AN EXPERIMENTAL STUDY ON MIXED REFORMING PERFORMANCE OF Co-BASED CATALYSTS

by

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to my family

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ABSTRACT

AN EXPERIMENTAL STUDY ON MIXED REFORMING PERFORMANCE OF Co-BASED CATALYSTS

The major purpose of this research study is to investigate the mixed reforming, both CDRM + SR and CDRM + POX, activity over Co-Ce/ZrO_2 bimetallic catalyst, and to experimentally determine the optimal mixture of oxygen sources for the improved catalytic performance. 10 wt.%Co-2 wt.%Ce/ZrO_2 catalyst was prepared and tested for its mixed reforming performance. Temperature, CH_4/CO_2 feed ratio and additional oxygen concentration levels in the feed during mixed reforming tests were used as experimental parameters. The results have shown that, mixed reforming, CDRM + SR and CDRM + POX, activity increase with an increase in temperature. The overall performance and stability in mixed reforming compared to those in individual CDRM has improved with the addition of steam and oxygen. It is observed that the lower CH_4/CO_2 feed ratios have resulted in higher CO_2 conversion and better selectivity. It is concluded that stable activity can be achieved and H_2/CO product ratio can be controlled by changing additional oxygen source concentration in the feed. Coke deposition in reactor is decreased with increasing O_2 concentration levels in the feed. It is also shown that the additional oxygen source, steam or oxygen, doesn't significantly affect activity, but the H_2/CO product selectivity is closer to unity in CDRM + POX mixed reforming. XPS analysis of freshly reduced and spent catalysts have shown that CO_2 conversion is positively affected by surface Co^{2+}/Co^{3+} ratio. In CDRM+POX mixed reforming, Ce^{3+}/Ce^{4+} ratio decreases at higher conversion values, due to high utilization of oxygen on active sites. The optimal mixed reforming condition is found as high temperature, low CH_4/CO_2 feed ratio and addition of O_2 with concentration level enough to prevent coke deposition.

ÖZET

METANIN KARIŞIK REFORMLANMASINDA KOBALT BAZLI KATALİZÖRLERİN PERFORMANSI HAKKINDA DENEYSEL ÇALIŞMA

Bu çalışmanın ana amacı, zirkonya üzerinde desteklenmiş kobalt bazlı çift metalli katalizörlerin karışık reformlanma, kuru + buhar reformanlanması ve kuru reformlanma + kısmi oksidasyon, reaksiyonundaki aktivitenin deneysel olarak incelenip geliştirilmesi, ve ideal oksijen kaynağı besleme değerlerinin bulunmasıdır. Co/ZrO_2 katalizörü, oksijen taşıma kapasitesini, elektron transfer regulasyonunu iyileştirerek, geliştirdiği bilinen Ce ile güçlendirilmiştir. 10 wt.%Co-2 wt.%Ce/ZrO_2 katalizörü hazırlanmıştır ve bu katalizör karışık reformlanma performansının ölçülmesi amacıyla deneysel testlere tabi tutulmuştur. Sıcaklık, CH_4/CO_2 besleme oranı ve ek oksijen konsantrasyon seviyesi, bu deneyin parametreleri olarak seçilmiştir. Sonuçlara göre, karışık reformlanma reaksiyonu aktivitesinde sıcaklığın artışı ile artış sağlanmıştır. Karışık reformlanmanın genel performansı ve stabilitesi kuru reformlanmaya göre iyileşme göstermiştir. CH_4/CO_2 besleme oranının düşük olduğu şartlarda, CO_2 dönüşümünün daha yüksek olduğu ve H_2/CO oranı seçiciliğinin istenen düzeye daha yakın oldüğu gözlemlenmiştir. Besleme karışımındaki ek oksijenin konsantrasyon seviyesi değiştirilerek aktivitenin daha kararlı hale gelmesinin sağlanabileceği ve ürün H_2/CO ürün oranının istenilen şekilde kontrol edilebileceği belirlenmiştir. Reaktördeki kok birikimi, besleme akışındaki O_2 oranı yükseltilince, azalmıştır. Ayrıca, ek O_2 kaynağının buhar veya oksijen olmasının aktiviteyi fazla etkilemediği gözlenmiştir. Ancak H_2/CO ürün oranının bire yakın olması için kuru reformlanma ve kısmi oksidasyondan oluşan karışık reformlanma daha uygundur. Taze indirgenmiş ve reaksiyonlarda kullanılmış katalizörlerin XPS analizleri CO_2 dönüşümünün yüzeydeki Co^{2+}/Co^{3+} oranında pozitif olarak etkilendiğini göstermiştir. O_2 ile gerçekleşen karışık reformlanmada kullanılan örneklerin yüzeyindeki Ce^{3+}/Ce^{4+} oranı düşüş göstermiştir, bu sonuç oksijenin aktif sitelerdeki kullanımındaki iyileşmeyi işaret etmektedir . İdeal reaksiyon şartları, yüksek sıcaklık, düşük CH_4/CO_2 besleme oranı ve yüzeydeki karbon temizlemeye yetecek oranda ek O_2 besleme oranları olarak bulunmuştur.

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C	Concentration
ΔH	Enthalpy of reaction

LIST OF ACRONYMS/ABBREVIATIONS

BOS	Birleşik Oksijen Sanayi
CDRM	Carbon Dioxide Reforming of Methane
EDX	Energy Dispersive X-Ray
FT	Fischer Tropsch
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatography
POX	Partial Oxidation
RWGS	Reverse Water Gas Shift
SEM	Scanning Electron Microscopy
SR	Steam Reforming
TCD	Thermal Conductivity Detector
WGS	Water Gas Shift
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

1. INTRODUCTION

Depletion of fossil fuel reserves combined with increasing energy demand of the world has lead researchers to find alternative and new ways of energy production. There has been a great interest on natural gas due to its abundance and energy potential. Many researchers have studied the catalytic reforming of methane, as it is the major component of natural gas (70-98%) (Albarazi *et al.*, 2013).

Currently the industrial processes use methane as a primary feedstock to produce synthesis gas, also called as syngas, a mixture containing CO and H_2. Syngas is utilized in production of liquid hydrocarbons by Fischer-Tropsch synthesis, methanol and oxygenated compounds. Also several carbonylation, hydrogenation and reduction processes are conducted with syngas. Methane reforming can be carried out in three different ways (Özkara-Aydınoglu, 2010):

CDRM $$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \; \Delta H^o_{298} = 247 kJmol^{-1} \quad (1.1)$$

SR $$CH_4 + H_2O \rightarrow 3H_2 + CO \; \Delta H^o_{298} = 206 kJmol^{-1} \quad (1.2)$$

POX $$2CH_4 + O_2 \rightarrow 4H_2 + 2CO \; \Delta H^o_{298} = -36 kJmol^{-1} \quad (1.3)$$

There are two main reasons for dry reforming of methane to receive further special interest from researchers; these are the consumption of two major greenhouse gases (CO_2 and CH_4) in the reaction and more suitable H_2/CO ratio in the produced syngas for further applications like Fischer-Tropsch synthesis, both of which have great importance for environmental and industrial aspects (Pichas *et al.*, 2011).

Catalytic dry reforming of methane (CDRM) has been widely studied over various catalysts containing noble metals such as Pt, Ru, Rh, Ir and Pd. It is shown that noble metal containing catalysts have higher activity and selectivity towards CDRM, but their high cost and low availability makes them economically incompetitive. On the other hand non-precious transition metals such as nickel, iron and cobalt also shows great promise with some drawbacks. CDRM is a highly endothermic reaction (800-900 °C), which causes

catalyst sintering. Additionally, methane cracking and Boudouard reactions creates carbon deposition which leads to catalyst deactivation (Luisetto *et al.*, 2012; Guczi *et al.*, 2010).

Methane Cracking $$CH_4 \rightarrow 2H_2 + C\ \Delta H^o_{298} = 17.9 kcal mol^{-1}$$ (1.4)

Bouduard Reaction $$CO \rightarrow CO_2 + C\ \Delta H^o_{298} = -41.2 kcal mol^{-1}$$ (1.5)

The drastic operating conditions impose the investigation on the development of new catalysts with improved stability and activity through preventing metal sintering and reducing coke formation. It is accepted that these aims can be achieved by using different supports, active metal precursors, synthesis methods and pretreatment procedures (Montoya *et al.*, 2000).

The previous studies have shown that activity loss for CDRM catalysts is caused mainly by coke deposition. Stable CDRM activity is achieved when carbon formed at the methane dehydrogenation sites are cleaned by the surface oxygen formed from CO_2 disproportionation. Relatively slower rate of carbon removal by surface oxygen compared to that of methane dehydrogenation leads to an increase in carbon deposition rate significantly, which subsequently results in activity loss (Huang *et al.*, 2008).

CDRM catalysts that suffer from severe coke deposition may sustain stable and high activity when additional oxygen source other than CO_2 is present in the process. In the current MS thesis, the mixed reforming, i.e. CDRM coupled with steam reforming or partial oxidation, performance of 10 wt.% Co-2 wt.% Ce/ZrO_2 catalyst was studied in a detailed fashion. Mixed reforming performance of catalyst is investigated by considering temperature, additional oxygen concentration of additional oxygen source in the feed, feed ratio and CH_4/CO_2 feed ratio as parameters.

In Chapter 2, theoretical background of CDRM and mixed reforming are presented by a detailed literature survey. Experimental work performed is presented in Chapter 3. The experimental results are shown and discussed in Chapter 4. In Chapter 5 the conclusions from the current study are drawn and the recommendations for future studies are made.

2. LITERATURE SURVEY

2.1. Carbon Dioxide Reforming of Methane

The catalytic dry reforming of methane (CDRM, Equation 2.1), which converts two of the cheap, thermodynamically stable and potent greenhouse gases (CO_2 and CH_4) into synthesis gas, a mixture of CO and H_2, has gained a lot of interest in recent years. CDRM produces syngas with H_2/CO ratio of 1, which is desired for the Fischer-Tropsch synthesis process to produce liquid hydrocarbons. The main reactions that take place CDRM are as follows (Akpan *et al.*, 2007):

CDRM:	$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$	(2.1)
RWGS:	$H_2 + CO_2 \leftrightarrow CO + H_2O$	(2.2)
Carbon dioxide methanation:	$4H_2 + CO_2 \leftrightarrow CH_4 + 2H_2O$	(2.3)
Carbon monoxide methanation:	$3H_2 + CO \leftrightarrow CH_4 + H_2O$	(2.4)
SR:	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	(2.5)
Boudouard reaction:	$2CO \leftrightarrow CO_2 + C$	(2.6)
Methane decomposition:	$CH_4 \leftrightarrow C + 2H_2$	(2.7)
Coke acidification:	$C + H_2O \leftrightarrow CO + H_2$	(2.8)

Synthesis gas (syngas), a mixture of two gases, H_2 and CO, is an important feed stock for industrial processes. Syngas is produced mainly through three main reactions; CDRM, steam reforming (Equation 2.10) and partial oxidation (Equation 2.11). CDRM has advantage over other syngas producing methods, like steam reforming and partial oxidation, with its H_2/CO production ratio of 1 (Yang *et al.*, 2010; Özkara-Aydınoğlu *et al.*, 2009;Arandiyan *et al.*, 2012; Newnham *et al.*, 2012).

CDRM	$CH_4 + CO_2 \leftrightarrow 2CO + 2\,H_2,\ \Delta H^0_{298} = +247\ kJ/mol$	(2.9)
SR	$CH_4 + H_2O \leftrightarrow CO + 3\,H_2\,,\ \Delta H^0_{298} = +206\ kJ/mol$	(2.10)
POX	$CH_4 + 1/2O_2 \leftrightarrow CO + 2\,H_2\,,\ \Delta H^0_{298} = -38\ kJ/mol$	(2.11)

CDRM utilizes natural gas, which involves CH_4 and CO_2, by producing highly valuable syngas. Syngas is primarily used in many industrial processes to produce wide range of chemical compounds, like formaldehyde, acetic acid, dimethyl ether, methyl tert-butyl ether, olefins (Equation 2.13) and liquid hydrocarbons, through Oxo and Fischer – Tropsch synthesis, and hydroformylation reactions. CDRM offers certain advantages over steam reforming and partial oxidation where the downstream processes like methanol (Equation 2.12) and Fischer – Tropsch synthesis requiring H_2/CO ratio close to unity (Arandiyan *et al.*, 2012; Newnham *et al.*, 2012; Djaidja *et al.*, 2006; Albarazi *et al.*, 2013).

Methanol Synthesis $$CO + 2H_2 \leftrightarrow CH_3OH \quad (2.12)$$

Olefin Production $$2nH_2 + nCO \leftrightarrow C_nH_{2n} + nH_2O \quad (2.13)$$

Syngas production accounts for 60-70% of typical commercial FT synthesis process on site capital costs, where FT synthesis process consists of three sections; syngas production and purification, FT synthesis, and product upgrade. As a result, CDRM has gained further research interest with industrial demand of cheaper syngas production. Thermodynamically it is more suitable to operate CDRM at high temperature with CO_2/CH_4 ratio far above unity to decrease the coke formation. However, CO_2/CH_4 feed ratio of unity is far more desirable from an industrial standpoint since H_2/CO ratio close to one will be more suitable for further downstream processes like FT synthesis. CDRM not only consumes two important greenhouses gases but also it utilizes abundant and cheap natural gas from readily available reservoirs with high methane content (70-98%) and substantial CO_2 content. Existence of such natural gas fields also opens up the possibility of employing CDRM in areas with little to no water availability (James *et al.*, 2010; Djaidja *et al.*, 2006; Albarazi *et al.*, 2013; Foo *et al.*, 2012; Cheng and Huang, 2010; Meshkani *et al.*, 2014; Ding *et al.*, 2014).

Although CDRM offers many advantages over other syngas production methods like SR and POX, its commercialization is yet prevented because it's a high-energy demanding reaction owing to its high endothermic character (ΔH^0_{298}=247kJ/mol). Thermodynamically higher temperature conditions are favored for better conversion rates. But coke forming Boudouard reaction (Equation 2.6), also called as carbon monoxide disproportionation, and methane decomposition (Equation 2.7) also occur under such severe conditions causing

coke-induced deactivation. Other drawbacks of high temperature dependence of CDRM are catalyst sintering, which decreases catalyst activation by preventing feed gases to reach active metal sites, and occurrence of reverse water gas shift (RWGS, Equation 2.2) reaction, which lowers the H_2/CO ratio below unity (Özkara-Aydınoglu and Aksoylu, 2010; Pichas *et al.*, 2011; Daza *et al.*, 2010; Luisetto *et al.*, 2012; Foo *et al.*, 2012).

Development of catalysts capable of inhibiting carbon deposition kinetically at conditions in which carbon disposing reactions are favored has been taking utmost interest from researchers. Development of the catalysts having high and stable activity under drastic conditions is a promising solution (Meshkani and Rezaei, 2011).

2.2. Mixed Reforming of Methane

Beside catalyst formulation, another method of suppressing the coke formation is the addition of another oxygen resource through changing the reaction conditions, like introducing water or oxygen to the reactant stream, which is called mixed reforming. Mixed reforming is CDRM simultaneous with steam reforming or partial oxidation. It is presented in prior studies that addition of steam into CDRM drastically reduced the carbon disposition rate. Partial oxidation of methane is an exothermic reaction. Coupling an endothermic reaction (CDRM) with an exothermic reaction (POX) facilitates better heat transfer on catalyst bed which incorporates safer reaction conditions and more efficient operation in terms of energy (Nematollahi *et al.*, 2011; Park *et al.*, 2013).

Reducing carbon disposition can be attained through adding steam, oxygen or both to CDRM press. Oxidation of the carbon precursor species, such as hydrogenated CH_x species, occurs in the presence of steam and/or O_2 results in reduced coke formation on catalyst surface (Choudhary and Mondal, 2006). Additional oxygen source not only decreases coke formation but also presents an opportunity to control H_2/CO ratio of the end product and temperature of catalyst bed. Steam reforming is still being used in industry widely to produce syngas. SR produces syngas with higher H_2/CO ratio (>3) than the scope of Fischer-Tropsch synthesis causing industries to require additional separating units thus increasing the overall plant cost. POX with explosion risk due to its exothermic nature is an operation unless hot spots are dealt with. By simultaneous CDRM (H_2/CO=1), SR

(H_2/CO>3) and/or POX (H_2/CO=2) the specs of the end product can be controlled for specified customer needs and the operational risks are subdued as well (Choudhary and Mamman, 2000; Koo *et al.*, 2009; Ji *et al.*, 2010).

2.3. Catalysts for Dry and Mixed Reforming of Methane

Fischer and Tropsch studied CDRM process as early as 1928 and presented that different metals have different activities for CDRM. Group VIII metals, also known as noble metals, such as Ru, Rh, Pt, Ir, Pd are immensely investigated by researchers and they are found to be significantly active in CDRM process. Especially rhodium and ruthenium have shown high selectivity with carbon free operation and high activity. However, due to their market price and lack of availability, those noble metals are not economically viable to be used in catalyst formulation (Bitter *et al.*, 1997; Wang and Ruckenstein, 2000; Foo *et al.*, 2012).

Group VII transition metals, such as Ni, Co and Fe, have been widely investigated, as they are more preferred by the industry since they are abundant, cheap and reactive materials. To make CDRM industrially viable it's a necessity to prepare transition-metal catalysts with higher activity, stability and selectivity. Nickel based catalysts are known to be the best catalysts in methane reforming, but the major drawback of Ni catalysts is the formation of carbon deposition on the catalyst surface which results in catalyst deactivation. The suppression of carbon deposition on Ni catalysts are widely studied but it still presents a great challenge in CDRM process (Sutthiumporn *et al.*, 2012).

2.3.1. Ni Based Catalysts

In recent years, CDRM is performed over supported Ni catalysts and it is reported that support may play an important role in the activity and resistance to carbon deposition. Thus, the supports are modified in order to improve stability and carbon resistance of nickel catalysts. Alkali, alkaline metal oxides and rare earth oxides are used generally as promoters. By increasing oxygen storage capacity and adding reversible oxygen storage ability, rare earth oxides have risen up interest in the research studies. Previous studies have shown that ceria and lanthanum oxide are effective in improving the dispersion of

active species as well as increasing stability, activity and resistance to carbon deposition. In their study, Yang et al., have used La_2O_3-CeO_2 binary promoted Ni-based catalysts to investigate their CDRM performance. The catalysts are evaluated on their stability and their resistance to carbon deposition. The performance tests are conducted at 773 K temperature under the flow of gaseous mixture of CH_4/CO_2/Ar with a volume ratio of 44.0:47.2:8.8. Activity of Ni/ɣ-Al_2O_3 catalyst with 10wt.% Ni loading was found to be higher than the catalysts with other Ni loadings. However, non-promoted catalysts were not stable due to large carbon deposition. Lanthanum oxide addition to Ni/ɣ-Al_2O_3 as a promoter did not increase the activity but it is reported that the carbon deposition was decreased to one third of that formed on unpromoted Ni catalyst. The alkaline function and dispersion effect of lanthanum are the reasons for this result. By addition of CeO_2 to the lanthanum oxide-promoted Ni/ɣ-Al_2O_3, the activity of the catalyst is increased in addition to the decreased coke deposition due to better electronic interactions conducted between ceria and nickel. Carbon formation is reported as filamentous, which is reactive, thus the stable activity was still observed with Ni/ɣ-Al_2O_3 (Yang *et al.*, 2010).

In their work, Barroso-Quiroga and Castro-Luna have investigated the catalytic performance of Ni catalysts on diverse ceramic oxides such as Al_2O_3, CeO_2, La_2O_3 and ZrO_2 in CDRM. The study also involves the addition of lithium and potassium oxides as promoters of Ni/CeO_2 system. The reaction was conducted in 823 K and the gas mixture CO_2/CH_4 with a molar ratio 1 was fed to system. Seven catalysts with a 10wt.% Ni loading were prepared via wet impregnation. Ni/ZrO_2 has shown an incredible performance with no deactivation during the reaction period. Ni/CeO_2 has shown the highest methane conversion but the performance loss was observed over time. Loadings and the performance of the 0.5wt.% K and Li promoted catalysts are compared with those of the unmodified Ni/CeO_2; the results show that promotion improved stability and suppressed coke deposition but the reactant conversion has decreased (Barroso-Quiroga and Castro-Luna, 2010).

Damyanova *et al.*, also worked on Ni catalysts supported on different alumina supports. Ni is supported on different materials such as θ, δ - Al_2O_3, SiO_2 – Al_2O_3, ZrO_2 - Al_2O_3 and $MgAl_2O_4$ synthesized by a plasma method. The behavior of catalysts was evaluated in terms of their CDRM performances. Fixed bed continuous flow quartz reactor

was used in the experiments. The reaction is conducted at 923 K. The system is fed with a gas mixture of CH_4/CO_2 with molar ratio of 1. The performance of Ni catalysts was found to be dependent on support type. Highest performance was shown by Ni/MgAl sample. The strong interaction between Ni oxide species and $MgAl_2O_4$ prevented metal sintering and coke formation, resulting high stability of the catalysts in CDRM (Damyanova *et al.*, 2012).

Nickel supported on common carrier materials such as silica and alumina has the rapid deactivation problem. On the other hand several novel nickel catalysts such as Ni/perovskite, Ni/La_2O_3, Ni/ZrO_2 have been reported as stable catalysts for CDRM. Meshkani and Rezaei, also report that MgO is another good anticoking support. In their article, Ni catalysts supported on nanocrystalline magnesium oxide with high surface were used in CDRM to investigate the effect of Ni loading, GHSV and feed ratio on the activity. It was found that both CH_4 and CO_2 conversions increased with the nickel loading up to 7 wt.%. However, both 10 and 15 wt.% Ni/MgO catalysts has activity lower than that of the 7 wt.% Ni/MgO catalyst. Especially 15 wt.% catalyst was observed to have drastically lower performance due to its limited metal dispersion. 15 wt.% Ni/MgO catalyst had higher CO_2 conversion than CH_4 due to the reverse water shift reaction (Equation 2.2) at temperatures as high as 700 °C. The H_2/CO ratio was observed as the lowest (0.72) over 15 wt.% Ni/MgO catalyst and the highest (0.96) over 7 wt.% Ni/MgO for the reaction performed at 700 °C with CH_4/CO_2 feed ratio of 1:1. Meshkani and Rezaei, investigated the effect of gas hour space velocity (GHSV) on the performance of 5 wt.% Ni/MgO catalyst. Both CH_4 and CO_2 conversions decrease with the increasing GHSV. Obviously the higher GHSV lowers the contact time for the adsorption and interaction of the reactants. 5 wt.% Ni/MgO catalyst was also used to investigate the effect of CH_4/CO_2 feed ratio. For the tests conducted at 700 °C, the CO_2/CH_4 feed ratio was changed between 1:2 to 3:1. As CO_2 fraction is increased in the feed, CH_4 conversion is increased while CO2 conversion is decreased. H2/CO molar ratio is also decrease with the increasing CO_2/CH_4 ratio in feed. It is reported that the occurrence of water gas shift reaction is enhanced at higher CO_2/CH_4 ratio (Meshkani and Rezaei, 2011).

