)	C ₂ H ₅ OH (ml.min ⁻¹)	H ₂ O (ml.min ⁻¹)	N ₂ (ml.min ⁻¹)	S/C	W/F _{EtOH} (mg.sec.ml ⁻¹)
1	10	12	72	156	3.0	50
2	20	12	72	156	3.0	100
3	25	12	72	156	3.0	125
4	30	12	72	156	3.0	150
5	35	12	72	156	3.0	175
6	40	12	72	156	3.0	200
7	10	12	72	87	3.0	50
8	20	12	72	87	3.0	100
9	25	12	72	87	3.0	125
10	30	12	72	87	3.0	150
11	35	12	72	87	3.0	175
12	40	12	72	87	3.0	200
13	10	12	72	49	3.0	50
14	20	12	72	49	3.0	100
15	25	12	72	49	3.0	125
16	30	12	72	49	3.0	150
17	35	12	72	49	3.0	175
18	40	12	72	49	3.0	200

4. RESULTS AND DISCUSSION

4.1. Introduction

The ethanol steam reforming reaction over the 0.2wt.%Pt-15wt.%Ni/ δ -Al₂O₃ catalyst was studied by Örüçü (2005) in order to find the effect of water to ethanol ratios and reaction temperatures. Preliminary kinetic studies have also been carried out on the same catalyst by Örüçü (2005) and Gökaliler (2005). These studies have indicated a positive dependence on ethanol with a reaction order close to unity and a slightly negative dependence on water vapor.

In the present work, ethanol steam reforming was studied over bimetallic Pt-Ni/ δ -Al₂O₃ catalysts with different Pt and Ni loadings at atmospheric pressure and temperatures ranging from 673 to 823 K. The kinetics of ethanol steam reforming over 0.3wt.%Pt-15wt.%Ni/ δ -Al₂O₃ catalyst were further studied over a relatively wide range of space time ($W_{cat} / F_{EtOH_{in}} = 50\text{-}200 \text{ mg sec ml}^{-1}$) at a fixed S:C ratio of 3.0 and a constant temperature of 723 K. The ethanol conversion and hydrogen yield were defined as follows:

$$\text{Ethanol conversion (\%)} = \frac{[EtOH]_{in} - [EtOH]_{out}}{[EtOH]_{in}} \times 100 \quad (4.1)$$

$$\text{H}_2 \text{ Yield} = \frac{[H_2]_{out}}{([EtOH]_{in} - [EtOH]_{out})} \quad (4.2)$$

The catalyst mass-based reaction rates in the kinetic measurements, ($-r_{EtOH}$), can be calculated from the conversion versus residence time ($W_{cat} / F_{EtOH_{in}}$) data as follows:

$$r_{EtOH} = \frac{dx_{EtOH}}{d(W_{cat} / F_{EtOH_{in}})} \quad (4.3)$$

where x_{EtOH} is ethanol conversion, $F_{EtOH\ in}$ is ethanol flow rate in the feed in ml.min^{-1} converted to mol.h^{-1} , W_{cat} is catalyst weight in g and $(-r_{EtOH})$ is the reaction rate in $\text{mol.g}^{-1}.\text{h}^{-1}$. Ethanol consumption rates were obtained from the slopes of the x_{EtOH} vs. $W / F_{EtOH\ in}$ curves at various points within the range of the operating conditions.

4.2. Steam Reforming of Ethanol over Pt-Ni/ $\delta\text{-Al}_2\text{O}_3$ Catalysts

Ni catalysts are efficient in steam reforming of hydrocarbons; however, their ATR performance is undermined by their tendency for deactivation by oxidation at ca 673 K. Pt catalysts are effective in hydrocarbon oxidation at elevated temperatures, and hence Pt-Ni catalysts are designed for thermally efficient fuel conversion and hydrogen production (Avcı *et al.*, 2004).

The effect of Ni and Pt loadings on the catalytic performance of the bimetallic Pt-Ni/ $\delta\text{-Al}_2\text{O}_3$ catalyst was studied at a reaction temperature of 723 K. Taking into account the global steam reforming of ethanol reaction (Reaction 2.12), the molar ratio of water/ethanol was fixed at 6.0 (corresponding to a steam/carbon ratio of 3) in order to work with an excess of water. On the basis of the results, increasing the Pt content increased the catalyst stability while increasing the Ni content increased both ethanol conversion and hydrogen production at 723 K, as depicted in Figure 4.1 and Figure 4.2, respectively. Based on the performance of the catalysts for higher hydrogen production rates and ethanol conversions, samples with 15wt. % Ni were further investigated at 673, 773 and 823 K.

The ethanol conversions and corresponding hydrogen production rates obtained at 375 min time-on-stream are presented in Figure 4.3 and Figure 4.4, respectively. Figure 4.3 shows remarkable effect of temperature on ethanol conversion. The most realistic increase in conversion was observed above 723 K for 0.3wt.%Pt-15wt.%Ni catalyst. Also, at temperatures below 723 K hydrogen production rates over 0.2wt.%Pt-15wt.%Ni and 0.3wt.%Pt-15wt.%Ni were rather slow, at 723 K they were almost equal and, above 723 K, 0.3wt.%Pt-15wt.%Ni performed better. These results are coinciding well with the study of Marino *et al.* (2001), who showed that high Ni and Cu content favored the hydrogen yield.

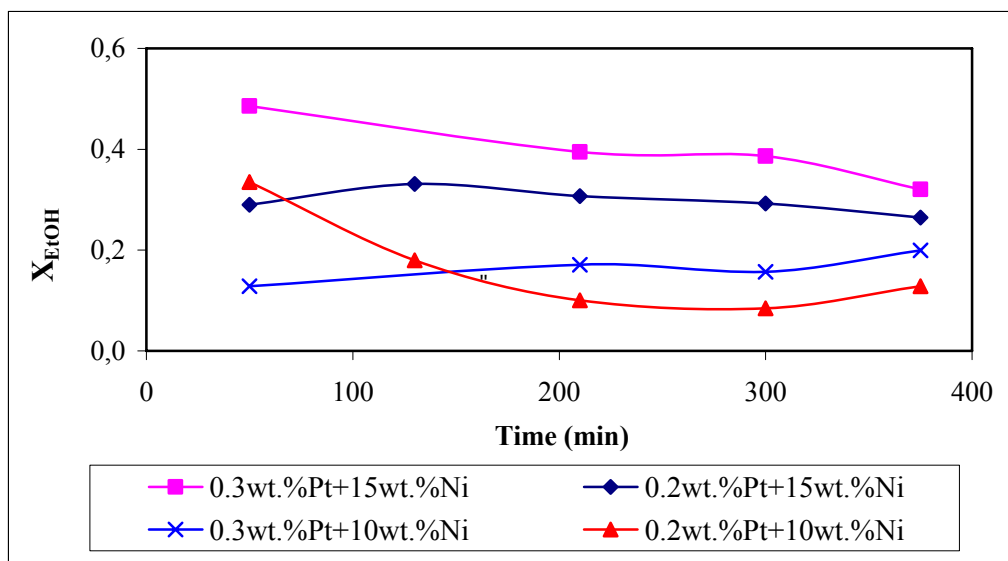


Figure 4.1. Effect of metal loading on ethanol conversion at 723 K

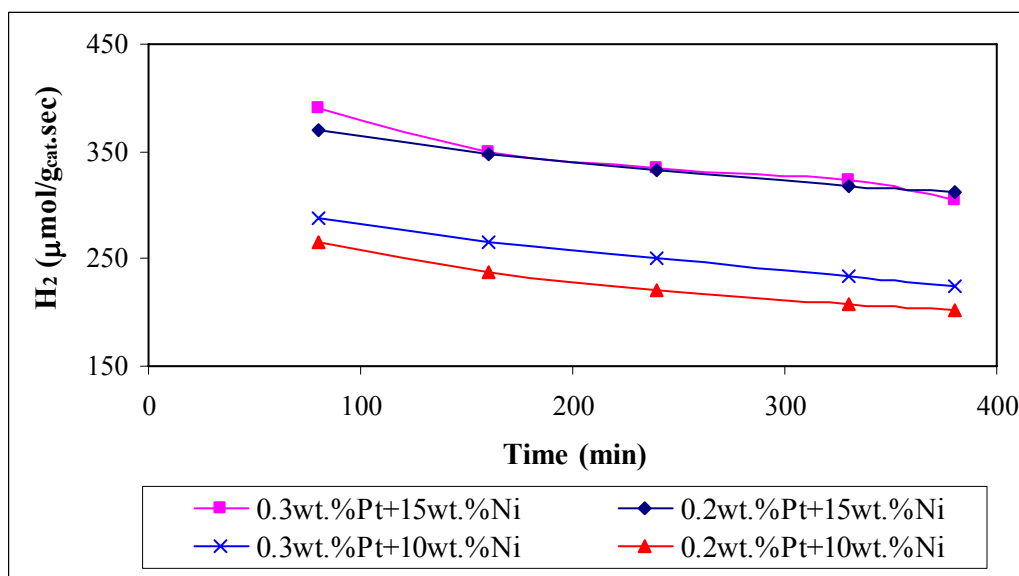


Figure 4.2. Effect of metal loading on hydrogen production rate at 723 K

The changes in fractional ethanol conversion and hydrogen production rate with temperature can be explained by the possibility of different side reactions in addition to ethanol steam reforming (Reaction 4.4), such as ethanol decomposition (Reaction 4.5) or methane reforming (Reaction 4.6) (Comas *et al.*, 2004; Vaidya and Rodrigues, 2006; Sahoo *et al.*, 2007).

