A STUDY ON BIMETALLIC WATER GAS SHIFT CATALYSTS TO BE USED IN FUEL PROCESSING

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to my family

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ABSTRACT

A STUDY ON BIMETALLIC WATER GAS SHIFT CATALYSTS TO BE USED IN FUEL PROCESSING

The aim of this study is to design and develop a Au-based, bimetallic WGS catalyst which has suitable activity and selectivity characteristics to be used in a fuel processor. The catalyst composition, preparation method, calcination temperature, reduction temperature and reduction mixture composition, and feed composition were the parameters used in the catalyst design and testing studies.

Nine different catalyst samples were prepared, tested and they are characterized by SEM. The optimum catalyst composition for WGS reaction was found to be 1% Re-2% Au/ZrO_2, prepared by impregnation of Re on ZrO_2 followed by deposition precipitation of Au (Re+Au). Addition of Re in this sequence was observed to improve the catalytic activity significantly, suggesting that rhenium is a good promoter for bimetallic gold based WGS catalysts. Together with five other different realistic feed compositions, a reaction mixture of 6% CO, 36% H_2O, 39% H_2, 10% CO_2, 9% He was used for most of the reaction tests performed. The WGS activities of the samples were determined for 250-350 ˚C range. Effect of W/F ratio (0.02, 0.03, 0.06) and H_2O/CO ratio (5, 6 and 7) on the WGS performance of Re-Au bimetallic catalysts were also investigated, and as expected, the general trend observed was that the catalytic activity increases with increasing W/F and H_2O/CO ratios, with the exception that the catalytic activity was found to be very close for all W/F ratios at 350 ˚C. For optimum catalyst composition and reaction conditions, the catalytic activity was observed to reach as high as 55% CO conversion at 350 ˚C.

Trace amounts of methane formation was observed only for the samples prepared by Au+Re sequence at 350 ˚C. No methane activity was observed for the rest of the samples. The results of the current study indicate that the bimetallic Re-Au catalyst supported on zirconia has a real potential to be used in the WGS unit of a real fuel processor.

ÖZET

YAKIT PROSESLEMEDE KULLANILACAK ÇİFT METALLİ SU-GAZ DEĞİŞİM KATALİZÖRLERİ ÜZERİNE BİR ÇALIŞMA

Bu çalışmanın amacı; bir yakıt prosesöründe kullanıma elverişli aktivite ve selektivite özelliklerine sahip, altın bazlı, çift metalli bir su-gaz değişim katalizörünün dizaynı ve geliştirilmesidir. Katalizör bileşimi, hazırlama metodu, kalsinasyon sıcaklığı, redüksiyon sıcaklığı ve redüksiyon karışımı bileşimi; katalizör dizaynı ve test çalışmalarında kullanılan parametrelerdir.

Dokuz farklı katalizör örneği hazırlanmış, test edilmiş ve SEM karakterizasyonları yapılmıştır. Su Gaz Değişim reaksiyonu için ideal katalizör bileşimi, Re impregnasyonunu izleyen Au tortu çökmesi (Re+Au) ile hazırlanan %1 Re-%2 Au/ZrO_2 olarak bulunmuştur. Re'un bu sırayla eklenmesinin katalitik aktiviteyi kaydadeğer şekilde artırdığı gözlendiğinden; renyumun iyi bir çift metalli, altın bazlı su-gaz değişim reaksiyonu katalizör destekleyicisi olduğu düşünülmüştür. Diğer beş farklı, gerçeğe uygun reaksiyon karışım bileşiminin yanısıra; yapılan testlerin birçoğunda %6 CO, %36 H_2O, %39 H_2, %10 CO_2, %9 He içeren bir reaksiyon karışımı kullanılmıştır. Örneklerin su-gaz değişim aktiviteleri 250-350 ˚C aralığında tespit edilmiştir. W/F (0.02, 0.03, 0.06) ve H_2O/CO (5, 6 and 7) oranlarının, Re-Au çift metalli katalizörlerinin su-gaz değişim performansı üzerindeki etkisi de incelenmiş, ve beklendiği gibi, katalitik aktivitenin 350 ˚C'de tüm W/F oranları için çok yakın olması haricinde, genel eğilimin katalitik aktivitenin artan W/F ve H_2O/CO oranlarıyla artması yönünde olduğu görülmüştür. İdeal katalizör bileşimi ve reaksiyon koşullarında, katalitik aktivitenin 350 ˚C'de %55'e kadar ulaştığı gözlenmiştir.

Eser miktarda metan oluşumu sadece Au+Re sırasıyla hazırlanan katalizöler için 350 ˚C'de gözlenmiştir. Diğer örnekler için metan aktivitesine rastlanmamıştır. Bu çalışmanın sonuçları, zirconium dioksit üzerinde Re-Au çift metalli katalizörün gerçek bir yakıt prosesöründe kullanım potansiyeli bulunduğunu göstermektedir.

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LIST OF ABBREVIATIONS

AFC	Alkaline Fuel cell
BOS	Birleşik Oksijen Sanayi
CATREL	Catalysis and Reaction Engineering Laboratory
EDAX	Energy Dispersive X-ray Analysis
ESEM-BCI	Environmental Scanning Electron Microscomopy-Backscattered Composition Imaging
GC	Gas Chromatograph
HTS	High Temperature Shift
LTS	Low Temperature Shift
MCFC	Molten-Carbonate Fuel Cell
PAFC	Phosphoric-Acid Fuel Cell
PEMFC	Polymer-Electrolyte-Membrane Fuel Cell
PROX	Preferential Oxidation
SOFC	Solid-Oxide Fuel Cell
TCD	Thermal Conductivity Detector
TPR	Temperature-Programmed Reduction
WGS	Water Gas Shift

1. INTRODUCTION

Water gas shift reaction is a well established industrial reaction used in H_2 production in large chemical facilities including refineries. However there is a renewed interest in WGS, due to its current role in fuel processors, which are devices that convert hydrocarbons to hydrogen by a series of catalytic reactions, namely reforming (Steam Reforming or Partial Oxidation or Autothermal Reforming), followed by Water Gas Shift and then Preferential Oxidation, which eliminates CO from the product stream. This new application introduces new challenges to the well established industrial water gas shift catalysts, like high activity and selectivity for a feed composition that is rich in reforming products, namely H_2, CO_2 and CH_4 besides CO and water vapor. Considering the fact that the utilities available in large scale conventional H_2 production facilities do not exist for fuel processors, long and complicated activation procedures or catalyst pyrophoricity should be avoided.

Water gas shift is a key reaction that utilizes the H_2 in water, converting the CO in the reformer product stream to CO_2. Thus, it is a key reaction for hydrogen production, which increases H_2 concentration while decreasing CO, which is poisonous to the fuel cell.

The industrial WGS catalysts are not suitable to be used in fuel processors as they have activation procedures that may cause them to become pyrophoric when exposed to air. Another drawback is that they are usually not sufficiently active for realistic feed compositions, having hydrogen and carbon dioxide. As WGS is an equilibrium reaction, presence of products in the feed stream usually has a dramatic effect on catalytic activity and this condition introduces also the possibility of methanation as a side reaction which consumes valuable hydrogen.

WGS reaction was studied before in CATREL, on Pt-Ni/Al_2O_3. (Caglayan and Aksoylu, 2009) Although very satisfactory results were obtained with an ideal feed composition, i.e. for the feed having only CO, water vapor and inert, introduction of CO_2 and H_2 to the system resulted in methanation and loss of even the hydrogen present in the

feed. Thus a new study on Au supported on CeO_2 has also been initiated by B.S. Caglayan recently.

The aim of the current study is to design and develop a Au-based, bimetallic WGS catalyst which has suitable activity and selectivity characteristics to be used in a fuel processor. The catalyst composition, preparation method, calcination temperature, reduction temperature and reduction mixture composition, and feed composition were the parameters used in the catalyst design and testing studies.

The optimal composition for Au-Re/ ZrO_2 catalyst was found to be one per cent Re, two per cent Au and 96 per cent ZrO_2. This catalyst, reduced under five per cent hydrogen flow at 180 °C for an hour before the activity tests, gave about 50 per cent CO conversion at 350 °C for a feed composition of 6% CO, 36% H_2O, 39% H_2, 10% CO_2, 9% He. It is also worth mentioning that no methane formation was observed during the WGS tests performed.

Section 2 of this report gives general information about the importance of fuel cells, and summarizes the reactions taking place in a fuel processor emphasizing the position of the WGS reaction within this system. Recent WGS studies, especially noble metal loaded over reducible oxide systems are investigated; with an emphasis on gold containing catalysts. Bimetallic gold systems are examined with special care. Experimental work is explained in detail on Section 3. The results are discussed in the 4^{th} Section and the conclusions that are drawn from this study are given in the 5^{th} Section.

2. LITERATURE SURVEY

Research for energy production through using more efficient and clean routes is of great interest, as the environmental impacts of conventional legislations about emissions get more stringent. One of the promising candidates as a future energy carrier is hydrogen, which can be produced from hydrocarbons by fuel processors and utilized in fuel cell applications.

2.1. Fuel Cells

Fuel cells are used to convert chemical energy to electrical energy, about twice as efficiently as an internal combustion engine and with comparably less pollutants. (Trimm, 2005) Within this context, hydrogen is the most probable future energy carrier and the difficulty of the storage of hydrogen is leading researchers to seek ways of on board, CO-free hydrogen production.

There are certain kinds of fuel cells developed for different applications, with different kinds of electrodes and operating temperatures: the alkaline fuel cell (AFC), the polymer-electrolyte-membrane fuel cell (PEMFC), the phosphoric-acid fuel cell (PAFC), the molten-carbonate fuel cell (MCFC), and the solid-oxide fuel cell (SOFC). The polymer-electrolyte-membrane fuel cell (PEMFC) is usually utilized in residential areas and vehicular applications as it operates at relatively lower temperatures and has good start-up performance. (Park *et al.*, 2008)

2.2. Reactions in a Fuel Processor

There are a series of reactions taking place in a fuel processor in production of hydrogen from hydrocarbons; reforming, water gas shift and preferential CO oxidation to decrease CO concentration down below 10-50 ppm.

2.2.1. Reforming

Steam reforming is a well established method in industrial hydrogen production.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad -\Delta H° = -206 kJ/mol \tag{2.1}$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \qquad -\Delta H° = -247 kJ/mol \tag{2.2}$$

Reforming takes place at high temperatures and the endothermicity of the reaction makes partial oxidation another favorable way of producing hydrogen.

$$CH_4 + \frac{1}{2}O_2 \leftrightarrow CO + 2H_2 \qquad -\Delta H° = 36 kJ/mol \tag{2.3}$$

If energy required for steam reforming is produced by simultaneous total oxidation utilizing the same hydrocarbon, the reaction system is called autothermal reforming (or Oxidative Steam Reforming).

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O \qquad -\Delta H° = 80 kJ/mol \tag{2.4}$$

2.2.2. Water Gas Shift

In water gas shift reaction, carbon monoxide produced in reforming step is reacted with water to form additional hydrogen, and at the same time, CO which is poisonous to the fuel cell, is converted to CO_2.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad -\Delta H° = 41 kJ/mol \tag{2.5}$$

Water gas shift reaction and catalysts utilized for the reaction will be discussed in more detail in section 2.3.

2.2.3. CO Removal

The gas mixture that leaves water gas shift reactor(s) still has a CO concentration that is harmful to the fuel cell, which can tolerate concentrations between 10-50 ppm. There are various methods to separate the carbon monoxide present in the WGS effluent; membrane separation by selective diffusion of hydrogen through a membrane, or methanation:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \tag{2.6}$$

Methanation reaction consumes valuable hydrogen, but it is considered still feasible for low carbon monoxide concentrations.

Another method, and maybe the most studied one, is removing CO in the syngas through preferential oxidation:

$$CO + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \tag{2.7}$$

The drawbacks are; the necessity to supply oxygen to the reaction system, to control the reaction temperature and possibility of hydrogen oxidation.

$$H_2 + \frac{1}{2}O_2(g) \rightarrow H_2O(g) \tag{2.8}$$

To minimize hydrogen oxidation, the catalyst properties and the reaction conditions must be decided accordingly. There are various PROX catalysts reported to have high activity and CO selectivity under realistic feed conditions. (Park *et al.*, 2008)

2.3. Water Gas Shift Reaction and Catalysts

Water gas shift is a reaction utilized in hydrogen production, where water in the form of steam reacts with carbon monoxide to produce hydrogen and carbon dioxide. The

reaction is reversible and exothermic, thus high temperatures are not favorable thermodynamically. On the other hand, as in every chemical reaction, the reaction kinetics is more favorable at higher temperatures. This is why the reaction is industrially conducted in two stages. The high temperature shift reaction takes place at 350-600 °C, while the low temperature reaction occurs at 150-300 °C. There are different types of catalysts used in industry for these stages, namely iron-based and copper-based catalysts for HTS and LTS operations, respectively. (Callaghan, 2006)

For fuel cell applications, it is desired to develop novel water gas shift catalysts which are active at a relatively low temperature range, as the reaction is equilibrium limited for high temperatures, and the desired carbon monoxide concentrations can not be achieved at elevated temperatures. The catalyst should be thermally stable, active for feed compositions typical for a reformer product stream and it should not catalyze side reactions like methanation, which consumes valuable hydrogen. (Panagiotopoulou and Kondarides, 2007)

There are certain drawbacks of commercial water gas shift catalysts that make them unsuitable for on-board fuel processing. They have activation procedures that can make them pyrophoric when exposed to air, and they can deactivate during shut-down/start-up conditions due to condensing steam. (Hilaire *et al.*, 2001)

Precious metals doped on reducible oxides are the most promising and so the most studied water gas shift catalysts in accordance to the renewed interest in water gas shift reaction within the context of fuel cell applications. In a study conducted by Panagiotopoulou and Kondarides, (Panagiotopoulou and Kondarides, 2006) activities of various noble metal-support catalysts were investigated for water gas shift reaction in the temperature range 150-550 °C with a feed composition of 3% CO and 10% H_2O, and balance He. Noble metals used in the study were Pt, Rh, Ru, and Pd, which were impregnated over TiO_2, CeO_2, La_2O_3, YSZ, Al_2O_3, MgO and SiO_2. The study concludes that among all metal-support combinations, Pt is more active than the others and that the reducible oxides (TiO_2, CeO_2, La_2O_3 and YSZ) have better support properties compared to irreducible ones (Al_2O_3, MgO, and SiO_2) in terms of catalytic activity.