As mentioned before the characteristics and nature of the support are important parameters in catalytic performance. Porosity, thermal stability and chemical properties of

support are the main reasons causing differences in catalyst performance. The use of argillaceous minerals in this regard attracts a lot attention due to their great abundance, low cost and physical-chemical properties. The starting material and the modifying species dictate the properties of these materials thus making them adaptable. Gamba *et al.*, investigated Ni-Pr system supported on a natural delaminated smectite in CDRM. They have considered the effect of calcination temperature and Pr content as their parameters. The tests were conducted in a vertical fixed bed quartz reactor at 700 °C over powder catalyst. The reactor was fed with a gas mixture of CH_4/CO_2 with 1:1 ratio. The temperature was increased 10 °C/min throughout the reaction. They have concluded that the Pr has a promoter effect and has optimum effect on catalytic system at a certain ratio owing to its role in electron transportation. Additionally, strong effect of calcination procedure is reported clearly. The catalysts treated at 800 °C have shown a greater stability and suffered less from coke deposition as compared to those calcined at 500 °C (Gamba *et al.*, 2011).

The carbon dioxide reforming of methane kinetics has been studied in detail over Ni-based catalysts. But there is still discussion on the plausible reaction mechanism. Previous studies have shown that CDRM have either one or two rate determining steps. Ş. Özkara-Aydınoglu and A. E. Aksoylu conducted a kinetic study on 0.2 wt.% Pt- 15 wt.%Ni/Al_2O_3 and 0.3 wt.% Pt- 10 wt.%Ni/Al_2O_3 catalysts. The aim of the article is to determine parameters in power type rate expression and find out the possible mechanistic expressions for the bimetallic Pt-Ni catalysts having different Pt:Ni loading ratio. Özkara-Aydınoglu and Aksoylu have shown that the kinetics of CDRM can be expressed as a simple power-law rate equation with reaction orders of 1 and 1.09 for CH4 and 0.87 and 1.40 for CO_2, respectively, for 0.2 wt.% Pt- 15 wt.% Ni/Al2O3 and 0.3 wt.% Pt- 10 wt.% Ni/Al_2O_3. It is also reported that the surface reaction mechanisms are different for both catalysts. Catalyst with high Ni:Pt loading ratio has experienced stronger CO inhibition effect resulting a lowered CO_2 utilization. On the catalyst with lower Ni:Pt ratio, CH_4 adsorption becomes weaker, thus the ability of utilizing CO_2 as the oxygen source becomes easier, resulting elimination of CO inhibition effect (Özkara-Aydınoglu and Aksoylu, 2013).

Synthetic layered double hydroxide materials (also known as hydrotalcites) have been investigated for some time due to their unique physicochemical properties. With

certain modifications, this material can be used as a catalyst precursor or even as a catalyst itself. Daza *et al.*, reported a new method to synthesize Ce promoted Ni/Mg-Al catalysts from hydrotalcite type precursors and they have investigated the effect of nominal Ce loading on the catalytic performance of catalysts. The tests were performed in a tubular quartz reactor. After the samples are reduced in situ at 700 °C, the tests are conducted at same temperature with various CO_2/CH_4/He compositions and total flow rate. They have concluded that Ce increased the degree of reduction and the total basicity resulting a promoting effect on catalytic performance. Increase in Ce load didn't increase the catalytic activity but the coke deposition was decreased. Catalysts doped with Ce stayed active up to 100h TOS under the flow of the diluted feed stream. Removal of the diluent He from the feed mixture results in carbon deposition leading deactivation (Daza *et al.*, 2010).

Dissociative CH_4 adsorption and CH_xO decomposition are two slow kinetic steps that dictate the mechanism of CDRM. It's also known that CO_2 produces OH groups through RWGS. Adsorbed CH_x intermediates reacting with OH groups would end up as a formate-type intermediate, CH_xO, which leads to H_2 and CO production. In this mechanism, formate support can take up the hydroxyl group as the sink, thus creating an opportunity for CH_xO formation and decomposition to occur at active metal-support interface. Aparicio *et al.*, developed the model for CDRM that suggested there might be more than one rate determining step. They additionally proposed that the surface oxygen availability might change the rate determining step. In their work, Tsipouriari and Verykios, presented the kinetic measurements over the Ni/La_2O_3 catalysts at 650-750 °C temperature range under varying partial pressures of CO_2 and CH_4. They have developed a mechanistic model from which kinetic model is derived. The mechanistic scheme suggested that adsorption of CH_4 on Ni, followed by cracking and carbon deposition, and oxycarbonate reaction with the Ni-$La_2O_2CO_3$ interface, which is produced from CO_2 with La_2O_3 surface (fast step), yielding CO through the slowest step. RWGS is found to be occurring simultaneously. The kinetic model they have developed from mechanistic predictions fitted well to experimental results (Tsipouriari and Verykios, 2001).

CDRM is a highly endothermic reaction dictating high reaction temperatures (800-1000 °C), resulting in coke deposition due to methane dehydrogenation (Equation 2.7). On the other hand steam reforming, dominant syngas production process, produces higher

H_2/CO ratio (>3) than the downstream processes require. In their study Ryi *et al.*, addressed these problems and combined two reactions with the expectation of reducing carbon formation by oxidizing the carbon precursor species, and to offer control over H_2/CO ratio in end product by adjusting $CH_4/H_2O/CO_2$ ratio in the feed stream. The experimental tests were conducted over catalytic nickel membrane with $(H_2O+CO_2)/CH_4$ molar feed ratio of 3. The molar ratio of H_2O/CO_2 was varied from 0 to 1 to understand the effect of the ratio of oxygen sources in the feed on the H_2/CO product ratio. They have carried out the experiments over the temperature range of 923-1023 K with residence time of 120ms. Ryi et al. have concluded that methane conversion is increased with increasing temperature and reached 96% at 1023 K with feed CO_2/H_2O ratio of 0. They have also shown that increase in CO_2/H_2O ratio decreased CH_4 conversion since catalytic nickel membrane is more active for stream reforming. This effect was most significant at 923 K. At temperatures ≥973 K influence of CO_2/H_2O ratio on CH_4 conversion was reduced. CO_2 conversion was increased with increasing temperature due to highly endothermic nature of CDRM, but due to the CH_4 limitation as reactant, CO_2 conversion was nearly constant for temperatures ≥973 K. Ryi *et al*. has illustrated that H_2/CO ratio in the product stream is controllable by changing the H_2O/CO_2 ratio in the feed stream. The H_2/CO molar ratios were 8.1, 5.7, 3.7 and 2.0 at 973K and 7.5, 5.3, 3.4 and 1.8 at 1023 K for H_2O/CO_2 ratios of 0, 0.11, 0.33 and 1, respectively. SEM and EDX analysis after the combined stream and dry reforming of methane tests have shown that catalytic nickel membranes were not affected by coke deposition (Ryi *et al.*, 2014).

He *et al.*, investigated the effect of different precursors used in catalyst preparation on combined CDRM and POX performance of the catalysts. Combination of CDRM and POX (CRPOX) removes the disadvantages and amplifies the advantages of both processes simultaneously. They have proposed developing Ni-MO_x/SiO_2(M: alkaline metal, alkaline earth metal, rare earth metal) starting from two different precursors, nitrate and citrate, as CRPOX catalyst due to mechanical strength of SiO_2 and higher dispersion tendency of Ni when promoted with MO_x. Two catalysts, Ni/SiO_2 and Ni-Al_2O_3/SiO_2 were prepared by incipient wetness impregnation. Ni/SiO_2 and Ni-Al_2O_3/SiO_2 samples were designated as NiSC and NiSN, NiAlSC and NiAlSN, being prepared from citrate and nitrate precursor respectively. Catalyst samples, 1-5 wt.% Ni , were dried overnight and afterwards calcined in air at 700 °C for 4h. Experimental tests were conducted by using a fluidized-bed reactor

under atmospheric pressure at 700 °C fed by a reactant gas stream consisting of CH_4, CO_2 and O_2 with molar ratio of 1/0.4/0.3. CH_4 conversion was increased with the increase in Ni loading for both NiSC and NiSN; for the former it was from 72.9% to 76.7% for the increase in Ni loading from 1 to 3%; and for the latter it was from 33.8% to 72.2% for the increase in Ni loading from 1 to 5%. NiSC have shown superior activity with lower Ni loadings. Stability was also significantly influenced by the precursor used in catalyst preparation. NiSC samples have shown no decline in methane conversion after 36h reaction time on stream where NiSN samples lost more than half of its activity in 2h reaction time on stream. He et al. have concluded that sintering might have been the main reason of the activity loss. NiSC also have shown superiority in selectivity and CO_2 conversion rates. In order to investigate the MO_x effect on catalyst performance, the catalysts were prepared with 0.5 to 3 n_{Al}/n_{Ni} ratios. NiAlSC catalyst have lost activity and shown increased deactivation rate with increasing n_{Al}/n_{Ni} ratios. On the contrary NiAlSN have significantly enhanced its activity with the increase in n_{Al}/n_{Ni} ratios, proving that MO_x has an important effect on catalytic performance. NiAlSC performed better in every aspects than NiALSN for the same n_{Al}/n_{Ni} ratios. These results have also been supported with XRD results. He et al. concluded that catalytic performance is affected by particle size of Ni, which is dependent on the precursor type used. Smaller particles of Ni were obtained over NiSC(4nm) than over NiSN (30 nm), which can be inferred as that nickel nitrate inhibits the redistribution of impregnation solution upon drying of the support bodies. The interaction strength between NiO and SiO_2 effects stability by preventing sintering. This strength has dropped by the addition of Al_2O_3 thus leading larger nickel particles over NiAlSC samples. He et al. have implied that stronger interaction between NiO leads to the smaller nickel particles after reduction and increased catalytic performance and stability (He *et al.*, 2009).

2.3.2. Co Based Catalysts

CDRM is deeply investigated over supported cobalt catalysts. Ruckenstein and Wang, in their study have studied the effect of support on CDRM performance. From previous studies it's illustrated that supported Ni, particularly MgO supported Ni catalysts have high activity and good coke resistance. It is suggest that NiO-MgO formation on catalyst is the primary reason of that high performance. Since lattice parameter and bond

distance of CoO is similar to NiO and MgO, Ruckenstein and Wang have suggested to explore MgO supported Co catalyst for CDRM. They have also investigated other alkaline earth metal oxides such as CaO, SrO and BaO. Moreover, Υ-Al_2O_3 and SiO_2 were also investigated as supports. All catalysts were prepared with the loading of 12 wt.%. The experimental tests were conducted under atmospheric pressure in a fixed-bed vertical down-flow quartz reactor at 900 °C with feed ratio of CH_4/CO_2 1:1. The results have shown that the performance of catalyst was strongly influenced by the support. MgO supported catalyst has shown the highest activity with CH_4 and CO_2 conversions of 92 and 94% respectively. In period of 50h TOS only MgO, which has shown the lowest carbon deposition on surface, had stable activity. Even though CaO, Υ-Al_2O_3 and SiO_2 have achieved high conversion rates, they have deactivated over time. Ruckenstein and Wang, have concluded that more difficult the reduction is, the stronger the CoO-support interactions. These interactions additionally prevent the sintering of the cluster and smaller clusters hinder coke formation (Ruckenstein and Wang, 2000).

Combination of non-precious metals such as Ni and Co is also shown to be promising in decreasing the carbon deposition during CDRM. In their work, Luisetto *et al.*, investigated the CDRM reaction on bimetallic Co-Ni/CeO_2 catalyst and compared it to the monometallic Ni/CeO_2 and Co/CeO_2 catalyst systems on the basis of the catalytic activity and carbon deposition. Ceria is chosen as the support due to its high oxygen storage capacity and oxygen mobility on the support, which is reported as promising in decreasing the carbon deposition. The experiments were conducted in a fixed-bed quartz reactor at atmospheric pressure and 600 °C. The gas mixture of CH_4/CO_2/Ar with 20:20:60 volume ratio is fed to reactor. The results show that surfactant assisted co-precipitation method is successful to obtain Co-Ni/CeO_2 catalysts. The bimetallic catalyst is reported to be more active and more selective then monometallic Ni and Co catalysts. Both cobalt containing catalysts Co-Ni/CeO_2 and Co/CeO_2 are shown better resistance against carbon deposition which is a clear indicator that the presence of cobalt suppresses carbon deposition (Luisetto *et al.*, 2012).

Cobalt as a transition metal has attracted a lot of interest to be used as an active metal in CDRM catalysts though it has coking problem. Özkara-Aydınoğlu and Aksoylu reported that metal additives affecting both support and active metals could be used to solve

deactivation results from coking. In order to achieve this aim they have produced and tested Co-X/ZrO_2 catalysts, X namely being lanthanum, cerium, manganese, potassium and magnesium. The experiments were conducted in a fixed-bed down-flow tubular quartz reactor under atmospheric pressure. The catalysts are calcined in situ in dry air and reduced in situ in H_2 at 773 K. The reactions were performed at 923 K by using a gas mixture having CH_4/CO_2 feed ratio of 1. They have reported that the metal additive has a significant effect on metal dispersion and catalytic performance. Monometallic Co/ZrO_2 had high activity but has suffered serious carbon deposition. La-modified catalyst has shown moderate activity with great stability. Co-Ce/ZrO_2 has shown the highest methane conversions and the activity loss was not as severe as that of the monometallic catalyst (Özkara-Aydınoğlu and Aksoylu, 2010).

Catalyst performance can be affected by its surface structure and acidity, which is directly linked to carbon deposition formed during CDRM. Basicity of catalyst increases surface CO_2 utilization which decreases coke formation. Based on this information, Foo *et al*. prepared lanthanide promoted bimetallic catalysts in order to investigate carbon gasification kinetics for a set of rare-earth metal (Ce, Pr and Sm) oxides-promoted Co-Ni catalysts. The catalysts were calcined in situ at 1073 K. The reactions are performed in a stainless steel fixed bed reactor. CDRM is performed with a gas mixture having CO_2:CH_4 ratio of 1-1.5 in 923-1023 K temperature range. They have modelled the kinetics of carbon deposition by a power law type expression, through which negative activation energy is calculated for carbon deposition. Their studies showed that there are two types of carbon species formed on the catalyst surface; one reactive and another relatively non-reactive, and lanthanide promotion only decreased the reactive carbon amount (Foo *et al.*, 2012).

Levenspiel suggested that when reaction and deactivation are inseparable, conversion data can be used to determine the kinetic parameters and deactivation rate coefficients simultaneously. The results of hydrocarbon dry reforming studies have been reported as if the carbon deposition doesn't affect the reforming rates. The carbon induced deactivation and steady state reaction kinetics were handled as if they have no interference. In their study, Foo *et al*., suggested the investigation of time-on-stream behavior of dry and oxidative reforming in order to better understand the underlying principle of usefulness of O_2 co-feeding in reducing activity decay without sacrificing from H_2/CO product ratio.

They have conducted the experiments on a bimetallic 5 wt.% Co-15 wt.% Ni catalyst, which was prepared by sequential wetness impregnation. Reaction runs were performed in a stainless steel fixed bed reactor. In the tests gas mixtures of CO_2:CH_4, with ratios between 1.5 and 3, were used and reactions were conducted in the temperature range of 873-973 K at atmospheric pressure. Oxidative CO_2 reforming was performed with the feed having O_2:CO_2:CH_4=0.5:1:1. The experiments have shown that oxygen co-feeding provided better stability with higher conversion. In the tests almost no coking was observed and H_2:CO product ratio was close to unity. Polymerization dehydrogenation mechanism was apparently found as the reason of deactivation at low CO_2:CH_4 feed ratios. At higher temperatures it was observed that at some point the deactivation of active sites accelerates. They have fitted reaction and deactivation kinetic parameters to a generalized reaction-deactivation model (Foo *et al.*, 2012).

As previously stated the nature of the support strongly influences the catalyst activity for CDRM. Takanabe *et al*. state that titania is one of the most promising oxides for suppressing carbon deposition since partially reduced TiO_x species would create strong metal support interaction by preventing large metal particle formation. The boundary between metal and support is a highly active site and it reduces the amount of carbon deposits. They have also proposed that carbon deposits can be minimized if carbide formation is prevented. By doping Ni to other metals, such as tin, chromium or manganese, carbide formation, subsequently coke deposition, is suppressed. From all the stated information Takanabe et al. have conducted a research on CDRM over Ni-Co/TiO_2 by comparing activity stability by changing Ni/Co loading ratio. The experimental tests were conducted under atmospheric pressure at 1023 K. They have set the metal loading to 10 wt.% for Co/TiO_2 and replaced a fraction of cobalt with the same amount of nickel in preparing different catalyst samples, where Co/Ni = m:n was denoted as CoNi(m:n)/TiO_2. The monometallic Co/TiO_2 have shown small activity and lost it even though there was no coke formation on the surface. Addition of Ni (10 mol%) has improved the catalytic activity and stability of monometallic Co/TiO_2 drastically. In comparison with monometallic catalyst, nickel has improved the resistance to oxidation for titanate and the reactivity toward methane decomposition on the metal. Excess nickel content (>80 mol%) has further improved the catalyst activity for CDRM but it also increased the occurrence of methane dehydrogenation and subsequently coke formation. They have also concluded

that a balance between performance and stability can be provided by adjusting Co/Ni loading ratio (Takanabe *et al.*, 2005).

The transition-metal carbides, such as tungsten and molybdenum carbide, are used in various reactions due to their incredible catalytic activity, stability and selectivity. In CDRM, these catalysts are known to show stable activity at high pressures. The structure of carbides can be modified by adding a second metal and these modifications are reported to increase their catalytic performance. In their work, Cheng and Huang, aimed to investigate the changes in catalytic performance of bimetallic Co and Ni-Mo carbide catalysts having different Me/Mo molar ratios. The relationships between catalytic performance, phase structure and surface properties are studied in detail. The activity tests were performed at 850 °C and atmospheric pressure. Stoichiometric feed mixture (CH_4:CO_2=1:1) was fed to the system. The results of the study reveal that high CDRM catalyst activity and stability can be associated to the formation of the Co, Ni-Mo carbide phase. The optimal Co/Mo and Ni/Mo ratio are to be reported as 0.4 and 0.2, respectively. The catalytic activity and stability are reported to have increased in comparison to molybdenum carbide catalyst. The higher molar ratios of Co/Mo and Ni/Mo than the optimal has led to a decrease in performance due to separated single metal formation of cobalt and nickel which decreased the structural and electronic promoting effect of the second metal added to transition-metal carbide (Cheng and Huang, 2010).

Ni/Al_2O_3-based catalysts have been available for fuel reforming commercially. These catalysts have been proven to be highly active and stable under excess steam. But CDRM is a process without steam, thus these catalysts undergo severe carbon deposition and deactivate. It has been illustrated that addition of Co, Cu and Sn to Ni-based catalyst increased its stability by improving catalyst's overall resistance to metal oxidation, subsequently to coke formation and catalyst deactivation. Promoter addition to catalyst has also been deeply investigated in many studies. Especially MgO and CaO-like promoters with high base strength increase the CO_2 adsorption on the surface of the catalyst. Son et al., have proposed developing a MgO promoted $CoNi/\Upsilon\text{-}Al_2O_3$ catalyst to increase resistance against coke deposition leading improvement in activity and stability. MgO promoted $CoNi/\Upsilon\text{-}Al_2O_3$ was prepared using wetness incipient impregnation with 3 wt.% loadings of Mg, Co and Ni. The experimental tests were conducted under atmospheric

pressure in a micro-tubular reactor at a temperature range 700-850 °C. Feed stream with $CH_4/CO_2/N_2$ ratio of 1:1:1 was fed to system. Son et al. have illustrated that the MgO promoted catalyst has superior activity and stability than the non-promoted catalyst. MgO promoted CoNi/ϒ-Al_2O_3 has shown stable activity at 850 °C for 200h TOS and it has also shown increased conversion rates for both CH_4 and CO_2. Non promoted catalyst has revealed three times more coke than the promoted one. Addition of MgO improved more than a single nature of the catalyst. In their work, it's shown that Ni crystallite size from samples that were chosen from spent catalyst is much smaller when MgO was used as a promoter, which clearly indicates that the sintering problem was prevented. In situ DRIFT spectra of CDRM over both promoted and non-promoted catalysts have shown that large amount of formate and carbonate species were formed. In previous studies it's reported that the carbonate (CO_3^{2-})/hydrocarbonate (HCO_3^-) are formed when CO_2 adsorps on basic support, which react with H atoms that are available from methane decomposition to form formate ($HCOO^-$) intermediates (Ferreira-Aparicio *et al.*, 2000). Furthermore, formate intermediates decompose into CO and adsorbed OH groups. It is also clearly shown that MgO has increased the adsorption of formate species, which indicates promotion effect resulted in accelerated decomposition/dissociation of CH_4 and CO_2 (Son *et al.*, 2014).

2.3.3. Noble Metal Based Catalysts

Type, nature and chemical properties of active metal, promoter and support are very important for catalytic activity. The activity can also be affected by impregnation strategy. In their work, Özkara-Aydınoğlu *et al.*, prepared Pt based CDRM catalysts supported on zirconia by using Ce as a promoter. Impregnation strategy, cerium amount, reaction temperature and reactant feeding ratio were used as the parameters. The experiments were performed in a fixed-bed down-flow tubular quartz reactor at atmospheric pressure. The catalyst was calcined in situ in dry air and reduced in situ in H_2 at 773 K. Reaction temperature was in range of 773-973 K. The reactants (CH_4:CO_2) were fed in ratios of 1:1 and 2:1. They have concluded that Ce addition have increased the CDRM activity of Pt/ZrO_2. The effect of the Ce as a promoter was studied when the impregnation strategy and Ce loading were used as the experimental parameters. 1 wt.% Ce addition with coimpregnation was found to lead better catalytic activity and stability results. At high temperature, H_2/CO product ratio close to unity was achieved. In coimpregnation, Pt is

dispersed better due to Ce^{3+} formation on ZrO_2 surface which lead to a performance increase. For the reaction with CH_4:CO_2 feeding ratio of 1:1, 1wt% Ce loaded sample performed better than 5 wt.% Ce loaded one. One the other hand at harsh conditions, like CH_4:CO_2= 2:1 feed ratio case, 1 wt.% Pt- 5 wt.% Ce/ZrO_2 gave the best results (Özkara-Aydınoğlu *et al.*, 2009).