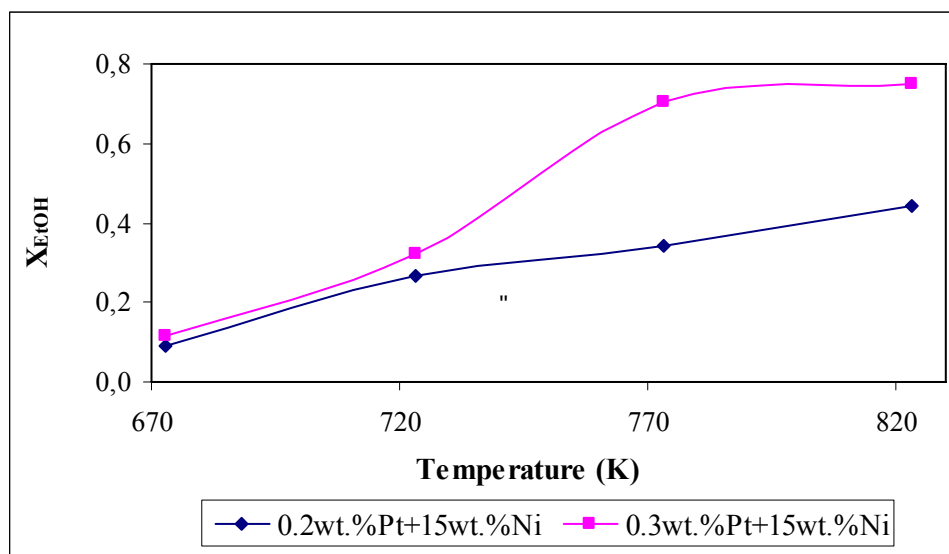
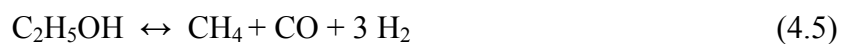
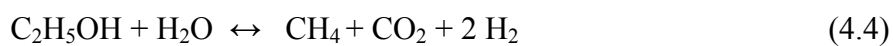


Figure 4.3. Effect of temperature on ethanol conversion

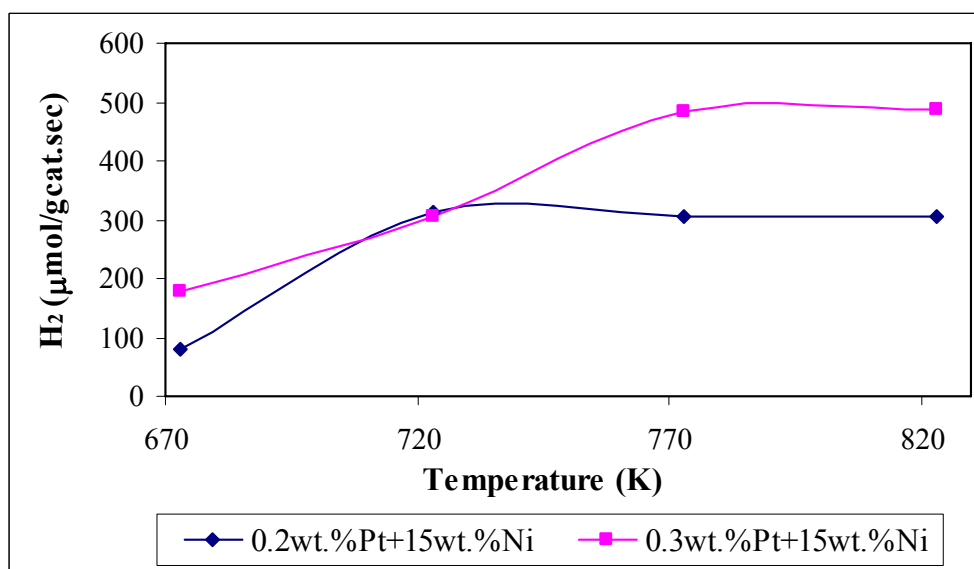


Figure 4.4. Effect of temperature on hydrogen production rate

The product distribution was also investigated in order to clarify this point. Methane production rate at 300 minutes time on stream is shown in Figure 4.5. No significant change was observed in the methane production rate for 0.3wt.%Pt catalyst with increasing temperature. On the other hand, the highest methane production rate for the catalyst with 0.2wt.% Pt content was observed at 723 K. Since the methane production rate decreased between the temperatures of 723 and 773 K, methane steam reforming reaction can be dominant for 0.2wt.% Pt catalyst in this temperature range. Figure 4.6 shows temperature effect on carbon dioxide production rate. Above 723 K, a significant increase in carbon dioxide production rate was observed for 0.3wt.%Pt catalyst. The results of Figures 4.4 and 4.5 are consistent with those observed from Figure 4.7 in the temperature range of 773 K and 823 K. The highest H_2/CH_4 ratio was observed at 773 K for both catalysts as shown in Figure 4.7.

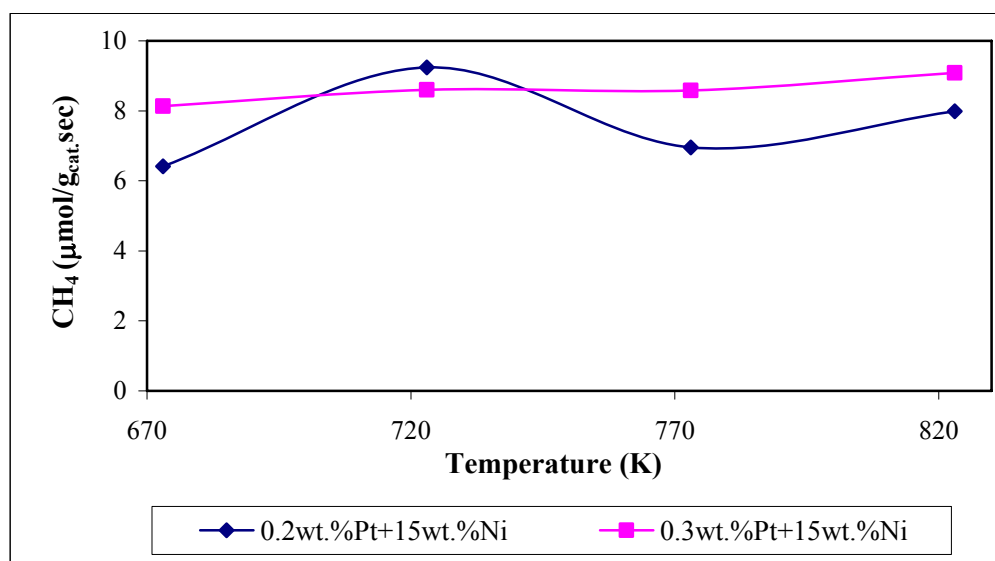


Figure 4.5. Effect of temperature methane production rate

Above 773 K, the relatively sharp decrease in H_2/CH_4 ratio can be the indication of methanation reactions (Reaction 4.7 and 4.8). Moreover, when CO_2/CO ratios were examined in Figure 4.8, it was seen that the steam reforming reaction became dominant with high temperatures.