Another study concerning the water gas shift activity of noble metals supported on ceria-zirconia oxides was published by Radhakrishnan et.al, (Radhakrishnan et.al, 2006a). The study investigates both high and low temperature regimes: The feed compositions 4.9% CO, 10.5% CO_2, 33% H_2O, 30.3% H_2 and 1.5% CO, 5% CO_2, 45% H_2O, 25% H_2 were used for HTS and LTS tests, both of which were conducted at the temperature range of 200-320 °C. The ceria-zirconia mixed oxide support was prepared by coprecipitation and noble metals (Ru, Rh, Ir, Au and Pt) were loaded on this support. It was found that for both high and low shift conditions; Pt has a higher activity in terms of CO conversion per number of noble metal atom loaded. The study concluded that the activity pattern of noble metals is Pt >Rh >Ru ≈Pd >Ir >Au. Methanation was found to occur for both Ru and Rh, favored at increasing temperatures. As Pt was found to be more active, different amounts of Pt was loaded on the Ce-Zr mixed oxide support and the samples were investigated for their catalytic activity. The results showed that it is not possible to reach equilibrium conversion below 320 °C with <4% Pt loaded for HTS conditions, and above that temperature only the samples loaded with ≥2 % Pt hit the equilibrium. It was concluded that a 1-2% Pt catalyst is the best choice in terms of activity/cost considerations, and that the addition of a metal promoter to the Pt/CeO_2-ZrO_2 catalyst might be necessary to reach equilibrium conversions at lower temperatures in a more cost effective manner. In their following study, the same researchers added Re to the Pt catalyst, and found that addition of Re enhances the water gas shift activity of the catalyst. It was seen that addition of 1% Re to a 2% Pt sample creates nearly the same improvement in the activity, as that of adding 1% more Pt; which means a 3% Pt sample shows the same catalytic activity with a 2% Pt-1%Re sample. But the latter was claimed to be a more cost effective solution. (Radhakrishnan *et.al*., 2006b)

Choung et al, (Choung *et al.*,2005) investigated the water gas shift activity of Pt-Re bimetallic catalysts supported on CeO_2-ZrO_2, and the enhancement of catalytic activity was explained to be a result of better dispersion of Pt on the support. But the catalytic activity evaluated on a "per m^2 of Pt exposed" basis showed that Re-Pt catalysts are more active compared to Pt only catalysts, which may point to a synergistic effect among Pt and Re. The TPR studies conducted in the study suggested that addition of Re prevents sintering of Pt, which explains the slower deactivation of Pt-Re samples observed, compared to monometallic Pt samples.

Addition of a promoter to a noble metal/reducible oxide water gas shift catalyst was also studied by Nguyen-Thanh *et al.* (Nguyen-Thanh *et al.*, 2008). Adding V to Pt supported on ZrO_2 was investigated under differential reaction conditions with a feed composition of 5.49% CO, 4.10% CO_2, 9.71% H_2, 49.95% N_2 and 30.75% H_2O. The addition of V was shown to increase catalytic activity up to twice as that of Pt on ZrO_2, which may be a result of enhanced surface reducibility or, if water gas shift occurs through a redox mechanism, the presence of V-O-ZrO_2 bonds which are expected to be very active in a redox mechanism. Effect of V as a promoter was also investigated for Pt on CeO_2 (Duarte de Farias *et al.*, 2008). The feed composition utilized was 6.0% CO, 16.0% H_2, 1.6% CO_2, 0.4% CH_4, 60.0% H_2O and balance N_2. After a reduction of 1hr under pure H_2 flow at 350 °C, the catalytic activity was investigated for the 200-350 °C temperature range with monometallic Pt and Pt-V samples having different amounts of V loaded. Addition of V to Pt-CeO_2 sample was shown to increase the catalytic activity, which was suggested to be the result of the formation of V-O-Ce bonds. It was also reported that methanation does not occur for any reaction conditions employed. It should be noted that the article makes a good point while comparing the catalytic activity reported for similar work in the literature. There are a variety of feed compositions used, which highly affects the activity, and one of the major differences is that some researchers use a basic CO/H_2O feed, ignoring the inhibitory effects of H_2 and CO_2 actually present in the feed stream. Thus, any comparison between different studies must be done with great care.

One of the most studied noble metal based systems for water gas shift reaction is gold supported on reducible oxides. In a study conducted by Fu *et al.* (Fu *et al.*, 2001), the catalytic activity of Au-CeO_2 catalysts was investigated. One important conclusion of this work was that the gold particle size is not the most important parameter for the activity of reducible oxide supported Au catalysts, but the crystal size of the support is also of great importance. The authors claimed that presence of Au is yet crucial as it increases the reducibility of the surface oxygen, but the amount of surface oxygen ready to be reduced depends on the crystal size of the ceria.

Another work that studies the influence of support structure on water gas shift activity was carried out by Águila *et al.* (Águila *et al.*, 2008). The study investigates the effect of crystalline structure of zirconia on the catalytic activity of Cu on ZrO_2 catalysts

for water gas shift reaction. There were two different zirconia crystalline structures investigated within this study, namely tetragonal and monoclinic ZrO_2. The monoclinic ZrO_2 support was prepared through the calcination of hydrous zirconium at 700 °C for 3 hours, while the tetragonal ZrO_2 was obtained by refluxing hydrous zirconium in a solution of 6.25 wt% of NH_4OH for 9 hours. The samples were dried overnight at 105 °C and then calcined at 700 °C for 3 hours. The catalytic activity tests performed in a tubular plug flow reactor with a feed composition of 2% CO, 6% H_2O and balance He concluded that for all temperatures, the tetragonal zirconia reaches far better activity than the monoclinic one. The reason for this difference was supposed be a result of the surface formates which are less stable on tetragonal zirconia. And the results of the study indicated that the decomposition of adsorbed formates is a key step for WGS.

The studies on gold supported on mesoporous zirconia, (Idakiev *et al.*, 2006) by Idakiev *et al.* showed that on ZrO_2, the particle size of Au is inversely related to the amount of Au in the sample, and that the catalytic activity increases with higher Au amounts and, thus, smaller particle size. The same authors concluded in another study that the size of gold particles on mesoporous titania increases with increasing amounts of gold in the sample which leads to a decrease in catalytic activity. The results indicated that the catalytic activity is related to the size of the gold particles rather than the amount of gold in the sample. Addition of cerium to the mesoporous titania catalyst was shown to enhance the catalytic activity. (Idakiev *et al.*, 2007) Au supported on cerium modified mesoporous titania was found to be more active than Au supported on CeO_2, or TiO_2, or mesoporous TiO_2, showing the important role of support in water gas shift reaction and suggesting a strong interaction between Ce and mesoporous TiO_2. It was actually claimed that Ce decreases the particle size of TiO_2 crystals and enhances the reducibility. Activity was observed to increase with increasing amounts of Au in the sample and space velocity was shown to be an important parameter on the activity, causing significant decreases at high space velocities like 8000 h^{-1}.

One inclusive study comparing WGS activity of Pt and Au on CeO_2-ZrO_2/ or ZrO_2 was published by Boaro *et al.* (Boaro *et al.*, 2008). The work mentions the role of support in the WGS reaction mechanism by employing both Ce-ZrO_2 mixed oxide and ZrO_2. The study compares the activity of Au and Pt supported on both supports. The metal loading

was kept constant at 4% for both Au and Pt. Au was added by deposition precipitation and Pt was impregnated on the supports mentioned. The catalyst samples were reduced under 5% H_2 at 180 °C and the reaction was carried out on the 180-350 °C temperature range with a realistic feed composition of 39% H_2, 24% N_2, 6% CO, 10% CO_2, and 21% H_2O. The products and reactants were analyzed with a gas chromatograph. The structure of zirconia was found to be mainly monoclinic with a small fraction of tetragonal phase, while addition of ceria was seen to stabilize the cubic phase. Effect of calcination temperature on support samples and metal precursors was also investigated. Although Au particle size was observed to increase with increasing calcination temperature, Pt particle size distribution was shown to be more dependent on the surface area of the support, and so to the calcination temperature of the support. Support samples that had been calcined at higher temperatures had lower surface areas; better dispersion of Pt crystals was observed on higher surface areas. Another important parameter that was shown to affect Pt particle size was observed to be the precursor; there, nitrates giving better results than chlorides. The catalytic activity of both monometallic catalysts changed with calcination temperature; for Au loaded samples activity decreased for increasing calcination temperature which resulted in bigger particle size, and for Pt the activity increased with calcination temperature. On the other hand, neither the surface area of support nor the calcination temperature of support was found to have a significant effect on the activity of Au catalysts. The support composition was shown to play an important role on the activity of gold catalysts; samples supported on pure zirconia giving better catalytic activity. An important finding of the study was that gold catalysts are more active compared to Pt samples at low temperatures.

There are various parameters affecting the catalytic activity of gold catalysts, mainly the preparation method. Deposition precipitation is one of the most successful preparation methods, where Au precursor is added slowly to a suspension of support whose pH is adjusted optimally between 8 and 9. Another important parameter is the calcination temperature for gold/metal oxide catalysts. The particle size of gold was shown to increase with increasing calcination temperatures. Optimum calcination temperature was determined as 200 °C. (Wolf and Schüth, 2002) Reproducibility is also a significant problem about Au/metal oxide catalysts, which is one of the main reasons for different results reported in literature.

The activity and stability of many gold/metal oxide WGS catalysts still need to be improved, especially under realistic feed conditions. So there is an increasing research interest on bimetallic Au catalysts to meet these criteria.

Various metals were loaded together with gold on iron (III) oxide by Venugopal *et al.*, namely Ag, Bi, Co, Cu, Mn, Ni, Pb, Ru, Sn, Tl, using deposition-coprecipitation. The catalytic activities of these samples were measured under a feed flow of 57.5 cm^3h^{-1} carbon monoxide and 920 cm^3h^{-1} water. The WGS activity of the samples were found to be Au-Ru ≥ Au-N i> Au > Au-Bi > Au-Sn > Au-Pb > Au-Mn ≥ Au-Cu > Au-Tl > Au-Co > Au-Ag at 100 °C, and Au-Ru > Au-Ni > Au-Bi > Au-Cu > Au-Pb > Au-Ag > Au-Tl> Au-Sn > Au > Au-Mn >Au-Co at 240 °C, Au-Ru catalyst being the most active sample. However, contributions of gold and ruthenium were suggested to be mostly independent; and a weak synergistic effect was claimed to be just a probability. It was also found likely that ruthenium dominates any contribution from gold, especially at high temperatures, but the probability of a promoter effect due to presence of gold could not be ruled out for low temperatures. (Venugopal *et al.*, 2003a)

Owing to its superior activity the gold-ruthenium/iron-oxide catalyst was further investigated. (Venugopal *et al.*, 2003b) WGS activities of gold/iron oxide, ruthenium/iron oxide and gold-ruthenium-iron oxide were investigated in the 100-240 °C temperature range, with a feed composition of 57.5Ncm^3 h^{-1} of CO in He (5.1 vol.% CO, balance He) and 125N cm^3 h^{-1} water. Au-Ru sample was more active than the other two for all temperatures, for which the difference was especially significant at lower temperatures. Activities of Ru and Au-Ru samples were closer for temperatures above 200 °C, but activity of Au was nearly only a quarter of others. An interaction between Au and Ru was proved by physicochemical characterizations, but a highly synergistic effect increasing the catalytic activity dramatically could not be mentioned

Bimetallic gold catalyst supported on ceria were prepared and investigated by Hurtado-Juan *et al.* (Hurtado-Juan *et al.*, 2008) Samples were prepared by coprecipitation and tested for WGS activity with an ideal feed composition that has a H_2O/CO ratio of 13.5. The WGS activities over these samples were found to be: Au–Pt > Pt > Au–Pd > Au–Ca ≥ Au–W > Pd >Au–Ni > Au. The presence of a metal promoter was shown to enhance

the catalytic activity. The study proposed that the metal promoters cause a local electronic band enlargement on ceria, enabling an easier reduction of the surface hydrogen. This idea was supported by the finding that the promoter that creates the highest band enlargement is Pt, and Au-Pt is the most active sample.

3. EXPERIMENTAL

3.1. Materials

3.1.1. Chemicals

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

Table 3.1. Chemicals used for catalyst preparation

Chemicals	Formula	Specification	Source	MW
Titanium IV oxide	TiO_2	99.2%	Merck	63.87
Zirconium oxide	ZrO_2	S.A.=90 m^2/g	Alfa Aesar	123.22
Cerium(III) nitrate hexahydrate	$Ce(NO_3)_3.6H_2O$	99.99%	Aldrich	434.22
Gold (III) chloride trihydrate	$HAuCl_4.3H_2O$	99.9+%	Aldrich	393.83
Ammonium perrhenate	NH_4ReO_4	99.999%	Aldrich	268.24
Ammonium carbonate	$CH_6N_2O_2$*CH_5NO_3(1:1)	-	Merck	157.13

3.1.2. Gases and Liquids

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

Table 3.2. Specifications and applications of the gases used

Gas/Standard	Specification	Application
Carbon monoxide	99.999% BOS	GC calibration, Reactant
Oxygen	99.999% BOS	GC calibration, Reactant
Carbon dioxide	99.999% BOS	GC calibration , Reactant
Helium	99.99% BOS	Reactant
Methane	99.99% BOS	GC calibration, Reactant
Hydrogen	99.99% BOS	GC calibration, Reactant, reducing agent

Helium	99.99% BOS	GC carrier

Table 3.3. Specifications and applications of the liquids used

Liquid	Specification	Application
Water	Distilled / De-ionized	Aqueous solutions, Reactant

3.2. Experimental Systems

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

- Catalyst preparation systems that are used to prepare the support and to carry out impregnation and deposition precipitation steps of catalyst preparation

- Catalyst characterization systems used to analyze the structural properties of the catalyst samples

- Catalytic reaction system which 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 a gas chromatograph and a CO analyzer that can be either used in parallel or in series fashion.

3.2.1. Catalyst Preparation System

The impregnation system includes a Retsch UR1 ultrasonic mixer, a vacuum pump, a buchner flask and a MasterFlex computerized-drive peristaltic pump.

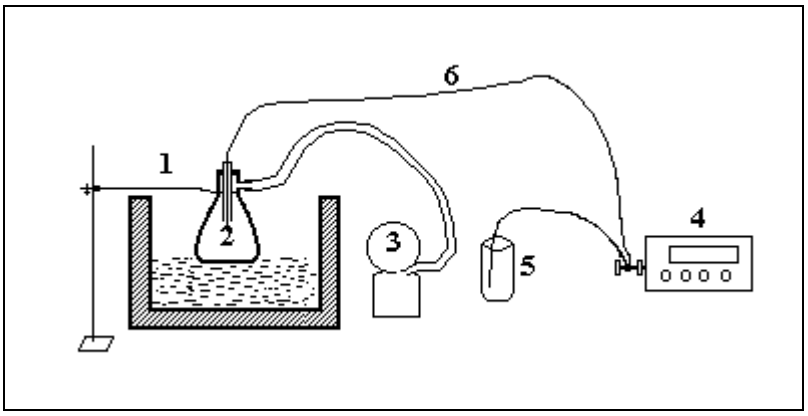

Figure 3.1. The impregnation system: 1. Ultrasonic mixer 2. Vacuum flask 3. Vacuum pump 4. Peristaltic (Soykal, 2008)

The deposition precipitation system consists of a Retsch UR1 ultrasonic mixer, flasks, a pH meter and a pipette.

3.2.2. Catalyst Characterization Systems

The structural analyses of the catalyst samples were carried out at Boğaziçi University Advanced Technologies R&D Center through Environmental Scanning Electron Microscopy-Backscattered Composition Imaging (ESEM-BCI), Energy Dispersive X-ray Analysis (EDAX) and particle size analysis techniques, using a Philips XL30 ESEM-FEG system which has a maximum resolution of 2 nm. In EDX analyses, the minimum detection limit was 50 ppm.

