AN EXPERIMENTAL STUDY ON THE EFFECT OF METAL LOADING ON WGS PERFORMANCE OF Au-Re SYSTEM

by

Burcu Yoğurtçu B.S., Chemical Engineering, Yıldız Technical University, 2009

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

Graduate Program in Chemical Engineering Boğaziçi University 2012

to my family

ACKNOWLEDGEMENTS

Firstly, I would like to express my sincere thanks to my thesis supervisor Prof. Ahmet Erhan Aksoylu. His advices helped me to improve my work and his guidance was invaluable throughout my thesis. It was a great honor for me to work with him during my graduate thesis.

I am very grateful to my thesis committee members; Prof. Ramazan Yıldırım and Assoc. Prof. Hasan Bedir for kindly revising and commenting on my thesis.

I wish to express my gratitude to Burcu Selen Çağlayan and Feyza Gökaliler who deserve special thanks for their guidance and help throughout my work.

Very special thanks goes to my friends Melek Selcen Başar, Aybüke Leba and Gülsüm Ersoy for their friendship and endless support throughout my master education without any hesitation.

I also would like to express my gratitude to other members of CATREL group, Ali Uzun, Merve Eropak, Bahadır Kara, Caner Ulguel, İpek Paksoy, Nilay Aktürk, Vasfiye Çimenoğlu, Murat Erol and İrfan Hösükoğlu for their suggestions and friendships. I would also like to thank all my friends in Chemical Engineering Department at Boğaziçi University, especially Tarık Can, Duygu Kocaman, Çağlar Meriçer, Bahar Nalbantoğlu and Mehmet Ünal Güneş.

Cordial thanks are for Bilgi Dedeoğlu, Nurettin Bektaş and Yakup Bal for their technical assistance and help during my thesis.

I would like to express my very great appreciation to my family. They always believed in me, even when I didn't. This thesis would not have been possible without their everlasting support. Finally, I cannot find the right words for the one person who I like to thank the most, my boyfriend Okan Yüzüak for his endless patience, support and encouragement during my thesis study.

Financial support provided by TÜBİTAK through project 111M144, and Boğaziçi University Research Fund through project BAP5570.

ABSTRACT

AN EXPERIMENTAL STUDY ON THE EFFECT OF METAL LOADINGS ON WGS PERFORMANCE OF Au-Re SYSTEM

The aim of the current work is to understand the effect of Au and Re loadings and Au:Re loading ratio on the WGS performance of the Au-Re/CeO₂ system under the flow of realistic feeds. In this experimental work, water-gas shift (WGS) reactions were performed over Au2-Re1/Ceria, Au2-Re0.5/Ceria, Au1-Re1/Ceria and Au0.5-Re0.5/Ceria catalysts which were prepared via rhenium impregnation followed by deposition precipitation of gold. The catalysts were characterized by XRD, XPS and HRTEM-EDS analyses. Besides catalyst composition, temperature, H₂O/CO ratio in the feed were used as experimental parameters. The performance tests were performed in the temperature range of 250-350°C under two different realistic feed compositions. HRTEM-EDS analyzes indicated that gold and rhenium are very well dispersed and both metals have small particle size. It was observed that with the increase in gold loading, CO conversion increased for fixed amount of rhenium. Similarly, catalysts with higher rhenium loading for fixed amount of gold also gave better performance. For the fixed Au:Re loading ratio, increase of metal loading enhances the catalyst performance. The combined evaluation of XPS and performance test results reveals that Ce^{3+} surface concentration and Ce^{3+}/Ce^{4+} surface ratio, which shows the ability to support to metal electron transfer, is dominantly determines performance, and this is more significant especially when the feed has high H₂O/CO ratio. The results showed that for fixed Au loading Ce^{3+}/Ce^{4+} surface ratio and hence the catalyst performance increases with the addition of Re; Au2-Re1/Ceria, which has the highest Ce^{3+}/Ce^{4+} ratio, showed the best performance in terms of CO conversion and the net hydrogen production.

ÖZET

Au-Re SİSTEMİNDE METAL YÜKLEMELERİNİN WGS PERFORMANSINA ETKİSİ ÜZERİNE DENEYSEL ÇALIŞMA

Bu çalışmanın amacı Au ve Re yüklemeleri ve Au:Re yükleme oranlarının gerçeğe uygun beslemelerle gerçekleştirilen WGS performansı üzerindeki etkisini anlamaktır. Bu deneysel çalışmada, su-gaz değişimi (WGS) reaksiyonları renyumun empregnasonu ve altının biriktirmeli çöktürülmesi metoduyla hazırlanan Au2-Re1/Ceria, Au2-Re0.5/Ceria, Au1-Re1/Ceria ve Au0.5-Re0.5/Ceria katalizörleri üzerinde gerçekleştirilmiştir. Bu katalizörler XRD, XPS ve HRTEM-EDS analizleri ile tanımlanmışlardır. Katalizör kompozisyonunun yanı sıra, beslemedeki H₂O/CO oranı da deneysel parametre olarak kullanılmıstır. Performans testleri 250-350 °C aralığında iki farklı gerçeğe uygun besleme kompozisyonu kullanılarak gerçekleştirilmiştir. HRTEM-EDS analizleri altın ve renyumun oldukça iyi dağıldığını ve her ikisinin de küçük parçacık büyüklüğüne sahip olduğunu göstermiştir. Renyum miktarı sabit tutulduğunda, altın yüklemesindeki artışın CO tüketimini yükselttiği gözlemlenmiştir. Benzer şekilde, sabit altın miktarı için de artan renyum yüklemesi daha iyi performans vermiştir. Metal yüklemeleri Au:Re oranı sabit tutularak yükseltildiğinde katalizör performansını arttırmıştır. XPS ve performans test sonuçlarının birlikte değerlendirilmesiyle; taşıyıcıdan metal kısma elektron transferi kabiliyetini gösteren Ce³⁺ yüzey konsantrasyonu ve Ce³⁺/Ce⁴⁺ yüzey oranının baskın şekilde performansı belirlediği, ve bunun yüksek H₂O/CO oranına sahip beslemelerde daha dikkat çekici olduğu ortaya çıkarılmıştır. Sonuçlar, sabit Au yüklemesi için Ce³⁺/Ce⁴⁺ yüzey oranının ve dolayısıyla katalizör performansının Re takviyesiyle arttığını; en yüksek Ce³⁺/Ce⁴⁺ oranına sahip olan Au2-Re1/Ceria katalizörünün CO tüketimi ve net hidrojen üretiminde en ivi performansı verdiğini göstermiştir.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	iv
ABSTRACT	vi
ÖZET	vii
LIST OF FIGURES	X
LIST OF TABLES	xii
LIST OF SYMBOLS	xiii
LIST OF ACRONYMS/ABBREVIATIONS	xiv
1. INTRODUCTION	1
2. LITERATURE SURVEY	3
2.1. Fuel Processor-Fuel Cell System	3
2.2. Reactions in a Fuel Processor	4
2.2.1. Reforming	4
2.2.2. Water Gas Shift	5
2.2.3. Preferential Carbon Monoxide Oxidation	5
2.3. Water Gas Shift Reaction and Catalysts	6
3. EXPERIMENTAL WORK	15
3.1. Materials	15
3.1.1. Chemicals	15
3.1.2. Gases and Liquids	15
3.2. Experimental Systems	16
3.2.1. Catalyst Preparation Systems	17
3.2.2. Catalyst Characterization Systems	18
3.2.2.1. X-Ray Diffraction	18
3.2.2.2. High Resolution Transmission Electron Microscopy	18
3.2.2.3. X-ray Photoelectron Spectroscopy	18
3.2.3 Catalytic Reaction System for WGS Reaction	19
3.2.4. Product Analysis System for WGS Reaction	21
3.3. Catalyst Preparation and Pretreatment	21
3.4. Reaction Tests	23

4. RESULTS AND DISCUSSIONS	24
4.1. Catalyst Characterization	24
4.2. Catalytic Activity Tests	29
5. CONCLUSIONS AND RECOMMENDATIONS	36
5.1. Conclusions	36
5.2. Recommendations	36
REFERENCES	38

LIST OF FIGURES

Figure 3.1.	Schematic diagram of the impregnation system.	17
Figure 3.2.	Schematic diagram of the deposition precipitation system	18
Figure 3.3.	Schematic diagram of the microreactor flow system	20
Figure 4.1.	XRD spectrum of ceria support.	25
Figure 4.2.	XP spectrum of Ce 3d region of catalyst samples.	26
Figure 4.3.	HRTEM images of catalysts.	28
Figure 4.4.	HRTEM images and corresponding surface EDS of the differential parts of Au2-Re1/Ceria sample area image involves both Au and Re particles.	28
Figure 4.5.	HRTEM images and corresponding surface EDS of the differential parts of Au2-Re1/Ceria sample area image involves only Au particles.	29
Figure 4.6.	Stability of Au2-Re1/Ceria catalyst in terms of CO conversion	30
Figure 4.7.	Stability of Au2-Re1/Ceria catalyst in terms of net H ₂ production	31
Figure 4.8.	Effect of Au-Re loading on CO conversion and net H ₂ production for Feed#1.	32
Figure 4.9.	Effect of Au-Re loading on CO conversion and net H ₂ production for Feed#2.	33

Figure 4.10.	Effect of H ₂ O/CO feed ratio on CO conversion.	34
Figure 4.11.	The effect of T on H_2/CO ratio in the product stream for Feed#1	35
Figure 4.12.	The effect of T on H_2/CO ratio in the product stream for Feed#2	35