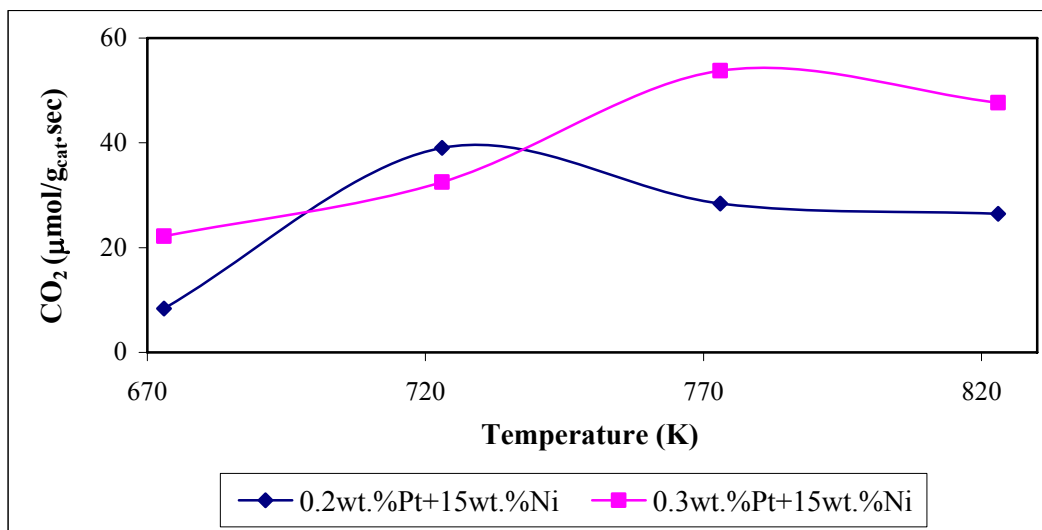


Figure 4.6. Effect of temperature carbon dioxide production rate

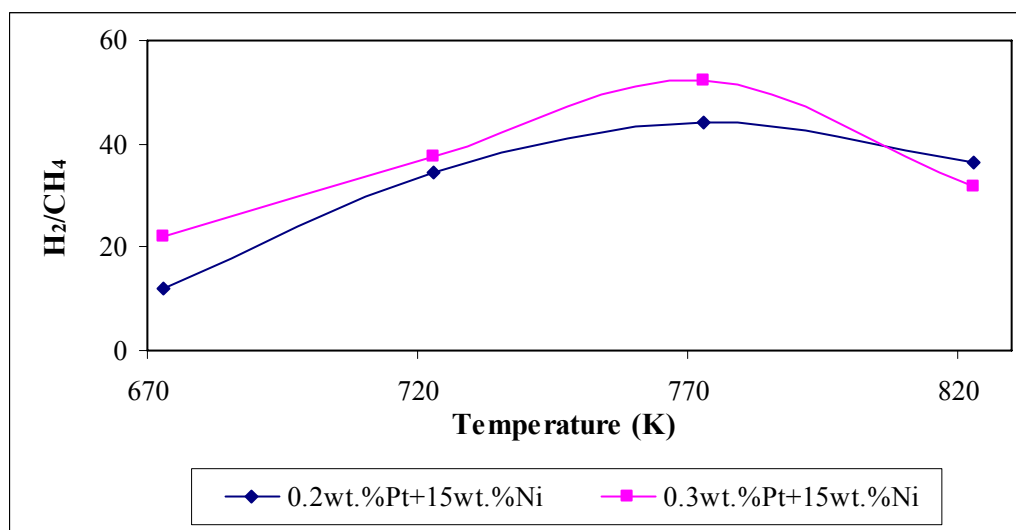


Figure 4.7. Effect of temperature on H₂/CH₄

In addition, hydrogen production rate is compared to carbon monoxide production rate at 773 K and 823 K in Figure 4.9. The H₂/CO ratio of 0.3wt.% Pt catalyst was decreased as the temperature increased while the reverse behavior was observed for the 0.2wt.% Pt catalyst.

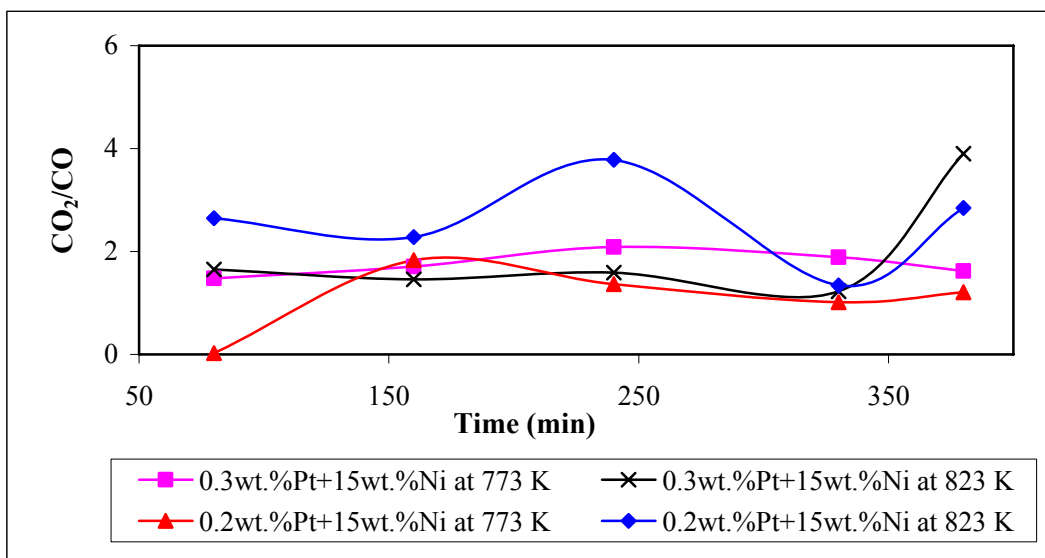


Figure 4.8. Effect of temperature on CO_2/CO ratio

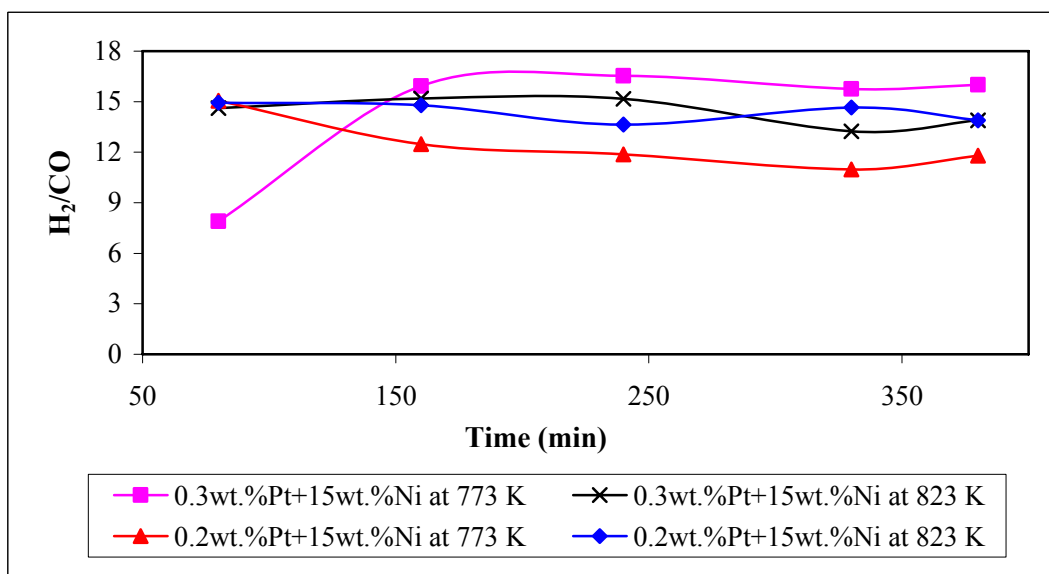


Figure 4.9. Effect of temperature on H_2/CO

On the basis of these results obtained at 723 K, it can be concluded that catalysts with 15wt.%Ni content are more efficient and that the Pt content also affects ethanol steam reforming performance. Although a Pt content of 0.3wt.% is better than 0.2wt.% in steam reforming in the absence of oxygen, higher Pt percentages may not be desirable in ATR where more fuel could be used up by oxidation.

4.3 Kinetic Study of Ethanol Steam Reforming

4.3.1. Steam Reforming of Ethanol

The criteria used to select operating conditions for investigating the effects of water and ethanol concentration on the kinetics of ethanol steam reforming over bimetallic Pt-Ni/ δ -Al₂O₃ catalyst were given in Section 3.4.3.

The dependence of ethanol steam reforming reaction rate on C₂H₅OH and H₂O partial pressures was studied over the bimetallic 0.3wt.%Pt-15wt.%Ni/ δ -Al₂O₃ catalyst. The measurements for the determination of reaction orders with respect to C₂H₅OH and H₂O were taken at 723 K by varying the residence time and the C₂H₅OH and H₂O concentrations in the feed at a fixed S:C ratio of 3.0 (Table 4.1). The data obtained at 375 minutes time-on-stream were used for the kinetic calculations.

The fractional conversions of ethanol (X) as a function of space time at various concentrations are presented in Figure 4.10 and 4.11 for different time-on-stream data. For a given value of $W / F_{EtOH_{in}}$, the ethanol conversion increased with increasing concentration, as expected. These results showed that the ethanol conversion initially increases rapidly with an increase in space time. Further increase in space time results in a slowing down of the corresponding increase of (X) for the three initial concentrations used.

The change in hydrogen production rate with space time is illustrated in Figure 4.12. As the $W / F_{EtOH_{in}}$ ratio increased from 0.33 to 1.17 g.h.mol⁻¹, the hydrogen production rate changed significantly at low space times for three initial concentration values, while above 1.17 g.h.mol⁻¹ no valuable changes were observed. Aupretre *et al.* (2005) showed that a hydrogen yield of 4.68 mol mol⁻¹ could be achieved over a Ni-Rh/1-Mg_{0.25}Al catalyst at 973 K. The hydrogen yield and corresponding ethanol conversion values given in Table 4.1 indicate that the higher the extent of reaction (ethanol conversion), the higher is the relative yield of hydrogen. These results are consistent with data in the literature obtained by Goula *et al.* (2004), Freni *et al.* (2003) and Comas *et al.* (2004).