3.2.3. Catalytic Reaction System

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

- Feed section
- Reaction section
- Product analysis section

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. helium, hydrogen, oxygen, carbondioxide, carbonmonoxide and methane. Water is fed to the system with an Agilent 1200 series HPLC pump at constant flow rates. The 1/16” tube, through which water is allowed to flow and the lines between the water inlet and the reactor are kept above 100˚C with a 2 m heating tape to enable vaporisation. The heating tape is controlled by an Omron E5AN PID controller with ± 3K sensitivity. The high purity gases are supplied by pressurized cylinders and their pressures are reduced via BOS 5850E model gas regulators to 1.5-2 atmospheres. The gases are passed through calibrated Brooks mass flow controllers. Two Brooks CC1A10 series control boxes are used to regulate the gas flows. On-off valves are placed in front of the mass flow controllers to protect them from possible back-pressure fluctuations.

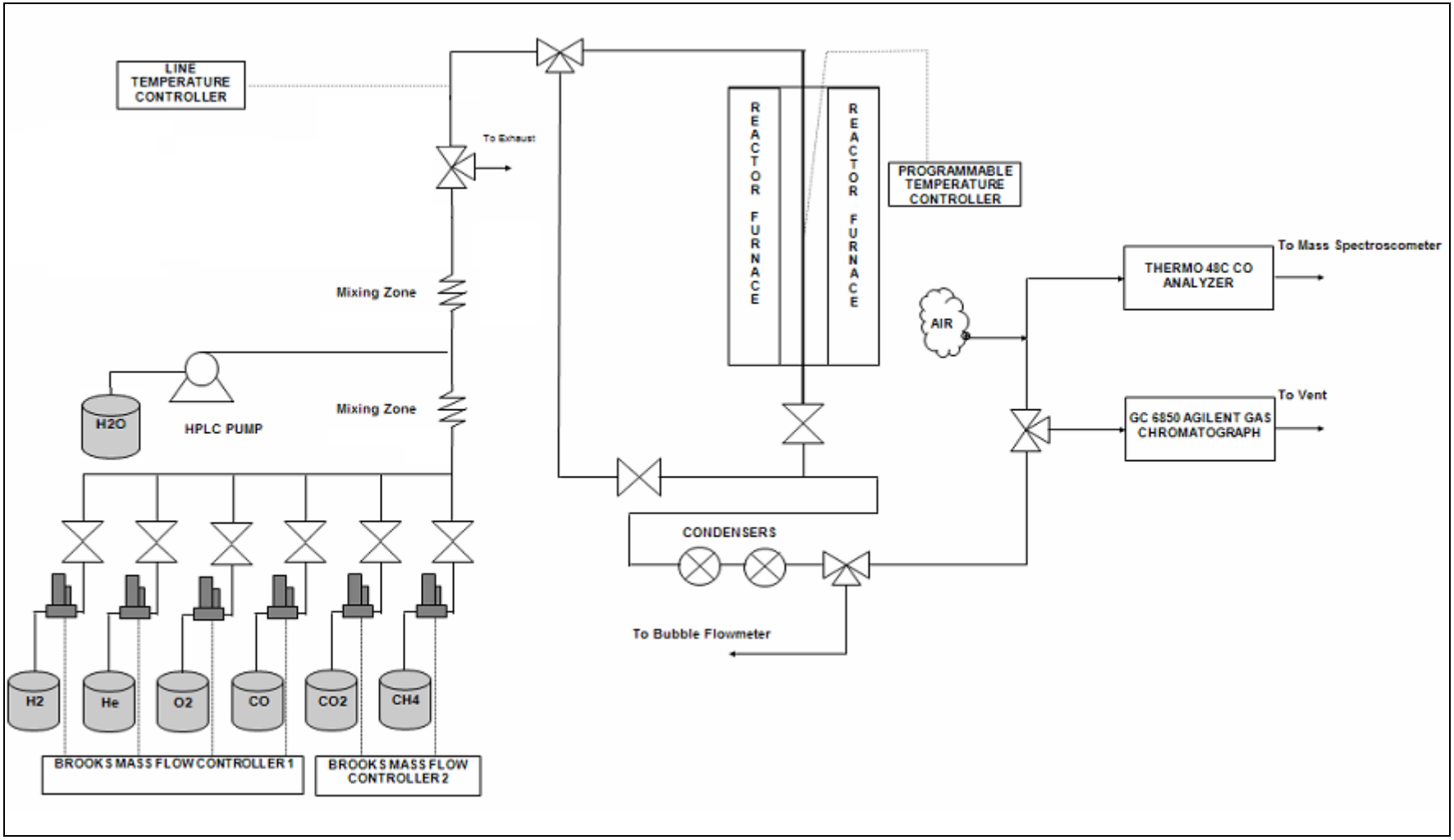

Figure 3.2. Flowsheet of the microreactor system (Soykal, 2008)

It is possible to divert flow using three way valves: The feed gases can be diverted to the bypass line, so that feed composition can be analyzed using the gas chromatograph and the CO analyzer. Another three way valve is used for diverting the flow to the bypass vent line for establishing steady state flow and mixing of the steam and other gaseous reactants prior to the reaction.

The reactants, metered and mixed in the feed section, are allowed to flow through the reaction section. This section is composed of a 50 cm x 2.4 cm ID tube furnace controlled to ± 0.5 K by a Eurotherm 3216 programmable temperature controller and a 1/4" stainless steel fixed-bed microreactor. The reactor, also constructed in CATREL has a length of 65 cm, so that it is 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. The position of the reactor and hence catalyst bed was adjusted to coincide with the constant-temperature zone of vertical 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. (Soykal, 2008)

3.2.4. Product Analysis Systems

For water gas shift reaction, the product gas needs to be tested for carbon monoxide and methane concentrations; there, CO concentration is needed to determine the conversion and CH_4 concentration is needed to investigate whether methanation occurs or not.

CO analyzer operates on the principle that CO absorbs infrared radiation at a wavelength of 4.6 microns. Infrared absorption is a non linear measurement technique therefore, it is necessary to transform the basic analyzer signal into a linear output. The CO analyzer uses an internally stored calibration curve to accurately linearize the instrument. This calibration curve limits the CO analyzers upper concentration range to 10000 ppm.

The operation diagram of the CO analyzer is given in Figure 3.5. The sample flows through an optical bench. Radiation from an infrared source is chopped then passed through a gas filter alternating between CO and N_2. The radiation then passes through a narrow bandpass interference filter and enters the optical bench where absorption by the sample gas occurs. The infrared radiation then exits the optical bench and falls on an infrared detector. The CO gas filter acts to produce a reference beam which cannot further be attenuated by CO in the sample cell. The N_2 side of the filter wheel is transparent to the infrared radiation and therefore produces a measurement beam which can be absorbed by CO in the cell. The chopped detector signal is modulated by the alternation between the two gas filters with an amplitude related to the concentration of CO in the sample cell. Other gases do not cause modulation of the detector signal since they absorb and measure beams equally. Therefore the system responds specifically to CO. The CO analyzer specifications are given in Table 3.4.

Agilent 6850C equipped with a Thermal Conductivity Detector (TCD) is used to analyze the product gas. An Alltech CTR1 column with the outer packing material of 6ft x 1/4" Packed with Activated Molecular Sieve and with the inner packing material of 6ft x 1/8” porous polymer mixture. Analysis conditions are given below in Table 3.5. (Soykal, 2008)

Table 3.4. CO analyzer specifications (Soykal, 2008)

Range	0-1 to 10000 ppm
Zero Noise	0.02 ppm RMS (30 second averaging time)
Lower Detectable Limit	0.04 ppm
Zero Drift	<0.1 ppm
Span Drift	±1 % full-scale
Response Time	60 seconds (30 second averaging time)
Linearity	±1% of full-scale ≤1000 ppm
	±2.5% of full-scale > 1000 ppm
Sample Flow Rate	1.0 LPM
Operating Temperature	20- 30˚C (may be safely operated over the range of 0-45˚C)

Table 3.5. Reactant and product gas analysis conditions (Soykal, 2008)

Column Type	CTR I (Packed Concentric Column)
Outer Column Packing	Activated Molecular Sieve
Inner Column Packing	Porous Polymer Mixture
Column Oven Temperature	353 K
Carrier Gas	Helium
Carrier Gas Flow Rate	20 ml/min
Detector Type	Thermal Conductivity
Detector Current	120 mA
Front Detector Temperature	493 K
Front Inlet Temperature	393 K
Auxillary Temperature	323 K

3.3. Catalyst Preparation and Pretreatment

3.3.1. Support Preparation

The support materials used in this study were TiO_2 and ZrO_2. TiO_2 supplied by Merck was calcined at 500 °C for 4 hours prior to being used as support, while ZrO_2 supplied by Alfa Aesar was crushed and sieved into 400-200 μm particle size and calcined at 650 °C for 3 or 4 hours.

3.3.2. Impregnation

The experimental set-up shown in Figure 3.2 was used for catalyst preparation by the incipient to wetness impregnation. Incipient wetness impregnation method that was used in the study consists of three parts:

- Evacuating the support,
- Contacting the support with the precursor solution, and
- Drying.

For incipient to wetness impregnation, support material was placed in the vacuum flask and kept under vacuum before, during and after the addition of precursor solutions. Since trapped air in the pores of the support could prevent penetration of the solutions, vacuum pump was used to remove the trapped air and to give a uniform distribution of the

active component. Before impregnating the solution, the support material was mixed with ultrasonic mixer for 25 min.

A Masterflex computerized-drive peristaltic pump was used to feed the precursor solution to the vacuum flask at a rate of 0.5 mL/min via silicone tubing. The slurry was mixed by an ultrasound mixer during the impregnation in order to maintain uniform distribution of the precursor solutions. After the precursor solution was added, the slurry was ultrasonically mixed for an additional 90 minutes. The thick slurry obtained was dried at 110 ˚C overnight.

3.3.3. Deposition Precipitation

To obtain highly dispersed gold particles on the surface of the catalysts, deposition precipitation technique was carried out as explained in the study by Boaro *et al.* (Boaro *et al.*, 2008).

The support was put in a beaker along with deionized water to obtain a suspension, and the suspension's pH was adjusted around 8 using a solution of $(NH_4)_2CO_3$. The beaker containing the suspension was placed in an ultrasonic bath to carry out the procedure in continuous agitation. The gold precursor was dissolved in deionized water to obtain a 10^{-3} M solution and this solution was added to the support suspension drop by drop. The resulting mixture was left in the ultrasonic bath for one more hour and then filtered. The sample was washed with deionized water several times and dried overnight at 110 ˚C.

The sample was then calcined at specified duration and temperatures given in Table 3.6.

3.3.4. Preparation of the Catalyst Samples

(i) Re-Au Supported on Ce Modified TiO_2: The composition of the catalyst is as follows: Support: 96%TiO_2, 4% Ce, Metals: 1% Au, 0.5% Re. The catalyst with the composition above was prepared as follows:

- Calcination of TiO_2 (4 hrs at 500 ˚C)
- Impregnation of Ce
- Calcination of Ce-TiO_2 (8 hrs at 500 ˚C)
- Impregnation of Re
- Calcination of Re/Ce-TiO_2 (8 hrs at 500 ˚C)
- Deposition Precipitation of Au
- Resulting powder was calcined at 400 ˚C for 4 hours.

(ii) Au Supported on ZrO_2 (3 batches): The compositions of the catalysts are as follows: 4 and 3% Au supported on ZrO_2. The catalysts with the compositions above were prepared as follows:

- Calcination of ZrO_2 (3 hrs at 650 ˚C)
- Deposition Precipitation of Au (one of the 4% batches was dried under vacuum)
- Resulting powder was calcined at 250 ˚C for 1 hour.

(iii) Au&Re on ZrO_2 (2 batches) sequence 1: The composition of the catalysts is as follows: Support: 96% ZrO_2, Metals: 3% Au, 1% Re. The catalyst with the composition above was prepared as follows:

- Calcination of ZrO_2 (3 hrs at 650 ˚C)
- Deposition Precipitation of Au
- Resulting powder was calcined at 250 ˚C for 1 hour.
- Impregnation of Re
    - One batch was calcined at 250 ˚C for 1 hr.
    - The other batch was calcined at 400 ˚C for 1 hr.

(iv)Au&Re on ZrO2 (3 batches) sequence 2: The compositions of the catalysts are 3, 2, 1 % Au, 1% Re supported on ZrO_2. The catalysts were prepared as follows:

- Calcination of ZrO_2 (3 hrs at 650 ˚C)
- Impregnation of Re

- Calcination at 250 ˚C for 1 hr.
- Deposition Precipitation of Au
- Resulting powder was calcined at 250 ˚C for 1 hour.

The compositions and preparation procedures of the catalyst samples prepared for this study are summarized in Table 3.6.

Table 3.6. Catalysts prepared for this study

Cat #	Composition	Calcination	Preparation
1	Support: 96%TiO_2, 4% Ce Metals: 1% Au, 0.5 % Re	TiO_2: 4 hrs 500C Ce-TiO_2: 8hrs 500 C Re/Ce-TiO_2 : 8hrs 500 C Au-Re/Ce-TiO_2 : 4hrs 400 C	Ce Impregnation Re Impregnation Au DP (vacuum dried)
2	96%ZrO_2, 4% Au	ZrO_2: 3 hrs 650C Au/ZrO_2: 1hrs 250 C	Au DP(vacuum dried)
3	96%ZrO_2, 4% Au	ZrO_2: 3 hrs 650C Au/ZrO_2: 1hrs 250 C	Au DP(normal dried)
4	97%ZrO_2, 3% Au	ZrO_2: 3 hrs 650C Au/ZrO_2: 1hrs 250 C	Au DP(normal dried)
5	96%ZrO_2, 3% Au, 1%Re	ZrO_2: 3 hrs 650C Au/ZrO_2: 1hrs 250 C Re-Au/ZrO_2: 1hrs 250 C	Au DP (normal dried) Re Impregnation
6	96%ZrO_2, 3% Au, 1%Re	ZrO_2: 3 hrs 650C Au/ZrO_2: 1hrs 250 C Re-Au/ZrO_2: 1hrs 400 C	Au DP (normal dried) Re Impregnation
7	96%ZrO_2, 3% Au, 1%Re	ZrO_2: 3 hrs 650C Re/ ZrO_2: 1hrs 250 C Re-Au/ ZrO_2: 1hrs 250 C	Re Impregnation Au DP (normal dried)
8	97%ZrO_2, 2% Au, 1%Re	ZrO_2: 3 hrs 650C Re/ ZrO_2: 1hrs 250 C Re-Au/ ZrO_2: 1hrs 250 C	Re Impregnation Au DP (normal dried)
9	98%ZrO_2, 1% Au, 1%Re	ZrO_2: 3 hrs 650C Re/ ZrO_2: 1hrs 250 C Re-Au/ ZrO_2: 1hrs 250 C	Re Impregnation Au DP (normal dried)

3.4. Reaction Tests

Once the amount of catalyst specified in Table 3.8 was placed in the reactor, the sample was heated to reduction temperature under 95 ml/min He flow and then the amount of hydrogen specified in Table 3.8 was introduced to the reactor to clear the catalyst surface from oxygen, which is present in the metal-oxide form, for a duration also specified in Table 3.8. After reduction, the sample was heated to reaction temperature under helium flow and trapped in helium while the reaction mixture, with the composition specified in Table 3.7 was bypassed for two hours to let it reach steady state. The

temperatures the reactions are carried out, along with other specifications are presented in Table 3.8.