LIST OF TABLES

Table 3.1.	Chemicals used in catalyst preparation.	15
Table 3.2.	Specifications and applications of the liquids used.	16
Table 3.3.	Specifications and applications of the gases used.	16
Table 3.4.	Reactant and product gas analysis conditions.	21
Table 3.5.	List of Au-Re/Ceria bimetallic catalysts.	22
Table 3.6.	Realistic feed compositions used in the current study	23
Table 4.1.	Ceria lattice constants and crystallite sizes of reduced samples	26
Table 4.2.	Ce ³⁺ and Ce ⁴⁺ percentages of the catalyst samples	27

LIST OF SYMBOLS

A	Lattice constant
D	Spacing between adjacent lattice planes
h, k, l	Miler indices
K	Shape factor
Μ	Molarity
Р	Density
Р	Pressure
R	Universal gas constant
Т	Crystallite size
Т	Temperature
V	Volume
β	Line broadeninig
λ	X-ray wavelength
θ	Bragg angle

LIST OF ACRONYMS/ABBREVIATIONS

DI	Deionized
EDS	Energy-dispersive X-ray Spectroscopy
FP	Fuel Processor
FTIR	Fourier Transform Infrared Spectroscopy
FWHM	Half the Maximum Intensity
GC	Gas Chromatography
GHSV	Gas Hourly Space Velocity
HPLC	High Performance Liquid Chromatography
HRTEM	High Resolution Transmission Electron Microscopy
LT-WGS	Low Temperature Water Gas Shift
MW	Molecular Weight
PEM-FC	Proton Exchange Membrane Fuel Cell
TCD	Thermal Conductivity Detector
WGS	Water Gas Shift
XPS	X-ray Photoelectron Microscopy
XRD	X-ray Diffraction

1. INTRODUCTION

Fuel Processor-Fuel Cell (FP-FC) systems have a crucial role to play in future sustainable energy generation, especially for decentralized, small-scale (2-5 kW range) stationary energy production (Çağlayan and Aksoylu, 2008; O'Connell *et al.*, 2012). The proton exchange membrane fuel cell (PEM-FC) is one of the most popular fuel cell systems which offers series of advantages such as compactness, low operating temperature, suitability to discontinuous operation, and long stack life, however it requires hydrogen with a low CO concentration (Tsang *et al.*, 2008; Yu *et al.*, 2006).

A typical fuel processor is a complex device composed of the reformer itself and carbon monoxide clean-up section in the case of PEM-FCs applications (O'Connell *et al.*, 2011). In a fuel processing system, the main part is the fuel reformer, which converts the fuels into hydrogen rich gas (Leung *et al.*, 2009). The water-gas shift unit, which follows reforming reactor, reduces the CO concentration from 10-15% to 1%. The preferential oxidation unit reduces CO content of hydrogen stream down below 50 ppm, which can be tolerated by PEM type FCs (Flytzani-Stephanopoulos *et al.*, 2005). Otherwise, the presence of CO in the reformate causes irreversible poisoning of the catalyst in the fuel cell electrodes, which will not only lead to cell voltage losses, but also limit the life of the fuel cell (Song *et al.*, 2005).

The water gas shift reaction is the key catalytic stage and considered as the main CO cleanup step in a fuel processor. The reaction is as follows:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H = -41.4 \, kJ/mol \tag{1.1}$$

In conventional systems, reduction of CO content in WGS unit is achieved by sequential processing the reformate, through a high temperature shift (350-450 °C) and low temperature water gas shift (180-250 °C) reactors, in order to reach near-to-equilibrium conversion levels with high reaction rates (Baier and Kolb, 2007). Although commercial catalysts are excellent to be used in large-scale industrial plants, they have some disadvantages such as thermodynamic limitations at high temperatures, sensitivity to

air/oxygen, the need of long pre-conditioning, and slow kinetics at low temperatures. Hence, conventional high temperature (Fe-Cr oxide) and low temperature (Cu-Zn-Al₂O₃) WGS catalysts cannot be used in fuel cell applications. Favorable WGS catalyst for fuel cell applications should be active, thermally stable, resistant to poisoning, and highly selective for a wide range of H₂O/CO ratios (Çağlayan and Aksoylu, 2008).

The aim of the current work is to understand the effect of Au and Re loadings and Au:Re loading ratio on the WGS performance of the Au-Re/CeO₂ system under the flow of realistic feeds. Au2-Re1/Ceria, Au2-Re0.5/Ceria, Au1-Re1/Ceria and Au0.5-Re0.5/Ceria catalysts were prepared via rhenium impregnation followed by deposition precipitation of gold. Besides catalyst composition, temperature, H₂O/CO ratio in the feed were used as experimental parameters. The catalysts were characterized by XRD, XPS and HRTEM-EDS analyses and their performance was tested in the temperature range of 250-350°C under two different realistic feed compositions.

Chapter 2 involves a literature survey containing a brief introduction to fuel cell-fuel processor systems, water gas shift reaction and the catalysts employed in water gas shift reaction, especially on gold over ceria systems. Experimental work is presented in detail on Chapter 3. The results obtained in the experiments discussed on Chapter 4 and the conclusions drawn from the study are given on Chapter 5.

2. LITERATURE SURVEY

2.1. Fuel Processor-Fuel Cell System

The increasing attention to the emissions from the conventional energy production routes and the internal combustion engines evokes fuel cells technology as clean alternative for reducing emissions from energy production units. Owing to their advantages such as high power density, low operating temperature, mechanical robustness, low weight, compactness, long stack life, fast start-up and dynamic response characteristics; the proton exchange membrane fuel cells (PEM-FCs) are considered as the most suitable electrochemical devices for vehicles application. Though hydrogen is considered as the best fuel for PEMFC, there is still no economically feasible solution available fot its storage, either as a liquid, as pressurized gas, or in the form of metal hydrides. Fuel processors which produce hydrogen *in-situ* from various hydrocarbon fuels offer an attractive alternative to hydrogen storage.

In a reformer unit converting hydrocarbons to hydrogen, carbon dioxide and carbon monoxide are also produced. However, in fuel cell applications, the presence of CO in the reformate causes irreversible poisoning of the catalyst in the fuel cell electrodes, which will not only lead to cell voltage losses, but also limit the life of the fuel cell (Song *et al., 2005*). This is the reason why a fuel processor has three catalytic units, namely reformer for hydrogen production, WGS unit for increasing hydrogen concentration while decreasing CO through utilizing hydrogen from water, and PROX unit for eliminating CO. The water-gas shift unit, which follows reforming reactor, reduces the CO concentration from 10-15% to 1%. The preferential oxidation unit reduces CO content of hydrogen stream down below 50 ppm, which can be tolerated by PEM type FCs (Flytzani-Stephanopoulos *et al., 2005*).

2.2. Reactions in a Fuel Processor

A typical fuel processor utilizes reforming, water-gas shift (WGS) and preferential carbon monoxide oxidation reactions in series in order to produce hydrogen from hydrocarbons.

2.2.1. Reforming

In a fuel processing system, the main part is the fuel reformer, which involves the conversion of hydrocarbons into hydrogen rich gas. There are three common methods of reforming: steam reforming, partial oxidation and autothermal reforming. Steam reforming is an extensively used method in industrial hydrogen production. Steam reforming is an endothermic reaction of steam with the fuel in the presence of a catalyst to produce H_2 and carbon monoxide.

$$C_n H_m + n H_2 O \rightarrow n C O + \left(\frac{1}{2}m + n\right) H_2$$
 (2.1)

Another option for fuel reforming is partial oxidation, which is an exothermic process and occurs when the feed reacts directly with air or pure oxygen at carefully balanced oxygen to fuel ratios.

$$C_n H_m + \frac{n}{2}O_2 \to nCO + \frac{m}{2}H_2 \tag{2.2}$$

Autothermal reforming combines endothermic steam reforming and exothermic total/partial oxidation reactions to maintain the required temperature without using external heat source; there, the heat produced by exothermic total/partial oxidation is used as the heat source for endothermic steam reforming.

$$C_n H_m + x O_2 + (2n - 2x)H_2 O \rightarrow nCO_2 + (2n - 2x + \frac{m}{2})H_2$$
 (2.3)

2.2.2. Water Gas Shift

The water gas shift reaction is the key catalytic stage and considered as the main CO cleanup step in a fuel processor. In the WGS reaction, carbon monoxide is converted to carbon dioxide by water vapor. The reaction is as follows:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H = -41.4 \ kj/mol$$
 (2.4)

Water gas shift reaction and its catalysts will be discussed in more detail in Section 2.3.

2.2.3. Preferential Carbon Monoxide Oxidation

The gas mixture that leaves water gas shift reactors still has a CO concentration that will cause irreversible poisoning of the catalyst in the fuel cell electrodes, which will not only lead to cell voltage losses, but also limit the life of the fuel cell (Song *et al., 2005*). The preferential oxidation unit reduces CO content of hydrogen stream down below 50 ppm, which can be tolerated by PEM type FCs (Flytzani-Stephanopoulos *et al., 2005*). The preferential oxidation term refers to selective oxidation of CO under the presence of high hydrogen concentration, usually between 45-60% by mole.

$$CO + \frac{1}{2}O_2 \to CO_2 \tag{2.5}$$

2.3. Water Gas Shift Reaction and Its Catalysts

The water gas shift reaction is a slightly exothermic reaction which is considered as the key catalytic stage, and the main CO cleanup step in a fuel processor. As WGS is an equilibrium reaction, in conventional systems; reduction of CO in WGS unit is achieved by sequential processing of the reformate, through a high temperature shift (350-450 °C) and low temperature water gas shift (180-250 °C) reactors, in order to reach near-to-equilibrium conversion levels with high reaction rates (Baier and Kolb, 2007).