As previously stated, combined CDRM and POX to produce syngas have been deeply investigated since it offsets both of the processes. Nematollahi *et al.* have studied combined CDRM and POX on noble metal catalysts (Ru, Rh, Ir, Pt and Pd) supported on alumina-stabilized magnesia. The experimental tests were conducted over 1 wt.% loaded catalysts a tubular fixed bed quartz reactor under atmospheric pressure at temperatures in range of 500-700 °C with steps of 50 °C with various molar feed ratios of CH_4, CO_2 and O_2. The results have shown that CH_4 conversion is increased with increasing temperature. Ru and Rh catalysts have the highest activity in dry and combined reforming, and in partial oxidation. In all reactions the lowest activity was shown by Pt and Pd catalysts. Nematollahi *et al.* have reported that methane conversion was higher in combined reforming than dry reforming and partial oxidation. In combined reforming at low and medium temperatures, the catalytic process is dominated by exothermic combustion and partial oxidation, while at higher temperatures are dominated by endothermic dry reforming. This trend influences CO_2 conversion rates. Increase in reaction temperatures also increases the CO_2 conversion. Due to RWGS reaction in CDRM, all catalysts have shown higher conversion rates for CO_2 than CH_4. In combined reforming, CO_2 conversions are lower than that observed for dry reforming. For different catalysts, the order of activity is observed similarly for both CH_4 and CO_2. It is also reported that at temperatures lower than 550 °C, negative CO_2 conversion rates have been reported due to domination of exothermic combustion reaction. Nematollahi *et al.* have also reported that with increase in reaction temperature, an increase in H_2 and CO selectivity is observed. H_2/CO ratios of 0.7, 2 and 1 have been observed with CDRM, POX and combined reforming respectively. The dominance of dry reforming and occurrence of RWGS have led to H_2/CO ratio of 1 in combined reforming at 700 °C. All catalysts have shown superior stability in activity and selectivity in combined reforming up to 50 h TOS at 700 °C. The H_2/CO ratios obtained were between 0.9 and 1.1 over different catalysts. Nematollahi *et al.* also investigated the

GHSV effect on catalytic performance of combined reforming. All catalyst have shown decreasing activity with increasing GHSV (Nematollahi *et al.*, 2011).

Noble metals have great activity in CDRM and high resistance to coke deposition. Since they are expensive and not widely available, using them in small amounts to promote the activity of a transition metal, such as Co, Ni and Fe, catalysts have been deeply investigated. Jabbour *et al.*, have tested cobalt promoted with ruthenium, which is widely known to increase the catalytic activity in FT synthesis, over mesoporous silica, SBA-15, which increases the cobalt dispersion. The catalysts were prepared by "two-solvents" impregnation method with metal loadings of 12 wt.% Co and 0.75,1,125 and 1.5 wt.% Ru. The experimental tests were conducted for two different modes. The activity measurements were done by increasing reaction temperature from 200 °C up to 800 °C with 5 °C/min increments. The stability measurements were done at 500 °C for 12 h. In all experiments, the feed having CH_4:CO_2 ratio as 1 used. Jabbour *et al,*. have reported that under similar conditions, pores of the support were filled with cobalt particulates while Ru particulates positioned outside of the pores. Even with lowest amount of Ru (0.75 wt.%), promotion enhanced reduction of cobalt species significantly. It was also reported that first hydrogen formation was observed at 600 °C, 500 °C and 510 °C reaction temperatures for 0.75, 1.125 and 1.5 wt.% Ru promoted catalysts, respectively. Highest Ru containing catalyst also has shown the highest activity (82% at 790 °C). All catalyst have deactivated due to either coke deposition and/or sintering. Jabbour *et al.*, concluded that catalyst deactivation was severe in all cases and another promotional metal with coke inhibition effect, such as Ce, should be investigated (Jabbour *et al*., 2014).

3. EXPERIMENTAL WORK

3.1. Materials

3.1.1. Chemicals

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

Table 3.1. Chemicals used in catalyst preparation.

Chemicals	Formula	Source	Molecular Weight (g/mol)
Cerium (III) nitrate hexahydrate	$Ce(NO_3)_3.6H_2O$	Merck	434.23
Cobalt (II) nitrate hexahydrate	$Co(NO_3)_2.6H_2O$	BDH	290.93
Zirconium oxide	ZrO_2	Alfa Aesar	123.22

3.1.2. Gases and Liquids

The gases used in this research were bought from Linde Group and Bileşik Oksijen Sanayi (BOS) A.Ş. The specification and applications of the gases and liquids used in this research are listed in Tables 3.2 and 3.3.

Table 3.2. Specification and application of the liquid.

Liquid	Specification	Application
Water	De-ionized	Aqueous solutions, Reactant

Table 3.3. Specifications and applications of the gases.

Gas	Specification	Application
Argon	99.998%	Inert, GC Carrier Gas
Carbon dioxide	99.995%	Reactant, GC calibration
Carbon monoxide	99.999%	GC calibration
Dry air	99.998%	Calcination, GC 6-way pneumatic valve
Hydrogen	99.990%	Reduction, GC calibration
Methane	99.500%	Reactant, GC calibration
Oxygen	99.999%	Reactant, GC Calibration
Nitrogen	99.990%	Inert, GC calibration

3.2. Experimental Systems

Four different experimental systems were used in this study:

- Catalyst Preparation System: The catalyst was prepared by incipient-to-wetness impregnation technique by using this system.
- Catalyst Characterization System: Various analytical and spectroscopic techniques were used to characterize the electronic properties of the freshly reduced and spent catalysts.
- Catalytic Reaction System: The catalytic activity, selectivity and stability were determined by using the catalytic reaction system. This system consists of a continuous flow microreactor system, including gas and liquid flow control, temperature controlled heating lines, a temperature controlled oven and a reaction chamber.
- Product Analysis System: This system is a gas chromatograph connected on-line to the microreactor flow system. Compositions of the feed and product streams were evaluated quantitatively by using this system.

3.2.1. Catalyst Preparation System

Catalyst preparation by incipient-to-wetness impregnation technique was performed by using the system including a Retsch UR1 ultrasonic mixer, a Buchner flask, a vacuum pump and a MasterFlex computerized-drive peristaltic pump.

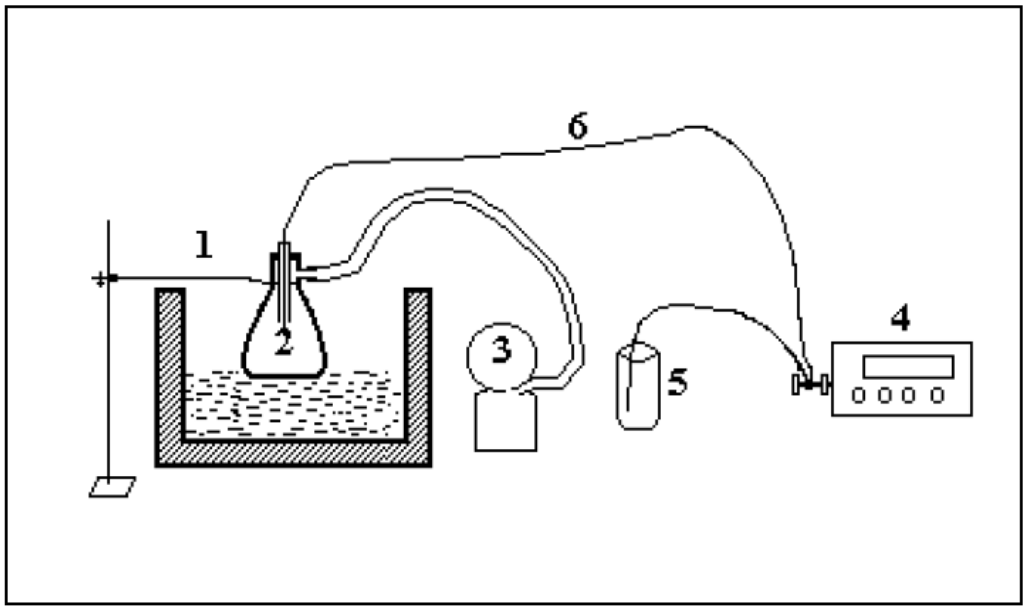

Figure 3.1. Schematic diagram of the impregnation system (Akın, 1996).
1. Ultrasonic mixer, 2. Büchner flask, 3. Vacuum pump, 4. Peristaltic pump, 5. Reactant storage tank, 6. Silicone Tubing.

3.2.2. Catalyst Characterization Systems

3.2.2.1 X-Ray Photoelectron Spectroscopy (XPS). The oxidation states of the metallic species present on the fresh and spent catalyst samples were measured by XPS. The tests were performed at Advanced Technologies Research and Development Center of Boğaziçi University using Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer equipped with a 180° double focusing hemispherical analyzer and Al-K_α micro-focused monochromater X-ray source.

3.2.3. Catalytic Reaction System for Mixed Reforming Reaction

The catalytic reaction system (Figure 3.2) was designed and constructed in the Catalysis and Reaction Engineering Laboratory of Chemical Engineering Department, Boğaziçi University. Feed, reaction and product analysts are three characteristic sections of the catalytic reaction system.

The feed section consists of mass flow control systems, 1/4", 1/8" and 1/16" stainless steel tubing, valves and fittings for gaseous species, i.e. carbon monoxide, carbon dioxide, dry air, hydrogen, methane, oxygen, nitrogen, and liquids, de-ionized water. The gases were supplied by pressurized gas cylinders. The flow rates of the gasses were controlled using Brooks Instrument mass flow controllers. The flow rates of gases; carbon monoxide, carbon dioxide, hydrogen, nitrogen and oxygen, were set by the Brooks Instrument 0154 series control box. The flow rates of gases; methane and dry air, were adjusted by the Brooks Instrument 0254 series control box. On-off valves were placed in front of the mass flow controllers to prevent the possible back-pressure fluctuations. Each of the gas species were fed from independent lines in order to adjust desired feed compositions. A three was way valve was placed before entering reactor to make it possible to divert the dry feed components to gas chromatograph by bypassing the reactor for feed analysis purposes.

Water was introduced to the system at constant flow rates using an Agilent 1100 series HPLC pump. The 1/16" stainless steel tubing, through which was fed, and the line going to reactor after on-off valve, consisting the reactant mixing zone, were kept at 140 ± 5 °C using a 1m Cole-Parmer heating tape connected to a 16-gauge wire K type sheathed thermocouple and Omron E5AN temperature controller. Heat losses were prevented by covering heated lines with ceramic wool insulation.

The reactants, mixed in the feed section in predetermined concentrations, were allowed to flow through the reaction section. This section consists of a 45 cm x 20 cm x 20 cm furnace with 2.4 cm ID controlled by a Eurotherm 3216P programmable temperature controller with ± 0.1 K precision, a K-type sheathed thermocouple and a 75 cm long, 12 mm ID quartz down-flow microreactor. Quartz reactor was connected to the system from both ends by using stainless steel fittings welded to 1/4" stainless steel tubes. Gas leakage

was prevented by using identical fittings with 12mm inner diameter, 24 mm outer diameter and 50 mm height. Center of the quartz micro reactor was filled with quartz wool to hold catalyst bed in a fixed position. Top and bottom ends of the reactor furnace were covered by ceramic glass wool insulations in order to prevent heat loss.

Two ice cold traps are placed after the reactor to remove steam fed and produced throughout the process in order to protect gas chromatograph column from any condensation.

3.2.4. Product Analysis System

3.2.4.1 CDRM + SR Mixed Reforming. Feed and product streams were analyzed by using an Agilent Technologies 6850 gas chromatograph (GC) equipped with a Thermal Conductivity Detector (TCD) and HayeSep D column. Analysis conditions are presented in Table 3.4.

Table 3.4. Reactant and product gas analysis conditions.

Gas Chromatograph	Agilent Technologies 6850
Detector type	TCD
Column temperature, °C	50
Inlet temperature, °C	100
Detector temperature, °C	150
Carrier gas	Argon
Carrier gas flow rate, ml/min	20
Column packing material	Hayesep D
Column tubing material	Stainless steel
Colum length & ID	3m x 3mm
Sample loop	1ml

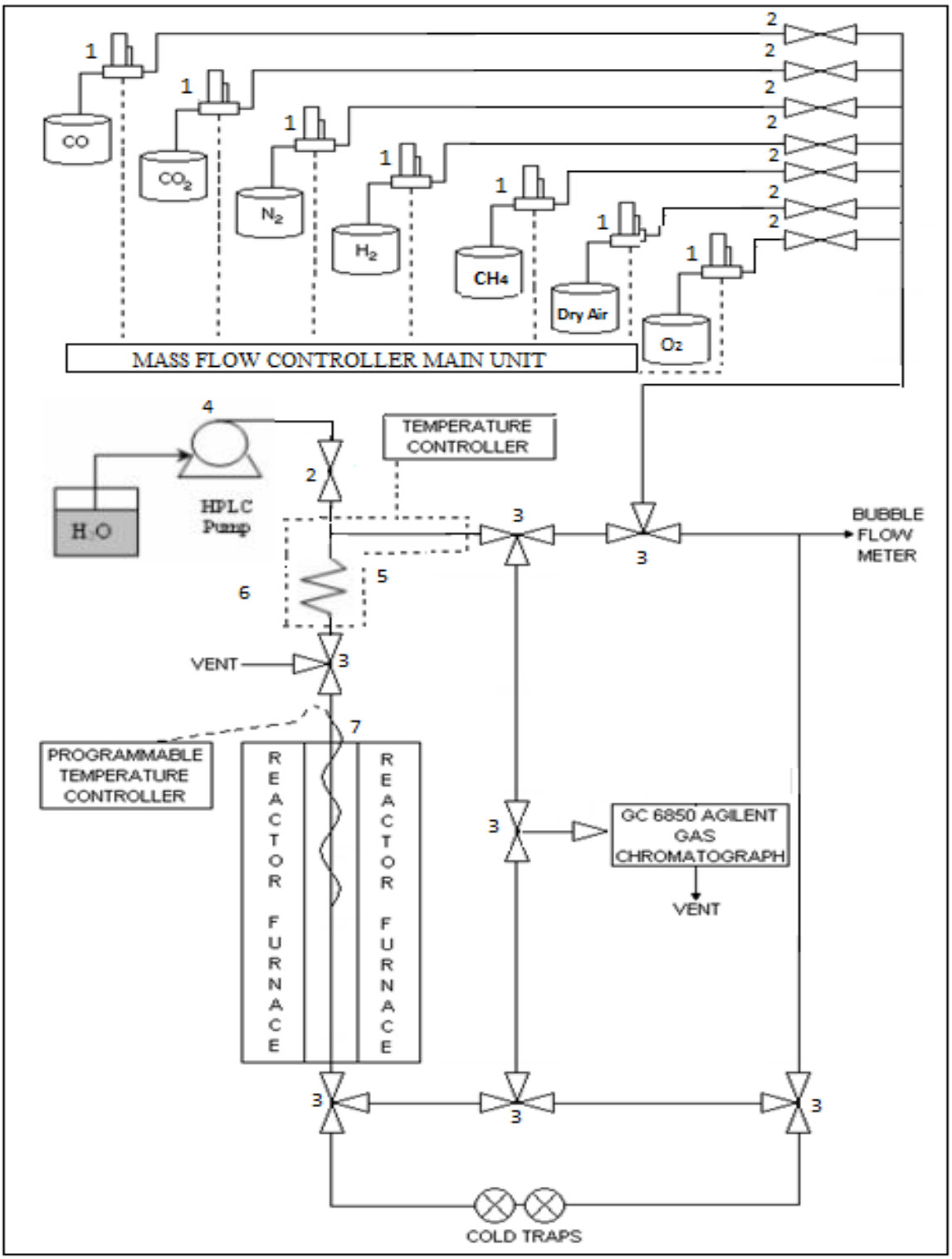

Figure 3.2. Schematic diagram of the microreactor flow system.

1. Mass flow controller, 2. On-off valve, 3. Three-way valve, 4. HPLC Pump, 5. Heating Zone, 6. Mixing Zone and 7. Differential Reactor.

The gas chromatograph was calibrated by sampling known values of the species to be analyzed under conditions given in Table 3.4. The volume vs peak area curves were established for each gas. The linear regression method is applied to analyze corresponding calibration factors.

3.2.4.1 CDRM + POX Mixed Reforming. Feed and product streams were analyzed by using an Agilent Technologies 6850 GC equipped with a TCD and Carboxen 1000 column. Analysis conditions are presented in Table 3.5.

Table 3.5. Reactant and product gas analysis conditions.

Gas Chromatograph	Agilent Technologies 6850
Detector type	TCD
Column temperature, °C	40-150
Inlet temperature, °C	110
Detector temperature, °C	175
Carrier gas	Argon
Carrier gas flow rate, ml/min	20
Column packing material	Carboxen 1000
Column tubing material	Stainless steel
Colum length & ID	15ft x 1/8”
Sample loop	1ml

The column temperature was increased from 40 °C to 150 °C with 55 °C/min ramp in order to analyze methane and carbon dioxide in both feed and reactor effluent streams. The gas chromatograph was calibrated by sampling known values of the gases to be analyzed under conditions given in Table 3.5. The volume vs peak area curves were constructed for each gas. The linear regression method is applied to analyze corresponding calibration factors.

3.3. Catalyst Preparation and Pretreatment

3.3.1. Support Preparation

High temperatures are required to reach high conversion levels since CDRM is an endothermic reaction. Therefore, high thermal capability of the catalyst support becomes as important as surface area. Zirconia support was used in this thesis, due to its characteristics. The support, meshed to 45-60 mesh size, was calcined at 1073 K for 4h in muffle furnace prior to the addition of the metals.

3.3.2. Preparation of Co-Ce/ZrO_2 Catalyst

The catalyst was prepared by using the experimental set-up shown in Figure 3.1 by applying incipient to wetness impregnation method. There are three characteristic steps of this method:

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

Five grams of support was placed in the Büchner flask and kept under vacuum throughout the process. Trapped air in support pores was removed by using a vacuum pump in order to obtain a uniform distribution of the active component. Prior to solution impregnation, the support material was mixed with ultrasonic mixer for 25 min.

Impregnation of aqueous precursor solution of cerium (cerium (III) nitrate hexahydrate) was performed under vacuum condition. This was followed by heat treatment in a muffle furnace at 773 K for 4h and impregnation of aqueous cobalt solution (cobalt (II) nitrate hexahydarate). The precursor solutions (ca. 0.6 mL/g) were fed by a Masterflex computerized-drive peristaltic pump to the flash under vacuum at a rate of 5 mL/min via silicone tubing. The slurry was mixed by an ultrasound mixer for 90 minutes after impregnation of each solution in order to sustain uniform distribution of the precursor

solutions. The thick slurry obtained was dried at 388 K overnight after each impregnation step.

3.3.3. Catalyst Pretreatment

10 wt.% Co-2 wt.% Ce/ZrO_2 catalyst was calcined *in situ* in dry air(30 mL/min) for 4h at 773 K and subsequently reduced *in situ* under H_2 flow (50 mL/min) for 2 h at 773 K. The temperature was increased to 773 K under nitrogen flow (25 mL/min) with 15 K/min increase rate. Mixing of dry air and hydrogen was prevented by introducing nitrogen flow between calcination and reduction procedures for 30 minutes. The reaction tests were performed on freshly calcined and reduced catalyst.

3.4. Reaction Tests

3.4.1. Blank Tests

Blank tests were conducted to confirm that material of construction, quartz wool and the reactor did not influence have activity. The results indicated that quartz wool and the reactor were inert under the conditions used in the reaction experiments.

3.4.2. CDRM +SR Mixed Reforming

The CDRM + SR mixed reforming has been studied over 10 wt.% Co-2 wt.% Ce/ZrO_2. The effect of temperature, CH_4/CO_2 feed ratio and steam to carbon (S/C) ratio in the feed was investigated. The nitrogen flow was set to 25 mL/min and the furnace temperature was increased with the rate of 15K/min. The GC operation was followed in the meanwhile. After both the GC and the system temperatures were ready, the reactions were performed at 873 K, 923 K and 973 K with CH_4/CO_2 feed ratios of 2 and 1 and S/C ratios of 1 and 0.5. The data from reactor effluent is collected at 30th min and every hour up to 6 hours after that. Then, feed data is collected after allowing feed gases to mix completely in bypass line. The experiments performed in this study are shown at Table 3.6 in detail.

Table 3.6. Summary of the experimental conditions used for mixed reforming, CDRM + SR.

Experiment No.	Temperature (K)	CH_4/CO_2	S/C	GHSV (mL/h g-cat)
1	873	2	1	20000
2	923	2	1	20000
3	973	2	1	20000
4	873	2	0.5	20000
5	923	2	0.5	20000
6	973	2	0.5	20000
7	873	1	0.5	20000
8	923	1	0.5	20000
9	973	1	0.5	20000

3.4.2. CDRM + POX Mixed Reforming

Same procedure was followed to obtain experimental data on CDRM + POX mixed reforming. The reactions were performed at 873 K, 923 K and 973 K with CH_4/CO_2 feed ratios of 2 and 1 and 4%, 7% and 10% O_2 concentrations in the feed. The experiments performed in this study are shown at Table 3.7 in detail.

Table 3.7. Summary of the experimental conditions used for mixed reforming, CDRM + POX.

Experiment No.	Temperature (K)	CH_4/CO_2	O_2 ratio (%)	GHSV (mL/h g-cat)
10	973	2	4	20000
11	973	2	7	20000
12	973	2	10	20000
13	923	2	10	20000
14	873	2	10	20000
15	973	1	7	20000
16	973	1	10	20000
17	923	1	7	20000
18	873	1	7	20000

4. RESULTS AND DISCUSSION

The aim of the current work is to study the mixed reforming, both CDRM + SR and CDRM + POX, activity of the Co-Ce/ZrO_2 system, and to determine the optimal mixture of the oxygen sources for the improved catalytic performance. CDRM catalysts lose activity due to excess carbon formation on active metal sites. Carbon is the side product of methane dehydrogenation. Active metal sites are not cleaned properly where surface oxygen formation rate, resulting from CO_2 disproportionation, is slower than the carbon formation rate from methane dehydrogenation. In previous studies it was shown that CDRM catalysts are capable of achieving better stable activity with additional oxygen source besides CO_2. Mixed reforming, i.e. CDRM coupled with steam reforming or with partial oxidation, is a way of providing excess surface oxygen enough to remove carbon formed by methane decomposition. Since surface oxygen takes main role in controlling deposition, not only the amount of surface oxygen but also the regulation of its transfer is important. Ce, which has an ability of going through a redox cycle, is impregnated to Co/ZrO_2 by sequential impregnation in order to achieve a surface enabling better oxygen transfer. In the current thesis, the mixed reforming performance of 10 wt.% Co-2 wt.% Ce/ZrO_2 was studied in a detailed fashion. The performance of catalyst was evaluated in a study for which CH_4/CO_2 feed ratio, the presence and amount of H_2O or O_2 in the feed stream and reaction temperature were used as the experimental parameters. The metal oxidation states of the fresh and used samples were analyzed by XPS.