Table 3.7. A summary of the feed flow compositions used during this study

Feed	Flow Composition
Feed #0	3% CO, 10% H_2O, 87% He
Feed #1	4.9% CO, 33% H2O, 30.3% H2, 10.5% CO2, 22.3% He
Feed #2	6% CO, 21% H_2O, 39% H_2, 10% CO_2, 24% He
Feed #3	6% CO, 36% H_2O, 39% H_2, 10% CO_2, 9% He
Feed #4	6% CO, 36% H_2O, 39% H_2, 10% CO_2, 4% He, 5% CH_4
Feed #5	6% CO, 30% H_2O, 39% H_2, 10% CO_2, 15% He
Feed #6	6% CO, 42% H_2O, 39% H_2, 10% CO_2, 3% He

Table 3.8. A summary of the experimental conditions used during this study

Exp #	Cat #	Cat(mg)	W/F (mg cat s ml^{-1})	Reduction	Feed Composition
1	1	75	W/F=0.012	5%H_2, 200 C, 1 hrs	Feed #0
2	1	200	W/F=0.033	50%H_2, 250 C, 2 hrs	Feed #1
3	1	200	W/F=0.033	50%H_2, 300 C, 2 hrs	Feed #1
4	2	75	W/F=0.012	5%H_2, 180 C, 1 hr	Feed #1
5	2	170	W/F=0.03	5%H_2, 180 C, 1 hr	Feed #1
6	2	170	W/F=0.03	5%H_2, 180 C, 1 hr	Feed #2
7	3	170	W/F=0.03	5%H_2, 180 C, 1 hrs	Feed #2
8	4	170	W/F=0.03	5%H_2, 180 C, 1 hrs	Feed #2
9*	5	170	W/F=0.03	5%H_2, 180 C, 1 hrs	Feed #2
10	5	170	W/F=0.03	5%H_2, 180 C, 1 hrs	Feed #2
11	5	170	W/F=0.03	5%H_2, 250 C, 1 hrs	Feed #2
12	5	170	W/F=0.03	50 %H_2, 250 C, 1 hrs	Feed #2
13	6	170	W/F=0.03	5%H_2, 180 C, 1 hrs	Feed #2
14	6	170	W/F=0.03	100% H_2, 180 C, 1 hrs	Feed #2
15	5	170	W/F=0.03	5% H_2, 180 C, 1 hrs	Feed #3
16	7	170	W/F=0.03	5% H_2, 180 C, 1 hrs	Feed #3
17*	7	170	W/F=0.03	5% H_2, 180 C, 1 hrs	Feed #3
18*	8	170	W/F=0.03	5% H_2, 180 C, 1 hrs	Feed #3
19	8	170	W/F=0.03	5% H_2, 180 C, 1 hrs	Feed #4
20	9	170	W/F=0.03	5% H_2, 180 C, 1 hrs	Feed #3
21*	9	170	W/F=0.03	5% H_2, 180 C, 1 hrs	Feed #3
22	9	170	W/F=0.03	5% H_2, 180 C, 1 hrs	Feed #4
23**	7	170	W/F=0.06	5% H_2, 180 C, 1 hrs	Feed #3
24**	7	170	W/F=0.02	5% H_2, 180 C, 1 hrs	Feed #3
25**	7	170	W/F=0.03	5% H_2, 180 C, 1 hrs	Feed #5
26**	7	170	W/F=0.03	5% H_2, 180 C, 1 hrs	Feed #6

(Experiments marked with * are analyzed with CO analyzer, ** indicates the experiments are analyzed both with CO analyzer and Gas Chromatograph)

The product gas composition was analyzed mostly by a gas chromatograph and the CO analyzer was used to confirm some results. The CO analyzer is designed to work in an open atmosphere and therefore it was calibrated according to the laboratory's ambient atmosphere. The trace amount of CO from the atmosphere is the base set value for the CO analyzer. The inlet flow rate of the CO analyzer was 1.089 l/min. The make-up stream of the CO analyzer was provided by air. The CO analyzer readings, which do not reflect the exact concentration of CO in the feed stream due to dilution with air, were corrected accordingly for finding the CO concentration in the reactor exit. (Soykal, 2008)

$$\text{CO in the product stream} = \frac{\text{What is read on the CO analyzer} \times 1089}{100} \qquad (3.1)$$

4. RESULTS AND DISCUSSIONS

The aim of this study is to optimize the composition and preparation technique of (an) active and selective bimetallic, gold based water gas shift catalyst(s) to be used in fuel processor applications. The promoter metal was chosen to be rhenium, and two different supports; ceria modified titania and zirconia were used throughout the study. Gold on zirconia was also synthesized and used as a reference catalyst, which forms a basis for a better understanding of the effects of Re. A parametric study was carried out on the Au-Re/ZrO_2 catalyst; parameters used were catalyst composition, the sequence of metal addition on the support, calcination temperature of the catalyst, reduction gas composition and temperature, and feed composition. The catalysts were prepared by Re impregnation followed by Au deposition precipitation, or visa versa.

4.1. Catalyst Characterization

Catalyst samples prepared for this study were investigated by ESEM for their micro-structural properties, especially analyzing for the dispersion of gold particles on the surface. EDAX analysis was also performed to determine the local bimetallic formations and their compositions. The samples prepared for analysis were all freshly reduced forms of the catalyst samples.

Figure 4.1 shows the SEM image of 4% Au/ZrO_2. The bright points are gold particles. The particle size is bigger than expected for a sample prepared by deposition precipitation and the particle distribution is not uniform.

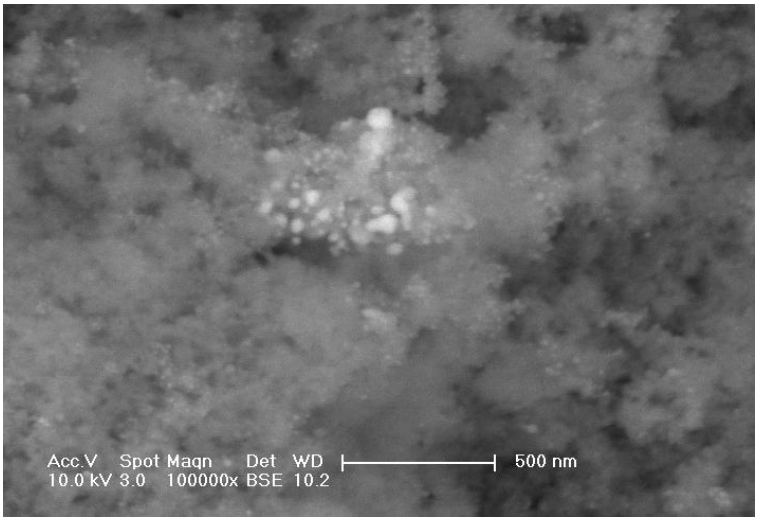

Figure 4.1. SEM image of 4% Au/ZrO_2 (catalyst #3)

An image of 3% Au/ZrO_2 is given in Figure 4.2 where there are no visible metal clusters/structures, suggesting that the distribution of gold particles is much better and the particle size is smaller, as concluded for Pt-Re/Ce-ZrO_2 in the literature, when no visible noble metal was observed in a sample micrograph. (Radhakrishnan *et al.*, 2006a)

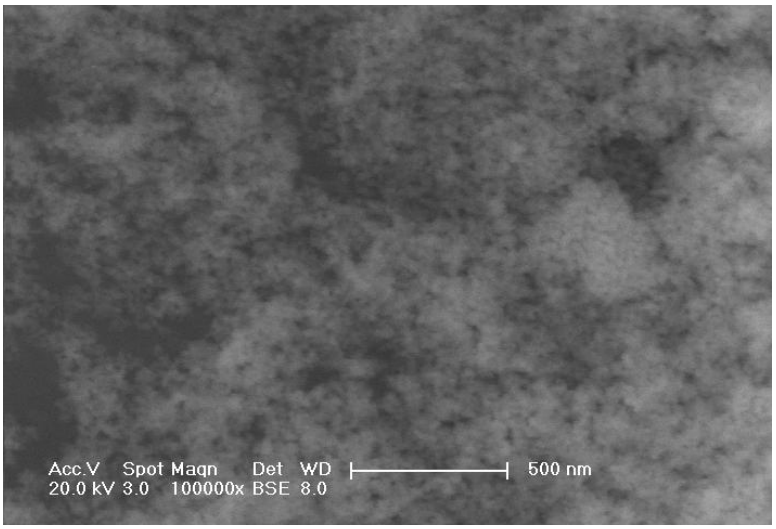

Figure 4.2. SEM image of 3% Au/ZrO_2 (catalyst #4)

The difference between 3% and 4% Au samples in terms of particle size and distribution suggests that 3% is a limit for obtaining well dipersed and small gold particles, however the reproducibility of Au catalysts is very low as stated by Wolf and Schüth,

(Wolf and Schüth, 2002) and there could have been another explanation for the poor distribution of gold particles for the 4% Au sample.

Rhenium promoter was first added on a sample that had already been deposited with 3% gold and the resulting sample was calcined at 250 ˚C (Catalyst #5). The addition of Re, through using Au+Re sequence, showed no improvement on the structure of the catalyst, and may have even caused formation of bigger gold particles, as shown in Figure 4.3.

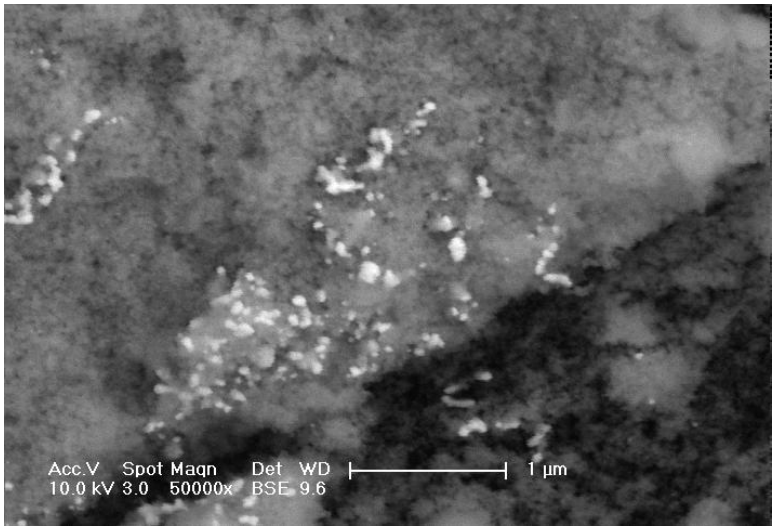

Figure 4.3. SEM image of 3% Au-1% Re/ZrO_2 (Catalyst #5)

Figure 4.4 shows the SEM image of a catalyst sample with same composition and that was prepared by the same procedure except the final calcination temperature, which is 400 ˚C. In the literature, formation of larger Au particles are reported when higher calcination temperatures are applied, the SEM image of Catalyst #6, on the other hand, is not indicative of formation of bigger gold particles. At this point, it is worth mentioning that this may be a result of non-uniform distribution of the particles, and the image would have been taken of an area with a better dispersion.

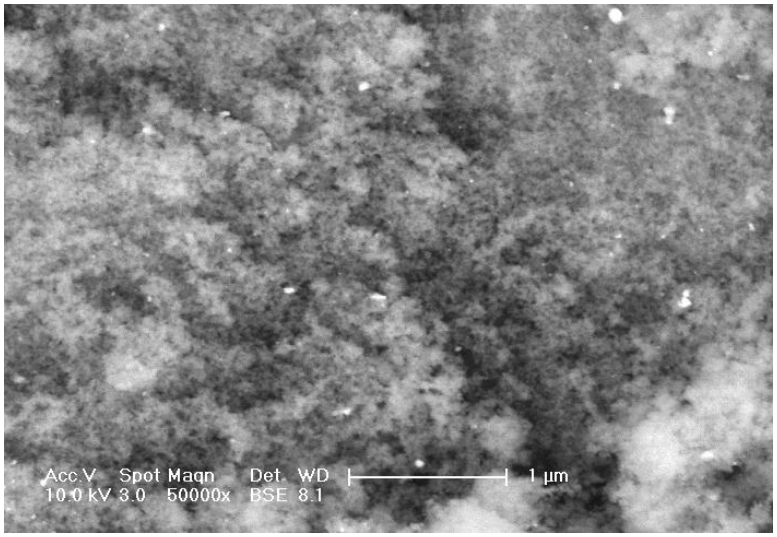

Figure 4.4. SEM image of 3% Au-1% Re/ZrO_2 (Catalyst #6)

Changing addition sequence of metal precursors to Re+Au resulted in better dispersion of gold particles in smaller sizes compared to that of the samples prepared through Re+Au sequence, which may be attributed to an interaction between Au and Re. The reason may be that gold particles already present on the surface kept their original sizes when Re was added afterwards, and on the other hand, when gold was added on ZrO_2 already impregnated with Re, the Re-ZrO_2 support led to a better Au dispersion by stabilizing gold particles on the surface during high temperature pretreatment steps and, as a consequence, smaller Au particle sizes were obtained. Figure 4.5 below shows the SEM image of a 3% Au-1% Re/ZrO_2 sample, that was prepared by impregnation of Re followed by deposition precipitation of Au, with a final calcination temperature of 250 ˚C.

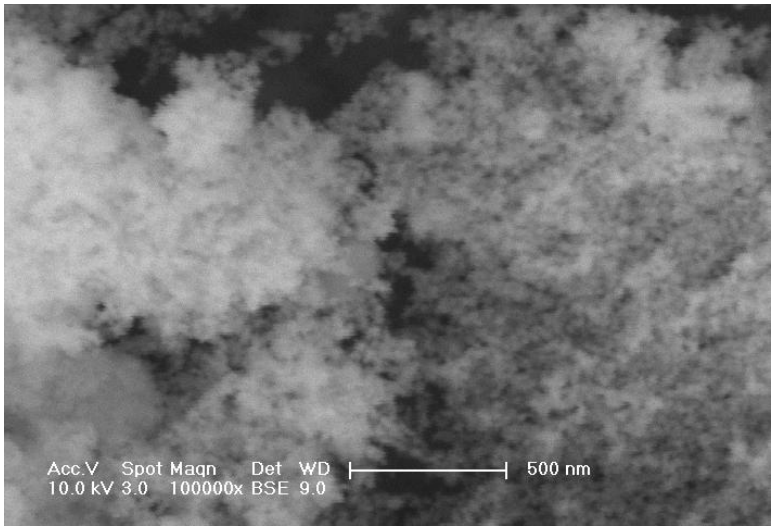

Figure 4.5. SEM image of 3% Au-1% Re/ZrO_2 (Catalyst #7)

To see the effect of gold loading on catalytic activity, 2% and 1% Au containing samples were also prepared. Figure 4.6 below shows an image of 2% Au-1% Re/ZrO_2 catalyst sample.