Although commercial catalysts are excellent to be used in large-scale industrial plants, they have some disadvantages such as thermodynamic limitations at high temperatures, sensitivity to air/oxygen, the need of long pre-conditioning, and slow kinetics at low temperatures. Hence, conventional high temperature (Fe_3O_4/Cr_2O_3) and low temperature ($Cu/ZnO/Al_2O_3$) WGS catalysts cannot be used in fuel cell applications. WGS catalysts for combined 'fuel processor-fuel cell' applications should be sufficiently active at relatively low temperatures, thermally stable, and resistant to coke deposition. Furthermore, they should be highly selective at high H₂O/CO feed ratios with no side reactions, such as methanation or hydrogen oxidation that would consume valuable hydrogen (Kondarides *et al.*, 2007) (Çağlayan and Aksoylu, 2008). Many catalytic systems have been investigated so far; however, an effective commercial catalyst, which guarantees high CO conversion levels without consuming hydrogen present in the reformer effluent fed to the WGS unit, is still not available.

The catalyst performance not only depends on the active metals, but also on the nature of the support used. Ceria, alumina, zirconia, titania, thoria and magnesia are oxides which have been widely tested in WGS reaction. Many precious metals such as Pt, Pd, Rh, Ru and Au have been reported to show high WGS reaction rate when they are supported on ceria (Hengrasmee *et al.*, 2011). Au and Pt group metals have been extensively studied in order to overcome the relatively weak performance specs of the commercial WGS catalysts. Moreover, they are generally superior to base-metal catalysts for the long time use. While platinum catalysts are generally more active than ruthenium, rhodium and palladium; gold is superior to platinum in terms of catalytic performance (Fraga *et al.*, 2008).

Gold-based catalysts have received enormous interest since the discovery by Haruta *et al.* of high catalytic activity and selectivity for a number of reactions when prepared in an appropriate manner (Holliday *et al.*, 2005). Gold exhibits surprisingly high catalytic activity when deposited as nano-particles on metal oxides, while it has long been regarded as a poorly active catalyst (Galletti *et al.*, 2011). Gold catalysts have high activity at low temperatures; hence they have received much interest during last 10 years (Park *et al.*, 2009; Naito *et al.*, 2005). Furthermore, gold has been regarded as a potentially useful element for CO abatement in WGS reaction at low temperature, considering its relatively lower price when compared to other noble metals such as platinum and rhodium (Galletti *et al.*, 2011). Moreover, the activity of well-prepared gold catalysts are significantly more active than platinum catalysts (Burch, 2006).

The catalytic activity and selectivity of the Au-based catalysts is strongly affected by the state and the structure of the carrier. In order to provide desirable contact between Au and the carrier, and for achieving good catalytic performance, the selection of an efficient carrier is thus a crucial parameter. One of the most studied noble metal based systems for water gas shift reaction is gold supported on reducible oxides. A comparative study on the effect of the activation temperature and the nature of the support for gold supported WGS was performed by Zanella and co-workers. The behavior of gold supported on reducible (TiO₂ and CeO₂) and non-reducible (SiO₂ and Al₂O₃) oxides was studied in order to determine the role of the support on the catalytic activity of gold particles. The results revealed that the activity of Au on TiO₂ and CeO₂ was much higher than Au supported on Al₂O₃ and SiO₂ due to the fast conversion of formate species in Au/TiO₂ and Au/CeO₂. In addition, Au/ SiO₂ catalyst was found practically inactive (Zanella *et al.*, 2007).

Another study that investigates gold catalysts promoted by CeO₂ and (α - γ)-Al₂O₃, is published by Galletti and co-workers. Au-based catalysts supported on alumina and ceria were prepared by deposition-precipitation method at different pH and molarity of the precursor solution. By considering the catalytic activity in terms of CO conversion for the WGS reaction, it was revealed that catalysts on alumina were not so active, despite a satisfactory gold deposition on the support; while ceria-based catalysts displayed better performances. Under the flow of a feed containing only H₂O and CO, with H₂O/CO ratio equal to 4, catalysts prepared at different pH and molarity (M=1x10⁻³) approached the equilibrium WGS conditions, especially the catalysts for which the preparation pH used was 8.5. The performance worsened by increasing or decreasing pH. Despite the satisfactory results with ideal feed conditions, catalytic activity tests conducted with a realistic reformate feed showed fairly low CO conversions. Moreover, HRTEM results indicated that catalyst with smaller Au cluster size gave better performance (Galletti *et al.*, 2011).

In case of noble metals or transition metals, the use of a high surface area mesoporous oxide support, rather than a commercial low surface area support, has some advantages in terms of the catalytic performance. The usage of mesoporous support would led to well dispersed and stable metal particles on the surface upon calcination and reduction, hence an improved catalytic performance can be observed. Idakiev et al. used mesoporous titania as a support for gold catalysts prepared by deposition precipitation method in their study, which investigate the influence of gold content and particle size on the catalytic activity. It has been reported that different loading, average particle size and dispersion of the gold profoundly influences the catalytic activity. Higher activity was observed for the sample which has lower average gold particle size and lower gold content. This is probably due to a better ratio between surface gold active sites and surface area of mesoporous titania (Idakiev et al., 2004). Later, Idakiev and co-workers analyzed the effect of CeO₂ to addition to mesoporous titania. It was concluded that ceria addition decreases the degree of crystallinity of mesoporous titania and its particle size. In addition, owing to the interaction of ceria with mesoporous titania, the reducibility of the support is affected strongly. The researchers concluded that the gold catalyst over ceria modified mesoporous titania is highly active catalyst for WGS reaction (Idakiev et al., 2007).

In the biphasic catalysts as the metal supported on oxides, many studies have been conducted to understand the role and the synergetic effect of the two phases in the catalytic reaction. One catalyst receiving much attention as a potential candidate is cerium oxide loaded with metals promoting the support reducibility (Naito *et al.*, 2005). Because of its ability to undergo rapid reduction and oxidation cycles, ceria is a highly promising support. It can also be used as a stabilizer for other metal oxide supports in order to maintain a high dispersion of the catalytic components and promoting WGS reaction (Guliants *et al.*, 2010). While the importance of ceria has been known for many years, the need for active

water-gas shift catalysts for nontraditional applications, such as fuel processing, has led to renewed interest in studying ceria-supported metals.

Support composition strongly affects the activity of WGS reaction. In recent years noble metal catalysts supported on CeO₂ and Ce-Zr mixed oxides have been intensely investigated as a promising next-generation WGS catalysts, which exhibited much faster high-temperature kinetics than conventional ferrochrome catalysts (Bi et al., 2009). It is possible to design very active gold catalysts by improving the oxygen storage capacity of ceria through incorporating it with other elements; CeO₂ can store and release oxygen to undergo oxidation-reduction cycles and promote catalytic activity for the water gas shift reaction, especially in case of metal-modified ceria (Hengrasmee et al., 2011). Flytzani-Stephanopoulos et al., also investigated the effect of preparation method on the enhancement of cerium oxide reducibility by gold. Nanoscale Au-(La doped) ceria catalysts was prepared by three methods: Deposition precipitation, coprecipitation and gelation methods. It was revealed that the presence of gold profoundly enhances the oxygen storage capacity of ceria, while the enhancement of ceria reducibility by gold is independent from the catalyst preparation method. In addition, a uniform gold distribution was observed for the sample which was prepared by deposition precipitation method, while relatively large large gold particles were observed for coprecipitated samples (Flytzani-Stephanopoulos et al., 2003).

A very active Au/Ce_xZr_{1-x}O₂ composition for LT-WGS reaction (LT: low temperature) has been reported by Thompsett and co-workers. It was found that Au supported on a CeZrO₄ prepared by a modified deposition-precipitation method has higher activity for the water-gas shift reaction than Au supported on CeO₂, TiO₂ and ZrO₂ prepared in a similar manner (Thompsett *et al.*, 2007). Surface area of ZrO₂ increases with the addition of CeO₂ due to the fact that cerium inhibits the crystallite growing and assists the production of smaller particles of monoclinic structure. Apesteguía and co-workers also tested the activity of Pt/CeO₂, Pt/ZrO₂ and Pt/Ce_xZr_{1-x}O₂ catalysts at the temperature of 250 °C. It was revealed that when the conversion of CO was greater or equal to 0.5 and the activity of Pt/Ce_xZr_{1-x}O₂ catalyst was seen to be greater than Pt/CeO₂ as Zr addition to CeO₂ increases both the surface area and reducibility of ceria. In contrast, the water gas shift activity on Pt/Ce_{0.25}Zr_{0.75}O₂ was lower than that of Pt/CeO₂ since the stability of the

formate species increases on Zr-rich Pt/Ce_xZr_{1-x}O₂ samples. It was indicated that lowering the formate decomposition rate would be rate-limiting in the WGS associative mechanism (Apesteguia *et al.*, 2011).