4.1. Performance Tests

The activity, stability and selectivity of the catalyst were determined under previously listed experimental conditions. The following formulas were used to calculate CH_4 and CO_2 conversion and H_2/CO product ratio:

$$Conversion(\%) = \frac{[C]_{in} - [C]_{out}}{[C]_{in}} x100 \quad (4.1)$$

$$\frac{H_2}{CO} = \frac{[C]_{H_2}}{[C]_{CO}} \tag{4.2}$$

where C is the volume percentage of the respective gas.

CH_4 and CO_2 conversion were considered as a measure of activity. Higher conversion values indicate higher activity. The selectivity of the catalyst was measured through the H_2/CO product ratio. In CDRM, it is preferred to have H_2/CO product ratios close to unity, for making the syngas composition suitable for the down-flow processes like Fischer-Tropsch synthesis.

4.2. CDRM + SR Mixed Reforming

4.2.1. The Effect of Temperature

The results of the experiments have clearly shown that, CH_4 and CO_2 conversions, in other words activity, increase with increasing temperature. As both CDRM and SR are endothermic reactions, this is an expected result. According to experiments with CH_4/CO_2 feed ratio of 2 and steam to carbon ratio (S/C ratio) of 1 (Figure 4.1), only small activity loss was observed throughout the experiments. Even for the tests conducted at high temperature with methane rich feed, which highly favor methane dehydrogenation thermodynamically, the activity losses observed were small. These losses in CH_4 conversions are 8.4%, 2.8% and 3% at 973 K, 923 K and 873 K respectively. The TOS CH_4 activity values for CH_4/CO_2 and S/C feed ratio combinations of 2-0.5 and 1-0.5 are presented in Figures 4.2 and 4.3, respectively.

Temperature effect on mixed reforming, CDRM + SR, was investigated in a detailed fashion. The experiments were conducted at temperature range of 873-973 K with CH_4/CO_2 feed ratios of 2 and 1, and S/C ratios of 1 and 0.5 at 20000 mL/h g cat space time. For CH_4/CO_2 feed ratio of 2 and S/C feed ratio of 1, at the end of the 6 h TOS methane conversions were recorded as 60%, 55% and 42% at 973 K, 923 K and 873 K, respectively. For S/C feed ratio of 0.5 at 973 K, 923 K and 873 K, CH_4 conversions at the

end of the 6 h TOS were found as 58%, 54% and 36% for CH_4/CO_2 feed ratio of 2 and 63%, 50% and 42% for CH_4/CO_2 feed ratio of 1.

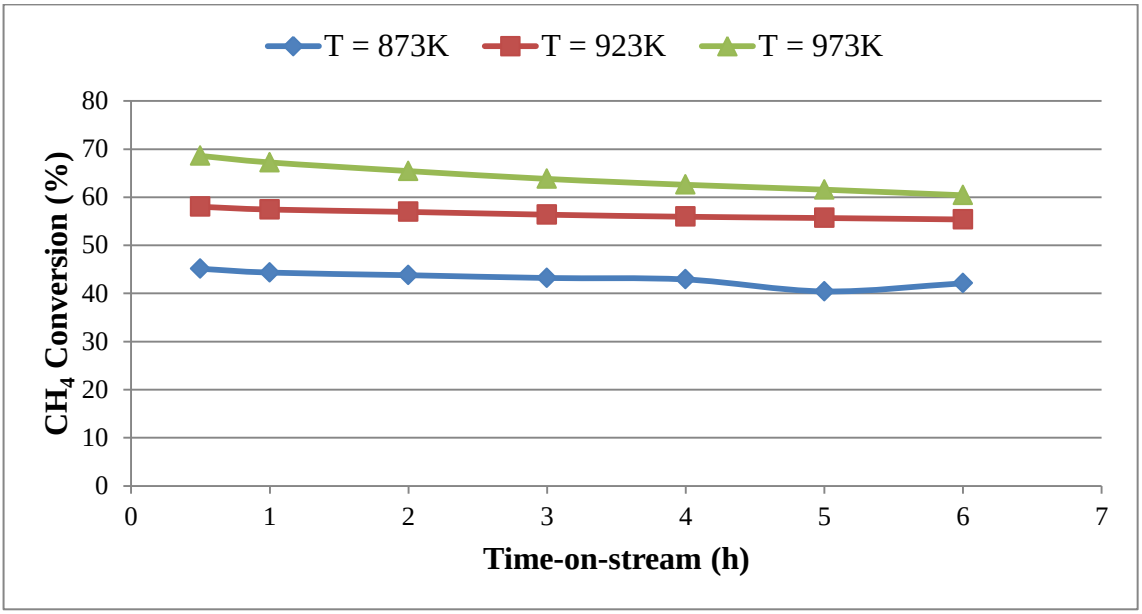

Figure 4.1. CH_4 TOS conversion values obtained for CH_4/CO_2 feed ratio of 2 and S/C feed ratio of 1.

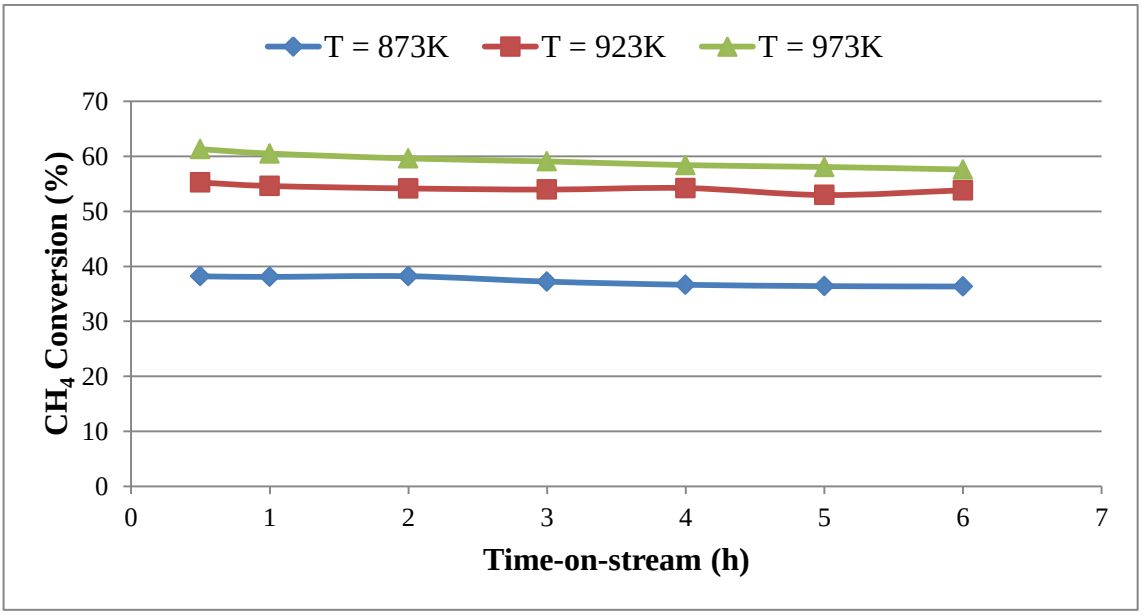

Figure 4.2. CH_4 TOS conversion values obtained for CH_4/CO_2 feed ratio of 2 and S/C feed ratio of 0.5.

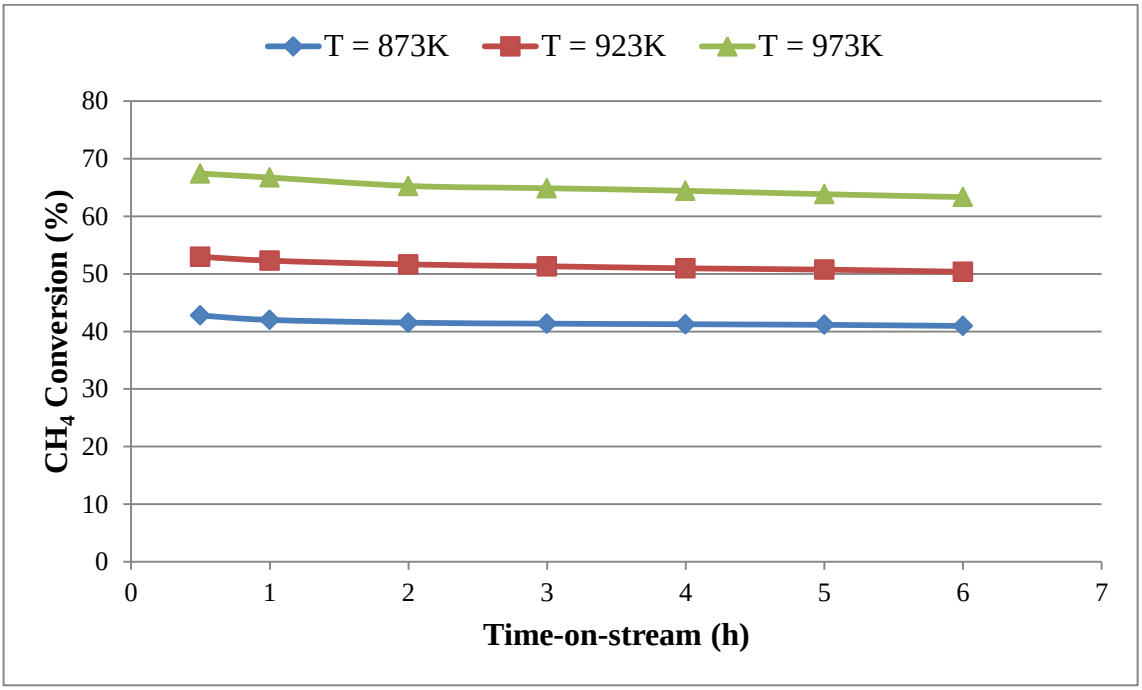

Figure 4.3. CH_4 TOS conversion values obtained for CH_4/CO_2 feed ratio of 1 and S/C feed ratio of 0.5.

CO_2 conversions were recorded in same fashion as CH_4 conversions. At lower temperatures CO_2 conversion is low and it shows drastic increase with increasing temperatures. The low CO_2 conversion at 873 K indicates that the utilization of steam as an oxygen source is favorable for Co-Ce/ZrO_2 system at low temperatures. As a consequence steam reforming is more favored than CDRM at lower temperatures. The increase in CO_2 conversion with the increase in temperature is expected due to two reasons. First, the increased methane conversion at higher temperatures led to an increase in oxygen requirement which cannot be satisfied only by oxygen coming from steam. Secondly, CDRM is favored at higher temperatures due to its extreme endothermicity, so CO_2 becomes thermodynamically more favorable to be consumed in the process. At the end of the 6 h TOS, CO_2 conversions were observed for CH_4/CO_2 feed ratio of 2 and S/C ratio of 1 are 39%, 29% and 8% at 973 K, 923 K and 873 K, respectively. For CH_4/CO_2 feed ratio of 2 and S/C ratio of 0.5 at 973 K, 923 K and 873 K the CO_2 conversion rates at the end of 6 h TOS are 61%, 54% and 28%, respectively. For CH_4/CO_2 feed ratio of 1 and for same temperature and S/C ratio levels, the CO_2 conversion rates at the end of 6 h TOS were

found to be 51%, 40% and 30%. The following figures (Figures 4.4-4.6) show all CO_2 conversion data obtained from CDRM + SR mixed reforming experiments.

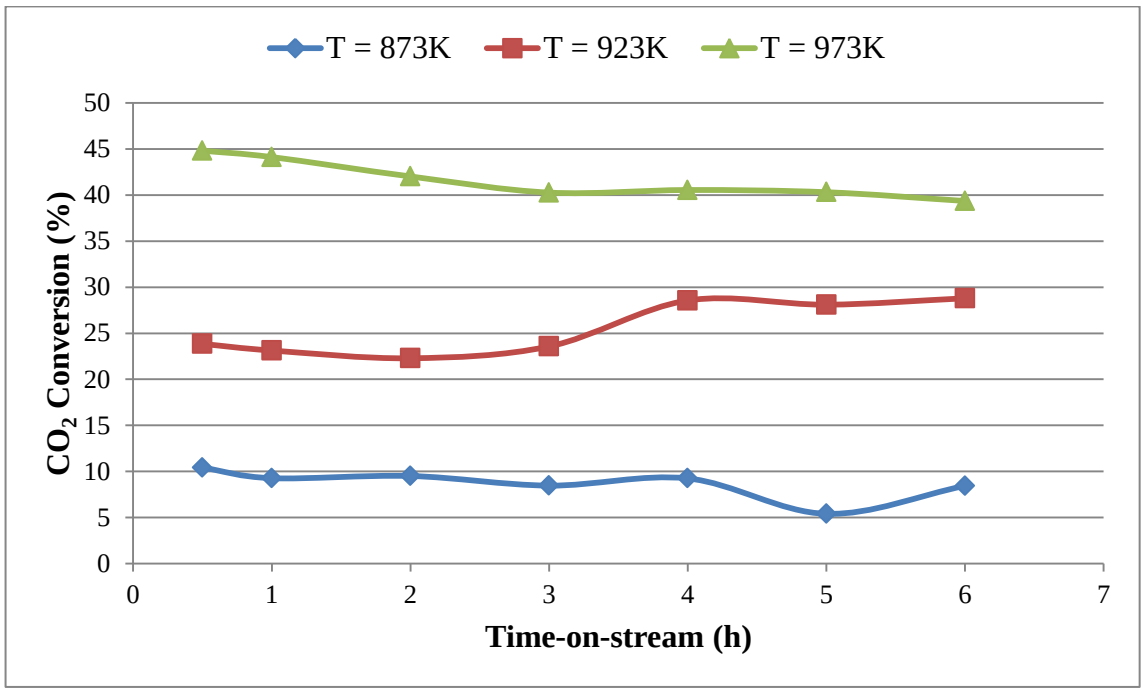

Figure 4.4. CO_2 TOS conversion values obtained for CH_4/CO_2 feed ratio of 2 and S/C feed ratio of 1.

H_2/CO ratio in the end product stream is considered as the selectivity measure. At 873 K for S/C of 1 and CH_4/CO_2 feed ratio of 2, steam reforming was extremely dominant (with CO_2 conversion less than 10%), so the H_2/CO ratio was higher than 3. As temperature was increased, the H_2/CO ratio decreased to 2.4 and 2.3 at 923 K and 973 K, respectively, due to enhanced CDRM activity. Considering that CDRM theoretically yields H_2/CO ratio of 1 while steam reforming yields 3, respectively, the H_2/CO ratio of end product can be controlled through regulating relative extents of those reactions. CDRM dominance in mixed reforming is influenced by steam amount fed to the system and reaction temperature. In all cases the H_2/CO product ratio decreases with an increase in temperature. As H_2/CO product ratio of 1 is desired, mixed reforming should be performed at high temperatures, which favor CDRM relatively more than SR. H_2/CO ratios at the end product were calculated as 2.1, 1.7 and 1.6 at 873 K, 923 K and 973 K, respectively for CH_4/CO_2 feed ratio of 2 and S/C ratio of 0.5. At same temperature levels and S/C, but for

CH_4/CO_2 feed ratio of 1, the H_2/CO ratios were calculated as 1.5, 1.4 and 1.3, respectively. The following figures (Figures 4.7-4.9) show the 6 h TOS H_2/CO ratio values.

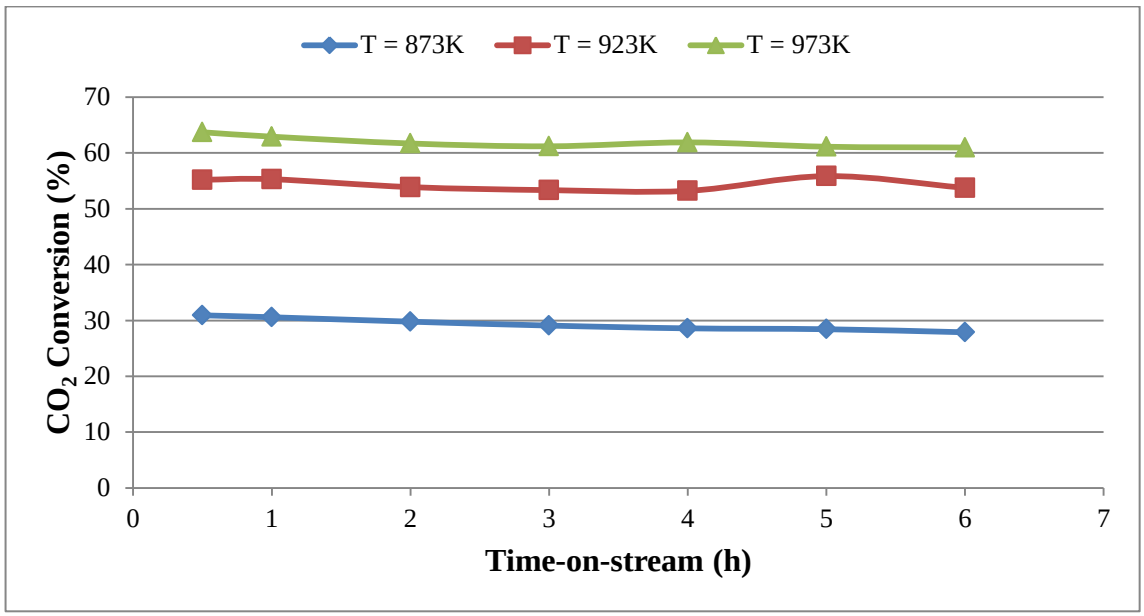

Figure 4.5. CO_2 TOS conversion values obtained for CH_4/CO_2 feed ratio of 2 and S/C feed ratio of 0.5.

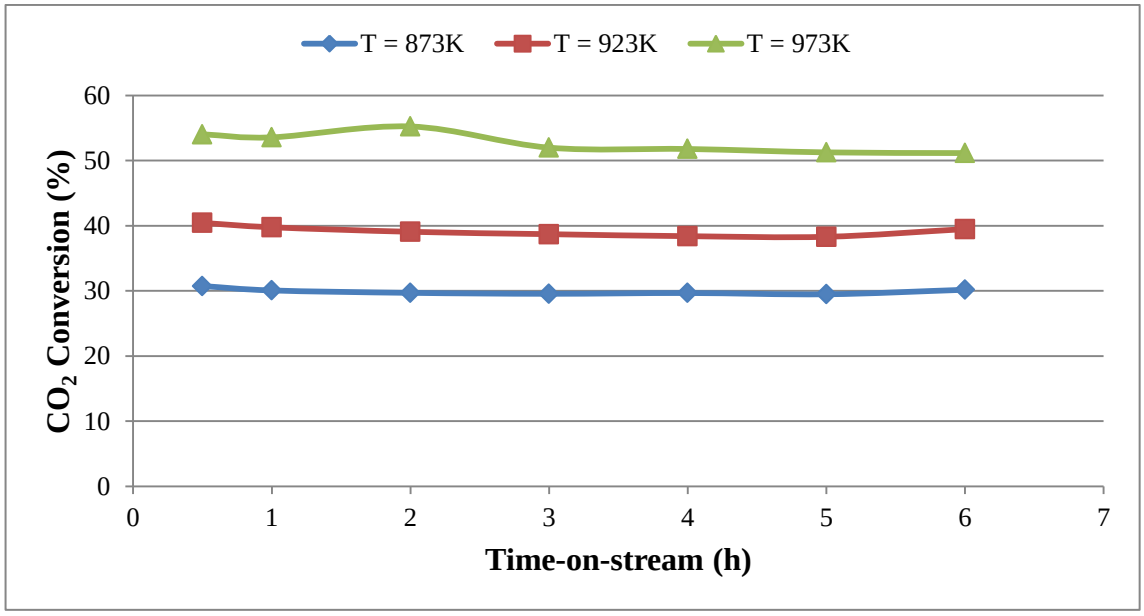

Figure 4.6. CO_2 TOS conversion values obtained for CH_4/CO_2 feed ratio of 1 and S/C feed ratio of 0.5.

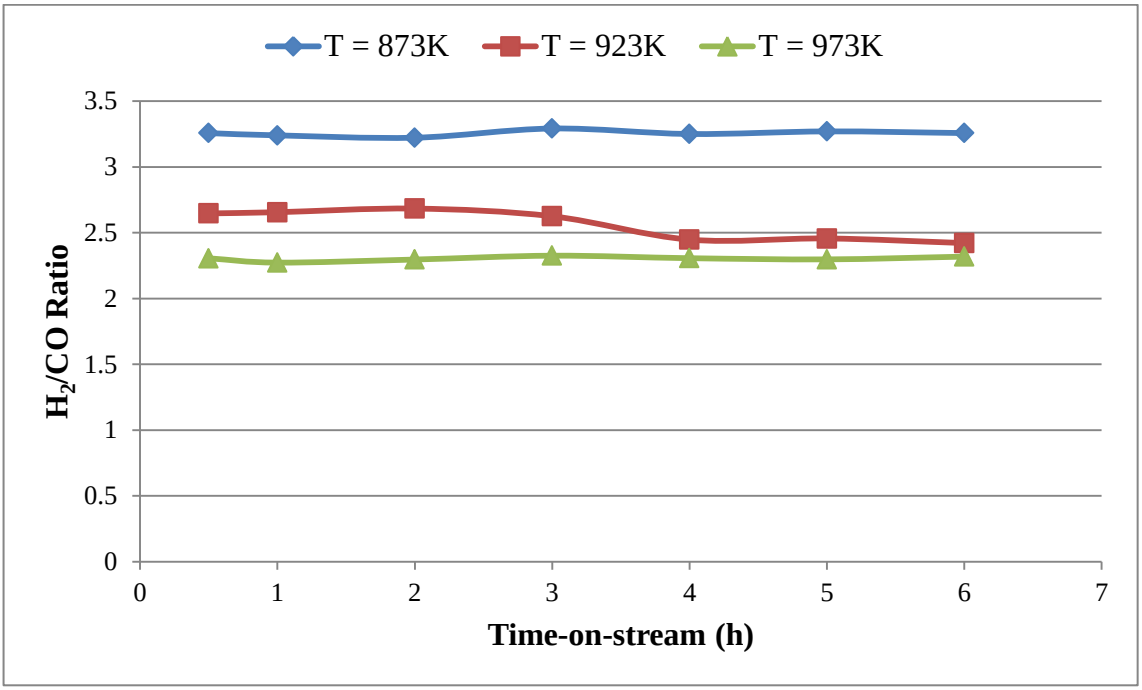

Figure 4.7. H_2/CO TOS ratio values obtained for CH_4/CO_2 feed ratio of 2 and S/C feed ratio of 1.