Table 4.1. Ethanol conversions and hydrogen yields over 0.3wt.%Pt-15wt.%Ni/ δ -
Al₂O₃ catalyst, T=723 K

Exp No	W_{cat} (mg)	Q_T (ml.min ⁻¹)	EtOH %	H ₂ O %	N ₂ %	300 min. TOS (fractional)	375 min. TOS (fractional)	375 min. TOS
						x_{EtOH}	x_{EtOH}	H ₂ Yield (mol.mol ⁻¹)
1	10	240	5.0	30.0	65.0	0.171	0.162	1.35
2	20	240	5.0	30.0	65.0	0.275	0.299	1.58
3	25	240	5.0	30.0	65.0	0.374	0.352	2.85
4	30	240	5.0	30.0	65.0	0.410	0.394	2.80
5	35	240	5.0	30.0	65.0	0.458	0.454	2.82
6	40	240	5.0	30.0	65.0	0.497	0.473	2.72
7	10	171	7.0	42.0	51.0	0.155	0.191	1.10
8	20	171	7.0	42.0	51.0	0.373	0.336	2.43
9	25	171	7.0	42.0	51.0	0.416	0.412	2.44
10	30	171	7.0	42.0	51.0	0.472	0.458	2.23
11	35	171	7.0	42.0	51.0	0.532	0.519	2.59
12	40	171	7.0	42.0	51.0	0.595	0.584	2.23
13	10	133	9.0	54.0	37.0	0.279	0.243	1.08
14	20	133	9.0	54.0	37.0	0.479	0.466	1.76
15	25	133	9.0	54.0	37.0	0.525	0.546	1.66
16	30	133	9.0	54.0	37.0	0.597	0.592	1.81
17	35	133	9.0	54.0	37.0	0.671	0.671	2.39
18	40	133	9.0	54.0	37.0	0.735	0.731	2.07

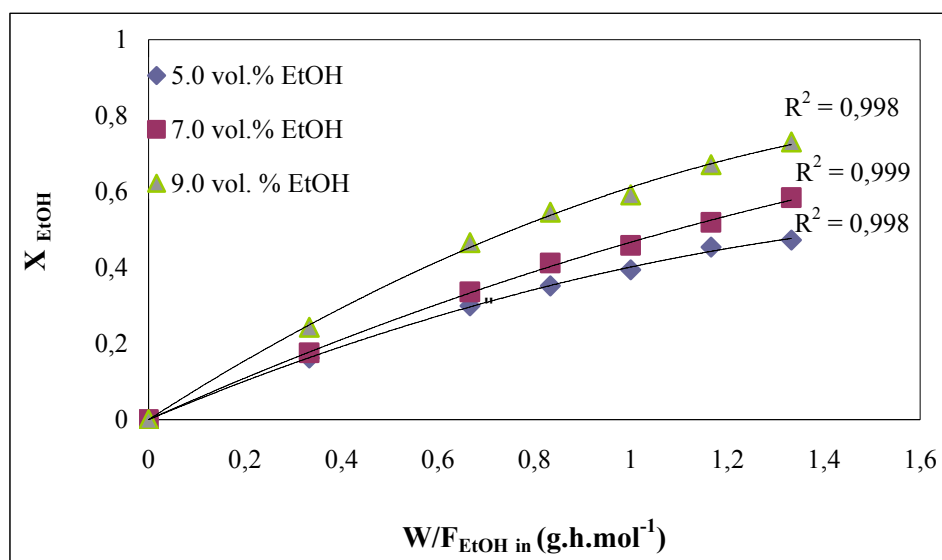


Figure 4.10. Fractional conversion of ethanol as a function of space time at various ethanol concentrations at 375 minutes TOS

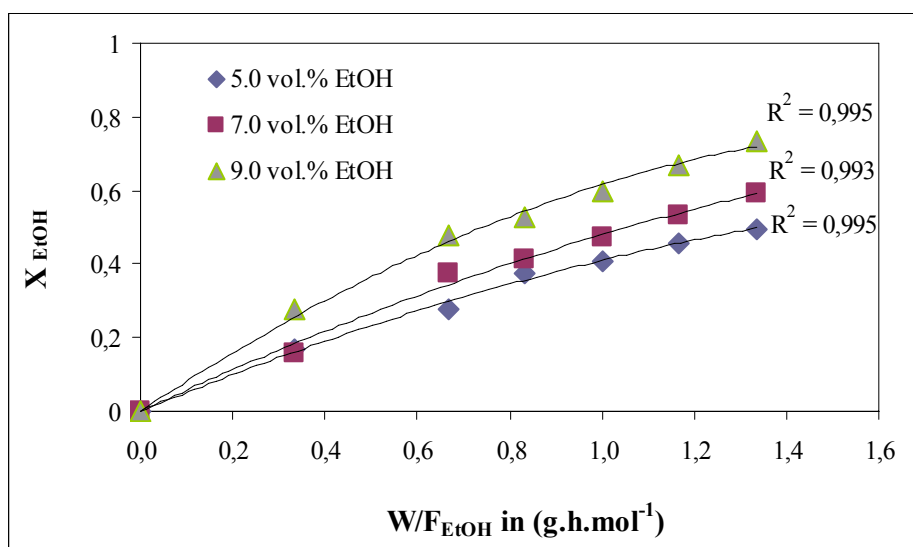


Figure 4.11 Fractional conversion of ethanol as a function of space time at various ethanol concentrations at 300 minutes TOS

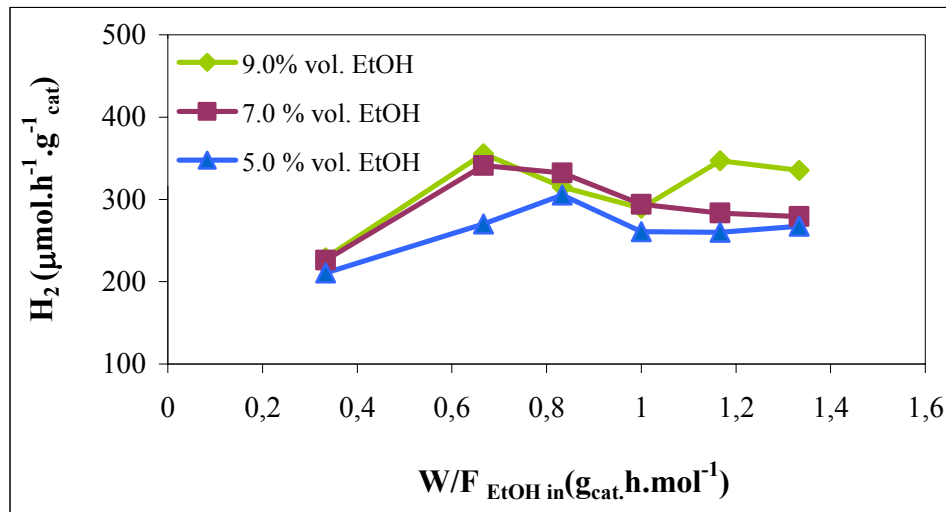


Figure 4.12. Effect of space time on hydrogen production rate at 300 min TOS

4.3.2. Power Law Modeling of the Kinetic Data

The ethanol steam reforming reaction kinetics were modeled by fitting a power function rate expression to the experimental data. The rate of reaction was represented as:

$$-r_{C_2H_5OH} = k(P_{C_2H_5OH})^\alpha (P_{H_2O})^\beta \quad (4.9)$$

Evaluation of the rate parameters requires first the determination of the reaction rates on the left-hand side of Equation 4.9. The rates of reaction were evaluated by fitting the ethanol conversion versus space time data (Figure 4.10) to a second order polynomial, followed by differentiation and evaluation of individual rates at various catalyst space times. These polynomials for 5.0 vol. per cent C₂H₅OH, 7.0 vol. per cent C₂H₅OH and 9.0 vol. per cent C₂H₅OH were obtained as follows, respectively:

$$x_{EtOH} = -0.1306(W / F_{EtOH})^2 + 0.5321(W / F_{EtOH}) \quad (4.10)$$

$$x_{EtOH} = -0.0997(W / F_{EtOH})^2 + 0.5661(W / F_{EtOH}) \quad (4.11)$$

$$x_{EtOH} = -0.2055(W / F_{EtOH})^2 + 0.8169(W / F_{EtOH}) \quad (4.12)$$

For each experiment, ethanol and steam concentrations were obtained from the effluent gas composition. Each calculated reaction rate and the corresponding effluent concentrations of ethanol and steam were employed in the determination of the ethanol SR rate equation. The resulting rate data given in Table 4.2 and 4.3 were processed by using nonlinear regression procedure according to the Levenberg-Marquardt algorithm to obtain rate parameters k , α and β appearing in Equation 4.9. The resulting rate data obtained by using polynomials for all conversions are given in Appendix A.