Tabakova *et al.* also investigated the impact of support composition on the performance in WGS reaction over Au/CeO₂-Fe₂O₃ catalysts. The gold particles were prepared via deposition-precipitation method on pure ceria, iron oxide and mixed Ce-Fe composite oxides. The following activity order Au/CeO₂ > Au/Ce50Fe50 > Au/Ce75Fe25 > Au/Ce25Fe75 > Au/Fe₂O₃ was observed. This tendency can be attributed to significant difference in gold particle size and in the ability of the supports to assist formation of oxygen vacancies (Tabakova *et al.*, 2011).

Guliants *et al.* studied a number of bimetallic $Cu_yNi_{20-y}/CeLaO_x$ catalysts and compared monometallic Cu and Ni catalysts supported on La-doped ceria. Supported Cu, Ni and bimetallic Cu-Ni catalysts were tested for the WGS reaction in 150-400 °C temperature range. The effect of the Cu/Ni ratio on the physicochemical properties and the catalytic performance was studied. It was concluded that Cu addition to Ni/CeLaO_x decreases the methane formation during WGS reaction and Ni addition to Cu/CeLaO_x increases the WGS activity (Guliants *et al.*, 2010).

It has been reported that some CeO₂-containing catalysts deactivate, and many factors may affect the extent of deactivation. Liu *et al.* used several techniques together in order to understand deactivation of Pt/CeO₂ water-gas shift catalysts under conditions simulating system/reactor shutdown. The reason for deactivation was seen to be the formation of carbonates on the catalyst surface which caused to shutdown, while Pt metal sintering was not found as a contributing factor to deactivation. Regeneration by air treatment removes the carbonates and restores activity. Ruettinger *et al.* suggested using ZrO₂-CeO₂ composites in order to minimize the deactivation problem. When Pt/CeO₂-ZrO₂ water gas shift catalyst was used, substantial aging was observed under both steady state operation at relatively low temperature (200-250 °C) and high temperature stress (up to 450 °C), whereas almost no reduction in activity was observed by simulating start-stop cycling, unlike with Pt/CeO₂. Moreover, the data indicated that the aging is mainly due to sintering of Pt particles and these materials are not appropriate for practical use. Lefferts *et*

al. also investigated deactivation scenarios for different supports and described possible ways to regenerate and stabilize catalyst activity. The activity of Pt/TiO_2 was seen to be better than Pt/CeO_2 . It was revealed that carbonate promoters did not affect the activity of Pt/TiO_2 due to the instability of carbonates on titania under WGS reaction conditions. Also the stability of Pt/TiO_2 can be increased by the addition of Re in order to prevent sintering. (Ruettinger *et al.*, 2006) (Liu *et al.*, 2005) (Lefferts *et al.*, 2007).

Cerium oxide has high oxygen mobility where its electronic conductivity and oxygen vacancy can be easily improved by using different promoters (Tsang, 2008). Studies on ceria supported precious metals such as Pd, Pt and Rh, have confirmed that these materials are effective catalysts for the WGS reaction (Andreeva et al., 2002). Song et al. used ceriasupported Pd-Cu & Pt-Cu bimetallic catalysts in order to clarify the characteristics of oxygen enhancement on WGS reaction. It was indicated that oxygen addition partially oxidizes chemisorbed CO leading to vacant sites for H₂O adsorption and the reaction. In terms of H₂ yield and CO conversion at temperatures lower than 300 °C, Pt-Cu and Pd-Cu showed better characteristics than monometallic catalysts owing to the strong interaction between metals, which provide more resistant catalysts toward oxidation (Song et al., 2011). Tsang et al. tested bimetallic Au-M (M=Pt,Pd) on ceria catalysts for low temperature WGS reaction. (Au-Pt)/Ceria and (Au-Pd)/Ceria catalysts exhibited higher WGS activity than that of the monometallic promoters. Tsang and co-workers proposed that the role of gold containing promoter is altering the local band structure of ceria to facilitate its redox properties at low temperatures (Tsang et al., 2008). They claimed that the role of the gold containing promoter is to alter the local band structure of ceria facilitating its redox properties at low temperature.

Another studies investigating the effect Re addition to the ceria supported catalyst, were conducted by Hengrasmee and her colleagues. Hengrasmee et al. studied the effect of Re addition on the activities of both Co/CeO_2 and Ni/CeO_2 catalysts for water gas shift reaction. The catalyst were prepared via incipient wetness impregnation technique and characterized by several standard methods. The conclusions attained from the studies confirm that Re influences the catalyst performance in several ways. It was revealed that addition of rhenium increases the reducibility on the surface ceria and facilitates the redox

process at the surface. It also increases the metal active sites and weakens the active metaladsorbate bonds (Hengrasmee *et al.*, 2011).

Radhakrishnan *et al.* also investigated the impact of using rhenium promoter for ceria-zirconia supported platinum catalysts on the WGS reaction. It was found that the reaction rate of the supported platinum catalyst was doubled by using rhenium as the promoter and long term stability for about 500 h was achieved. The optimal platinum to rhenium ratio was proposed as 2:1 by weight with the nominal platinum loading of 2 wt. %. In addition, the introduction of the rhenium promoter lowered the amount of total noble metal was required to handle the targeted 6000 ppm carbon monoxide concentration in a realistic feed coming from the reformer (Radhakrishnan *et al.*,2006).

Presence of divalent elements also lowers the necessary loading levels of precious metals and the rare earths, which are becoming increasingly expensive. Davis *et al.* revealed the effects of Ca-doping on Pt/CeO₂ catalysts and observed improved LT-WGS rates over Ca-doped Pt/CeO₂. They concluded that divalent elements weaken the Ce-O bond and hence enhance both O-mobility and CeO₂ reducibility (Davis *et al.*, 2011).

The activity and stability of ceria-supported catalysts strongly depend on preparation conditions. Hence, understanding the effect of preparation conditions, gaining insights into mechanism and limiting steps for WGS reaction are important for obtaining catalysts with improved performance (Gorte *et al.*, 2004). Specchia *et al.* tested the catalytic activity of Rh-based catalysts supported on CeO₂ with the aim of evaluating the influence of the preparation method on the catalytic activity in WGS reaction. CeO₂ was prepared by two methods which are solution combustion synthesis and hard template. For the feed having 5% CO and 20% H₂O, the conversion of CO was started at slightly lower temperatures over the catalysts prepared by the hard template method, however CH₄ outlet concentrations were found to be higher than the catalysts prepared by the solution combustion synthesis method. Moreover, the catalysts prepared with solution combustion method, showed the best performance weight space velocity is lowered (Specchia *et al.*, 2011). (Gorte *et al.*, 2004).

There are various parameters affecting the catalytic activity of gold catalysts, mainly the preparation method. The preparation technique strongly influences catalytic activity due to the large differences in size of gold particles and the availability of active gold sites at the surface. Tabakova and co-workers have compared the structural and catalytic properties of Au/ceria catalysts prepared by deposition-precipitation and modified deposition-precipitation method in low temperature WGS reaction. The results indicated that the deposition-precipitation is a more promising technique than modified depositionprecipitation technique because large portion of gold occur in the form of nanoparticles on the surface, as confirmed by XPS and FTIR data (Tabakova *et al.*, 2004).

The correlation between gold loading and catalytic activity was investigated by Andreeva and co-workers. Ceria supported gold catalysts, especially the ones with higher gold content, exhibited a high and stable activity for the WGS reaction. It was indicated that the high and stable activity of the catalysts is probably due to the high stability of the gold dispersion. When the effects of space velocity on CO conversion was studied, it was observed that CO conversion noticeably decreases with the increasing space velocity. In addition catalytic activity of the catalysts slightly increased as a function of H_2O/CO (Andreeva *et al.*, 2002).

Tabakova *et al.* conducted a FTIR study for understanding the chemisorption and reactivity of the molecules use the information gained in designing highly active and stable gold-based catalysts. (Tabakova *et al.*, 2003). The FTIR results indicated that gold is covered by oxygen atoms, and causes a strong modification of the ceria surface properties. More coordinatively unsaturated sites appear on the surface due to this modification. The reduction of the catalyst in the presence of hydrogen leads negatively charged gold sites and oxygen vacancies at the surface. In addition, CO adsorption on gold nanoparticles increases after the reduction. During the reaction, the adsorption of CO occurs on the gold particles, while the dissociation of steam on the ceria. Therefore, the WGS reaction proceeds at the metal support interface, which plays a crucial role in clarifying the noticeable high stability of Au/CeO₂ catalysts (Tabakova *et al.*, 2003).

The studies on gold-based catalysts bimetallic catalysts received great attention due to their extraordinary activities. Suo *et al.* investigated a bimetallic structure with gold and

other metals (Ni, Cu, Ag, Pt and Pd) on ceria support. The catalytic activity of the catalysts studied was found to be related to the metal added. It was revealed that Au-Pt/CeO₂ had the highest activity at 78% conversion level. The benefits of using Pt and Au, such as reduction of ceria to Ce^{3+} , as well as the creation of oxygen vacancies which makes the average size of ceria smaller (Suo *et al.*, 2010). Another study focuses on the effects of doping different metals (Al and Sm) on gold supported on ceria catalysts was conducted by Andreeva and co-workers. The results attained from this study confirm that the Sm and Al dopants increase the oxygen mobility, and improve the stability of the catalysts through preventing the gold and ceria particles from agglomeration (Andreeva *et al.*, 2010).