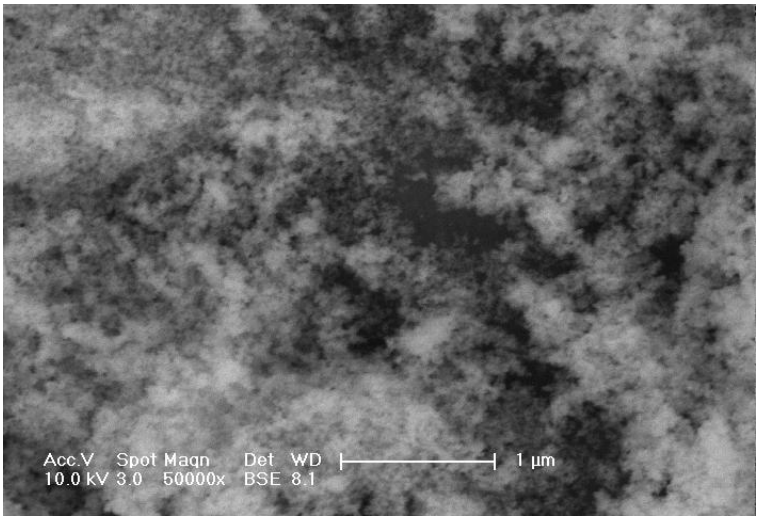

Figure 4.6. SEM image of 2% Au-1% Re/ZrO_2 (Catalyst #8)

The following image in Figure 4.7, which also belongs to Catalyst #8, indicates well dispersed Au particles, showing no agglomeration to form large crystallites.

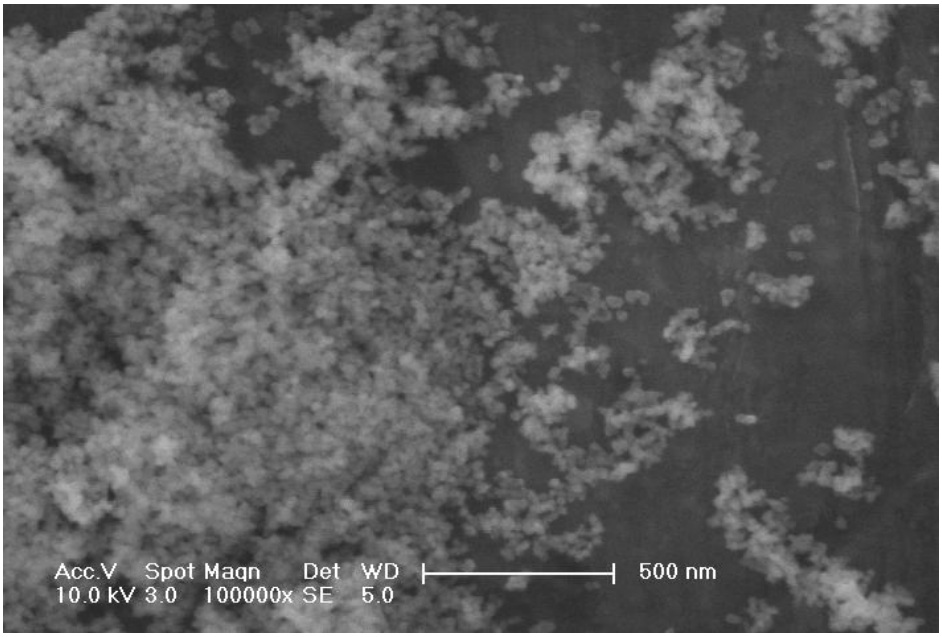

Figure 4.7. SEM image of 2% Au-1% Re/ZrO_2 (Catalyst #8)

A similar SEM image obtained from 1% Au-1% Re/ZrO_2 (Catalyst #9) sample is presented below in Figure 4.10 which also indicates well dispersion of gold particles.

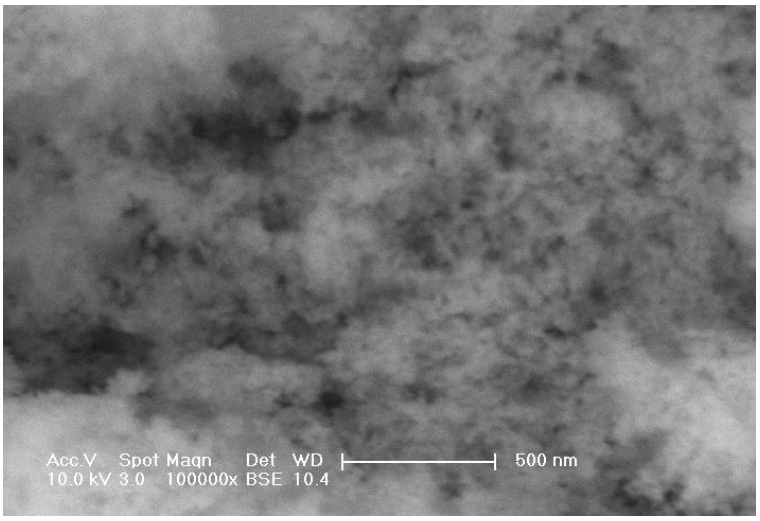

Figure 4.8. SEM image of 1% Au-1% Re/ZrO_2 (catalyst #9)

4.2. Catalytic Activity Tests

The concentrations of CO, CO_2 and CH_4 in the product stream were determined by a gas chromatograph. The catalysts prepared for this study were highly selective, showing almost no methane formation up to 350 ˚C; for some samples only trace levels of methane was detected at 350 ˚C. Thus, CO conversion is taken as a measure of catalytic activity through this study. It should be mentioned that the CO conversion levels in the product stream was double-checked by the CO analyzer connected to the system whenever necessary. Carbon monoxide conversions were evaluated by the following formula:

$$\text{CO conversion (\%)} = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} x100 \quad (4.1)$$

The amount of liquid water used in the experiments was calculated by the formula:

$$V_{Steam(H_2O)} = \frac{V_{Liquid(H_2O)} \times \rho_{H_2O} \times R \times T}{MW_{H_2O} \times P} \quad (4.2)$$

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

4.3. Water Gas Shift Activity of Au-Re Bimetallic Catalysts

4.3.1. WGS Tests Conducted on Au-Re/Ce-TiO_2 Catalysts

The first catalyst sample synthesized for this part of the study was Au-Re/Ce-TiO_2 (Catalyst #1). Ceria and Rhenium were impregnated sequentially and gold was added by deposition precipitation. The catalytic activity of this catalyst upon reduction under 5% H_2, balance He flow at 200 ˚C was first investigated on a bed of 75 mg sample, with an ideal feed composition which has 3% CO, 10% H_2O and balance He (Feed #0). Figure 4.9 shows the CO conversion attained over the sample in the 150-400 ˚C temperature range.

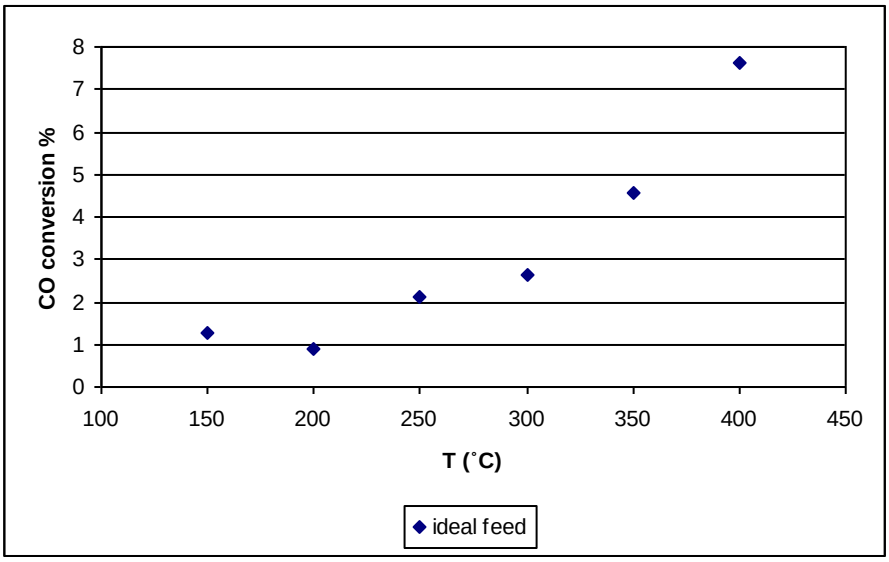

Figure 4.9. CO conversion % for Au-Re/Ce-TiO_2 for ideal feed; 3% CO, 10% H_2O and balance He (Experiment 1)

Considering the fact that a WGS catalyst, Pt-Ni/Al_2O_3, having satisfactory activities very close to equilibrium conversion levels with ideal feed compositions has already been synthesized in CATREL, and the Au-Re system on Ce-TiO_2 has limited activities, this was the only test performed under ideal feed conditions. Two more experiments were performed on this sample, to check whether the activity could be improved with changes in the reduction procedure. Figure 4.10 shows the results of those two experiments, performed on 200 g samples at a constant temperature of 350 ˚C with a realistic feed composition, Feed #1 (4.9%CO, 33%H_2O, 30.3% H_2, 10.5% CO_2, 22.3%He). For those tests the length of reduction procedure was increased to 2 hours, the H_2 concentration used in reduction was increased to 50%, and reduction treatments were performed at 250 and 300 ˚C, respectively.

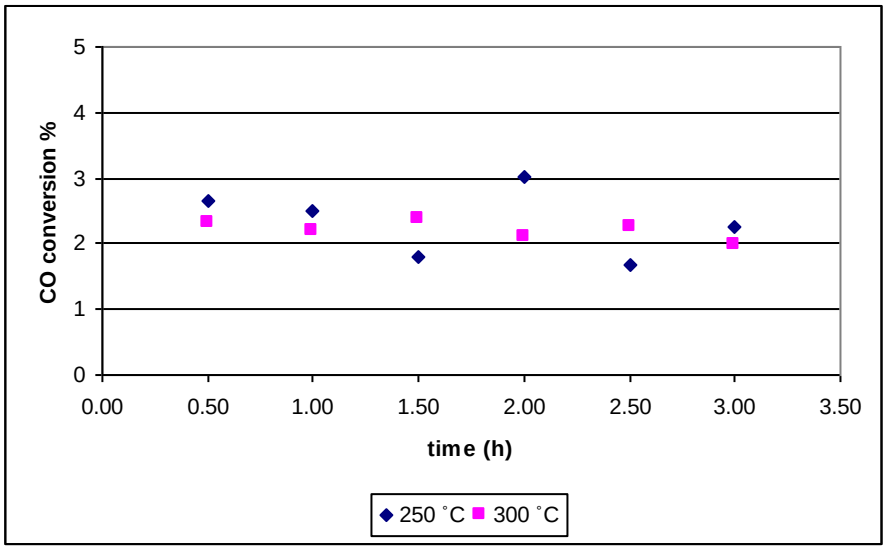

Figure 4.10. Effect of reduction temperature on the catalytic activity of Au-Re/Ce-TiO_2; reaction temperature: 350 ˚C, reaction mixture: 4.9%CO, 33%H_2O, 30.3% H_2, 10.5% CO_2, 22.3%He (Experiments 2&3)

Both samples, reduced at 250 and 300 ˚C, gave very low CO conversions, and the reduction temperature did not show a significant effect on the activity of the samples. Considering the fact that the catalysts showing very low activity under ideal feed conditions can not perform better under realistic conditions, no further tests were performed on Au-Re/Ce-TiO_2 samples.

No methane formation was observed for this sample, in any of these experiments.

4.3.2. WGS Tests Conducted on Au/ZrO_2 Catalysts

The activity of monometallic Au/ZrO_2 was investigated prior to the tests on bimetallic Au-Re/ZrO_2. The first Au/ZrO_2 sample synthesized contained 4% Au, and was named as Catalyst #2.The amount of catalyst sample used in the reaction test was 75 mg, and the sample was reduced under 5% H_2 flow at 180 ˚C for 1 hour. The catalytic activity was investigated under the flow of Feed #1 (4.9% CO, 33% H_2O, 30.3% H_2, 10.5% CO_2, 22.3% He). Activity of this sample, in terms of CO conversion, is presented in Figure 4.11 along with the results for a 200 mg sample tested under same conditions.

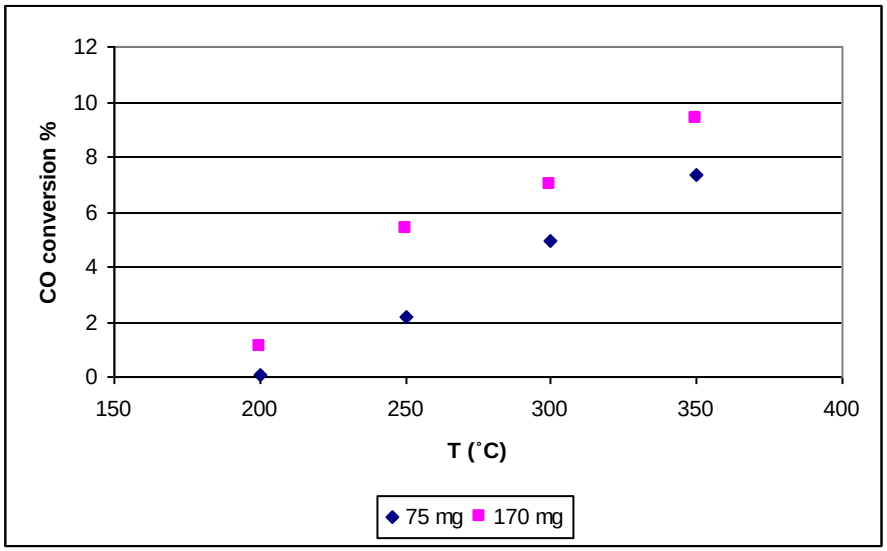

Figure 4.11. Effect of amount of catalyst on the catalytic activity of 4% Au/ZrO_2 (Catalyst #2); reaction mixture: 4.9%CO, 33%H_2O, 30.3% H_2, 10.5% CO_2, 22.3%He (Experiments 4&5)

As seen from Figure 4.11, catalytic activity increases with increasing amounts of catalyst sample and Catalyst #2 samples have better activity than Catalyst #1. Effect of feed composition on the activity of Catalyst #2 is presented in Figure 4.12. Note that the second feed composition used, which has 6% CO, 21% H_2O, 39% H_2, 10% CO_2 and balance He, is referred as Feed #2.