The Levenberg-Marquardt algorithm is an iterative technique that locates the minimum of a function that is expressed as the sum of squares of nonlinear functions. The sum of the squared differences of the measured reaction rates, $(-r)_m$, and the calculated reaction rates, $(-r)_c$, for N experiments and p parameter values is defined as the variance of experimental error given by the following equation:

$$\sigma^2 = \sum_{i=1}^n \frac{[(-r)_{im} - (-r)_{ic}]^2}{(N - p)} \rightarrow \text{minimum} \quad (4.13)$$

All parameters found by linearised least squares are used as initial estimates in nonlinear least squares analysis. The reaction orders with respect to ethanol (α) and steam (β) and the rate constant (k) found by using MATLAB computer software in the 0-45 per cent ethanol conversion region are presented in Table 4.4.

Table 4.2. Concentrations of C₂H₅OH and H₂O and calculated reaction rates over 0.3wt.%Pt-15wt.%Ni/ δ -Al₂O₃ for 5.0 vol.% EtOH, T = 723 K

No	$W / F_{C_2H_5OH_{in}}$ (g.h.mol ⁻¹)	Concentrations (mol.l ⁻¹) 5.0 vol.%		$(-r_{C_2H_5OH})$ (mol.g ⁻¹ .h ⁻¹)
		C ₂ H ₅ OH	H ₂ O	
1	0.05	0.0020	0.0123	0.5190
2	0.08	0.0020	0.0122	0.5112
3	0.10	0.0020	0.0122	0.5060
4	0.15	0.0019	0.0120	0.4929
5	0.20	0.0019	0.0119	0.4799
6	0.25	0.0018	0.0117	0.4668
7	0.30	0.0018	0.0116	0.4537
8	0.33	0.0017	0.0115	0.4450
9	0.35	0.0017	0.0114	0.4407
10	0.40	0.0017	0.0113	0.4276
11	0.45	0.0016	0.0112	0.4146
12	0.50	0.0016	0.0110	0.4015
13	0.55	0.0016	0.0109	0.3884
14	0.60	0.0015	0.0108	0.3754
15	0.65	0.0015	0.0107	0.3623
16	0.67	0.0015	0.0106	0.3580
17	0.70	0.0014	0.0106	0.3493
18	0.75	0.0014	0.0105	0.3362
19	0.80	0.0014	0.0104	0.3231
20	0.83	0.0013	0.0103	0.3144
21	0.85	0.0013	0.0103	0.3101
22	0.90	0.0013	0.0102	0.2970
23	0.95	0.0013	0.0101	0.2840
24	1.00	0.0013	0.0100	0.2709
25	1.05	0.0012	0.0099	0.2578
26	1.10	0.0012	0.0098	0.2448
27	1.15	0.0012	0.0098	0.2317
28	1.17	0.0011	0.0097	0.2274

Table 4.3. Concentrations of C₂H₅OH and H₂O and calculated reaction rates over 0.3wt.%Pt-15wt.%Ni/ δ -Al₂O₃ for 7.0 vol. % and 9.0 vol.% EtOH, T = 723 K

NO	$W / F_{C_2H_5OH_{in}}$ (g.h.mol ⁻¹)	Concentrations (mol.l ⁻¹) 7.0 vol. %		$(-r_{C_2H_5OH})$ (mol.g ⁻¹ .h ⁻¹)	Concentrations (mol.l ⁻¹) 9.0 vol. %		$(-r_{C_2H_5OH})$ (mol.g ⁻¹ .h ⁻¹)
		C ₂ H ₅ OH	H ₂ O		C ₂ H ₅ OH	H ₂ O	
1	0.05	0.0028	0.0173	0.5561	0.0036	0.0221	0.7964
2	0.08	0.0028	0.0171	0.5501	0.0035	0.0218	0.7840
3	0.10	0.0028	0.0171	0.5462	0.0035	0.0217	0.7758
4	0.15	0.0027	0.0168	0.5362	0.0033	0.0212	0.7553
5	0.20	0.0026	0.0166	0.5262	0.0032	0.0208	0.7347
6	0.25	0.0025	0.0164	0.5163	0.0030	0.0204	0.7142
7	0.30	0.0025	0.0161	0.5063	0.0029	0.0200	0.6936
8	0.33	0.0024	0.0160	0.4996	0.0028	0.0198	0.6799
9	0.35	0.0024	0.0159	0.4963	0.0028	0.0196	0.6731
10	0.40	0.0023	0.0157	0.4863	0.0027	0.0192	0.6525
11	0.45	0.0022	0.0155	0.4764	0.0025	0.0189	0.6320
12	0.50	0.0022	0.0153	0.4664	0.0024	0.0185	0.6114
13	0.55	0.0021	0.0151	0.4564	0.0023	0.0182	0.5909
14	0.60	0.0020	0.0149	0.4465	0.0022	0.0179	0.5703
15	0.65	0.0020	0.0147	0.4365	0.0021	0.0176	0.5498
16	0.67	0.0019	0.0146	0.4332	0.0020	0.0173	0.5429
17	0.70	0.0019	0.0145	0.4265	0.0020	0.0173	0.5292
18	0.75	0.0019	0.0143	0.4166	0.0019	0.0170	0.5087
19	0.80	0.0018	0.0141	0.4066	0.0018	0.0167	0.4881

Table 4.4. Power law reaction parameter estimations by linear and nonlinear regression

Regression	Linear	Nonlinear
α	0.99 ± 0.09	1.01 ± 0.03
β	-0.10 ± 0.04	-0.09 ± 0.02
k (mol.g _{cat} ⁻¹ .h ⁻¹ .atm ^($\alpha+\beta$))	8.55 ± 3.0	9.23 ± 0.3

The nonlinear regression analysis resulted in a value of 1.01 for α and of -0.09 for β . The reaction rate constant is determined as 9.23 mol.g_{cat}⁻¹.h⁻¹.atm^{-0.92}. Thus, the resulting power law rate expression for ethanol steam reforming takes the following form:

$$-r_{C_2H_5OH} = 9.23(P_{C_2H_5OH})^{1.01}(P_{H_2O})^{-0.09} \quad (4.14)$$

Figure 4.13 illustrates a comparison between the calculated reaction rate from the above expression and the experimental reaction rate. In the range of experiments, the model predicted reaction rates were in agreement with the experimental data for all three ethanol compositions. Also, the reaction rates estimated by differentiating the polynomials at different space times fits well the model-predicted rate data as illustrated in Figure 4.14.

The value of α indicates that the reaction rate is first order in ethanol while the value of β indicates that steam mildly inhibits the steam reforming reaction due to competition between steam and ethanol for active sites on the catalyst surface. This result is in agreement with the literature for steam reforming of n-butane over the bimetallic Pt-Ni/ δ -Al₂O₃ catalyst (Avcı, 2003; Avcı *et al.*, 2004). A comparison with data reported in the literature for steam reforming of ethanol over Ni-based catalysts is shown in Table 4.5.

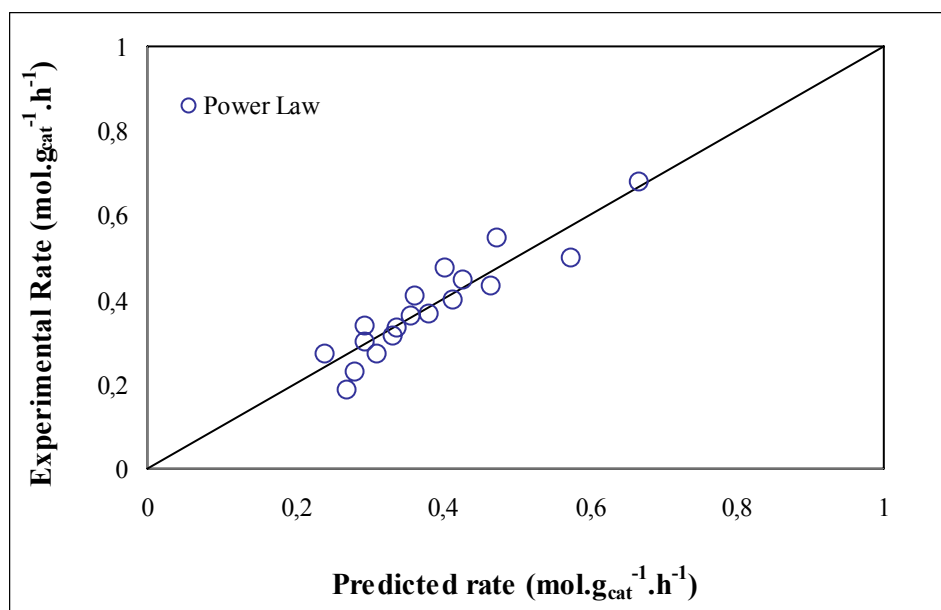


Figure 4.13. Diagonal chart of measured and predicted rates of ethanol steam reforming at 723 K