While many research groups have reported that Re can improve the activity of many reaction when it is used as a second metal, Çağlayan and Aksoylu was the first group that conducted a study in case of ceria supported Au-Re catalysts in WGS reaction. Çağlayan and Aksoylu investigated water gas shift activity under ideal feed conditions on ceria supported gold catalysts promoted by rhenium, by using the effect of temperature, rhenium incorporation, metal addition sequence, GHSV and H₂O/CO ratio as the test parameters. Test results showed that rhenium increases steam tolerance of the catalysts, hence highest activity was observed on a novel Au-Re/ceria bimetallic catalyst, especially at high H₂O/CO feed ratios. The application sequence of rhenium impregnation and gold deposition precipitation causes pronounced changes in catalytic properties. Higher dispersion and CO conversion was obtained when gold deposition precipitation applied on impregnated Re/Ceria catalysts, while poor WGS activity was observed for the catalysts which were Re impregnated before gold deposition precipitation. This is probably due to the blockage of active sites (Çağlayan and Aksoylu, 2011).

3. EXPERIMENTAL WORK

3.1. Materials

3.1.1. Chemicals

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

Table 3.1. Chemical	s used in o	catalyst pro	eparation (all	l specifications:	research	grade).	•
---------------------	-------------	--------------	----------------	-------------------	----------	---------	---

Chemicals	Formula	Source	Molecular Weight (g/mol)
Ammonium carbonate	CH ₆ N ₂ O ₂ .CH ₅ NO ₃	Merck	157.13
Ammonium perrhenate	NH ₄ ReO ₄	Aldrich	268.24
Cerium (III) nitrate hexahydrate	Ce(NO ₃) ₃ .6H ₂ O	Merck	434.23
Sodium carbonate	Na ₂ CO ₃	Merck	105.99
Tatrachloroauric (III) acid trihydrate	AuCl ₄ H.3H ₂ O	Merck	393.83

3.1.2. Gases and Liquids

All of the gases used in this research were supplied by the Linde Group. The specifications and applications of the liquids and gases in this study are listed in Table 3.2. and Table 3.3.

Table 3.2. Specification and application of the liquid used.

Liquid	Specification	Application	
Water	De-ionized	Aqueous solutions, Reactant	

Table 3.3. Specifications and application area of the gases used.

Gas/Standard	Specification	Application
Argon	99.998%	Inert, GC Carrier Gas
Carbon dioxide	99 995%	Reactant, GC
	<i>,,,,,,,,,,,</i> ,,,,,,,,,,,,,,,,,,,,,,,,,	calibration
Carbon monoxide	99 999%	Reactant, GC
	<i><i>yyyyyyy</i></i>	calibration
Dry air	99 998%	Calcination, GC 6-way
Diyun	<i>уу.уу</i> био	pneumatic valve
Helium	99.999%	Inert, GC Carrier Gas
Hydrogen	99 990%	Reactant, Reduction,
inguiogen	<i>,,,,,</i> ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	GC calibration
Nitrogen	99.998%	Inert, GC calibration

3.2. Experimental Systems

There are three main groups of experimental systems used in this study:

- (i) Catalyst Preparation Systems: These are the systems used to prepare the support and to carry out impregnation and deposition precipitation steps of catalyst preparation.
- (ii) Catalyst Characterization Systems: These systems were used to analyze the structural properties of the catalyst samples.
- (iii) Catalytic Reaction System: This catalytic reaction system was used for determining the catalytic activity, selectivity and stability. The continuous flow microreactor

system consists of a feed section including mass flow controllers, HPLC pump and a mixing zone; a reaction section including a temperature controlled oven, and an analysis section consisting of two gas chromatographs that are connected on-line to the microreactor flow system.

3.2.1. Catalyst Preparation Systems

The impregnation system (Figure 3.1) consists of a Retsch UR1 ultrasonic mixer, a vacuum pump, a büchner flask and a MasterFlex computerized-drive peristaltic pump. The system used for deposition precipitation method (Figure 3.2) includes a Julabo water bath, a 400 ml beaker, a Heidolph impeller and a Mettler Toledo pH-meter.



Figure 3.1. Schematic diagram of the impregnation system(a) Ultrasonic mixer, (b) Büchner flask, (c) Vacuum pump, (d) Peristaltic pump,(e) Reactant storage tank and (f) Silicone tubing.



Figure 3.2. Schematic diagram of the deposition precipitation system (a) Water bath, (b) Beaker, (c) Impeller and (d) pH-meter.

3.2.2. Catalyst Characterization Systems

<u>3.2.2.1. X-Ray Diffraction (XRD).</u> In order to identify the crystalline phases of the catalyst samples and calculating their particle sizes, a Rigaku D/MAX-Ultima+/PC X-ray diffraction equipment having an X-ray generator with Cu target and scan speed of 2°/min was used. The experiments were performed at the Advanced Technologies Research and Development Center of Bogazici University.

<u>3.2.2.2. High Resolution Transmission Electron Microscopy (HR-TEM).</u> HR-TEM analyses were carried out using JEOL 2100 LaB_6 HRTEM operating at 200 kV in order to obtain information on the microstructural characterization of the catalyst surface and the surface variation upon reduction. The tests were conducted at the Institute of Materials at TUBITAK-MAM.

<u>3.2.2.3. X-ray Photoelectron Spectroscopy (XPS).</u> The extent of electronic interaction between metal components of the freshly reduced catalyst samples was examined through determination the amounts of metallic phases by X-ray photoelectron spectroscopy (XPS). The analyses were performed at the Middle East Technical University Central Laboratory using PHI 5000 XPS spectrometer equipped with a hemispherical electron analyzer and monochromatic Al anode.

3.2.3. Catalytic Reaction System for WGS Reaction

The catalytic reaction system was designed and constructed in the Catalysis and Reaction Engineering Laboratory of Chemical Engineering Department, Boğaziçi University, and involves feed, reaction and product analysis sections.

Feed preparation section, which is stationed before the reactor, consists of mass flow control systems, 1/4", 1/8" and 1/16" stainless steel tubes and fittings for feeding liquid water and gaseous species, i.e. hydrogen, nitrogen, carbon dioxide and carbon monoxide. The reactant gases were supplied by pressurized gas cylinders with an optimum pressure of 1.5 bar. Water is fed to the system with an Agilent 1100 series HPLC pump while the flow rates of the gases were controlled by Brooks Instrument mass flow controllers. The set of flow rate values were adjusted by the Brooks Instrument 0154 series control box. On-off valves were placed in front of the mass flow controllers to protect them from possible back-pressure fluctuations. Each gas was fed from its independent line, in order to adjust desired feed ratios and evaluate the flow of individual species. The system configuration enables diverting the flow direction of feed gases before entering the reactor via using a three way valve in order to protect gas chromatographs from steam.

The liquid water was introduced into the reaction system at constant flow rates using an Agilent 1100 series HPLC pump. The 1/16" stainless steel tubing, through which water was allowed to flow and the line going to reactor after the on-off valve, including the reactant mixing zone (the transfer line), were kept about at 130 °C using a 1 m Cole-Parmer heating tape for preventing condensation. The temperature level of the transfer line was controlled by an Omron E5AN.

The reactants, metered and mixed in the feed section, were allowed to flow through the reaction section. This section was composed of a 45 cm \times 20 cm \times 20 cm furnace whose temperature was controlled by ± 0.1 K through using a Eurotherm 3216P programmable temperature controller connected to a K type sheathed thermocouple, having the down-flow, 56.5 cm long, 1/4" OD, stainless steel tubular microreactor inside. Silane treated glass wool was placed to the center of the reactor in order to hold the catalyst. 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 stable temperature profile. The steam in the product flow was removed by two cold traps which were placed after the reactor. The line between the reactor and cold traps was kept at about 130 °C to prevent steam to condense along the stainless steel tubing (Çağlayan, 2011).



Figure 3.3. Schematic diagram of the microreactor flow system (a) Mass flow controller, (b) On-off valve, (c) Three-way valve and (d) Mixing zone.

3.2.4. Product Analysis System for WGS reaction

Two Agilent Technologies 6850 gas chromatographs equipped with Porapak Q and Molecular Sieve 5A columns, and a Thermal Conductivity Detector (TCD) were used to detect feed and dry product streams. The data used for reporting the catalyst performance were 1 h time-on-stream data. Analysis conditions are given below in Table 3.4.

CC	Agilent Technologies	Agilent Technologies
GC	6850-GC1	6850-GC2
Detector type	TCD	TCD
Column temperature, °C	80	40
Inlet temperature, °C	65	65
Detector temperature, °C	200	200
Carrier gas	Helium	Argon
Carrier gas flow rate, ml/min	20	20
Column packing material	Porapac Q	Molecular Sieve 5A
Column tubing material	Stainless steel	Stainless steel
Column length & ID	2m x 3 mm	2m x 3 mm
Sample loop	1 ml	1 ml

Table 3.4. Reactant and product gas analysis conditions.

Before proceeding with the experiments, the gas chromatographs were calibrated by injecting known values of the gases to be analyzed under the conditions given in Table 3.4. Using this procedure, volume versus peak area curves were obtained for each gas and the corresponding calibration factors were determined by linear regression (Çağlayan, 2011).

3.3. Catalyst Preparation and Pretreatment

Ceria support was prepared from cerium (III) nitrate hexahydrate precursor, by homogeneous precipitation method. The pH of the solution was controlled by Na₂CO₃ solution in order to adjust the pH to 8. The suspension was then allowed to mix for an hour in a water bath at 60 °C under controlled temperature and pH. A thoroughly stirred mixture

was then filtered by using Watman filter paper and washed with deionized water, and then dried overnight at 105 °C and calcined for 4 hours at 400 °C (Çağlayan, 2011).