As a result, for Co-Ce catalyst increase in temperature increases overall activity (CH_4 conversion), CDRM activity (CO_2 conversion) and push H_2/CO product ratio close to unity as well.

4.2.2. The Effect of S/C Feed Ratio

Results of the mixed reforming experiments performed with S/C feed ratios of 1 and 0.5 on 10 wt.%Co- 2wt.% Ce/ZrO_2 are compared with results of the CDRM experiments performed on the same catalyst. In those tests, a fixed CH_4/CO_2 feed ratio of 2 was used. Both mixed reforming and CDRM tests were conducted at three temperature levels, 873, 923 and 973 K. The effect of S/C in mixed reforming performance is explained in detail by using these results. The experiments were conducted at 873, 923 and 973 K for S/C ratios of 0, 0.5 and 1 for a space time of 20000 mL/h g cat. The following figures (Figures 4.10-4.12) illustrate the effect of S/C on overall activity (CH_4 conversion).

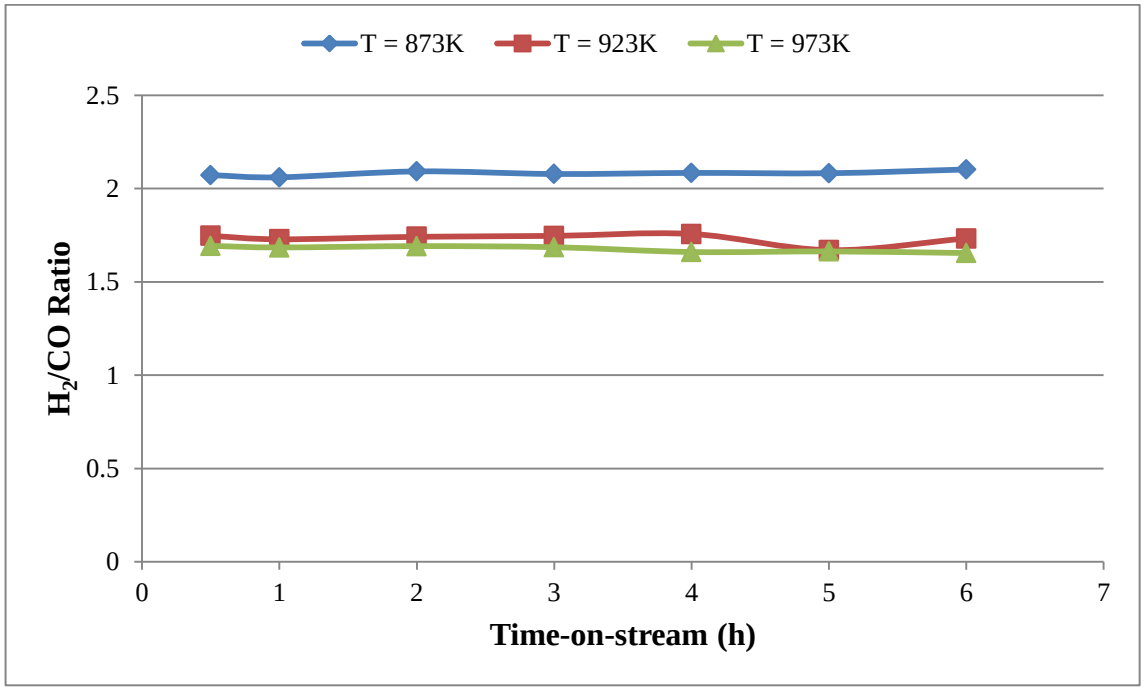

Figure 4.8. H_2/CO TOS ratio values obtained for CH_4/CO_2 feed ratio of 2 and S/C feed ratio of 0.5.

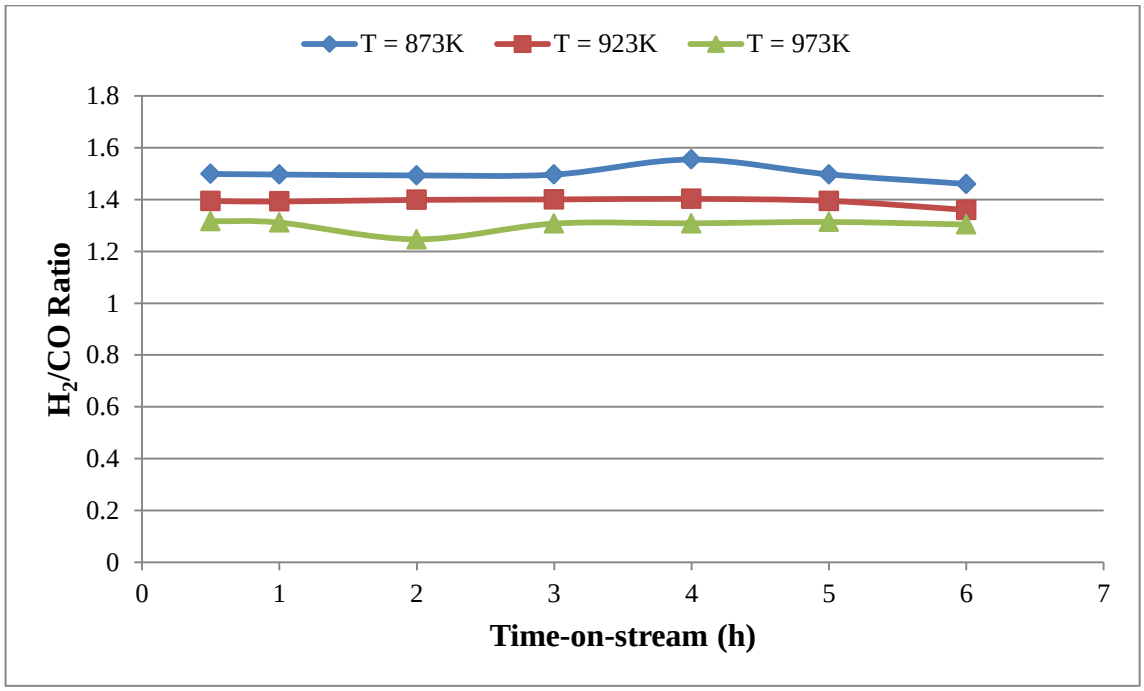

Figure 4.9. H_2/CO TOS ratio values obtained for CH_4/CO_2 feed ratio of 1 and S/C feed ratio of 0.5.

It is clearly shown that for CH_4/CO_2 feed ratio of 2 for temperature range of 873-973 K, addition of steam increases overall activity at the end of 6 h TOS. A comparison with the CDRM results clearly reveals that the performance stability is improved drastically in mixed reforming even for the lower S/C feed ratio. The improvement of stability in activity stems from the enhanced coke resistance of catalyst in mixed reforming. Minimal to no coke deposition was observed on the spent catalyst used in mixed reforming at the end of 6 h TOS.

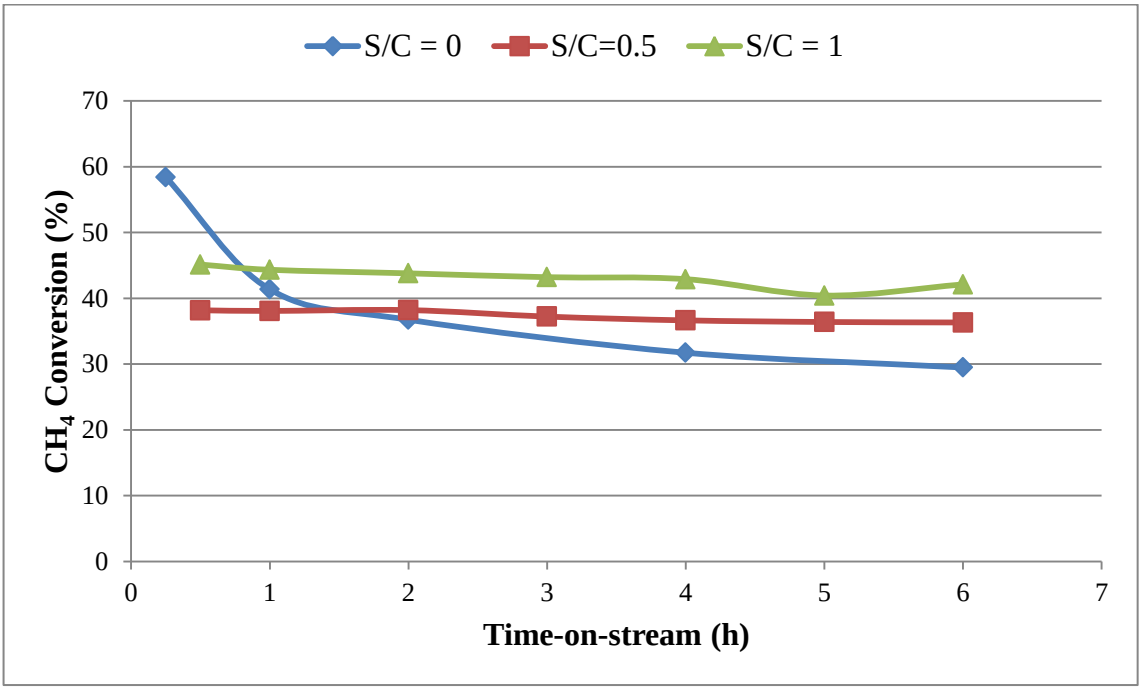

Figure 4.10. CH_4 TOS conversion values obtained for CH_4/CO_2 feed ratio of 2 at 873 K.

In the experiments performed at CH_4/CO_2 feed ratio of 2 in temperature range of 873-973 K, the CH_4 conversion values are measured at the end of the 6 h TOS for S/C feed ratios of 0, 0.5 and 1. These results are illustrated in Figure 4.13. The methane conversion values for S/C ratios of 0, 0.5 and 1 were observed as 29%, 26% and 42% at 873 K, 34%, 53% and 55% at 923 K and 55%, 58% and 60% at 973 K, respectively. For CH_4/CO_2 feed ratio of 2, it's clearly shown that overall activity increases with increasing temperature and S/C feed ratio. As both CDRM and SR are endothermic reactions, the increase in activity with an increase in temperature is expected.

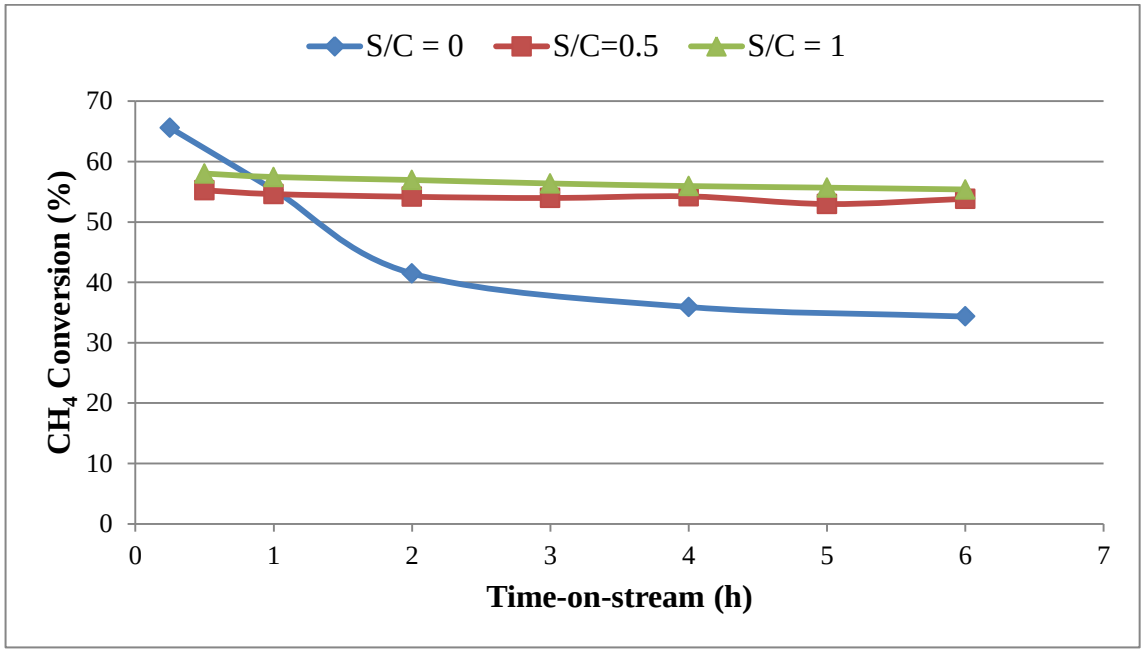

Figure 4.11. CH_4 TOS conversion values obtained for CH_4/CO_2 feed ratio of 2 at 923 K.

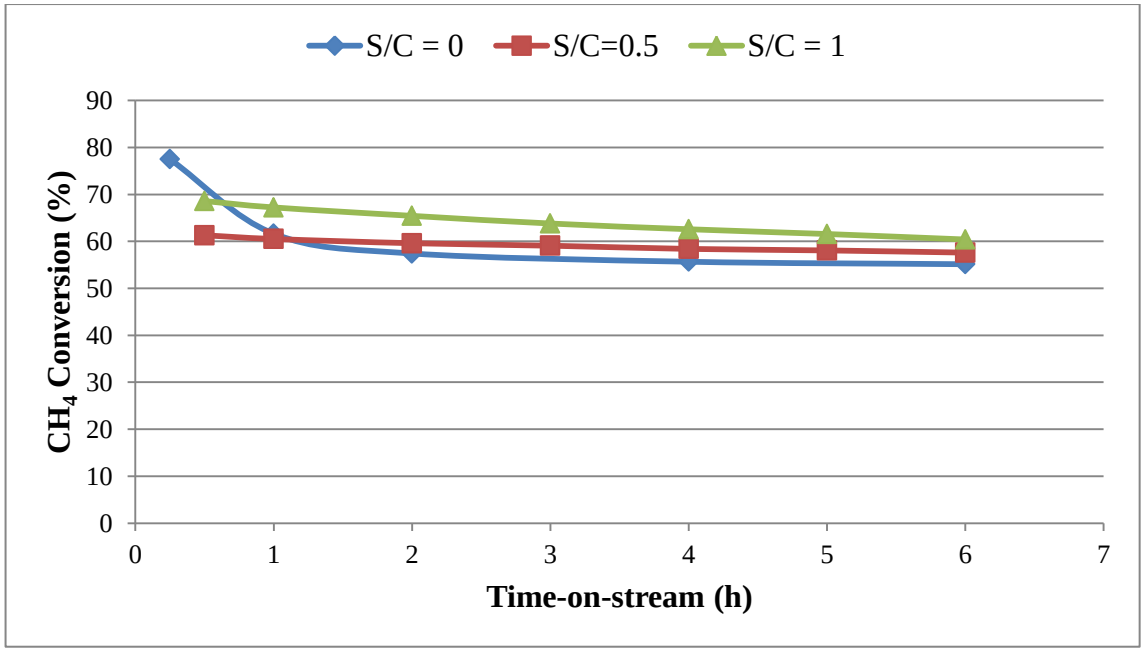

Figure 4.12. CH_4 TOS conversion values obtained for CH_4/CO_2 feed ratio of 2 at 973 K.

For the same experimental conditions, the CO_2 conversion at the of the 6 h TOS were found as 58%, 28% and 8% at 873K; 74%, 54% and 29% at 923K; and 86%, 61% and 39% at 973 K for S/C ratios of 0, 0.5 and 1, respectively. These results are shown in Figure

4.14. The results show that CO_2 utilization increases with the increase in temperature. On the other hand, CO_2 utilization decreases with the increase in steam addition. Relative extent of CDRM compared to SR gets higher with the increase in temperature. The difference between CDRM activity, i.e. S/C=0, and mixed reforming activity gets smaller with the increase in temperature.

The results indicate that oxygen rich steam is preferred by Co-Ce system as the oxygen source, especially at lower temperatures. The addition of steam drastically decreases the CO_2 conversion and subsequently the CDRM activity. The CO_2 conversion at 873 K with S/C feed ratio of 0 is higher than the CO_2 conversion at 973 K with S/C feed ratio of 0.5, which clearly states that oxygen source preference of the surface is steam.

H_2/CO product ratio values were calculated for S/C feed ratio of 0.5 as 2.1, 1.7 and 1.6 at 973, 923 and 873 K, respectively (Figure 4.15). Same trend is observed for S/C ratios of 1; at the end of 6 h TOS, H_2/CO ratios were observed as 3.3, 2.4 and 2.3 at 973, 923 and 873 K, respectively.

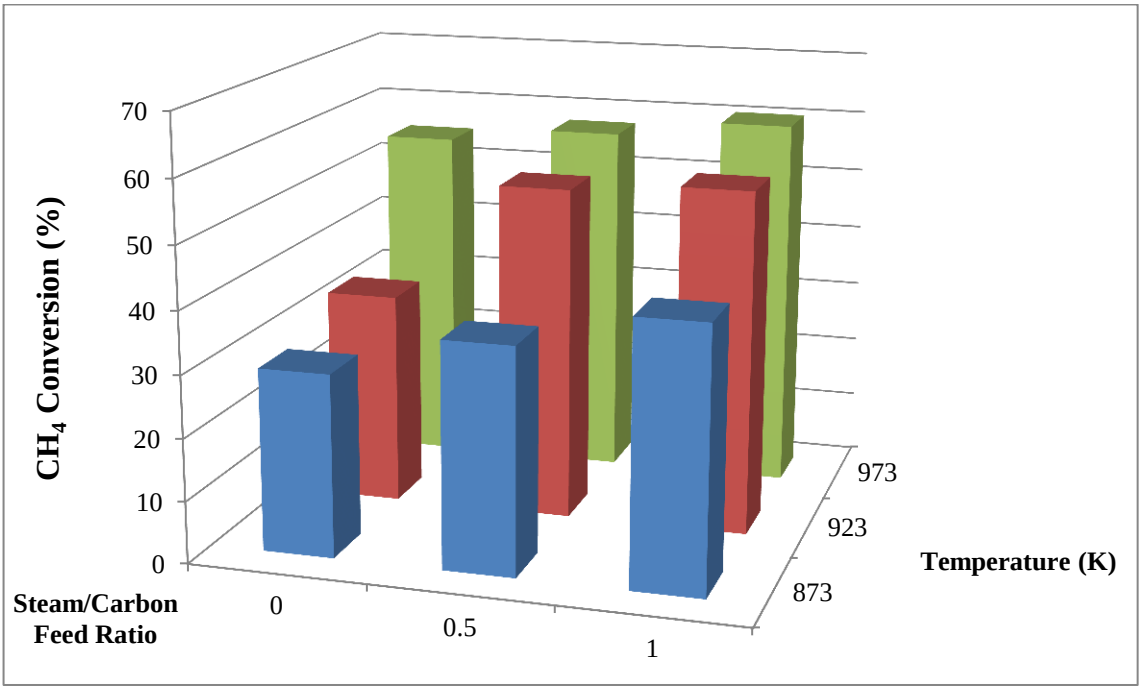

Figure 4.13. CH_4 at the end of 6 h TOS conversion values obtained for CH_4/CO_2 feed ratio of 2.

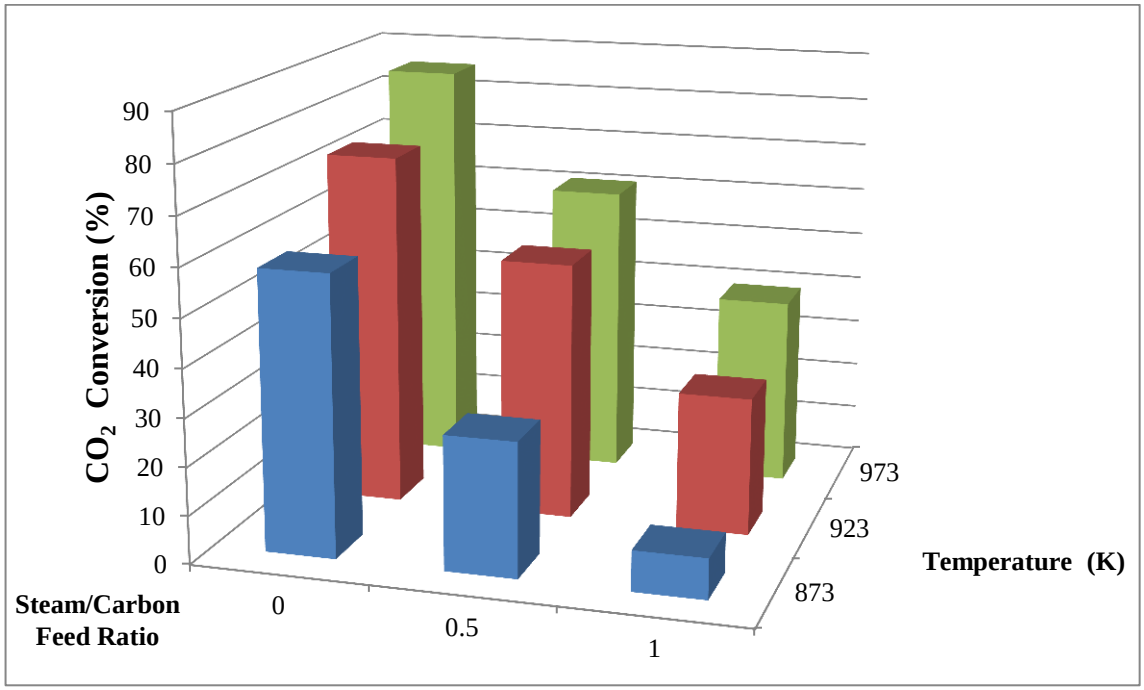

Figure 4.14. CO_2 at the end of 6 h TOS conversion values obtained for CH_4/CO_2 feed ratio of 2.