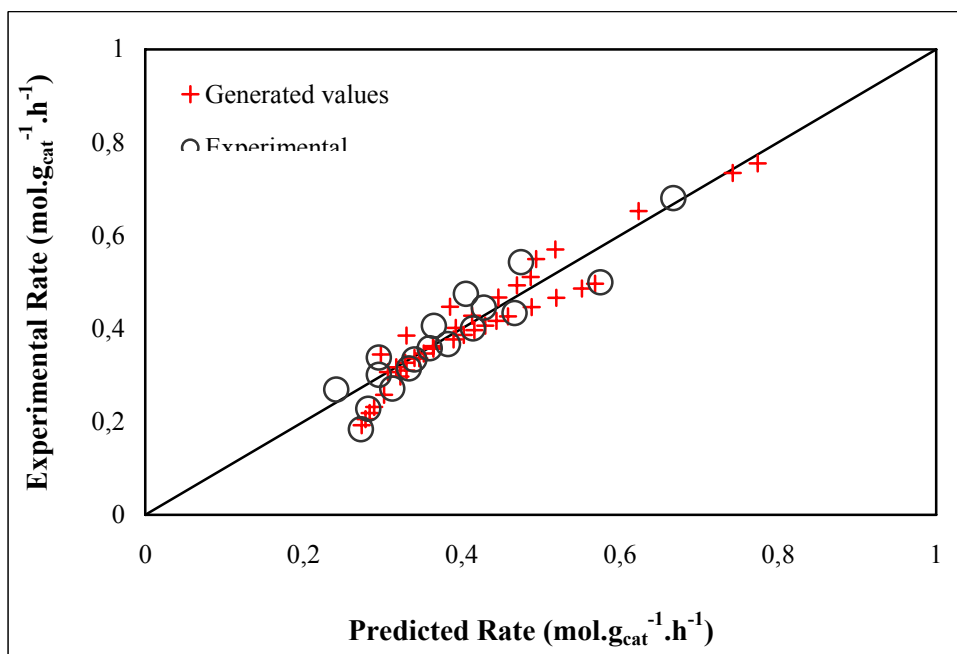


Figure 4.14. Observed rate versus predicted rate for the steam reforming of ethanol

Table 4.5. Kinetics of steam reforming of ethanol over Ni-based catalysts

Catalyst	T (K)	Rate constant	Order w.r.t ethanol	Order w.r.t steam	References
0.3wt.%Pt- 15wt.%Ni/Al ₂ O ₃	723	$9.23 \text{ mol.g}_{\text{cat}}^{-1}.\text{h}^{-1}.\text{atm}^{-0.92}$	1.01	-0.09	This work
Ni/Y ₂ O ₃	403	$2.95 \times 10^{-3} \text{ m}^3.\text{kg}_{\text{cat}}^{-1}.\text{s}^{-1}$	1		Sun et al., (2005)
Ni/Al ₂ O ₃	403	$2.32 \times 10^{-3} \text{ m}^3.\text{kg}_{\text{cat}}^{-1}.\text{s}^{-1}$	1		Sun et al., (2005)
Ni/La ₂ O ₃	403	$19.1 \times 10^{-3} \text{ m}^3.\text{kg}_{\text{cat}}^{-1}.\text{s}^{-1}$	1		Sun et al., (2005)
Ni/Al ₂ O ₃	593–793		0.43		Akande , (2005)
0.2wt.%Pt- 15wt.%Ni/Al ₂ O ₃	673-723	$1.3 \times 10^{-2} \text{ mol.g}_{\text{cat}}^{-1}.\text{s}^{-1}.\text{kPa}^{-1.07}$	1.25	-0.22	Gökaliler, (2005)
Cu-plated Raney nickel	523–573		1		Morgenstern and Fornango, (2005)

For a first-order reaction in a packed-bed reactor, the following relation holds true:

$$\ln(1 - X) = k(W/Q_T) \quad (4.15)$$

Plots of $\ln(1 - X)$ versus W/Q_T data are shown in Figure 4.15 and 4.16 for experimental and generated data, respectively. The data reasonably fall on a straight line confirming that the reaction is first order with respect to ethanol. This result is in agreement with the estimated reaction order for ethanol as shown in the power law equation.

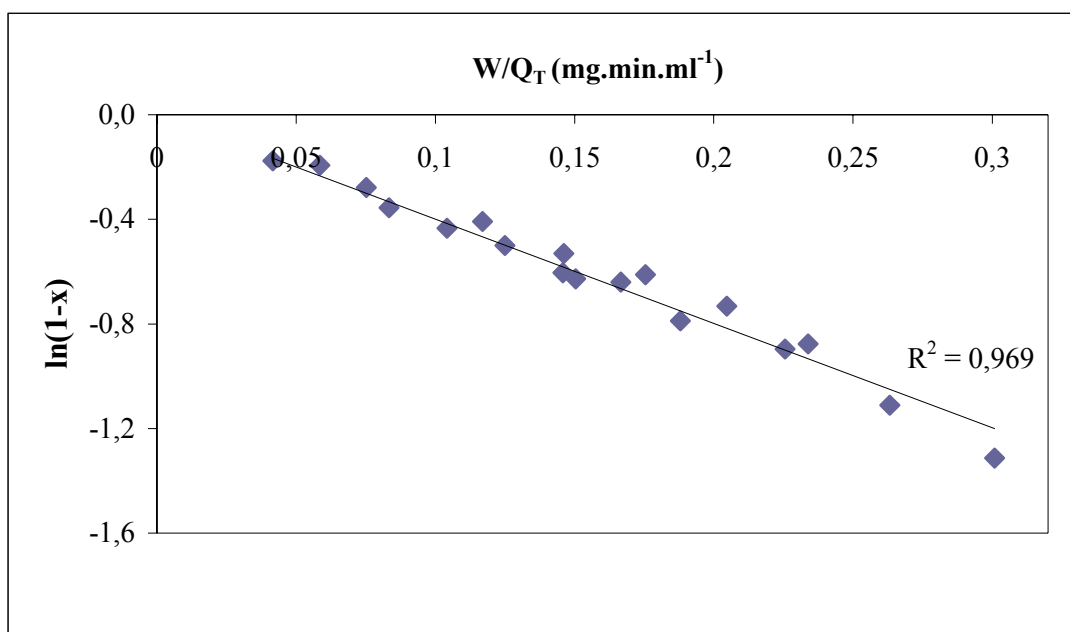


Figure 4.15. Semilog plot of the mole fraction of unreacted ethanol as a function of W/Q_T at 723 K

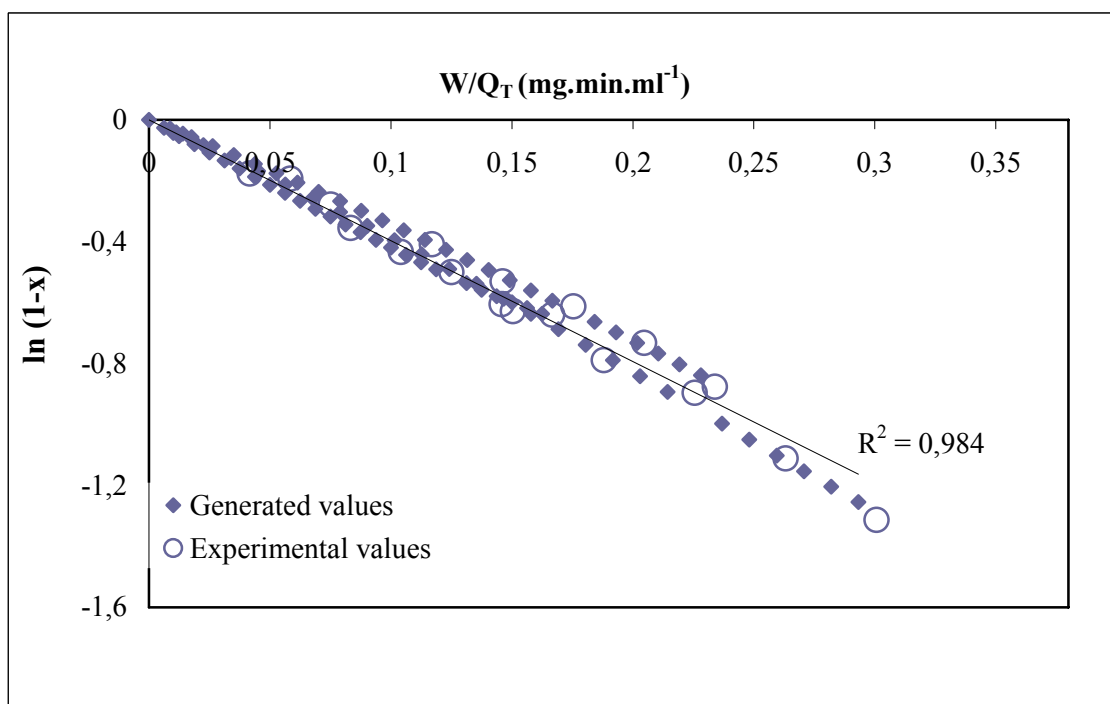


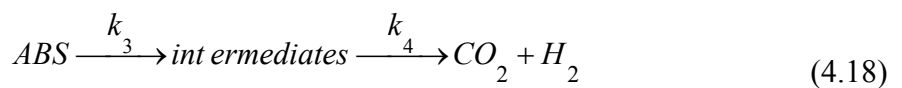
Figure 4.16. Semilog plot of generated the mole fraction of unreacted ethanol as a function of W/Q_T at 723 K

4.3.3. Langmuir–Hinshelwood–Hougen–Watson Kinetics

The rate expression for heterogeneously catalyzed reactions may be stated in the form of a power function or as a LHHW-type (Langmuir–Hinshelwood–Hougen–Watson) equation. The power law expression provides limited insight into the reaction mechanism and may be considered as a limiting case of the LHHW kinetics. The development of LHHW kinetic models requires the assumption of a rate-determining step for each product.