Re addition to ceria support was conducted via incipient to wetness impregnation method in the system described in Figure 3.1 by using aqueous solution of ammonium perrhenate. The ceria support was placed in a Buchner flask and kept under vacuum during the process. The support was mixed ultrasonically for 25 min. before impregnating the aqueous solution. The precursor solution was impregnated on the support by using Masterlex computerized-drive peristaltic pump at a rate of 0.5 ml/min. The resulting slurry was mixed ultrasonically in order to obtain uniform distribution of the precursor solution on the ceria support. After 1.5 h, the resulting slurry was dried overnight (Çağlayan, 2011).

Deposition precipitation technique was used to obtain highly dispersed gold particles on the Re impregnated ceria supports. The Re impregnated support was put in a beaker along with DI water at a pH of 8.0-8.5 by adding aqueous solution of ammonium carbonate. Tetrachloro auric (IV) acid was dissolved in DI water and added dropwise under vigorous stirring. The resulting precipitate was aged for 1 h, filtered and washed with DI water at 65 °C. The filtrate was allowed to dry overnight at 75 °C under vacuum and calcined at air in a muffle furnace at 400 °C for 4 h (Çağlayan, 2011).

All catalysts tested in this study are prepared in the sequence mentioned above. The list of gold and rhenium loadings on ceria supports are shown in Table 3.5. Before the reaction tests were performed, the catalyst samples were reduced *in situ* under 5% hydrogen and 95% nitrogen flow feed for 1 h at 200 °C.

Denoted as	Au wt. %	Re wt. %
Au2-Re1/Ceria	2	1
Au1-Re1/Ceria	1	1
Au2-Re0.5/Ceria	2	0.5
Au0.5-Re0.5/Ceria	0.5	0.5

Table 3.5. List of Au-Re/Ceria bimetallic catalysts.

3.4. Reaction Tests

The WGS performance of Au-Re/Ceria catalysts (given in Table 3.5) in a realistic feed composition (i.e. feed having CO, H_2 , H_2O , CO_2) was investigated at 250, 300 and 350 °C for two different feed compositions (given in Table 3.6). Each experiment was conducted over 75 mg freshly reduced catalyst with 120000 ml/g.h GHSV.

Table 3.6. Realistic feed compositions used in the current study.

Feed #	H ₂ O/CO	CO%	H ₂ O %	H ₂ %	CO ₂ %	N ₂ %
1	16.24	2.1	34.1	23.7	12.3	27.8
2	6.67	4.9	32.7	30	10.4	22

After reduction, the catalyst bed heated to the reaction temperature, and nitrogen gas trapped in the reactor while the reactants with specified compositions were bypassed for 1.5 hour in order to obtain steady state gas composition.

4. RESULTS AND DISCUSSIONS

The WGS catalysts designed to be used in fuel processor of the combined FP-PEMFC system must reach high CO conversion activity (ie. near to equilibrium level) for the feed stream having composition of the typical reformer product -which is rich in H₂ and has CO₂, H₂O, CO and N₂, ie. real feed- without leading any decrease in the H₂ concentration due to unwanted reactions like methanation. Though there are many research papers reporting WGS performance data under ideal feed conditions, the publications reporting WGS data obtained with real feed are very rare and none of those report H₂ concentration at the WGS product and/or change in H₂ content through comparing WGS feed and product streams. The aim of the current work is to understand the effect of Au and Re loadings and Au:Re loading ratio on the WGS performance of the Au-Re/CeO₂ system under the flow of representative realistic feeds. Besides catalyst composition, temperature, H₂O/CO ratio in the feed were used as experimental parameters. The catalysts were characterized by XRD, XPS and HRTEM-EDS analyses, and their performance was tested in the temperature range of 250-350 °C under two different realistic feed compositions.

4.1. Catalyst Characterization

X-ray diffraction (XRD) measurements were performed using Cu K_{α} irradiation at a scan rate 2 degree at a minute. XRD spectrum of ceria support of all Au-Re/CeO₂ system tested are presented in Figure 4.1 as an example. XRD spectra revealed that ceria samples obtained in this study exhibit cubic fluorite structure. In addition, ceria retained its fluorite structure after rhenium impregnation and deposition precipitation of gold. No detectable diffraction peaks of gold and rhenium crystallites were observed probably because of high dispersion of metals with small particle sizes. Table 4.1 shows the lattice constants and crystallite sizes for ceria determined from (111) diffraction peaks of XRD spectrum through using Scherrer equation,

$$\tau = \frac{K \lambda}{\beta \cos \theta} \tag{4.1}$$

where K is the shape factor, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) in radians, θ is the Bragg angle and τ is the mean size of the crystallites. The lattice constants calculated via using the following equation,

$$a = d\sqrt{h^2 + k^2 + l^2} \tag{4.2}$$

Ceria lattice constants and crystallite sizes of reduced catalysts are presented in Table 4.1.

Results indicated that rhenium and gold addition to ceria support did not influence the ceria lattice constant to a great extent. On the other hand, it is observed that the ceria crystallite size of the with higher Re content (Au2-Re1/Ceria) is calculated 4.5% smaller than the one with lower Re loading (Au2-Re0.5/Ceria). XRD results revealed that there is a strong interaction between both Au-CeO_x and Re-CeO_x enough to leading changes in Ce crystallite size.



Figure 4.1. XRD spectrum of ceria support.

Sample	Lattice constant, a (nm)	Crystallite size, τ (nm)
Ceria	0.538	11.97
Au2-Re1/Ceria	0.538	11.95
Au1-Re1/Ceria	0.540	11.87
Au2-Re0.5/Ceria	0.539	12.49
Au0.5-Re0.5/Ceria	0.539	13.00

Table 4.1. Ceria lattice constants and crystallite sizes of reduced samples.

Ceria exhibits unique redox properties which can be analyzed by X-ray photoelectron spectroscopy (XPS). XPS analyzes performed to characterize the oxidation state of cerium in cerium oxides; the difference between Ce^{3+} and Ce^{4+} can be illustrated from the Ce 3d signal shapes. It is observed that the XP spectrum of Ce 3d region of catalyst samples were in accordance with the literature. The XPS binding energies of Ce 3d lines are presented in Figure 4.2.



Figure 4.2. XP spectrum of Ce 3d region of catalyst samples *: Ce³⁺, **: Ce⁴⁺, (a) Au2-Re0.5/Ceria, (b) Au1-Re1/Ceria, (c) Au0.5Re0.5/Ceria and (d) Au2-Re1/Ceria.

The Ce 3d lines have 10 peaks suggesting the presence of both Ce^{3+} (*) and Ce^{4+} (**). After peak deconvolution via using the XPSPEAK 4.1 program, it was revealed that the Ce³⁺ concentration seems to be relatively higher in the case of the catalyst which exhibit high WGS activity. This result is in accordance with the explanation that Ce³⁺ plays a crucial role in increasing electron transfer ability from the support to metallic sites, hence resulting in higher catalytic activity (Çağlayan and Aksoylu, 2011), which is also the case in the current study. The Ce³⁺ and Ce⁴⁺ percentages of the catalysts samples are presented in Table 4.2.

Sample	Ce^{3+} (%)	Ce^{4+} (%)
Au2-Re1/Ceria	63.00	37.00
Au1-Re1/Ceria	37.36	62.64
Au2-Re0.5/Ceria	52.51	47.49
Au0.5-Re0.5/Ceria	20.63	79.37

Table 4.2. Ce^{3+} and Ce^{4+} percentages of the catalyst samples.

HR-TEM analyses were carried out to obtain information on the microstructural properties of the reduced catalyst samples. The HRTEM images of the Au0.5-Re0.5/Ceria and Au2-Re1/Ceria samples clearly showed that gold and Re particles are well dispersed on the CeO_x support; Figure 4.3 shows selected images of the same magnification showing the high dispersion. The Au2-Re1/Ceria sample studied further by HRTEM. Two selected images from different regions of the sample and the corresponding surface analytical analysis results by EDS are given in Figure 4.4 and Figure 4.5. Figure 4.4 clearly shows the highly dispersed Au-Re sites. Figure 4.5, the area which lacks Re sites, revealed that gold sites are formed as small clusters with different crystallite faces; however Re may form as very small agglomerations (Figure 4.4).



Figure 4.3. HRTEM images of catalysts (a) Au0.5-Re0.5/Ceria and (b) Au2-Re1/Ceria.



Figure 4.4. HRTEM images and corresponding surface EDS of the differential parts of Au2-Re1/Ceria sample: area image involves both Au and Re particles.



Figure 4.5. HRTEM images and corresponding surface EDS of the differential parts of Au2-Re1/Ceria sample: area image involves only Au particles.

4.2. Catalytic Activity Tests

Activity and stability characteristics of the catalysts (given in Table 3.5) investigated at 250, 300, 350 °C under atmospheric pressure using 75 mg freshly reduced catalyst with 120000 ml/g.h GHSV. The experiments were performed under flow of two different realistic feeds (given in Table 3.6) including H_2 , CO, CO₂ and balance N₂, and varied mainly in terms of H_2O/CO ratio. The concentrations of the gases in the product and feed stream were determined by two gas chromatographs. During the experiments, methane formation was not observed. CO conversion was taken as a measure of catalytic activity, stability and net H_2 production was also used as an indication of selectivity. CO conversion, net H_2 production and the amount of water vapor in the feed stream were evaluated by using the following formulas:

$$C0 \ conversion \ (\%) = \frac{[C0]_{in} - [C0]_{out}}{[C0]_{in}} \times 100$$
(4.3)

net
$$H_2$$
 production (%) = $\frac{[H_2]_{out} - [H_2]_{in}}{[H_2]_{in}} \times 100$ (4.4)

$$V_{steam(H_2O)} = \frac{V_{liquid (H_2O)} \times \rho_{H_2O} \times R \times T}{MW_{H_2O} \times P}$$
(4.5)

where $\rho = 1000 \text{ g.L}^{-1}$; P=1 atm; R=0.082 L.atm.mol⁻¹.K⁻¹; T=298 K and MW_{H2O}=18 gmol⁻¹.