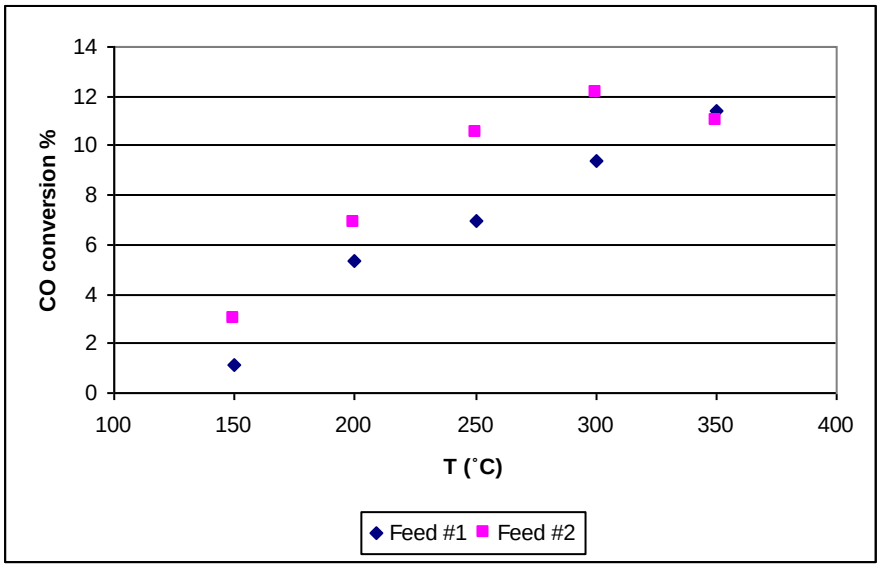

Figure 4.12. Effect of feed composition on the catalytic activity of 4% Au/ZrO_2, (Catalyst #2), reaction mixture: Feed #1: 4.9%CO, 33%H_2O, 30.3% H_2, 10.5% CO_2, 22.3%He & Feed #2: 6%CO, 21%H_2O, 39% H_2, 10% CO_2 and balance He (experiments 5&6)

Catalytic activity was found to increase for the new feed composition, which has almost same amount of CO_2 and even more H_2, but a lower H_2O/CO ratio. This can lead to a conclusion that the sample is more active for relatively lower H_2O/CO ratios.

Catalyst #3, which has the same composition as the Catalyst #2, but only atmospheric drying was applied upon deposition precipitation step, was tested next. Table 4.1 below shows the CO conversion levels obtained from the tests conducted on Catalyst #2 and Catalyst #3. In those tests, 170 mg samples were reduced under 5% H_2 flow at 180 ˚C for 1 hour, and Feed #2 was used as the feed stream.

Table 4.1. Effect of drying technique on catalytic activity, Catalyst #2 vacuum drying and Catalyst #3 atmospheric drying (Experiments 6&7)

Reaction Temperature (˚C)	Catalyst #2	Catalyst #3
300	12.1	11.4
350	11.0	13.6

The samples have very close CO conversion activities, suggesting that the drying technique is not an important parameter affecting the catalytic activity. The effect of gold loading was also investigated; for that purpose a 3% Au sample, namely Catalyst #4 was synthesized and tested. Table 4.2 shows the CO conversion levels obtained from Catalyst #3 and Catalyst #4.

Table 4.2. Effect of amount of gold loaded on catalytic activity, 4% Au (Catalyst #3) and 3% Au (Catalyst #4) (Experiments 7&8)

Reaction Temperature (˚C)	Catalyst #3	Catalyst #4
300	11.4	11.43
350	13.6	10.92

No concrete conclusion can be drawn on the effect of gold loading, as the WGS conversions obtained from those two samples are really close.

4.3.3. WGS Tests conducted on Au-Re/ZrO_2 Catalysts

First two bimetallic Au-Re samples supported on ZrO_2, Catalyst #5 and Catalyst #6, were prepared by a preparation procedure for which Au deposition was followed by Re impregnation (3% Au and 1% Re). Catalyst #5 and #6 were just different in their final calcination temperatures, which were 250 and 400 ˚C, respectively.

In order to investigate the influence of Re addition on the catalytic activity, CO conversion per cent results of 3%Au/ZrO_2 (Catalyst #4) and 3%Au-1% Re (Catalyst #5) are given together in Table 4.3.

Table 4.3. Effect of Re addition on the catalytic activity of 3% Au/ZrO_2 (Catalyst #4 & Catalyst #5) (Experiments 8&10)

Reaction Temperature (˚C)	Au	Au-Re
300	11.43	4.52
350	10.92	13.55

The results show that rhenium addition slightly increases the catalytic activity at 350 ˚C, but the activity decreases significantly at 300 ˚C. Low activity levels obtained from

both samples are in agreement with the SEM images of samples indicating relatively poor dispersion of Au on both samples. As explained in section 4.1 of this study, addition of Re in this sequence results in relatively poor dispersion and bigger gold particle sizes, which are parameters affecting the catalytic activity.

Effect of reduction temperature on the catalytic activity of Catalyst #5 was investigated for Feed #2, on samples reduced under 5% H_2 flow for 1 hour at 180 and 250 ˚C. The CO conversion per cent results are given in Table 4.4.

Table 4.4. Effect of reduction temperature on the catalytic activity of 3% Au-1%Re/ZrO_2 (Catalyst #5) (Experiments 10&11)

Reaction Temperature (˚C)	180 ˚C	250 ˚C
300	4.52	6.80
350	13.55	15.54

The increase in reduction temperature may have resulted in a slight increase of the catalytic activity, but the values are still very close. CO conversion values taken at 300 ˚C are worse compared to the Au/ZrO_2 samples.

Aiming to study the effect of H_2 content of the reduction mixture on WGS activity, the WGS activities of Catalyst #5 samples, which were reduced under the flow of 5% H_2 and 50% H_2 mixtures, were determined. The reduction was conducted at 250 ˚C for 1 hour for both cases. The activity results obtained for Feed #2 are given in Table 4.5.

Table 4.5. Effect of H_2 composition in reduction on the catalytic activity of 3% Au-1%Re/ZrO_2 (Catalyst #5) (Experiments 11&12)

Reaction Temperature (˚C)	5%	50%
300	6.80	4.96
350	15.54	15.94

The CO conversion results obtained in both cases are very similar, indicating that H_2 concentration of the reduction mixture has no significant effect on the activity of the samples.

The activities of the samples under the flow of Feed #3 with a composition of 6% CO, 36% H_2O, 39% H_2, 10% CO_2 and balance He, were also determined in order to see the effect of H_2O/CO ratio on the WGS activity. Table 4.6 gives the CO conversion levels obtained from Catalyst #5, reduced under 5% H_2 flow, at 180 ˚C for 1 hour under flow of Feed #3 having H_2O/CO=6 and Feed #2 having a H_2O/CO ratio of 3.5.

Table 4.6. Effect of H_2O/CO ratio on the catalytic activity of 3% Au-1% Re/ZrO_2 (Catalyst #5) (Experiments 10&15)

Reaction Temperature (˚C)	H_2O/CO=3.5	H_2O/CO=6
300	4.52	7.64
350	13.55	17.98

As observed from Table 4.6, catalytic activity is enhanced with increasing H_2O/CO ratios, unlike the case for Catalyst #2. It can be said that the presence of Re led to an enhanced activity when H_2O is used in excess amounts.

Catalytic activities of samples with different final calcination temperatures were investigated by comparing the CO conversion performances of Catalyst #5 and Catalyst #6.

Table 4.7. Effect of final calcination temperature on the catalytic activity of 3% Au-1% Re/ZrO_2 (Catalysts #5&#6) (Experiments 10&13)

Reaction Temperature (˚C)	Calcination T=250 ˚C	Calcination T=400 ˚C
300	4.52	4.12
350	13.55	11.25

The activity results indicated that the final calcination temperature have very limited effect on catalytic activity.

Aiming to study the effect of H_2 concentration in reduction stream on water gas shift activity of Catalyst #6, two samples were reduced under flows of 5% and 100% H_2 streams, respectively and both for a duration of 1 hour at 180 ˚C, were determined.

Table 4.8. Effect of H_2 composition in reduction on the catalytic activity of 3% Au-1% Re/ZrO_2 (Catalyst #6) (Experiments 13&14)

Reaction Temperature (˚C)	5%	100%
300	4.12	3.38
350	11.25	10.05

As can be seen from activity levels in Table 4.8, H_2 composition of the reduction mixture does not have an important effect on the catalytic activity. These were the last experiments performed to understand the influence of reduction mixture composition on bimetallic Au-Re samples, as it is concluded not to have a significant effect on activity.

It should be noted that trace amounts of methane formation was observed in WGS activity tests conducted on Catalyst #5 and Catalyst #6 at 350 ˚C.

In order to observe the influence of metal precursor introduction sequence on activity, 3% Au-1% Re/ZrO_2 (Catalyst #7), for which Re impregnation was carried out first and then Au was added with deposition precipitation, was prepared and tested in WGS. The results obtained were compared with those obtained from the tests conducted on Catalyst #5 with the same reaction conditions. The effect of preparation sequence on WGS activity can be seen in Table 4.9.

Table 4.9. Effect of preparation sequence on the catalytic activity of 3% Au-1% Re/ZrO_2 (Catalysts #5 & #7) (Experiments 15&16)

Reaction Temperature (˚C)	DP first	Imp. first
300	7.64	30.49
350	17.98	50.55

According to the WGS test results, the preparation sequence is found to be an important parameter on the catalytic activity of Au-Re bimetallic samples; the results clearly showed that adding gold by using deposition precipitation on Re/ZrO_2 support results in a significant increase in the CO conversion.

An overall evaluation of the WGS activities of Au-Re bimetallic samples prepared by Re+Au sequence clearly shows that Re+Au samples have higher WGS activities compared to monometallic Au/ZrO_2 samples. The probable reasons may be;

(i) the stabilizing effect of Re/ZrO_2 support leading to a higher dispersion of gold,
(ii) the synergistic interaction between Au and Re, and
(iii) the possible surface alloy formation between Au and Re.

Two new Au-Re catalyst samples, having fixed Re loading as 1% and two different levels of Au loadings, as 2% Au (Catalyst #8) and 1% Au (Catalyst #9), were prepared by Re impregnation followed by Au deposition.

In order to see the effects of Au loading on WGS performance; Catalysts #7, #8 and #9 were tested in 250-350 ˚C temperature range; the results of the activity tests are given in Figure 4.13.

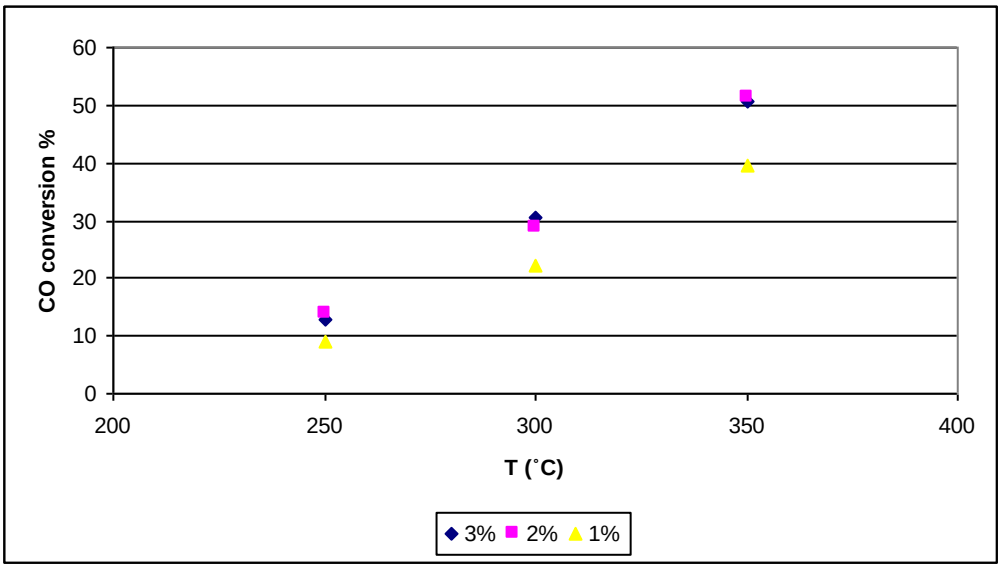

Figure 4.13. Effect of Au loading % on the catalytic activity of Au-Re bimetallic catalysts (Experiments 16, 18 and 20)

The performance results showed that samples having 2 and 3% Au loads have very similar activities and they both have shown significantly better activity compared to 1% sample especially at high temperature. Thus, the optimum gold loading for 1% Re loaded bimetallic Au-Re samples is postulated to be 2%.

Activities of 1 and 2% samples were also investigated for the effect of presence of methane in the feed stream. Figure 4.14 and Figure 4.15 shows the WGS activities of Catalyst #8 and Catalyst #9 under the flow of feeds with (Feed #4) and without (Feed #3) methane.

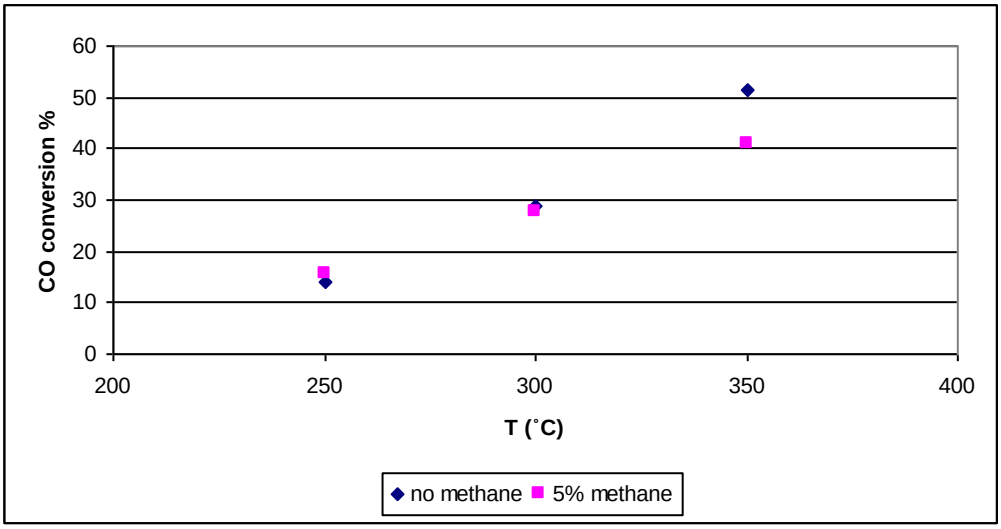

Figure 4.14. Effect of presence of methane on the catalytic activity of 2% Au-1% Re/ZrO_2 bimetallic catalyst (Experiments 18 and 19)

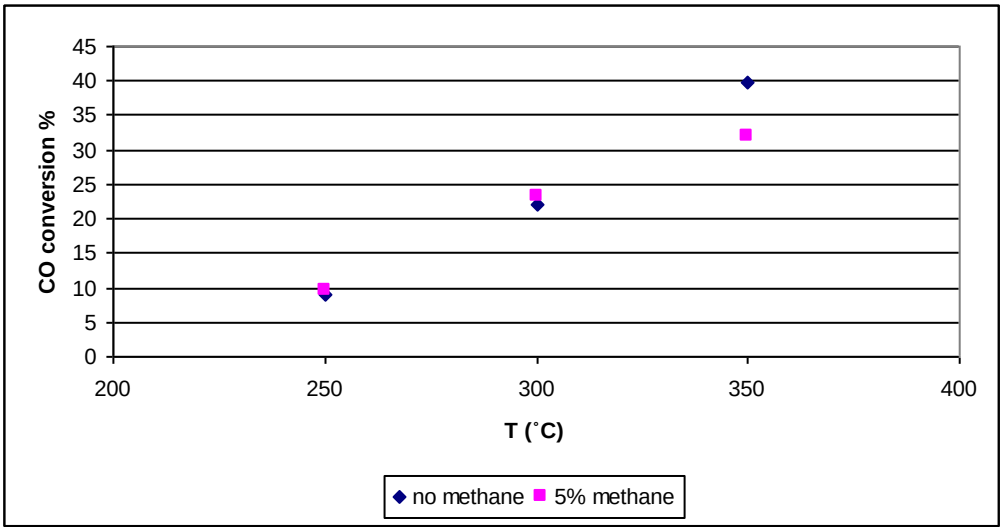

Figure 4.15. Effect of presence of methane on the catalytic activity of 1% Au-1% Re/ZrO_2 bimetallic catalyst (Experiments 21 and 22)

As observed from the figures, CO conversion is very similar for both cases up to 300 ˚C, but there is a slight decrease in the activity at 350 ˚C in the presence of methane for both samples.