There are different pathways suggested for the ethanol steam reforming. The main reaction mechanism involves dehydrogenation or dehydration reactions. Dehydration reactions produce intermediate products such as ethylene, which is easily transformed into carbon that is deposited on the active phase producing the catalyst poisoning. In the dehydrogenation step ethanol converted to the acetaldehyde which further transformed in to the reforming products. In the present study, the results obtained in Section 4.2 showed that hydrogen, carbon dioxide, carbon monoxide and methane were present in the product distribution.

Vaidya and Rodrigues (2006) proposed that the steam reforming of ethanol occurred via reaction intermediates such as CH_3CHO , C_2H_4 , C_2H_6 , and CH_4 , over the $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst and reported that the formation of these intermediates could be the rate-controlling step. They also proposed the following mechanism by which a complex ABS is formed as a result of the reaction between adsorbed ethanol and water from the gas phase, assuming the formation of adsorbed intermediates by the decomposition of this complex as the rate determining step, and expressed the dependence of the rate on reactant partial pressure in Equation 4.19. Adsorbed water did not participate in the reaction.



where A and B denote ethanol and water, respectively and S denotes an active site.

$$r = \left[\frac{k_1 k_2 P_A P_B}{k_{-1} + k_1 P_A + k_2 P_B + k_1 k_2 P_A P_B / k_3} \right] \quad (4.19)$$

Since the water in far excess and pressure was constant $P_B \approx P_{B0}$ and Equation 4.19 could be expressed in a simple form as

$$r = \frac{k_R P_A P_B}{[1 + b P_A]} \quad (4.20)$$

where k_R and b were defined as follows:

$$k_R = \left[\frac{k_1 k_2 P_{B0}}{k_{-1} + k_2 P_{B0}} \right] ; \quad b = \frac{k_1 + (k_1 k_2 P_{B0} / k_3)}{[k_{-1} + k_2 P_{B0}]} \quad (4.21)$$

When $(b P_A) \ll 1$, Equation 4.20 became

$$r = k_R P_A \quad (4.22)$$

Thus, the results of Vaidya and Rodrigues (2006) study indicated a linear relationship with the ethanol partial pressure. This is in agreement with the results obtained in Section 4.3.2.

In this study, Langmuir-Hinshelwood rate expressions with single and dual site mechanisms and Equation 4.19 proposed by Vaidya and Rodrigues (2006) were used to fit experimental ethanol steam reforming rate data. The rate parameters were estimated with nonlinear least-squares analysis and the Marquardt-Levenberg algorithm by using MATLAB and POLYMATH 5.1 computer software. Models giving either poor correlation coefficients or negative parameter values were rejected during the estimation of the kinetic parameters. Among the mechanisms, rate expressions for dissociative adsorption of

ethanol was not evaluated because of negative parameter values. The values of the parameters for optimal fit determined using non-linear regression and proposed models are given in Table 4.6.

Table 4.6. Langmuir-Hinshelwood rate expressions analyzed for ethanol steam reforming at 723 K

Model No	Proposed Rate Equations	Rate Parameters	σ^2 (mol.g ⁻¹ .h ⁻¹) ²	References
1	$r = \frac{k_1 k_2 P_A P_B}{[k_{-1} + k_1 P_A + k_2 P_B + k_1 k_2 P_A P_B / k_3]}$	$k_1 = 24.1 \text{ atm}^{-1}$ $k_{-1} = 19.3 \text{ atm}^{-1}$ $k_2 = 5.0$ $k_3 = 2.0 \text{ mol.g}^{-1}.\text{h}^{-1}.\text{atm}^{-1}$	0.0015	Vaidya and Rodrigues, 2006
2	$r = \frac{k P_A P_B}{(1 + K_A P_A + K_B P_B)^2}$	$k = 94.8 \text{ mol.g}^{-1}.\text{h}^{-1}.\text{atm}^{-1}$ $K_A = 6.5 \text{ atm}^{-1}$ $K_B = 1.5 \text{ atm}^{-1}$	0.0015	Praharso <i>et al.</i> , 2004
3	$r = \frac{k K_A K_B P_A P_B}{(1 + K_A P_A + K_B P_B)}$	$k = 0.6 \text{ mol.g}^{-1}.\text{h}^{-1}.\text{atm}^{-1}$ $K_A = 36.2 \text{ atm}^{-1}$ $K_B = 6.5 \text{ atm}^{-1}$	0.0012	Fogler, 2005
4	$r = \frac{k K_A K_B P_A P_B}{(1 + K_A P_A + K_B P_B^2)}$	$k = 0.9 \text{ mol.g}^{-1}.\text{h}^{-1}.\text{atm}^{-1}$ $K_A = 15.9 \text{ atm}^{-1}$ $K_B = 4.5 \text{ atm}^{-1}$	0.0012	Acharya <i>et al.</i> , 2006

As reported in Table 4.6, models 1-2 and 3-4 have the same variance of the experimental error (σ^2). Among these models, model I proposed by Vaidya and Rodrigues (2006), model III and power law were compared with the experimental rate data in Figure 4.17 and 4.18. Three models give reasonably good fit to the observed experimental data.

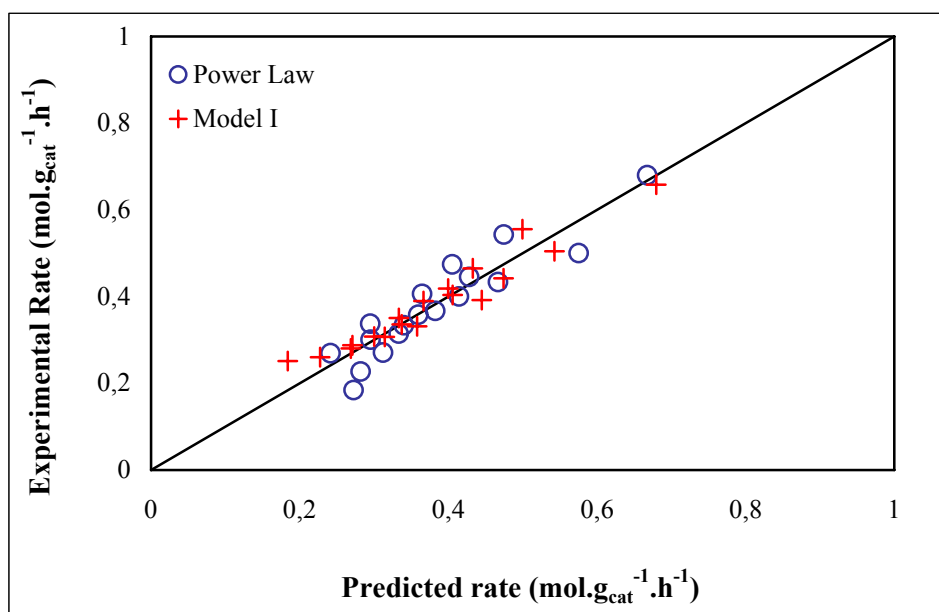


Figure 4.17. Predicted (Eley Rideal Model I and Power law) versus observed rate for ethanol steam reforming

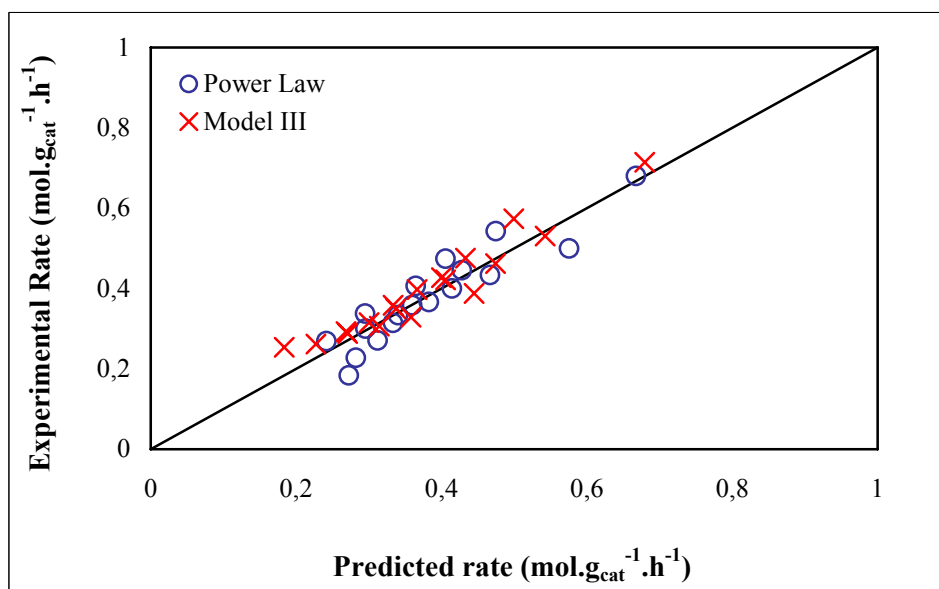


Figure 4.18. Predicted (Langmuir-Hinshelwood Model III and Power law) versus observed rate for ethanol steam reforming