In the present study, the performance test conditions were designed to investigate the effects of the Au-Re loading, H_2O/CO feed ratio and reaction temperature on the WGS activity of the bimetallic Au-Re/Ceria catalysts.

All of the catalysts was tested for 3 h and it was revealed that none of them showed stability loss. The catalytic stability of Au2-Re1/Ceria catalyst, which showed the maximum conversion during the performance studies, was tested for 3 h at 350 °C. The test was carried out with a feed stream consisting of 4.9% CO, 30% H₂, 32.7% H₂O and balance N₂. The stability of the catalyst is shown in Figure 4.6 and Figure 4.7 in terms of CO conversion and net H₂ production, respectively.



Figure 4.6. Stability of Au2-Re1/Ceria catalyst in terms of CO conversion. (4.9% CO, 30% H₂, 32.7% H₂O, 22% N₂; 350°C)



Figure 4.7. Stability of Au2-Re1/Ceria catalyst in terms of net H_2 production. (4.9% CO, 30% H_2 , 32.7% H_2O , 22% N_2 ; 350°C)

It was observed that the catalyst with higher gold content give both better CO conversion and net H₂ production for the fixed rhenium loading. In addition, catalysts with higher rhenium loading for fixed amount of gold also give better performance. As it also demonstrated by XPS results (given in Table 4.2), addition of both Au and Re improves the reducibility of ceria. The evaluation of performance and XPS test results in a combined fashion clearly shows that there is a direct relation between the activity of the catalysts and their Ce³⁺ surface concentration (in other words Ce³⁺/Ce⁴⁺ concentration ratio). There, Ce³⁺ enhance the activity via increasing the ability of electron transfer from the support to metallic sites. Additionally, it should be worth mentioning that for the fixed Au loading (ie. Au2-Re1/Ceria and Au2-Re0.5/Ceria), increase in Re loading led to an increase in Ce³⁺/Ce⁴⁺ ratio, which enhance the catalysts at 250, 300 and 350 °C are presented in the following figures (Figure 4.8, Figure 4.9) as a function of temperature. The feed compositions used in the figures are Feed#1 and Feed#2 is given in Table 3.6, respectively. The equilibrium conversion of CO is also displayed for comparison.



Figure 4.8. Effect of Au-Re loading on (a) CO conversion and (b) net H₂ production for Feed#1 (♦Au2-Re1/Ceria; ■Au1-Re1/Ceria; ▲Au2-Re0.5/Ceria; x Au0.5-Re0.5/Ceria; * Equilibrium).



Figure 4.9. Effect of Au-Re loading on (a) CO conversion and (b) net H₂ production for Feed#2 (♦Au2-Re1/Ceria; ■Au1-Re1/Ceria; ▲Au2-Re0.5/Ceria; x Au0.5-Re0.5/Ceria; * Equilibrium).

CO conversions for the two feeds having different H_2O/CO ratios give nearly the same activities at 250°C because of slow reaction kinetics at low temperatures (Figure 4.10). At 300°C, high steam content of Feed#1 suppressed reverse WGS reaction, hence higher CO conversion was obtained. It is worth to mention that, at 300 °C net H_2 production was lower when compared to high CO conversion for Feed#1, which is probably due to oxidation of excess of hydrogen. In addition, no methane formation was observed during the experiments. As indicated by peak CO conversion levels at 300 °C, the suppression of reverse WGS by higher steam content of Feed#1 and the consequent high CO conversion loses its dominance at 350 °C, most probably due to moderately exothermic nature of the reversible WGS reaction.



Figure 4.10. Effect of H_2O/CO feed ratio on CO conversion (F1: Feed#1 $H_2O/CO=16.24$; F2: Feed#2 $H_2O/CO=6.67$).

It is evident from the plots of net H₂ production vs. temperature that H₂ consumption was not observed for most of the catalysts. In the case of Feed#1, net H₂ production was observed at 300 and 350 °C almost for all catalysts except Au0.5-Re0.5/Ceria. Note that with its lowest Ce^{3+}/Ce^{4+} ratio indicated by XPS results, Au0.5-Re0.5/Ceria has very limited electron transfer ability from support to metal sites; this limits the facilitation of water during WGS reaction, and severely effect the catalyst performance for the feeds with

high H₂O/CO ratio, like Feed#1. As can be expected from CO conversion and net H₂ production levels, H₂/CO product ratio makes a peak for Feed#1 (Figure 4.11) at 300 °C for all catalysts except Au0.5-Re0.5/Ceria. This peak observed at 300 °C for H₂O/CO ratio seems shift to higher temperatures when the H₂O/CO ratio in the feed decreases, as can be observed form Figure 4.12 showing H₂/CO product ratio obtained for Feed#2. Furthermore, all of the catalyst consumed the H₂ at 250 °C. When the experiments were performed with lower steam/carbon monoxide ratio (H₂O/CO=6.67), net H₂ production level follows an increasing trend as a function of temperature for the range tested, and net H₂ consumption was observed only for Au0.5-Re0.5/Ceria at 250 °C.



Figure 4.11. The effect of T on H_2/CO ratio in the product stream for Feed#1.



Figure 4.12. The effect of T on H_2/CO ratio in the product stream for Feed#2.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The purpose of this experimental study was to investigate the effects of Au:Re loading, H_2O/CO feed ratio and temperature on WGS reaction under realistic feed compositions. The conclusions from this study were summarized as follows:

- As gold loading increases, CO conversion increases for fixed amount of rhenium.
- Catalysts with higher rhenium loading for fixed amount of gold gave better performance.
- HRTEM-EDS analyzes indicated that gold and rhenium are very well dispersed and both metals have small particle size.
- The combined evaluation of XPS and performance test results reveals that Ce³⁺ surface concentration and Ce³⁺/Ce⁴⁺ surface ratio, which shows the ability to support to metal electron transfer, is dominantly determines performance, and this is more significant especially when the feed has high H₂O/CO ratio.
- For fixed Au loading Ce³⁺/Ce⁴⁺ surface ratio and hence the catalyst performance increases with the addition of Re.
- For the fixed Au:Re loading ratio, increase of metal loading enhances the catalyst performance.
- Addition of both Au and Re improves the reducibility of ceria, as demonstrated by XPS analysis.

5.2. Recommendations

Considering the resulst of this experimental study, following ideas are suggested for future studies which will use Au-Re/Ceria system as a WGS catalyst:

- Performing stability tests for a long period to investigate the stability of the catalyst, although loss of activity was not observed during the experiments for 3 hours.
- Studying wide range of steam/carbon monoxide ratios in order to understand the effect of steam content, more accurately.

REFERENCES

- Andreeva, D., V. Idakiev, T. Tabakova, L. Ilieva, P. Falaras, A. Bourlinos, and A. Travlos, 2002, "Low Temperature Water Gas Shift Reaction over Au/CeO₂ Catalysts", *Catalysis Today*, Vol. 72, pp. 51-57.
- Andreeva, D., M. Kantcheva, I. Ivanov, L. Ilieva, J. W. Sobczak, and W. Lisowski, 2010, "Gold-supported on Ceria Doped by Me³⁺ (Me=Al and Sm) for Water Gas Shift Reaction: Influence of Dopant and Preparation Method", *Catalysis Today*, Vol. 158, pp. 69-77.
- Azzam, K. G., I. V. Babich, K. Seshan, and L. Lefferts, 2007, "A Bifunctional Catalyst for the Single Stage Water Gas Shift Reaction in Fuel Cell Applications. Part II. Roles of the Support and Promoter on Catalyst Activity and Stability", *Journal of Catalysis*, Vol. 251, pp. 163-171.
- Baier, T. and G. Kolb, 2007, "Temperature Control of the Water Gas Shift Reaction in Micro-structured Reactors", *Chemical Engineering Science*, Vol. 62, pp. 4602-4611.
- Bi, Y., H. Xu, W. Li, and A. Goldbach, 2009, "Water Gas Shift Reaction in a Pd Membrane Reactor over Pt/Ce_{0.6}Zr_{0.4}O₂ Catalysts", *International Journal of Hydrogen Energy*, Vol. 34, pp. 2965-2971.
- Bickford, E. S., S. Velu and C. Song, 2005, "Nano-structured CeO₂ Supported Cu-Pd Bimetallic Catalysts for the Oxygen-assisted Water Gas Shift Reaction", *Catalysis Today*, Vol. 99, pp. 347-357.
- Burch, R., 2006, "Gold Catalysts for Pure Hydrogen Production in the Water Gas Shift Reaction: Activity, Structure and Reaction Mechanism", *Physical Chemistry Chemical Physics*, Vol. 8, pp. 5483-5500.