Aiming to see the on-line real-time performance of the samples as well as to verify the results obtained from gas chromatograph under the same reaction conditions, the WGS performance tests on Catalysts #7, #8, and #9 were repeated in experiments 17, 18 and 21, respectively, for which the CO levels in the product stream were determined by CO analyzer. In those tests, an increasing temperature progression was applied for 50 ˚C increments for which the conversion data were taken when steady state values were reached for one temperature level and then the reaction temperature was increased to the next level. The results obtained from these experiments are given in Figures 4.16, 4.17 and 4.18 below:

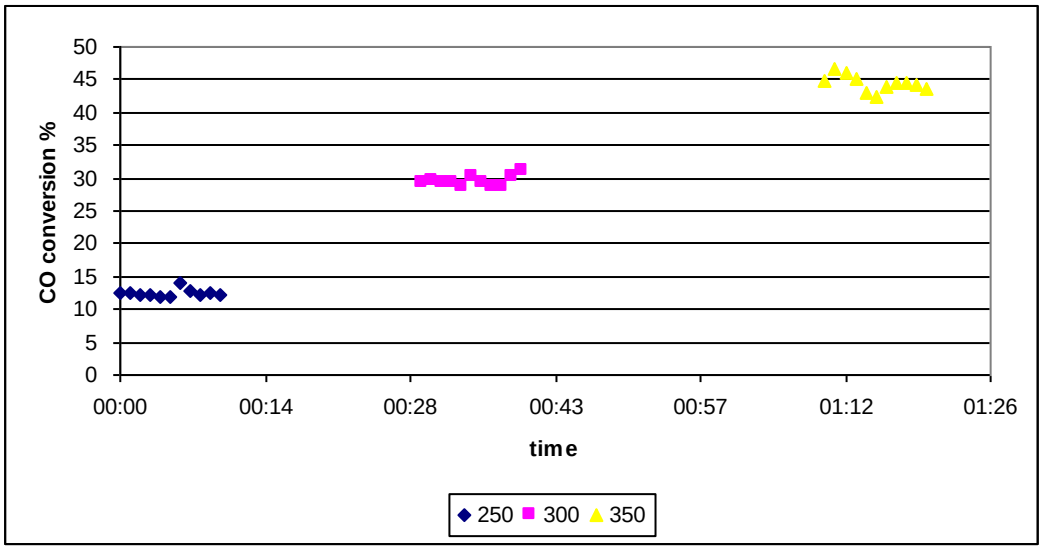

Figure 4.16. Catalytic activity of 3% Au-1% Re/ZrO_2 (Catalyst #7) determined with the CO analyzer (Experiment 17)

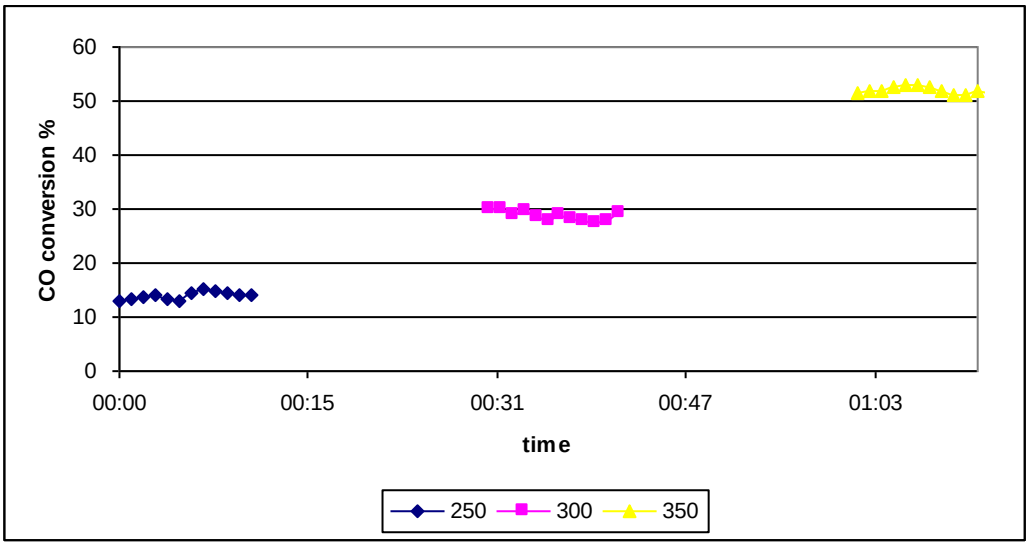

Figure 4.17. Catalytic activity of 2% Au-1% Re/ZrO_2 (Catalyst #8) determined with the CO analyzer (Experiment 18)

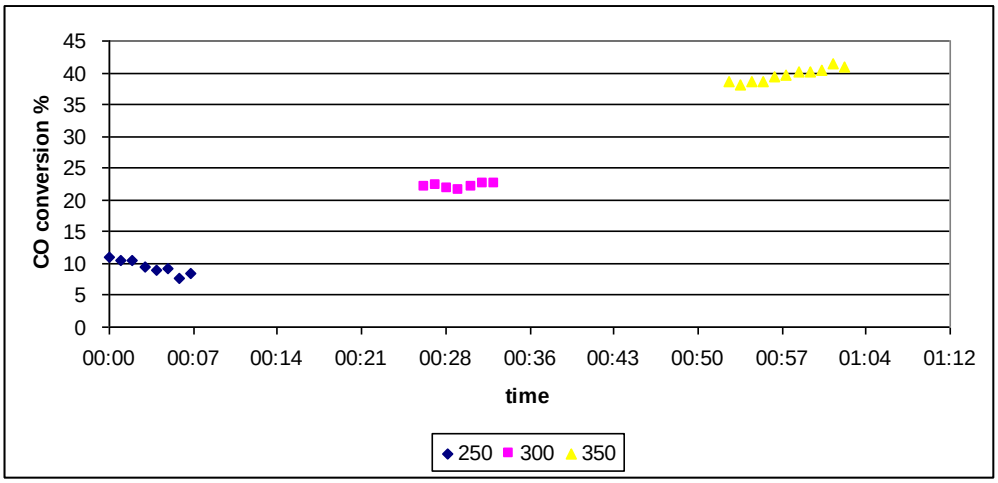

Figure 4.18. Catalytic activity of 1% Au-1% Re/ZrO_2 (Catalyst #9) determined with the CO analyzer (Experiment 21)

The results confirm that the best performing Au-Re catalyst in WGS reaction conducted under the flow of realistic feed is 2% Au-1% Re/ZrO_2 and the CO conversion values obtained from GC and CO analyzer are in good agreement. It is also worth mentioning that no methane formation was observed during any of the activity tests.

In order to investigate the effect of W/F ratio on the WGS performance, W/F ratios of 0.02 and 0.06 were also used, apart from the W/F ratio of 0.03 used for almost all other experiments. Figure 4.19 and 4.20 below show the activities obtained over Catalyst #7 from the experiments performed by using GC and CO analyzer in the product analysis.

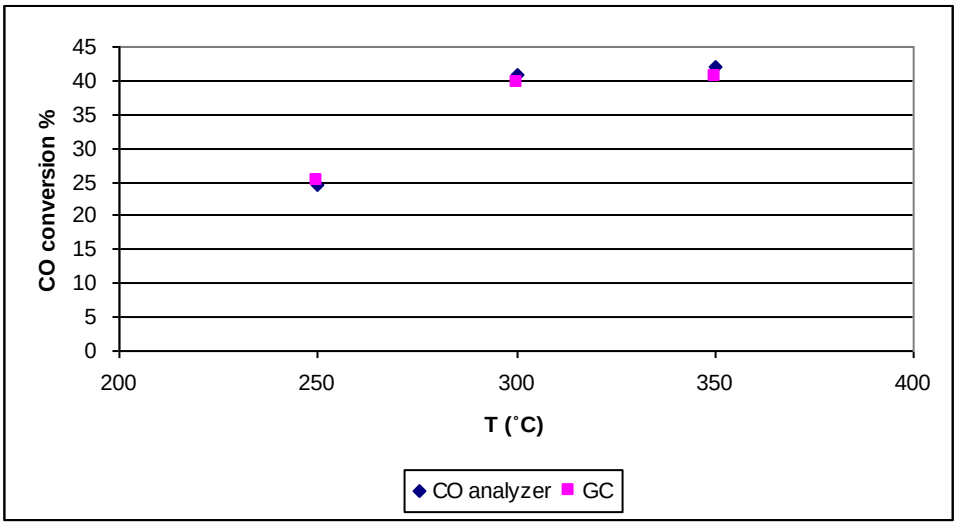

Figure 4.19. Catalytic activity of 3%Au-1%Re/ZrO_2 (Catalyst #7) determined with GC and CO analyzer for W/F=0.06 mg cat s ml^{-1} (Experiment 23)

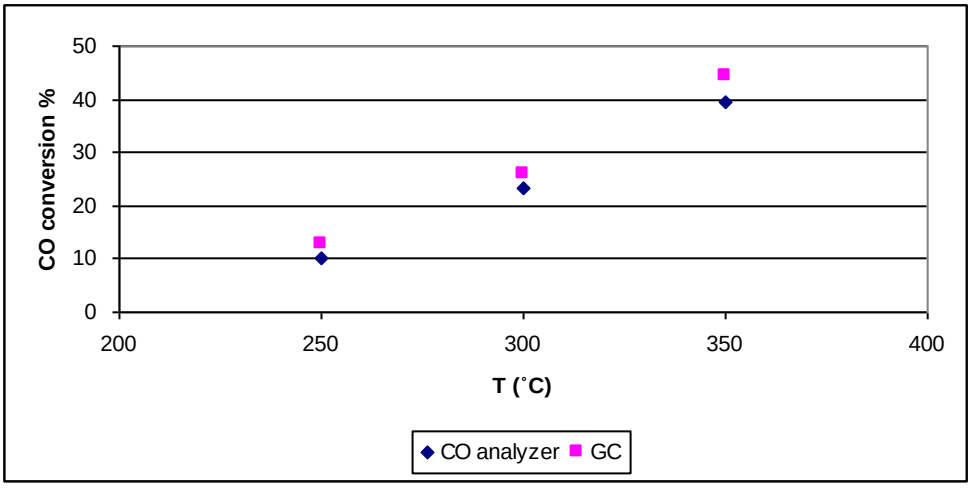

Figure 4.20. Catalytic activity of 3%Au-1%Re/ZrO_2 (Catalyst #7) determined with GC and CO analyzer for W/F=0.02 mg cat s ml^{-1} (Experiment 24)

The effect of W/F ratio on the WGS performance of 3%Au-1%Re/ZrO_2 (Catalyst #7), can be observed in Figure 4.21 below.

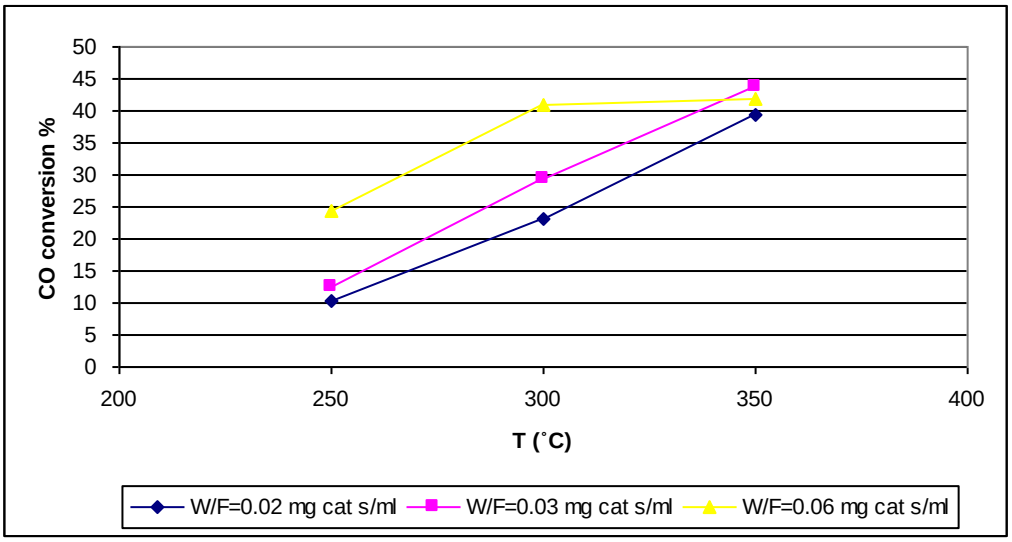

Figure 4.21. Effect of W/F ratio on the WGS performance of 3%Au-1%Re/ZrO_2 (Catalyst #7) (Experiments 17, 23 and 24)

As expected, the general trend observed from Figure 4.21 is that the catalytic activity increases with increasing W/F ratios, with the exception that the catalytic activity is very close for all W/F ratios at 350 ˚C.

In order to further investigate the effect of H_2O/CO ratio in the feed stream on the catalytic activity of Catalyst #7, two experiments were performed with H_2O/CO ratios of 5 and 7, Feed #5 and Feed #6 respectively, to be compared with the previous H_2O/CO ratio of 6 utilized in experiments tested under a feed flow of composition Feed #3. Figures 4.22 and 4.23 below show the activity results obtained for these experiments, using both CO analyzer and GC for product stream analysis.