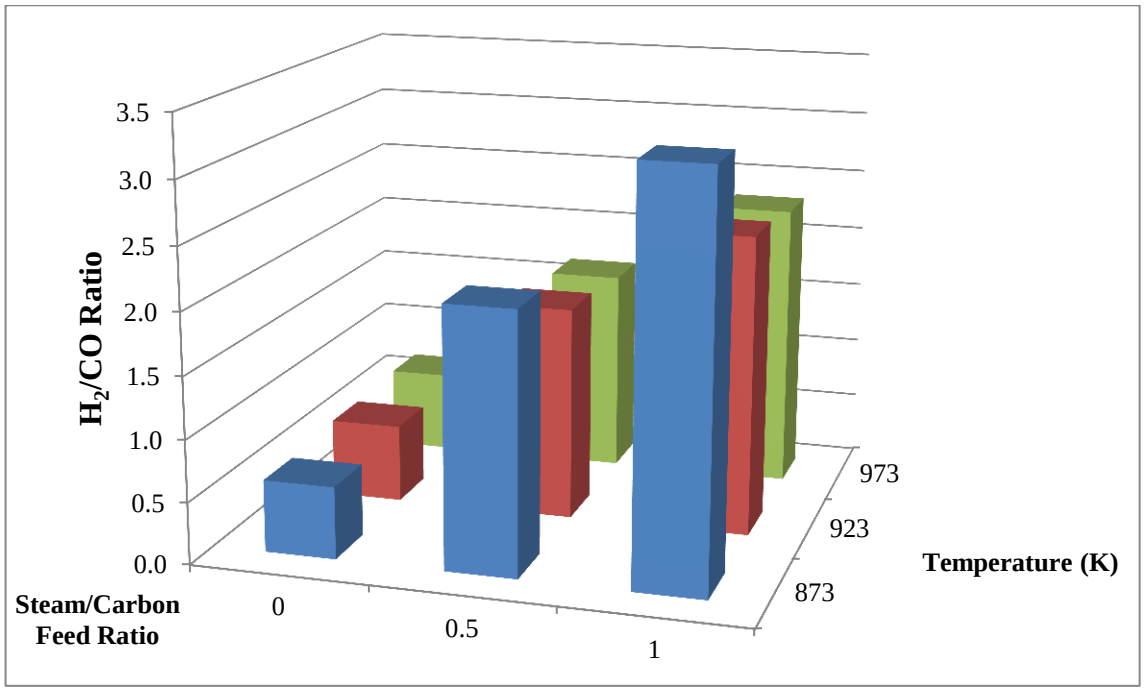

Figure 4.15. H_2/CO at the end of 6 h TOS product ratio values obtained for CH_4/CO_2 feed ratio of 2.

The results show that at higher temperatures and lower S/C ratios, the H_2/CO ratios is closer to unity, i.e. the syngas is more suitable for down-flow processes like FT synthesis. Increasing S/C ratio and lowering temperature increase H_2/CO ratio immensely. SR is more dominant than CDRM at low temperatures and high S/C ratios and moderately exothermic WGS possibly takes place increasing H_2/CO ratio even higher than 3. The results clearly indicate that, by changing the reaction conditions and relative extents of CDRM and SR, it's possible to control H_2/CO ratio.

It is clear that the Co-Ce catalyst has improved overall performance and stability in mixed reforming compared to those in individual CDRM. On the other hand, H_2/CO product ratio was observed to be higher than the required value. The possibility of controlling the H_2/CO product ratio and reaching the same activity at lower temperatures are the other advantages of mixed reforming over CDRM.

4.2.3. The Effect of CH_4/CO_2 Feed Ratio

The effect of CH_4/CO_2 feed ratio on the mixed reforming performance was studied for CH_4/CO_2 feed ratio level of 2 and 1 in the tests conducted at 973 K for a fixed S/C feed ratio of 0.5. The following figures illustrate TOS CH_4 and CO_2 conversions (Figures 4.16 and 4.17) achieved as well as H_2/CO (Figure 4.18) selectivity of the catalyst.

In Figure 4.18, methane conversion values achieved are given as a function of time for CH_4/CO_2 values of 2 and 1. The results show that methane conversion increases with decreasing CH_4/CO_2 feed ratio indicating the additional methane is not fully utilized by the catalyst. The opposite trend is observed in CO_2 conversion values. In Figure 4.19 CO_2 conversion increases with increasing CH_4/CO_2 ratio points out the higher CO_2 utilization when methane is fed in excess amount.

Another advantage of using low using low CH_4/CO_2 ratio in mixed reforming is suppressing H_2/CO ratio close to unity. For CH_4/CO_2 feed ratio of 2, the H_2/CO ratio was found as 1.6, and for CH_4/CO_2 feed ratio of 1, the H_2/CO was found as 1.3 at the of the 6h TOS. Another interpretation of this result is that at higher CH_4/CO_2 feed ratio, RWGS is limited due to lack of CO_2, resulting in higher H_2/CO ratio.

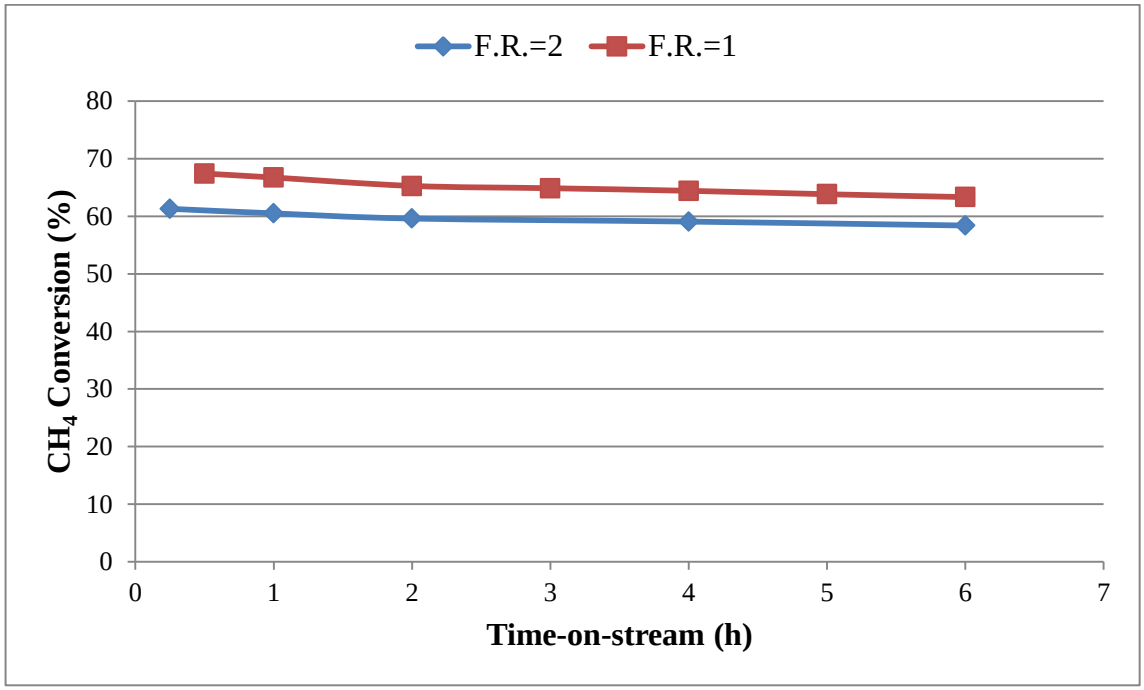

Figure 4.16. CH_4 TOS conversion values obtained for S/C feed ratio of 0.5 at 973 K.

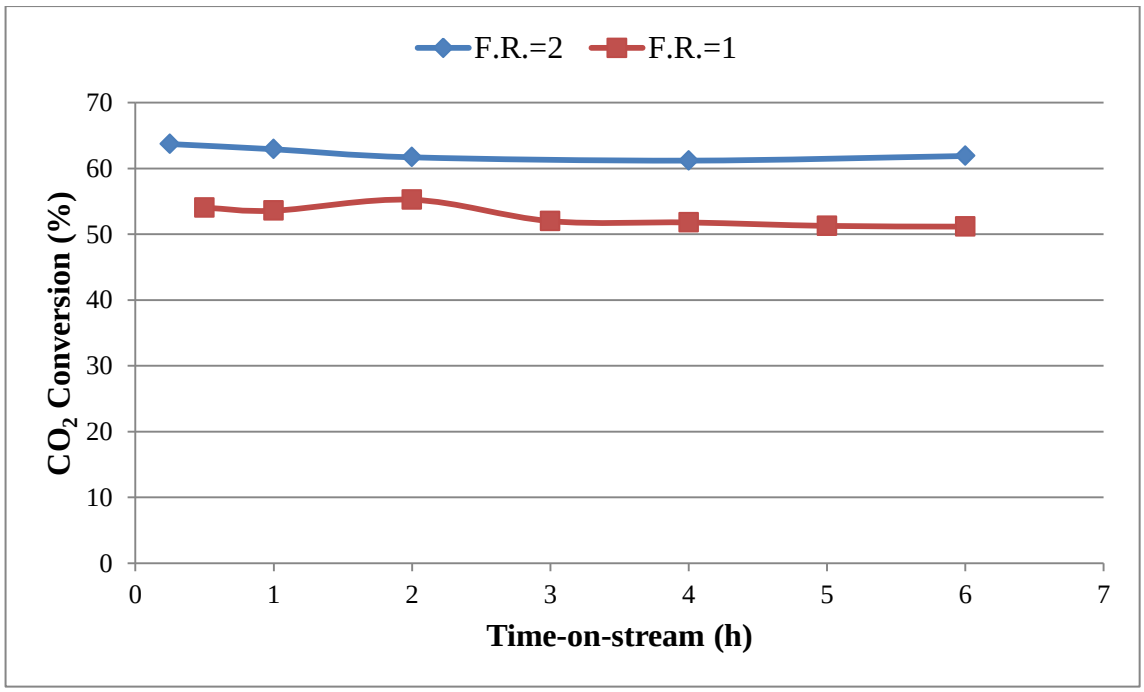

Figure 4.17. CO_2 TOS conversion values obtained for S/C feed ratio of 0.5 at 973 K.

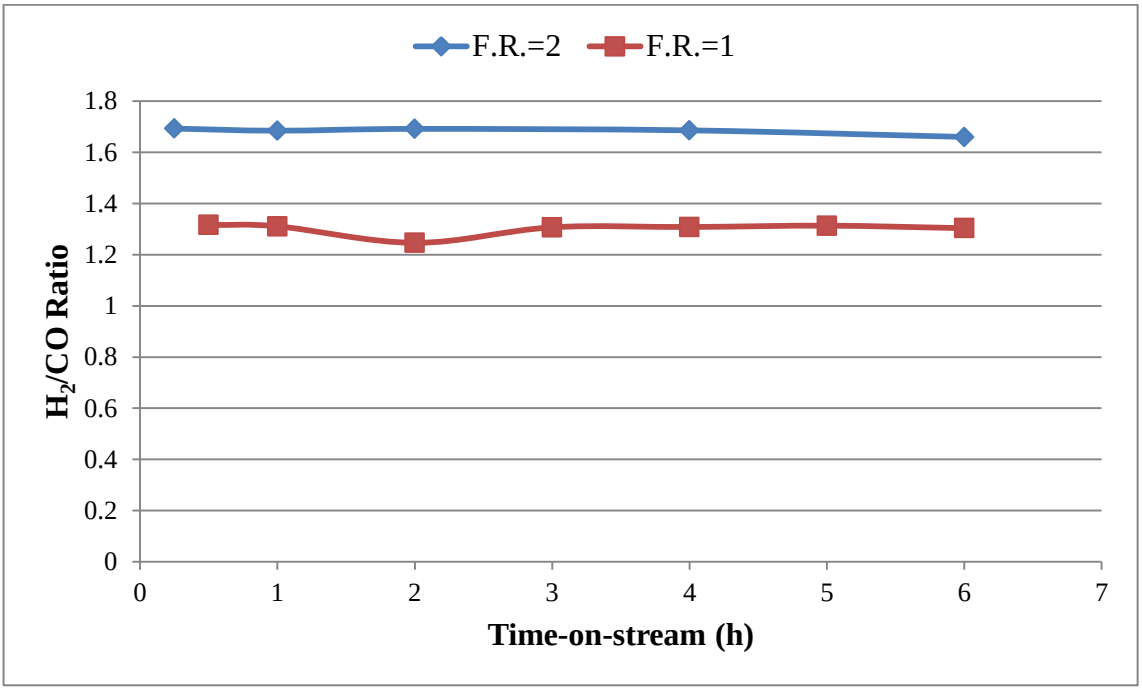

Figure 4.18. H_2/CO TOS ratio values obtained for S/C feed ratio of 0.5 at 973 K.

4.3. CDRM + POX Mixed Reforming

4.3.1. The Effect of Temperature

As in the case of mixed CDRM + SR, the activity in mixed CDRM + POX increases with increasing temperature. In order to see the effect of temperature on mixed CDRM + POX reforming performance, the activity and selectivity data obtained from the tests conducted at three temperature levels, 873, 923 and 973 K by using CH_4/CO_2 feed ratio of 2 with 10% O_2 in the feed, and CH_4/CO_2 feed ratio of 1 with 7% O_2 in the feed are comparatively analyzed.

CH_4 conversion was found increasing with the increase in temperature for both feed mixtures. For CH_4/CO_2 feed ratio of 2 with 10% O_2 in the feed, CH4 conversions were found as 57%, 51% and 37% at 973, 923 and 873 K, respectively, at the end of the 6 h TOS (Figure 4.19). For CH_4/CO_2 feed ratio of 1 with 7% O_2 in the feed case, CH_4 conversions were calculated as 63%, 51% and 40% at 973, 923 and 873 K, respectively

(Figure 4.20). In almost all cases there is no activity loss at the end of 6 h TOS and highest activity loss observed is lower than 7%.

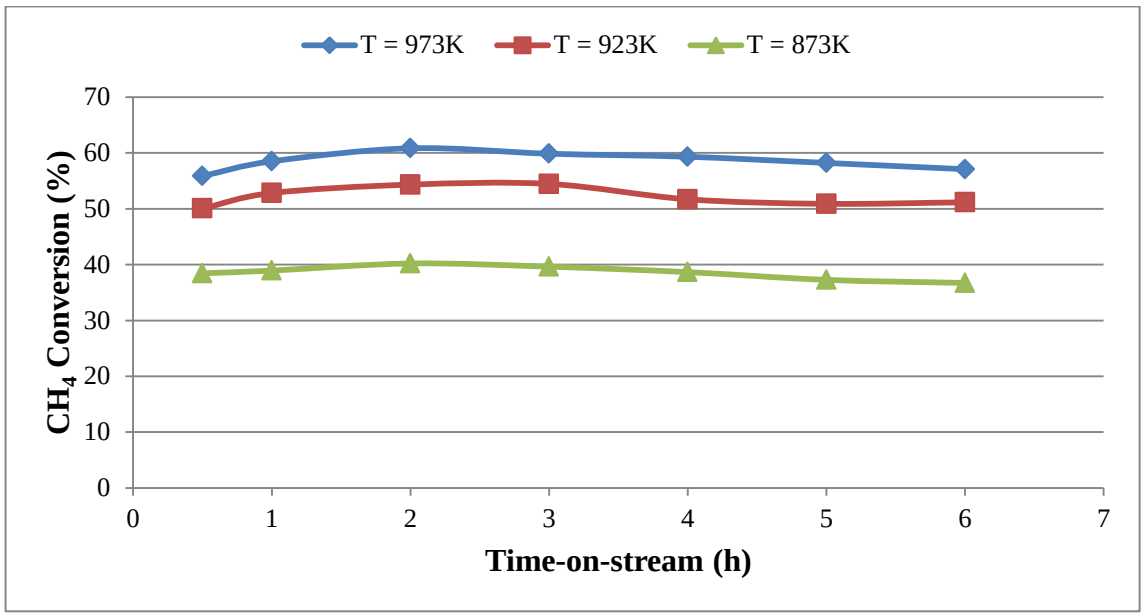

Figure 4.19. CH_4 TOS conversion values obtained for CH_4/CO_2 feed ratio of 2 with 10% O_2 in the feed.

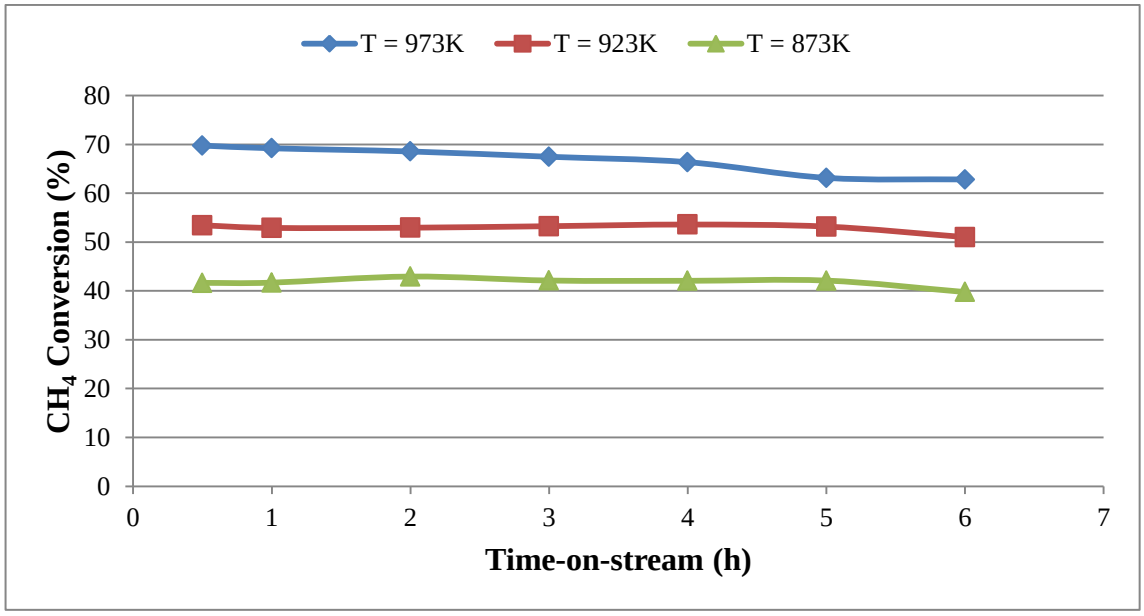

Figure 4.20. CH_4 TOS conversion values obtained for CH_4/CO_2 feed ratio of 1 with 7% O_2 in the feed.

Owing to endothermicity of CDRM, CO_2 conversion rates increases with the increase in temperature. On the other hand, this increase in CO_2 conversion cannot directly be interpreted as the dominance of CDRM in mixed reforming due to the fact that H_2/CO product selectivity remains almost constant when the reaction temperature is increased. CO_2 conversions were found as 70%, 57% and 38% at 973, 923 and 873 K, respectively, for CH_4/CO_2 feed ratio of 2 with 10% O_2 in the feed (Figure 4.21). Relatively lower CO_2 conversions, 55%, 43% and 31%, were obtained at for CH_4/CO_2 feed ratio of 1 with 7% O_2 in the feed at 973, 923 and 873 K, respectively at the end of 6 h TOS (Figure 4.22).

The selectivity of the mixed CDRM + POX is almost constant in temperature range of 873-973 K and close to unity. H_2/CO ratios were calculated as 1.08, 1.12 and 1.08 for CH_4/CO_2 feed ratio of 2 with 10% O_2 in the feed at 973, 923 and 873 K, respectively. For CH_4/CO_2 feed ratio of 1 with 7% O_2 in the feed, relatively lower H_2/CO product ratios, 0.84, 0.82 and 0.80 were calculated at 973, 923 and 873 K, respectively. These values are presented in Figure 4.23 and 4.24.

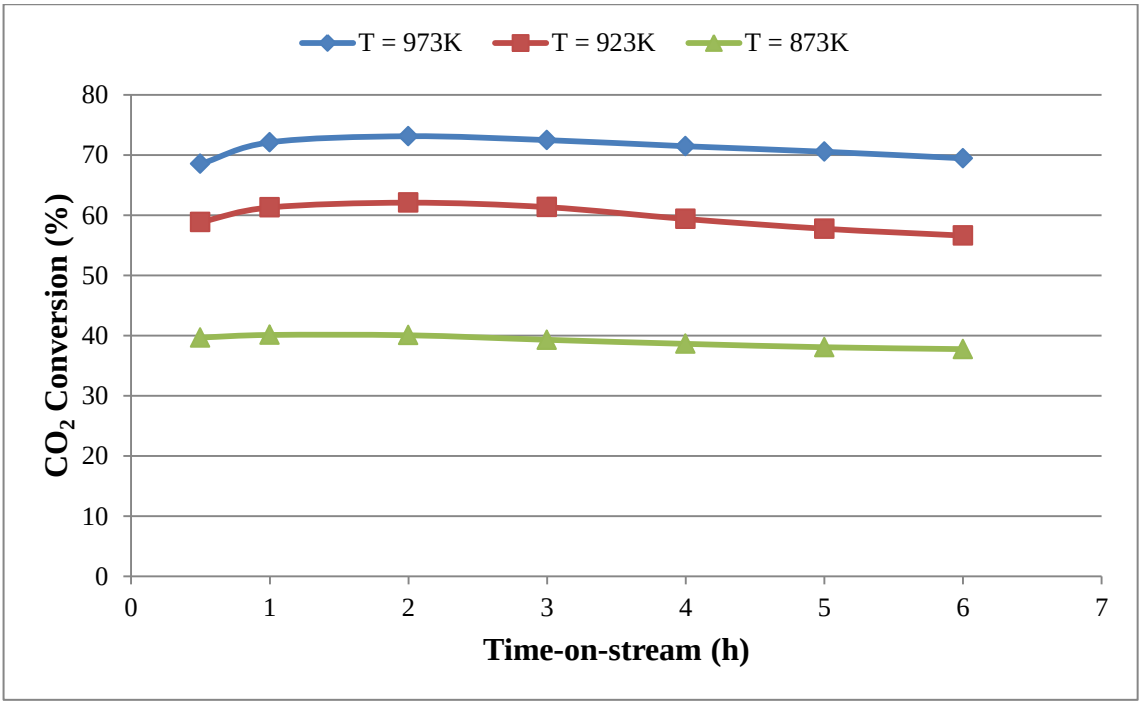

Figure 4.21. CO_2 TOS conversion values obtained for CH_4/CO_2 feed ratio of 2 with 10% O_2 in the feed.