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The kinetics of ethanol steam reforming was studied over bimetallic Pt-Ni/ δ -Al₂O₃ catalysts prepared by sequential incipient-to-wetness impregnation. The first part of the thesis involved parametric study of the bimetallic Pt-Ni/ δ -Al₂O₃ catalysts with different Pt and Ni contents for hydrogen production by ethanol steam reforming. After evaluating the effects of Pt-Ni loadings and temperature on ethanol conversion and product distribution, kinetic studies were carried out at atmospheric pressure and a temperature of 723 K. The experimental rate data were used to estimate the kinetic parameters of power law type and Langmuir-Hinshelwood type rate equations. The major conclusions that can be drawn from this study are given as follows:

- The parametric studies over bimetallic Pt-Ni/ δ -Al₂O₃ catalysts showed that increasing the Pt content increases catalyst stability while increasing the Ni content increases both ethanol and hydrogen production rates, and the catalysts with 15wt.%Ni content give the best catalytic performance.
- The reaction temperature has a remarkable effect on both ethanol conversion and hydrogen production rates, and the most significant increase is observed above 723 K over the 0.3wt.%Pt-15wt.%Ni/ δ -Al₂O₃ catalyst.
- Hydrogen, methane, carbon dioxide and carbon monoxide are the main products in the temperature range studied. At 823 K, hydrogen production rate decreases slightly and carbon monoxide production is favored rather than carbon dioxide together with methane and hydrogen over the catalyst with 0.3wt.%Pt-15wt.%Ni content.
- The results of ethanol steam reforming kinetics over 0.3wt.%Pt-15wt.%Ni/ δ -Al₂O₃ at 723 K showed that the reaction is well described by both a power rate law and a Langmuir-Hinshelwood model and indicated that the model fits reasonably well to the experimental data at all contact-times and conversion levels. The reaction orders with respect to ethanol and steam were found as 1.01 and -0.09, respectively, indicating the mild inhibition effect of steam on the reaction.

5.2. Recommendations

Under the light of the results of the present work, the following are recommended for further studies:

- Kinetic studies may be repeated and improved by performing several experiments at different temperatures to calculate the activation energy of the ethanol steam reforming reaction, and hence, to obtain the effect of temperature on the reaction mechanism over the 0.3wt.%Pt-15wt.%Ni/ δ -Al₂O₃ catalyst.
- Kinetic experiments can be performed at different steam to carbon ratios in order to investigate the reaction rate dependence on steam partial pressure, especially at lower steam to carbon ratios, and hence to propose an LHHW-type kinetic model resting on a more inclusive reaction mechanism.
- Additional kinetic experiments can be conducted by including hydrogen into the feed stream in order to clarify the effect of hydrogen on the reaction mechanism and to obtain rate expressions that are more generally applicable.

APPENDIX A: ADDITIONAL EXPERIMENTAL RATE DATA

Additional kinetic data calculated by differentiation of polynomials obtained from conversion versus space time graphs in Section 4.3 are given below.

Table A.1. Concentrations of C₂H₅OH and H₂O and calculated reaction rates data over 0.3wt.%Pt-15wt.%Ni/ δ -Al₂O₃ for 5.0 vol.% EtOH, T = 723 K

NO	$W / F_{C_2H_5OH_{in}}$ (g.h.mol ⁻¹)	Concentrations (mol.l ⁻¹) 5.0 vol.%		$(-r_{C_2H_5OH})$ (mol.g ⁻¹ .h ⁻¹)
		C ₂ H ₅ OH	H ₂ O	
1	0.05	0.0020	0.0123	0.5190
2	0.08	0.0020	0.0122	0.5112
3	0.10	0.0020	0.0122	0.5060
4	0.15	0.0019	0.0120	0.4929
5	0.20	0.0019	0.0119	0.4799
6	0.25	0.0018	0.0117	0.4668
7	0.30	0.0018	0.0116	0.4537
8	0.33	0.0017	0.0115	0.4450
9	0.35	0.0017	0.0114	0.4407
10	0.40	0.0017	0.0113	0.4276
11	0.45	0.0016	0.0112	0.4146
12	0.50	0.0016	0.0110	0.4015
13	0.55	0.0016	0.0109	0.3884
14	0.60	0.0015	0.0108	0.3754
15	0.65	0.0015	0.0107	0.3623
16	0.67	0.0015	0.0106	0.3580
17	0.70	0.0014	0.0106	0.3493
18	0.75	0.0014	0.0105	0.3362
19	0.80	0.0014	0.0104	0.3231
20	0.83	0.0013	0.0103	0.3144
21	0.85	0.0013	0.0103	0.3101
22	0.90	0.0013	0.0102	0.2970
23	0.95	0.0013	0.0101	0.2840
24	1.00	0.0013	0.0100	0.2709
25	1.05	0.0012	0.0099	0.2578
26	1.10	0.0012	0.0098	0.2448
27	1.15	0.0012	0.0098	0.2317
28	1.17	0.0011	0.0097	0.2274
29	1.20	0.0011	0.0097	0.2187
30	1.25	0.0011	0.0096	0.2056
31	1.30	0.0011	0.0096	0.1925
32	1.33	0.0011	0.0095	0.1838

Table A.2. Concentrations of C_2H_5OH and H_2O and calculated reaction rates over 0.3wt.%Pt-15wt.%Ni/ δ - Al_2O_3 for 7.0 vol. % and 9.0 vol.% EtOH, T = 723 K

NO	$W / F_{C_2H_5OH_{in}}$ (g.h.mol ⁻¹)	Concentrations (mol.l ⁻¹) 7.0 vol. %		$(-r_{C_2H_5OH})$ (mol.g ⁻¹ .h ⁻¹)	Concentrations (mol.l ⁻¹) 9.0 vol. %		$(-r_{C_2H_5OH})$ (mol.g ⁻¹ .h ⁻¹)
		C_2H_5OH	H_2O		C_2H_5OH	H_2O	
1	0.05	0.0028	0.0173	0.5561	0.0036	0.0221	0.7964
2	0.08	0.0028	0.0171	0.5501	0.0035	0.0218	0.7840
3	0.10	0.0028	0.0171	0.5462	0.0035	0.0217	0.7758
4	0.15	0.0027	0.0168	0.5362	0.0033	0.0212	0.7553
5	0.20	0.0026	0.0166	0.5262	0.0032	0.0208	0.7347
6	0.25	0.0025	0.0164	0.5163	0.0030	0.0204	0.7142
7	0.30	0.0025	0.0161	0.5063	0.0029	0.0200	0.6936
8	0.33	0.0024	0.0160	0.4996	0.0028	0.0198	0.6799
9	0.35	0.0024	0.0159	0.4963	0.0028	0.0196	0.6731
10	0.40	0.0023	0.0157	0.4863	0.0027	0.0192	0.6525
11	0.45	0.0022	0.0155	0.4764	0.0025	0.0189	0.6320
12	0.50	0.0022	0.0153	0.4664	0.0024	0.0185	0.6114
13	0.55	0.0021	0.0151	0.4564	0.0023	0.0182	0.5909
14	0.60	0.0020	0.0149	0.4465	0.0022	0.0179	0.5703
15	0.65	0.0020	0.0147	0.4365	0.0021	0.0176	0.5498
16	0.67	0.0019	0.0146	0.4332	0.0020	0.0173	0.5429
17	0.70	0.0019	0.0145	0.4265	0.0020	0.0172	0.5292
18	0.75	0.0018	0.0143	0.4166	0.0019	0.0170	0.5087
19	0.80	0.0018	0.0141	0.4066	0.0018	0.0167	0.4881
20	0.83	0.0017	0.0139	0.3999	0.0017	0.0164	0.474
21	0.85	0.0017	0.0140	0.3966	0.0017	0.0164	0.468
22	0.90	0.0017	0.0138	0.3866	0.0016	0.0161	0.447
23	0.95	0.0016	0.0136	0.3767	0.0015	0.0159	0.426
24	1.00	0.0016	0.0135	0.3667	0.0015	0.0159	0.406
25	1.05	0.0015	0.0133	0.3567	0.0014	0.0154	0.385
26	1.10	0.0015	0.0131	0.3468	0.0013	0.0152	0.365
27	1.15	0.0014	0.0130	0.3368	0.0012	0.0150	0.344
28	1.17	0.0014	0.0130	0.3335	0.0012	0.0150	0.337
29	1.20	0.0014	0.0128	0.3268	0.0012	0.0148	0.324
30	1.25	0.0013	0.0127	0.3169	0.0011	0.0147	0.303
31	1.30	0.0013	0.0126	0.3069	0.0011	0.0145	0.283
32	1.33	0.0012	0.0124	0.3002	0.0010	0.0143	0.269

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