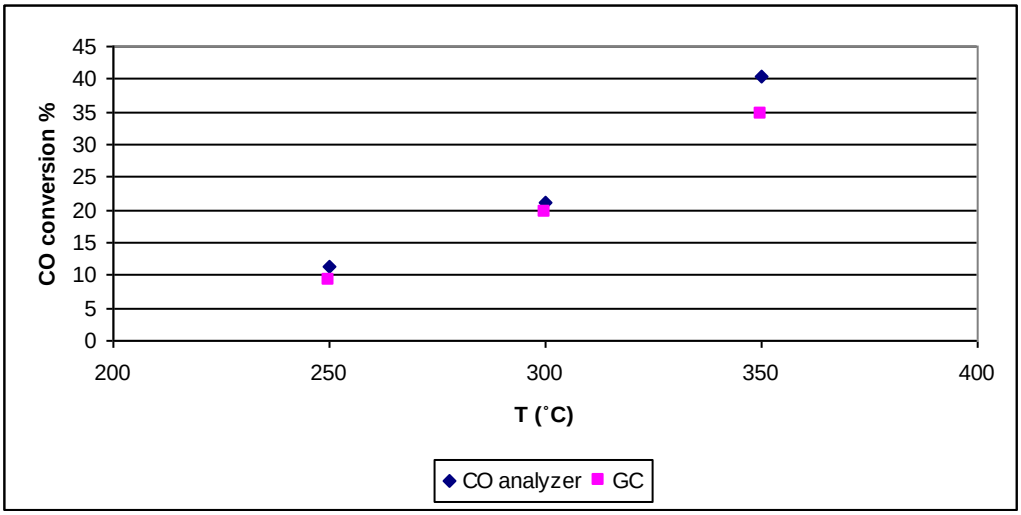

Figure 4.22. Catalytic activity of 3% Au-1% Re/ZrO_2 (Catalyst #7) determined with GC and CO analyzer for $H_2O/CO=5$ (Experiment 25)

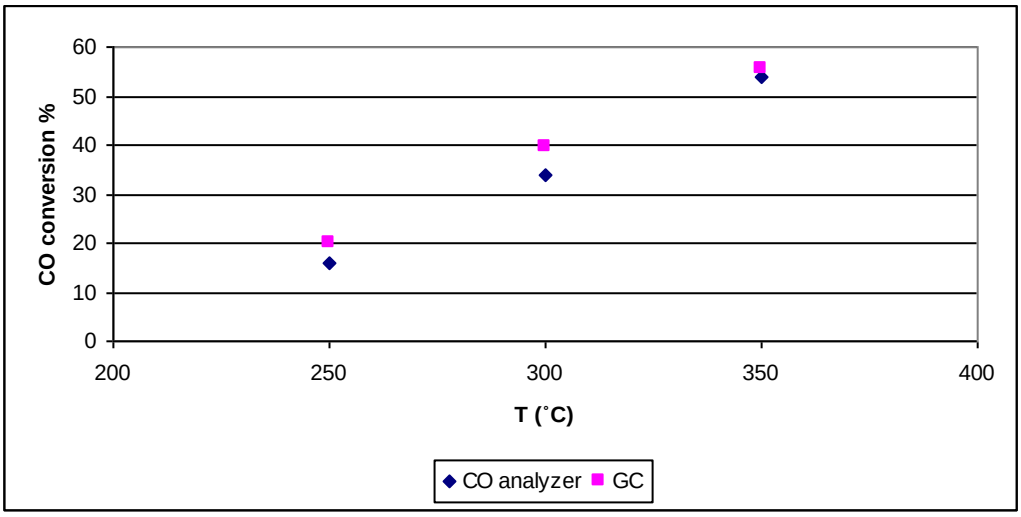

Figure 4.23. Catalytic activity of 3% Au-1% Re/ZrO_2 (Catalyst #7) determined with GC and CO analyzer for $H_2O/CO=7$ (Experiment 26)

The effect of H_2O/CO ratio on the WGS performance of 3% Au-1% Re/ZrO_2 (Catalyst #7), can be observed in Figure 4.24 below.

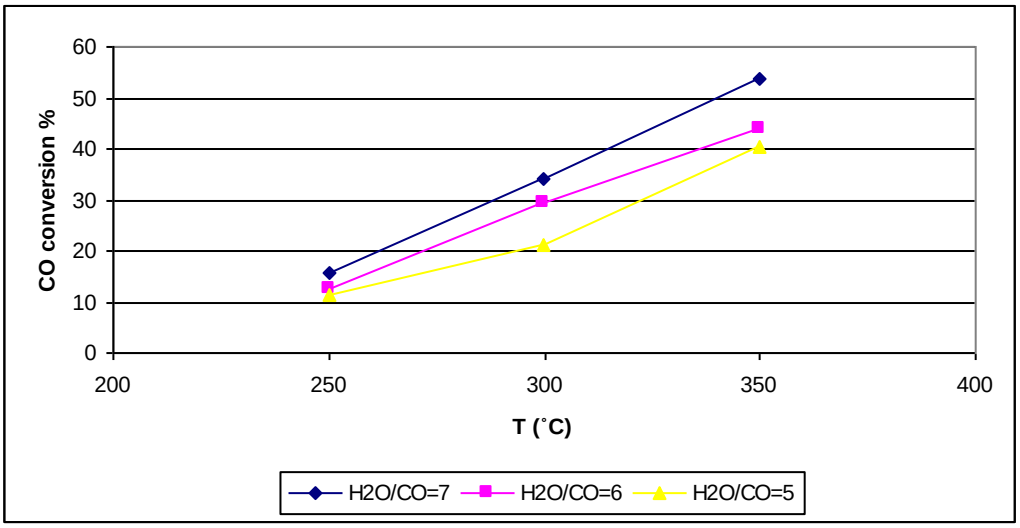

Figure 4.24. Effect of H_2O/CO ratio on the WGS performance of 3%Au-1%Re/ZrO_2 (Catalyst #7) (Experiments 17, 25 and 26)

As seen from the figure above, increasing the H_2O/CO ratio in the feed composition has a positive effect on the WGS activity of Au-Re/ZrO_2 samples.

Table 4.10 summarizes the CO conversion activities of all samples tested in this study. In the tests marked with ** the product stream was analyzed both with GC and CO analyzer; for those tests both results are presented in consequent rows. The average activity levels obtained from CO analyzer are underlined in the table.

Table 4.10. Summary of CO conversion results for all experiments performed for this study

Exp #	Cat #	W/F (mg cat s ml^{-1})	Feed Composition	CO conversion %		
				250 ˚C	300 ˚C	350 ˚C
1	1	W/F=0.012	Feed #0	-	2.6	4.6
2	1	W/F=0.033	Feed #1	-	-	2.67, 2.49, 1.78, 3.01,1.67, 2.25
3	1	W/F=0.033	Feed #1	-	-	2.32,2.18,2.39, 2.11,2.25,1.97
4	2	W/F=0.012	Feed #1	-	4.94	7.33
5	2	W/F=0.03	Feed #1	-	9.40	11.40
6	2	W/F=0.03	Feed #2	-	12.11	11.04
7	3	W/F=0.03	Feed #2	-	11.39	13.62
8	4	W/F=0.03	Feed #2	-	11.43	10.92
9*	5	W/F=0.03	Feed #2	-	-	13.47
10	5	W/F=0.03	Feed #2	-	4.52	13.55
11	5	W/F=0.03	Feed #2	-	6.80	15.54
12	5	W/F=0.03	Feed #2	-	4.96	15.94
13	6	W/F=0.03	Feed #2	-	4.12	11.25
14	6	W/F=0.03	Feed #2	-	3.38	10.05
15	5	W/F=0.03	Feed #3	-	7.64	17.98
16	7	W/F=0.03	Feed #3	12.97	30.49	50.55
17*	7	W/F=0.03	Feed #3	12.60	29.51	43.88
18*	8	W/F=0.03	Feed #3	13.84	28.78	51.45
19	8	W/F=0.03	Feed #4	15.63	27.58	41.01
20	9	W/F=0.03	Feed #3	9.07	22.11	39.66
21*	9	W/F=0.03	Feed #3	10.99	21.88	38.02
22	9	W/F=0.03	Feed #4	9.44	23.11	31.88
23**	7	W/F=0.06	Feed #3	25.04	39.60	40.53
				24.51	40.99	41.98
24**	7	W/F=0.02	Feed #3	12.78	25.93	44.19
				10.16	23.25	39.29
25**	7	W/F=0.03	Feed #5	19.91	39.77	55.40
				15.80	34.03	53.73
26**	7	W/F=0.03	Feed #6	9.22	19.65	34.66
				11.24	21.26	40.56

The CO conversion activities of the samples tested by using the same reaction conditions are given and compared in Figures 25 and 26.

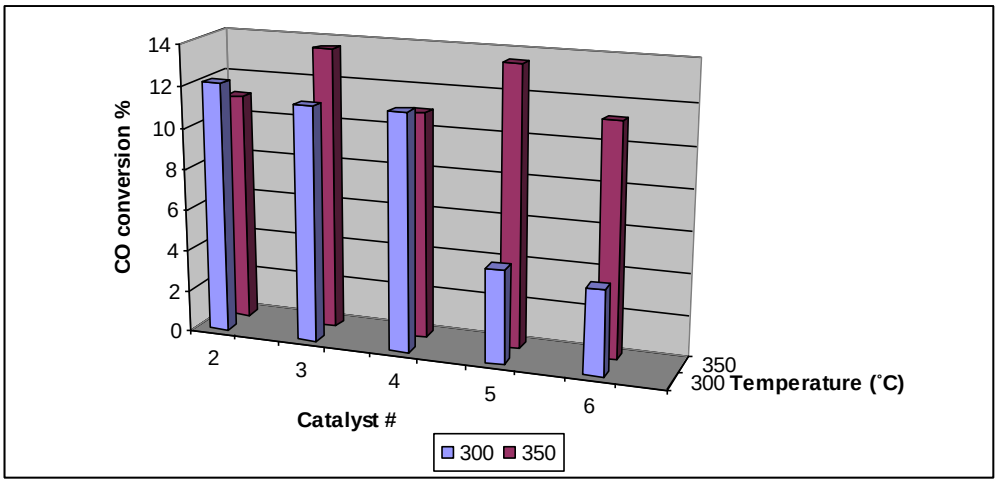

Figure 4.25. WGS performances of Catalyst #2, #3, #4, #5 and #6 tested with Feed #3 (Experiments 15, 16, 18 and 20)

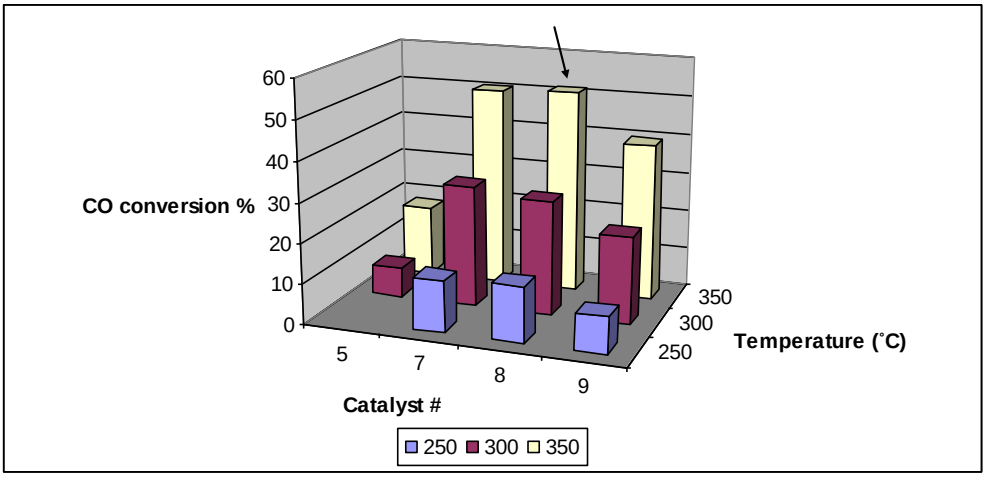

Figure 4.26. WGS performances of Catalyst #5, #7, #8 and #9 tested with Feed #2 (Experiments 6, 7, 8, 10 and 13)

The results clearly show that 1%Au-2% Re (Catalyst #8) prepared by sequential impregnation, for which Re is introduced first, has the highest activity. It can also be observed from the performance results, that samples having 2 and 3% Au loads have very similar activities and they both attain significantly better activities compared to 1% sample, especially at 350 ˚C.

It is worth remembering that activities of 1 and 2% samples prepared by Re+Au sequence were also studied for determining the effect of presence of methane in the feed stream. CO conversion values obtained were very similar for both cases up to 300 ˚C, but there was a slight decrease in the activity at 350 ˚C in the presence of methane for both samples.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

A comparison of the SEM images of 3% and 4% Au samples in terms of particle size and distribution suggested that 3% gold loading may be a limit for obtaining well dispersed gold. However, although particle size and dispersion are known to be important parameters for catalytic activity, the activity tests performed to understand the effect of gold loading on both samples gave very similar results. Increasing calcination temperature did not lead to formation of larger gold particles, which is in accordance with the fact that the catalytic activities of samples with different final calcination temperatures were found to be very similar.

WGS activity tests performed aiming to investigate the effect of reduction temperature and H_2 composition of reduction mixture on the catalytic activity showed that these two parameters have no significant effect on the activity of the samples prepared in this study. Additionally, tests conducted on samples dried with different drying techniques (vacuum and atmospheric drying) showed that drying technique is not an important parameter affecting the catalytic activity.

Addition of Re, through using Au+Re sequence, showed no improvement on the micro-structure of the catalyst samples, and might have even caused formation of bigger gold particles indicated by SEM images obtained. In accordance with that finding, the catalytic activity tests performed on samples prepared by this sequence showed that the catalytic activity was even lower than that had been obtained over monometallic samples at 300 ˚C. Changing impregnation sequence to Re+Au, however, resulted in better dispersion of gold particles in smaller sizes compared to that of the samples prepared through Au+Re sequence. According to the WGS test results, adding gold by using deposition precipitation on Re/ZrO_2 support results in a significant increase in the CO conversion, when compared to CO conversion values obtained for tests performed on both monometallic Au/ZrO_2 samples and $Au\text{-}Re/ZrO_2$ samples prepared by Au+Re sequence. The probable reasons were suggested to be;

(i) the stabilizing effect of Re/ZrO_2 support leading to a higher dispersion of gold,

(ii) the synergistic interaction between Au and Re, and

(iii) the possible surface alloy formation between Au and Re.

In order to see the effects of Au loading on WGS performance; catalyst samples prepared by Re+Au sequence and containing 3%, 2% and 1% Au respectively, were tested in the 250-350 ˚C temperature range. The performance results showed that samples having 2 and 3% Au loads have very similar activities and they both attained significantly better activities compared to 1% sample, especially at 350 ˚C. Thus, the optimum gold loading for 1% Re loaded bimetallic Au-Re samples was postulated to be 2%.

Activities of 1 and 2% samples prepared by Re+Au sequence were studied for determining the effect of presence of methane in the feed stream. CO conversion values obtained were very similar for both cases up to 300 ˚C, but there was a slight decrease in the activity at 350 ˚C in the presence of methane for both samples.

Effect of W/F ratio on the WGS performance was also investigated by using W/F ratios of 0.02 and 0.06, apart from the W/F ratio of 0.03 used for almost all other experiments. As expected, the general trend observed was that the catalytic activity increases with increasing W/F ratios, with the exception that the catalytic activity was found to be very close for all W/F ratios at 350 ˚C.

H_2O/CO ratios of 5, 6 and 7 were utilized in experiments to observe the effect of H_2O/CO in the feed. Increasing the H_2O/CO was shown to have a positive effect on the WGS activity of $Au\text{-}Re/ZrO_2$ samples, whereas an inverse effect was observed for monometallic Au/ZrO_2 samples. Thus, it was suggested that the presence of Re led to an enhanced activity when H_2O was used in excess amounts.

Trace amounts of methane formation was observed only for the samples prepared by Au+Re sequence at 350 ˚C. No methane activity was observed for the rest of the samples.

5.2. Recommendations

Considering the results obtained in this study, following ideas are suggested for future studies that will use Au-Re/ZrO_2 as a selective WGS catalyst under realistic feed conditions:

- Although no indication of loss of activity was observed during reaction tests performed, it is worth performing a stability test for a long period to investigate whether the catalyst is highly stable.
- The de-ionized water source was seen to be a very important parameter on the reproducibility of the catalyst samples. Grade and source of de-ionized water must be fixed and great care should be given to obtain a standard water composition.

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