- Chayakul, K., T. Srithanratana, and S. Hengrasmee, 2011, "Catalytic Activities of Re-Ni/CeO₂ Bimetallic Catalysts for Water Gas Shift Reaction", *Catalysis Today*, Vol. 175, pp. 420-429.
- Chayakul, K., T. Srithanratana, and S. Hengrasmee, 2011, "Effect of Re Addition on the Activities of Co/CeO₂ Catalysts for Water Gas Shift Reaction", *Journal of Molecular Catalysis*, Vol. 340, pp. 39-47.
- Chen, Y., C. Yu, Y. Liu, and C. Lee, 2006, "Start-up Strategies of an Experimental Fuel Processor", *Journal of Power Sources*, Vol. 160, pp. 1275-1286.
- Corti, C. W., R. J. Holliday, and D. T. Thompson, 2005, "Commercial Aspects of Gold Catalysis", *Applied Catalysis A: General*, Vol. 291, pp. 253-261.
- Çağlayan, B. S. and A. E. Aksoylu, 2009, "Water Gas Shift Reaction over Bimetallic Pt-Ni/Al₂O₃ Catalysts", *Turkish Journal of Chemistry*, Vol. 33, pp. 249-256.
- Çağlayan, B. S. and A. E. Aksoylu, 2011, "Water Gas Shift Activity of Ceria Supported Au-Re Catalysts", *Catalysis Communications*, Vol. 12, pp. 1206-1211.
- Çağlayan, B.S., Design and Development of Catalysts & Adsorbents for CO_x Free H₂ Production, Ph.D. Thesis, Boğaziçi University, 2011.
- Farias, A. M. D., P. Bargiela, M. G. C. Rocha, and M. A. Fraga, 2008, "Vanadiumpromoted Pt/CeO₂ Catalysts for Water Gas Shift Reaction", *Journal of Catalysis*, Vol. 260, pp. 93-102.
- Fonseca, A. A., J. M. Fisher, D. Özkaya, M. D. Shannon, and D. Thompsett, 2007, "Ceriazirconia Supported Au as Highly Active Low Temperature Water Gas Shift Catalysts", *Topics in Catalysis*, Vol. 44, pp. 223-235.

- Fu, Q., S. Kudriavtseva, H. Saltsburg, and M. Flytzani-Stephanopoulos, 2003, "Gold-ceria Catalysts for Low Temperature Water Gas Shift Reaction", *Chemical Engineering Journal*, Vol. 93, pp. 41-53.
- Fu, Q., W. Deng, H. Saltsburg, and M. Flytzani-Stephanopoulos, 2005, "Activity and Stability of Low-content Gold-cerium Oxide Catalysts for the Water Gas Shift Reaction", *Applied Catalysis B: Environmental*, Vol. 56, pp. 57-68.
- Galletti, C., P. Djinovic, S. Specchia, J. Batista, J. Levec, A. Pintar, and V. Specchia, 2011,
 "Influence of the Preparation Method on the Performance of Rh Catalysts on CeO₂ for WGS Reaction", *Catalysis Today*, Vol. 176, pp. 336-339.
- Hilaire, S., X. Wang, T. Luo, R. J. Gorte, and J. Wagner, 2004, "A Comparative Study of Water Gas Shift Reaction over Ceria-supported Metallic Catalysts", *Applied Catalysis A: General*, Vol. 258, pp. 271-276.
- Hurtado-Juan, M., C. M. Y. Yeung, and S. C. Tsang, 2008, "A Study of Co-precipitated Bimetallic Gold Catalysts for Water Gas Shift Reaction", *Catalysis Communications*, Vol. 9, pp. 1551-1557.
- Idakiev, V., T. Tabakova, Z. Y. Yuan, and B. L. Su, 2004, "Gold Catalysts Supported on Mesoporous Titania for Low Temperature Water Gas Shift Reaction", *Applied Catalysis A: General*, Vol. 270, pp. 135-141.
- Idakiev, V., T. Tabakova, K. Tenchev, Z. Yuan, T. Ren, and B. Su, 2007, "Gold Nanoparticles Supported on Ceria-modified Mesoporous Titania as Highly Active Catalysts for Low Temperature Water Gas Shift Reaction", *Catalysis Today*, Vol. 128, pp. 223-229.
- Kim, Y. T., E. D. Park, H. C. Lee, D. Lee, and K. H. Lee, 2009, "Water Gas Shift Reaction over Supported Pt-CeO_x Catalysts", *Applied Catalysis B: Environmental*, Vol. 90, pp. 45-54.

- Kugai, J., J. T. Miller, N. Guo, and C. Song, 2011, "Oxygen-enhanced Water Gas Shift on Ceria-supported Pd-Cu and Pt-Cu Bimetallic Catalysts", *Journal of Catalysis*, Vol. 277, pp. 46-53.
- Lenite, B. A., C. Galletti, and S. Specchia, 2011, "Studies on Au Catalysts for Water Gas Shift Reaction", *International Journal of Hydrogen Energy*, Vol. 36, pp. 7750-7758.
- Lin, J., P. Biswas, V. V. Guliants, and S. Misture, 2010, "Hydrogen Production by Water Gas Shift Reaction over Bimetallic Cu-Ni Catalysts Supported on La-doped Mesoporous Ceria", *Applied Catalysis A: General*, Vol. 387, pp. 87-94.
- Linganiso, L. Z., G. Jacobs, K. G. Azzam, U. M. Graham, B. H. Davis, D. C. Cronauer, A. J. Kropf, and C. L. Marshall, 2011, "Low Temperature Water Gas Shift: Strategy to Lower Pt Loading by Doping Ceria with Ca²⁺ Improves Formate Mobility/WGS Rate by Increasing Surface O-mobility", *Applied Catalysis A: General*, Vol. 394, pp. 105-116.
- Liu, X., W. Ruettinger, X. Xu, and R. Farrauto, 2005, "Deactivation of Pt/CeO₂ Water Gas Shift Catalysts due to Shutdown/startup Modes for Fuel Cell Applications", *Applied Catalysis B: Environmental*, Vol. 56, pp. 69-75.
- O'Connell, M., G. Kolb, K. P. Schelhaas, M. Wichert, D. Tiemann, H. Pennemann, and R. Zapf, 2012, "Towards Mass Production of Micro-structured Fuel Processors for Application in Future Distributed Energy Generation Systems: A Review of Recent Progress at IMM", *Chemical Engineering Research and Design*, Vol. 90, pp. 11-18.
- Panagiotopouolu, P., J. Papavasiliou, G. Avgouropoulos, T. Ioannides, and D. I. Kondarides, 2007, "Water Gas Shift Activity of Doped Pt/CeO₂ Catalysts", *Chemical Engineering Journal*, Vol. 134, pp. 16-22.
- Radhakrishnan, R., R. R. Willigan, Z. Dardas, and T. H. Vanderspurt, 2006, "Water Gas Shift Activity and Kinetics of Pt/Re Catalysts Supported on Ceria-zirconia Oxides", *Applied Catalysis B: Environmental*, Vol. 66, pp. 23-28.

- Ruettinger, W., X. Liu, and R. J. Farrauto, 2006, "Mechanism of Aging for a Pt/CeO₂-ZrO₂
 Water Gas Shift Catalysts", *Applied Catalysis B: Environmental*, Vol. 65, pp. 135-141.
- Sandoval, A., A. Gomez-Cortes, R. Zanella, G. Diaz, and J. M. Saniger, 2007, "Gold Nanoparticles: Support Effects for the WGS Reaction", *Journal of Molecular Catalysis A: Chemical*, Vol. 278, pp. 200-208.
- Sato, Y., K. Terada, S. Hasegawa, T. Miyao, and S. Naito, 2005, "Mechanistic Study of Water Gas Shift Reaction over TiO₂ Supported Pt-Re and Pd-Re Catalysts", *Applied Catalysis A: General*, Vol. 296, pp. 80-89.
- Tabakova, T., F. Boccuzzi, M. Manzoli, and D. Andreeva, 2003, "FTIR Study of Low Temperature Water Gas Shift Reaction on Gold/ceria Catalyst", *Applied Catalysis A: General*, Vol. 252, pp. 385-397.
- Tabakova, T., F. Boccuzzi, M. Manzoli, J. W. Sobczak, V. Idakiev, and D. Andreeva, 2004, "Effect of Synthesis Procedure on the Low Temperature WGS Activity of Au/ceria Catalysts", *Applied Catalysis B: Environmental*, Vol. 49, pp. 73-81.
- Tabakova, T., M. Manzoli, D. Panevai F. Boccuzzi, V. Idakiev, and I. Mitov, 2011, "COfree Hydrogen Production over Au/CeO₂-Fe₂O₃ Catalysts: Part II. Impact of the Support Composition on the Performance in the Water Gas Shift Reaction", *Applied Catalysis B: Environmental*, Vol. 101, pp. 266-274.
- Vignatti, C. I., M. S. Avila, C. R. Apesteguia, and T. F. Garetto, 2011, "Study of the Water Gas Shift Reaction over Pt Supported on CeO₂-ZrO₂ Mixed Oxides", *Catalysis Today*, Vol. 171, pp. 297-303.
- Xuan, J., M. K. H. Leung, D. Y. C. Leung, and M. Ni, 2009, "A Review of Biomassderived Fuel Processors for Fuel Cell Systems", *Renewable and Sustainable Energy Reviews*, Vol. 13, pp. 1301-1313.

Yu, Q., W. Chen, Y. Li, M. Jin, and Z. Suo, 2010, "The Action of Pt in Bimetallic Au-Pt/CeO₂ Catalysts for Water Gas Shift Reaction", *Catalysis Today*, Vol. 158, pp. 324-328.