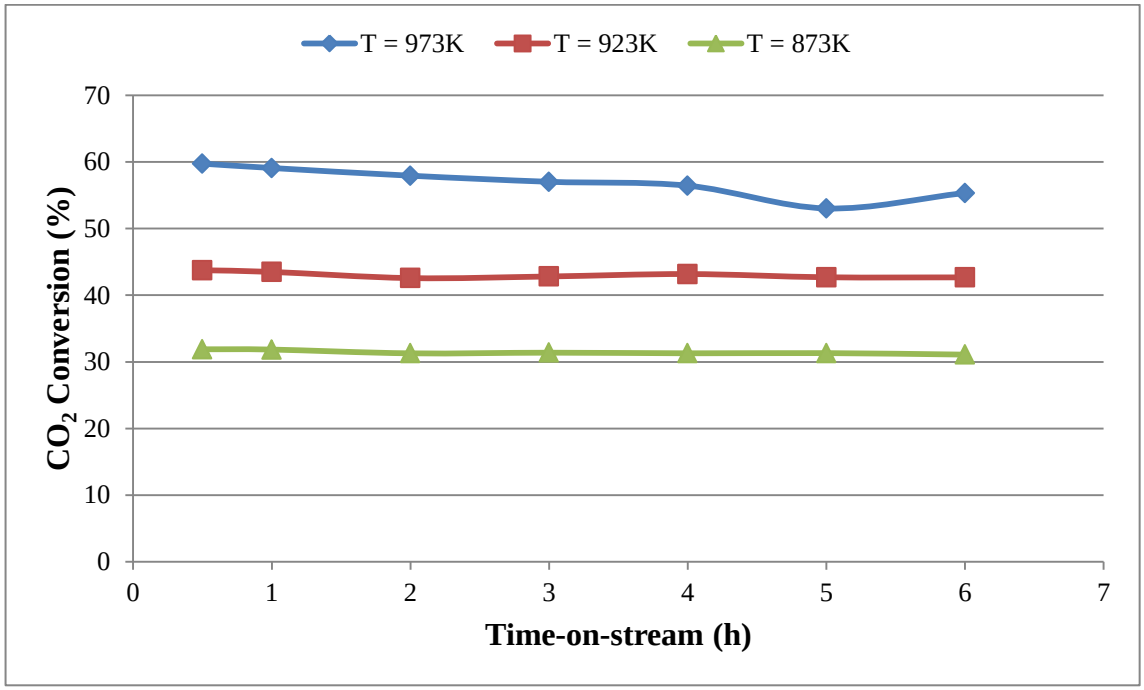

Figure 4.22. CO_2 TOS conversion values obtained for CH_4/CO_2 feed ratio of 1 with 7% O_2 in the feed.

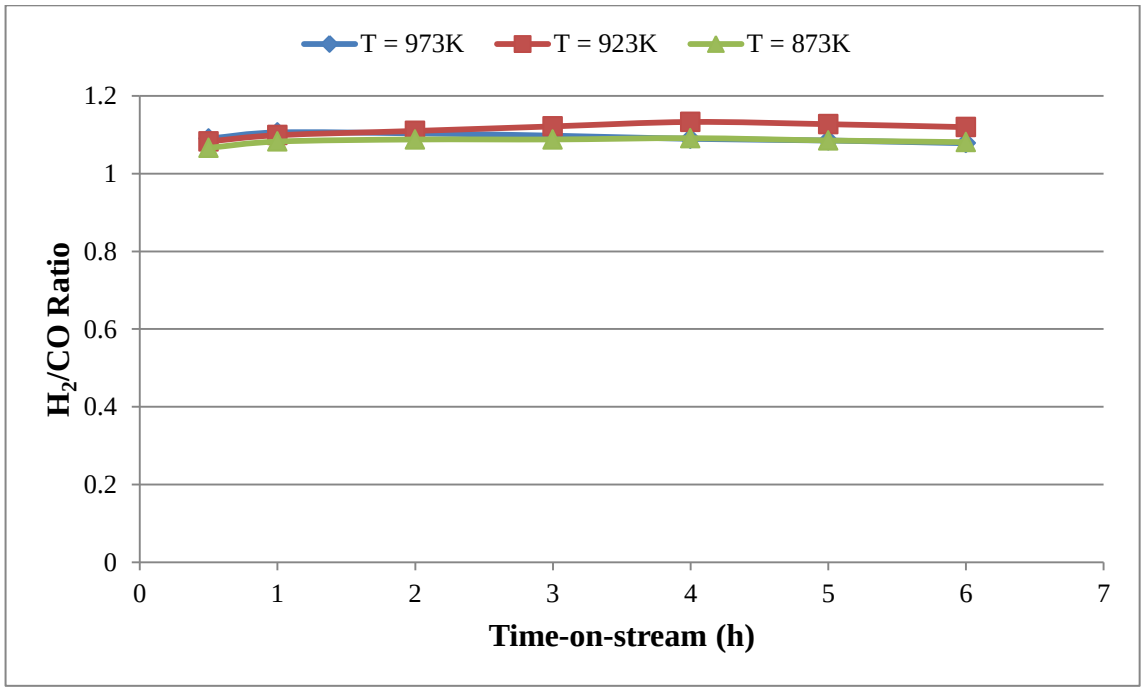

Figure 4.23. H_2/CO TOS ratio values obtained for CH_4/CO_2 feed ratio of 2 with 10% O_2 in the feed.

H_2/CO product ratios obtained at different temperature for different feed composition clearly show that with addition of oxygen to the system selectivity towards targeted H_2/CO ratio of unity can be achieved.

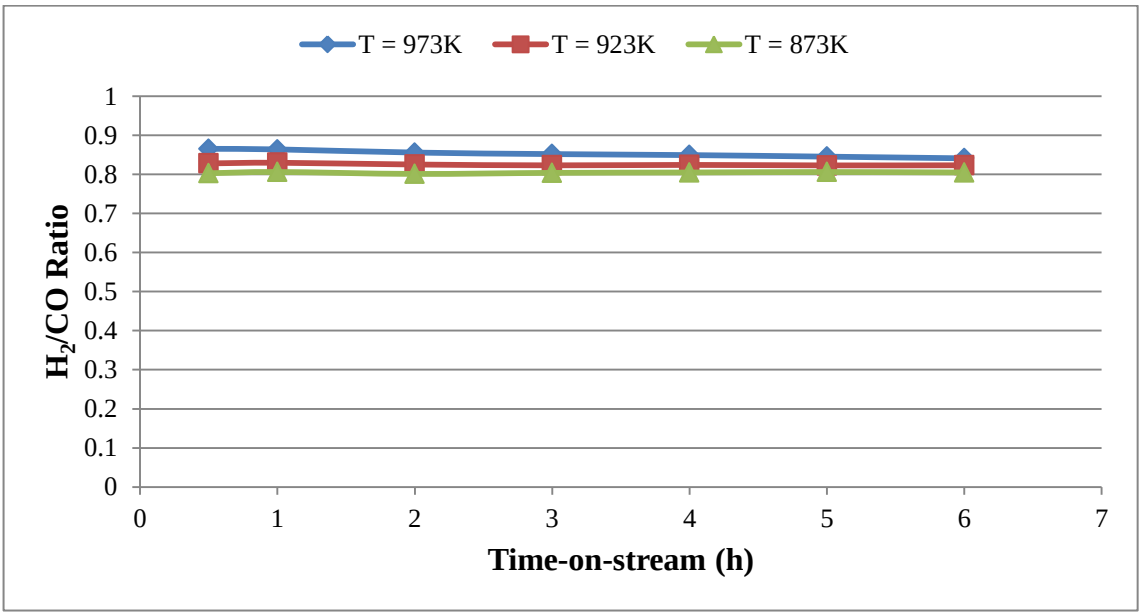

Figure 4.24. H_2/CO TOS ratio values obtained for CH_4/CO_2 feed ratio of 1 with 7% O_2 in the feed.

4.3.2. The Effect of O_2 Concentration in the Feed

In order to understand the effect of O_2 concentration in the feed on mixed CDRM+POX performance of Co-Ce system, the results of the performance tests conducted for CH_4/CO_2 feed ratio of 2 at 973 K with the O_2 feed concentrations of 0%, 4%, 7% and 10% and for CH_4/CO_2 feed ratio of 1 at 973 K with the O_2 feed concentrations of 0%, 7% and 10% were comparatively analyzed (Figures 4.25 and 4.26). As a general trend, increase in O_2 concentration in the feed leads to increased stability.

In the tests performed for CH_4/CO_2 feed ratio of 2 at 973 K, it was observed that 0% and 10% O_2 concentrations in the feed resulted almost same CH_4 conversion values after 6 h TOS, while O_2 concentration of 10% led higher stability and no activity loss. The results clearly indicated that the catalyst showed almost the same starting activity in the tests performed with 4%, 7% and 10% O_2 presence in the feed.

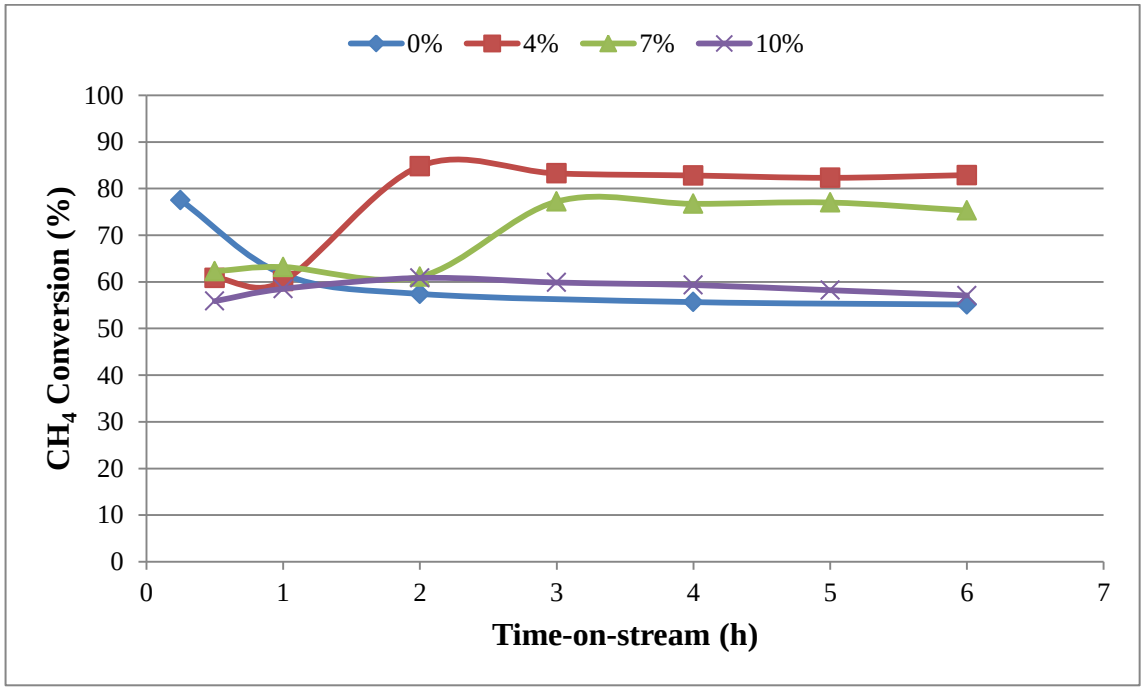

Figure 4.25. CH_4 TOS conversion values obtained for CH_4/CO_2 feed ratio of 2 at 973 K.

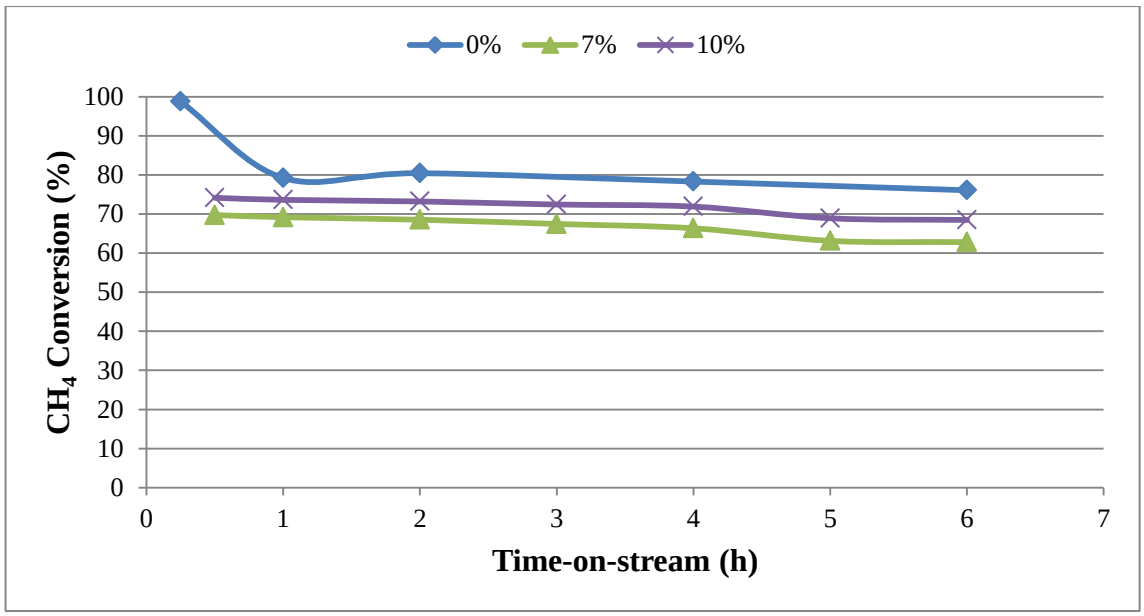

Figure 4.26. CH_4 TOS conversion values obtained for CH_4/CO_2 feed ratio of 1 at 973 K.

On the other hand, it is observed that there is a rise in activity for the feed having 7% and 4% O_2, especially when the feed is richer in CH_4. The spent catalysts had less deposited coke when O_2 feed concentration was higher. This result confirms that as long as

the surface oxygen is enough to clean carbon deposition, activity is stable. The instantaneous increase of CH_4 concentration in Figure 4.25 for O_2 feed concentrations of 4 and 7% hints the possible change in the reaction route led by the stabilization of the surface concentrations. In the tests conducted for CH_4/CO_2 feed ratio of 1 at 973 K for both 7 and 10% O_2 feed concentrations, the activities are stable for the whole TOS tests. It should be noted that for the lower CH_4/CO_2 feed ratio, i.e. when it is 1, there is a slight decrease in TOS methane conversion values with the introduction of O_2 to the feed (Figure 4.26). CO_2 conversion values are given in Figures 4.27 and 4.28 for the same reaction conditions. As the CO_2 conversion values also show a similar trend (Figure 4.28) with a larger decrease with O_2 addition, it may be suggested that either CDRM becomes relatively more favorable when CH_4/CO_2 feed ratio is low, i.e. 1, compared to the conditions with a higher CH_4/CO_2 feed ratio.

In the tests conducted for CH_4/CO_2 feed ratio of 2 at 973 K, both CH_4 and CO_2 conversions showed drastic changes midway through reaction for 4 and 7% oxygen addition. Possible increase in total oxidation, resulting in CO_2 and H_2O production, might cause a decrease in apparent CO_2 conversion values. It should be noted that with increasing O_2 concentration in the feed, the CO_2 conversion values decreased due to increased partial oxidation and total oxidation activity.

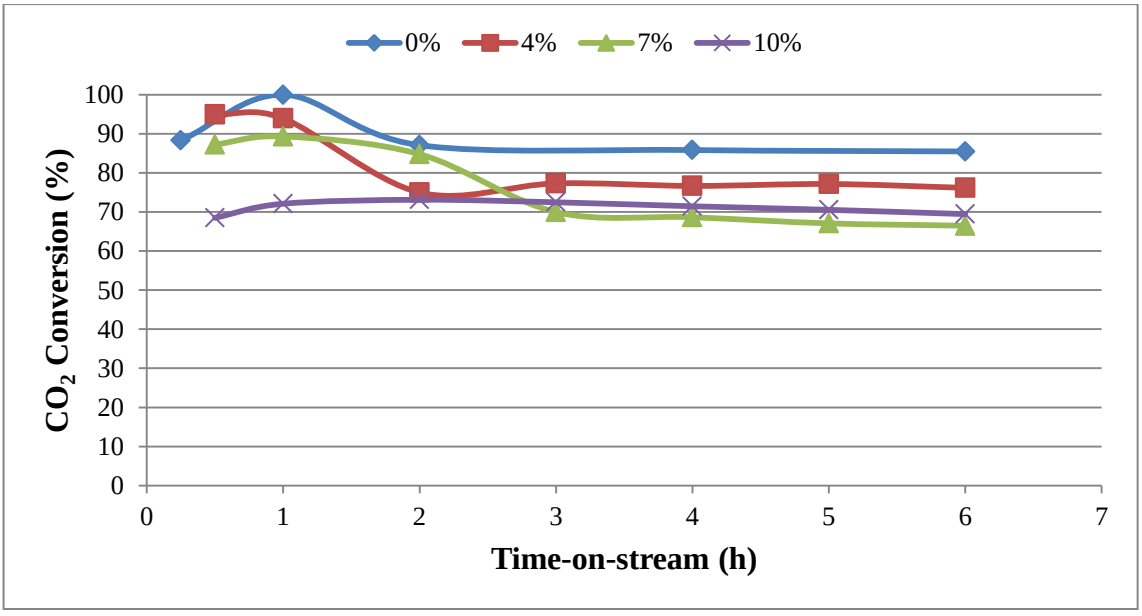

Figure 4.27. CO_2 TOS conversion values obtained for CH_4/CO_2 feed ratio of 2 at 973 K.

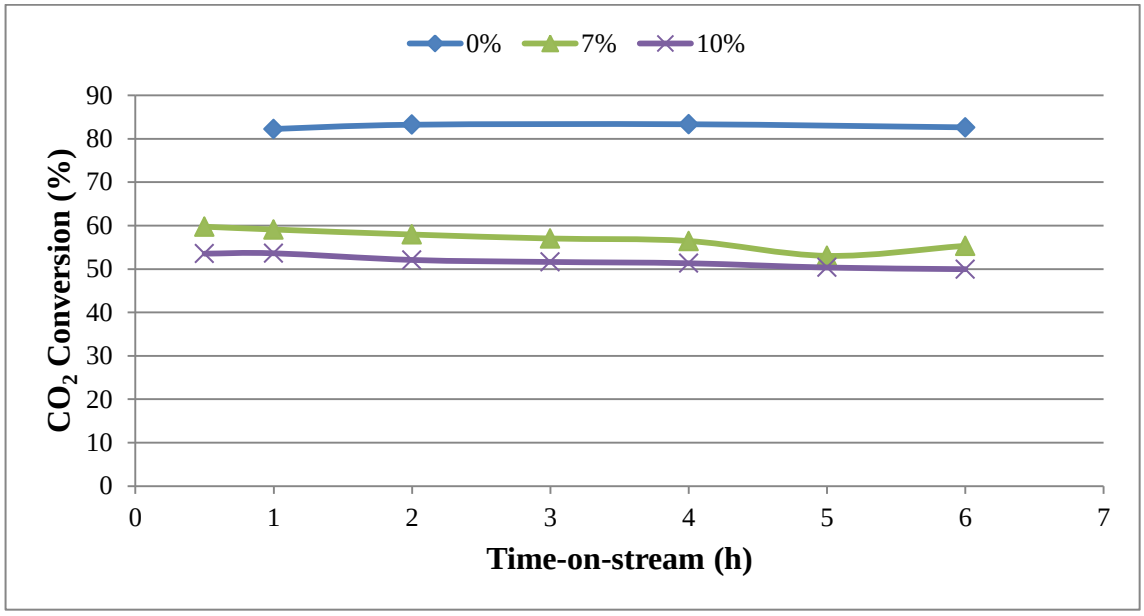

Figure 4.28. CO_2 TOS conversion values obtained for CH_4/CO_2 feed ratio of 1 at 973 K.

The results show that H_2/CO product selectivity is immensely improved for mixed reforming case compared to the CDRM-only process. For CH_4/CO_2 feed ratio of 2 at 973 K with 7% O_2 feed concentration the H_2/CO ratio of 0.96 was achieved at the end of 6h TOS. All the H_2/CO ratios calculated are presented in Figures 4.29 and 4.30.

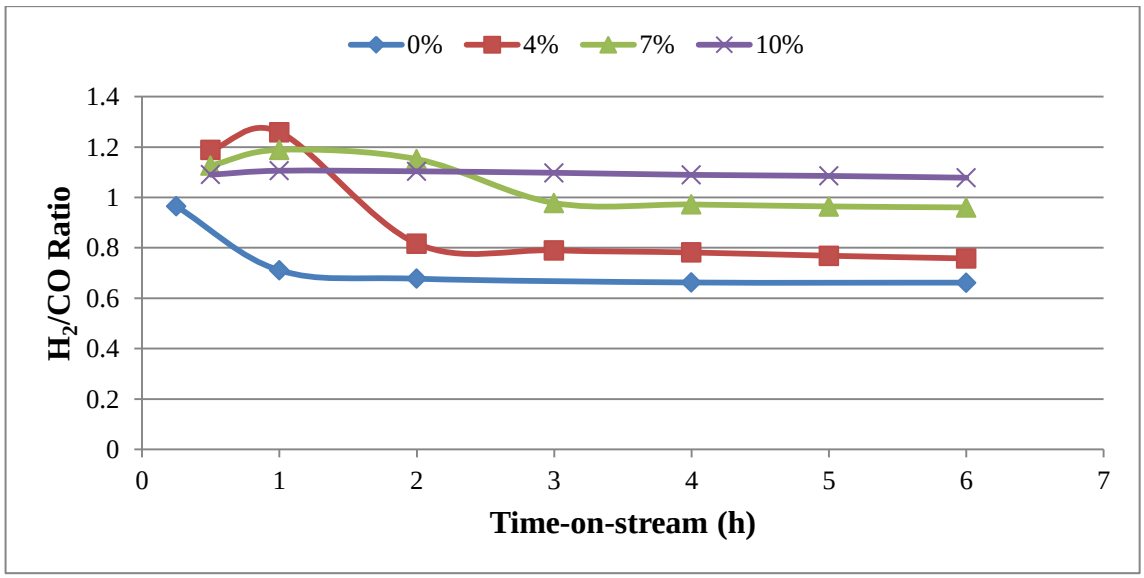

Figure 4.29. H_2/CO TOS ratio values obtained for CH_4/CO_2 feed ratio of 2 at 973 K.

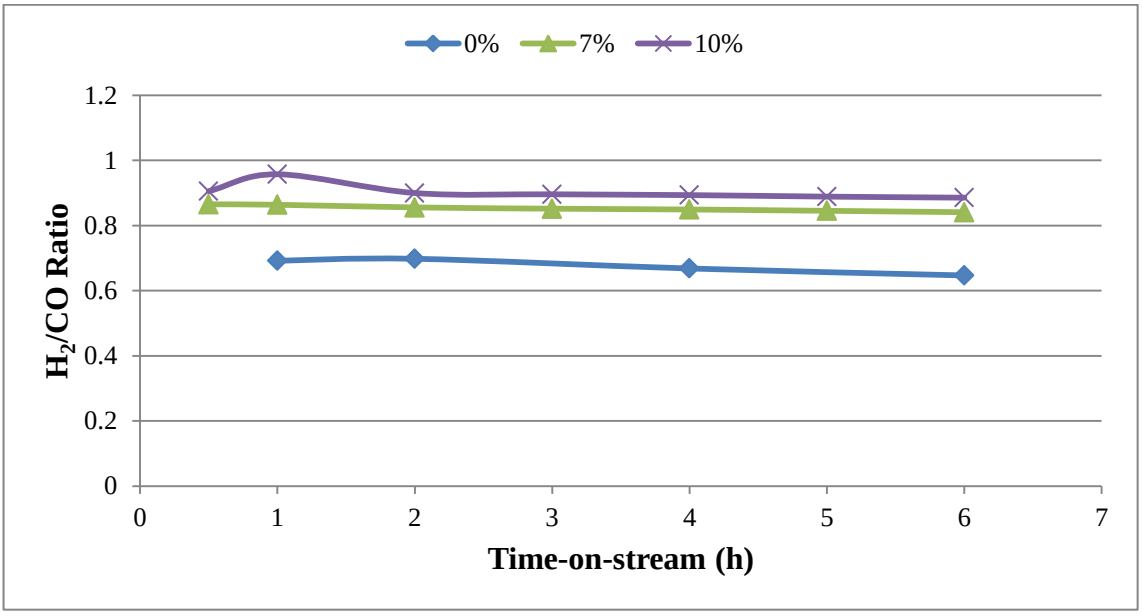

Figure 4.30. H_2/CO TOS ratio values obtained for CH_4/CO_2 feed ratio of 1 at 973 K.

In the experiments conducted for both CH_4/CO_2 feed ratios, increasing O_2 feed ratios has increased the H_2/CO product ratio, which is an expected result led by increasing POX activity. The results clearly show for both cases that with changing additional O_2 amount, stable activity can be achieved and the H_2/CO product ratio can be controlled. The ability to control the selectivity is a clear advantage of mixed reforming over CDRM.

4.3.3. The Effect of CH_4/CO_2 Feed Ratio

The experiments were conducted at 973 K with additional 10% O_2 in the feed for two different CH_4/CO_2 feed ratio to understand the effect of CH_4/CO_2 feed ratio on the performance of the catalyst. The tests gave similar trends to the ones obtained for mixed reforming with SR (Figures 4.31-4.33). CH_4 conversion was decreased by increasing CH_4/CO_2 feed ratio, since surface utilization of CH_4 did not increase as much as its increase in amount. CO_2 conversions were increased with the increase in CH_4/CO_2 feed ratio due to the increased need to surface oxygen. H_2/CO product ratios were also increased with increasing CH_4/CO_2 feed ratio. This can be explained by the fact that as hydrogen is produced by methane/methyl dehydrogenation, there is an increase in H_2 production with an increase in the amount of CH_4 fed.

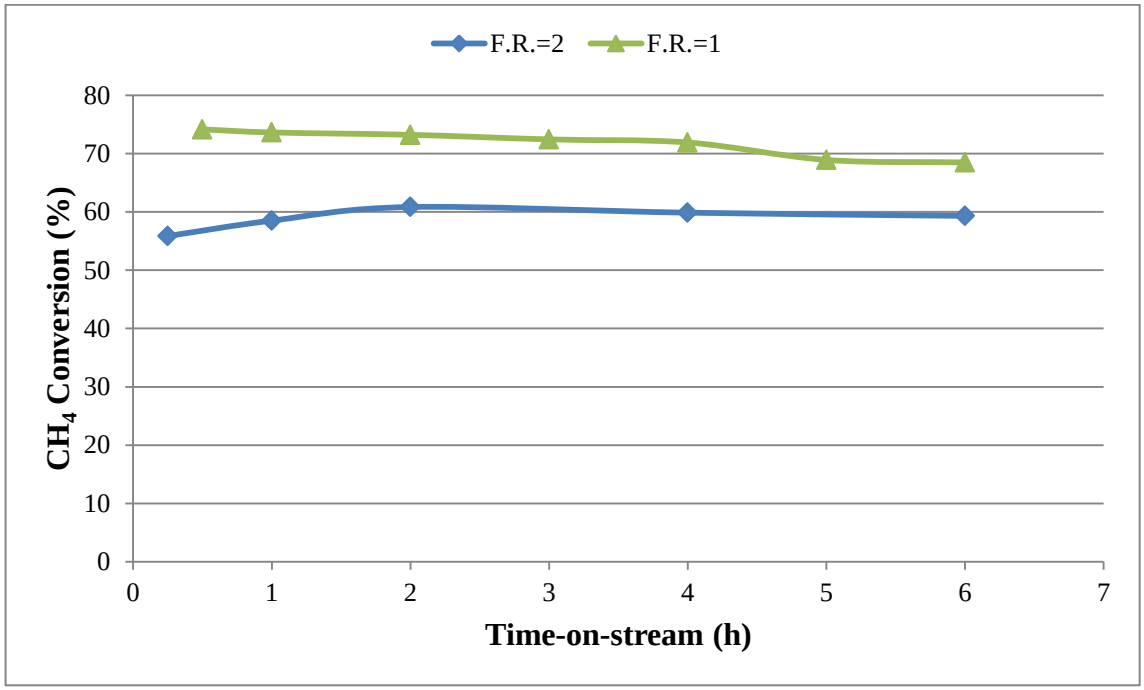

Figure 4.31. CH_4 TOS conversion values obtained for 10% O_2 concentration in feed at 973 K.

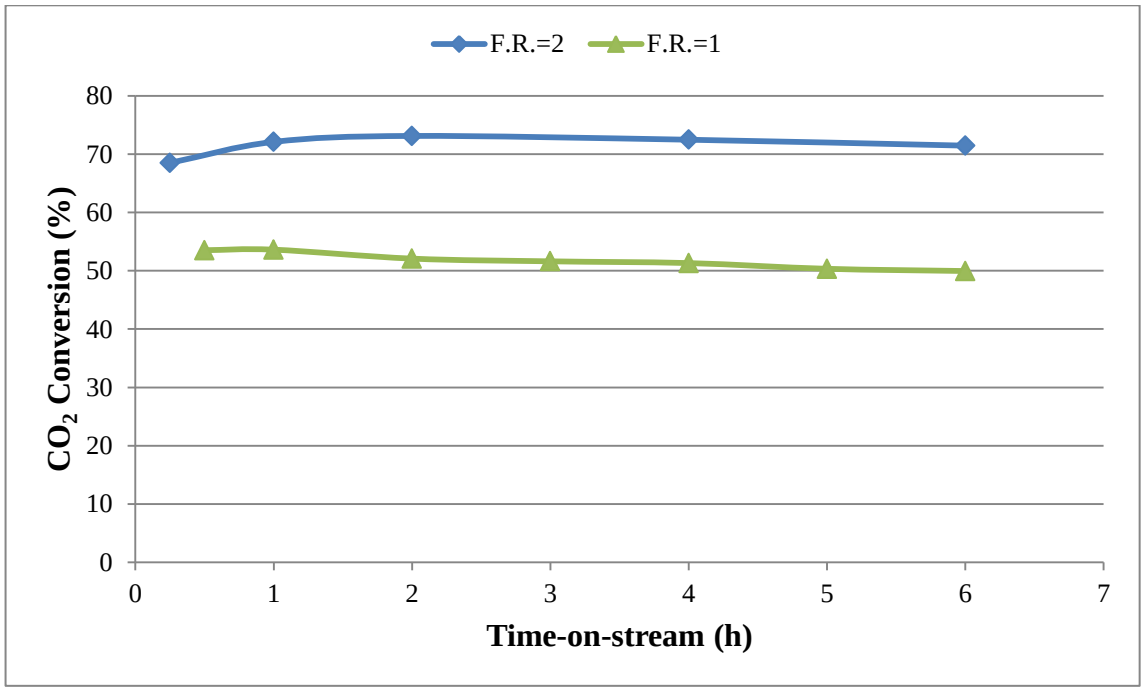

Figure 4.32. CO_2 TOS conversion values obtained for 10% O_2 concentration in feed at 973 K.

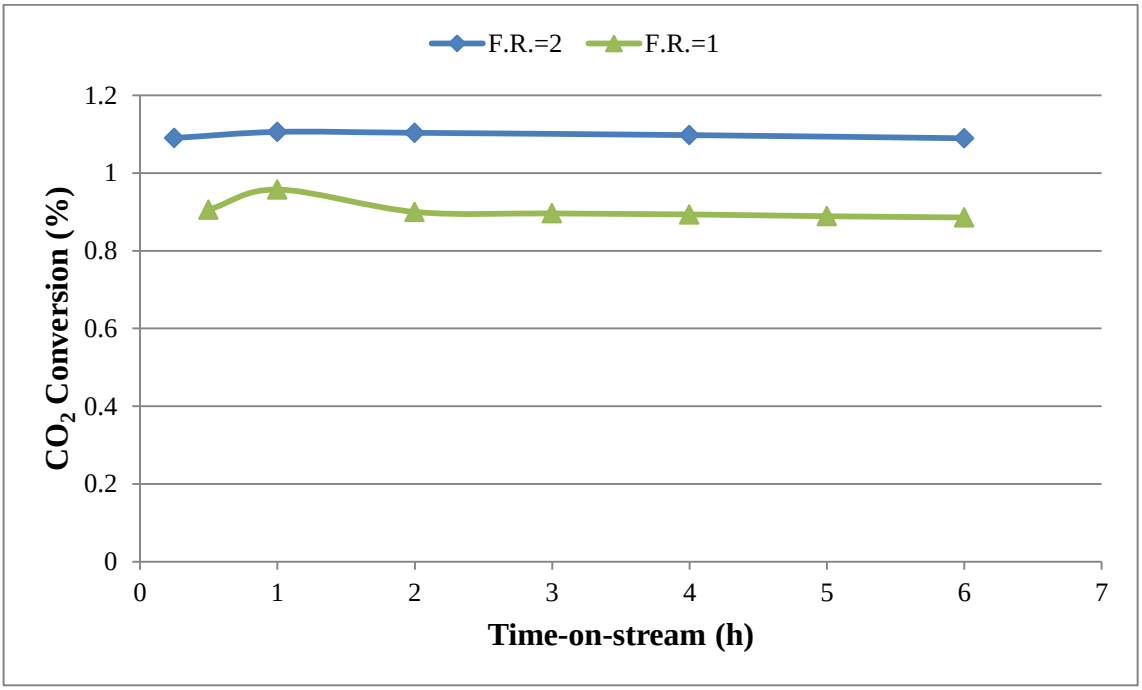

Figure 4.33. H_2/CO TOS ratio values obtained for 10% O_2 concentration in feed at 973 K.

4.4. XPS Characterization of Co-Ce System

Considering oxidative nature of SR and POX, and redox properties of CeO_x, oxidation states of both Co and Ce on freshly reduced and spent Co-Ce systems are of crucial importance. XPS spectra of Co 2p core level and Ce 3d core level were analyzed and presented in Figures 4.34 and 4.35, respectively. The XPS spectra of Co and Ce for freshly reduced catalyst, and spent catalysts that had been used in both CDRM+SR and CDRM+POX mixed reforming were obtained. The spent samples used at performance tests conducted under extreme conditions, i.e. the ones tested at high temperature for high CH_4/CO_2 feed ratio and high additional oxygen concentration in feed, and the ones tested at low temperature, for low CH_4/CO_2 feed ratio and low additional oxygen concentration in feed, were selected for XPS analysis in order to comparatively analyze the effect of mixed reforming conditions on oxidation state changes of Co and Ce active sites clearly.

The results of Co 2p XP spectra were compared to the results presented in the literature. There are two main peaks, at 780 eV and 796 eV, in Co 2p spectra; between those the former indicates the Co^{3+} formation while the latter indicates Co_3O_4 species on

the surface. It is observed from the comparison between XPS spectra of the freshly reduced and spent samples that additional oxygen content in the feed during the tests increases the intensities of these main peaks. Both peaks move to higher binding energy levels after the reaction. Co^{3+}, formed at 780 eV, reduce in to Co^{2+} in reaction (Lin *et al.*, 2010). On the other hand Co_3O_4 species, observed at 796 eV, move to a higher binding energy and form Co_2O_3 species (Biesinger *et al.*, 2010). The higher binding energy level may also point to increased metal-support interaction strength. The extent of oxidizing agents used is observed at 786 eV and 803 eV. The peak at 786 eV, which illustrates $Co(OH)_2$, was intensified in spent samples compared to their freshly reduced form. The freshly reduced catalyst did not show any $Co(OH)_2$ (satellite peak), which was reported at 803 eV (Tan *et al.*, 1990).

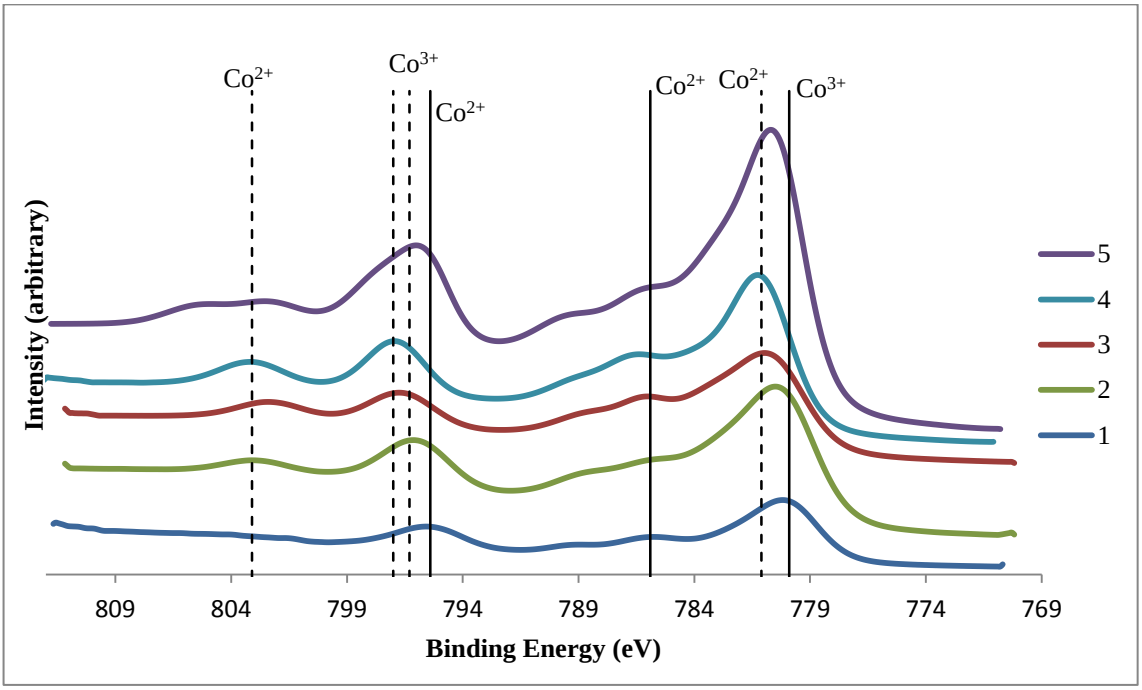

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Figure 4.34. XP spectrum of Co 2p region of catalyst samples. 1. Freshly reduced; 2. Spent at CH_4/CO_2 ratio of 1 and S/C of 0.5 at 873 K; 3. Spent at CH_4/CO_2 ratio of 2 and S/C of 1 at 973 K; 4. Spent at CH_4/CO_2 ratio of 1 with 7% O_2 in feed at 873 K; 5. Spent at CH_4/CO_2 ratio of 2 with 10% O_2 in feed at 973 K.

Co^{2+}/Co^{3+} ratios on the surface were also calculated and comparatively analyzed (Table 4.1). It seems that Co^{2+}/Co^{3+} ratio is increased on the spent samples that had yielded high H_2/CO product ratio; for those samples, high H_2 probably led to an increase in reduced Co^{3+} form. On the other hand, the results have shown that Co^{2+}/Co^{3+} ratios of

spent catalysts used in CDRM + POX are smaller than those of the spent catalysts used in CDRM + SR, which indicates that metal oxidation by O_2 is stronger than that by H_2O. XPS results show that for the spent samples used in CDRM + POX, the CO_2 conversion values increase directly with the increase in their surface Co^{2+}.

In the XPS spectra of Ce species, the main peaks at 882.3, 888.9, 898.2 and 916.5 eV show the Ce^{4+} species, and the peak at 906.6 eV shows Ce^{3+} species (Leppelt *et al.*, 2006). As previously mentioned, Ce is capable of going through redox cycle. Because of this feature, increase in the amount of the Ce^{3+} species, which has increased electron transfer capability, on the surface increase reaction activity where oxidizing agents are involved. In mixed reforming, both H_2O and O_2 are oxidizing agents with different extents. The results show H_2O addition in CDRM+SR mixed reforming doesn't change Ce oxidation states significantly, hence the overall Ce^{3+}/Ce^{4+} ratio is almost the same as that obtained from freshly reduced form. On the other hand, compared to data obtained from freshly reduced form, the Ce^{3+}/Ce^{4+} ratio decreases significantly when the reaction is conducted with high O_2 content in the feed. It is interesting to note that the Ce^{3+}/Ce^{4+} ratio is higher than that of the freshly reduced catalyst when CDRM+POX mixed reforming is conducted with low O_2 ratio in feed (Table 4.2). The results have indicated that Ce^{3+}/Ce^{4+} ratio decreases at higher conversion values, due to high utilization of oxygen on active sites. Similar to Co 2p spectra, some of the main peaks, at 882.3, 906.6 and 916.6 eV, move to higher binding energy levels, which may be an indicator of higher metal-support interaction strength (Biesinger *et al.*, 2011; Lin *et al.*, 2010).

Table 4.1. Co^{2+}/Co^{3+} ratios obtained from XPS at different conditions.

Catalyst Condition	Co^{2+}/Co^{3+} ratios
Freshly reduced	1.1
Spent at CH_4/CO_2 ratio of 1 and S/C of 0.5 at 873K	4.5
Spent at CH_4/CO_2 ratio of 2 and S/C of 1 at 973K	4.7
Spent at CH_4/CO_2 ratio of 1 with 7% O_2 in feed at 873K	1.9
Spent at CH_4/CO_2 ratio of 2 with 10% O_2 in feed at 973K	3.7

Table 4.2. $Ce3^{+}/Ce^{4+}$ ratios obtained from XPS at different conditions.

Catalyst Condition	Ce^{3+}/Ce^{4+} ratios
Freshly reduced	0.36
Spent at CH_4/CO_2 ratio of 1 and S/C of 0.5 at 873K	0.38
Spent at CH_4/CO_2 ratio of 2 and S/C of 1 at 973K	0.33
Spent at CH_4/CO_2 ratio of 1 with 7% O_2 in feed at 873K	0.52
Spent at CH_4/CO_2 ratio of 2 with 10% O_2 in feed at 973K	0.20

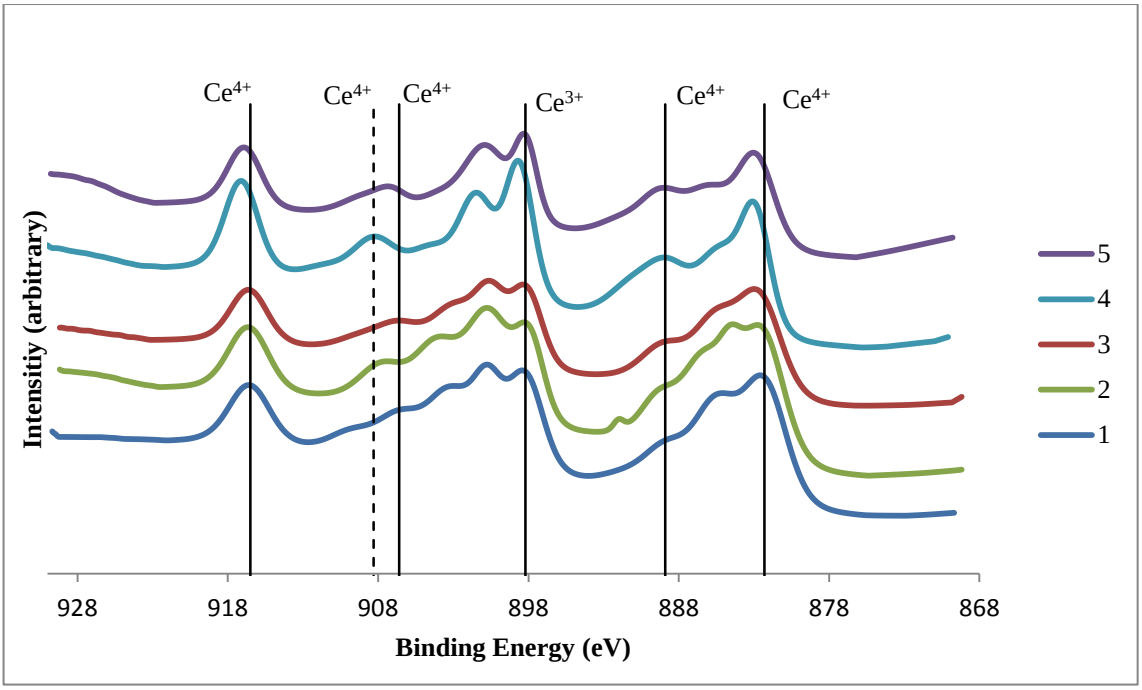

Figure 4.35. XP spectrum of Ce 3d region of catalyst samples. 1. Freshly reduced; 2. Spent at CH_4/CO_2 ratio of 1 and S/C of 0.5 at 873 K; 3. Spent at CH_4/CO_2 ratio of 2 and S/C of 1 at 973 K; 4. Spent at CH_4/CO_2 ratio of 1 with 7% O_2 in feed at 873 K; 5. Spent at CH_4/CO_2 ratio of 2 with 10% O_2 in feed at 973 K.

4.5. Comparison of H_2O and O_2 as Additional Oxygen Source

Both H_2O and O_2 are additional O_2 sources yielding mixed reforming of CDRM with SR and POX, respectively. In comparative analysis of H_2O and O_2 addition on the mixed reforming performance, the tests were conducted for water addition (S/C=0.5) and oxygen addition (7% and 10%) cases. The mixed reforming tests were performed for two CH_4/CO_2 feed ratios, 1 and 2, at 873 and 923 K.

The results clearly show that as long as coke deposition is prevented, the catalyst activity is stable. In the tests conducted, for CH_4/CO_2 feed ratio of 1 at 873 K and CH_4/CO_2 feed ratio of 2 at 923 K, both CO_2 and CH_4 values are almost equal even after 6 h TOS (Figures 4.36-4.39).

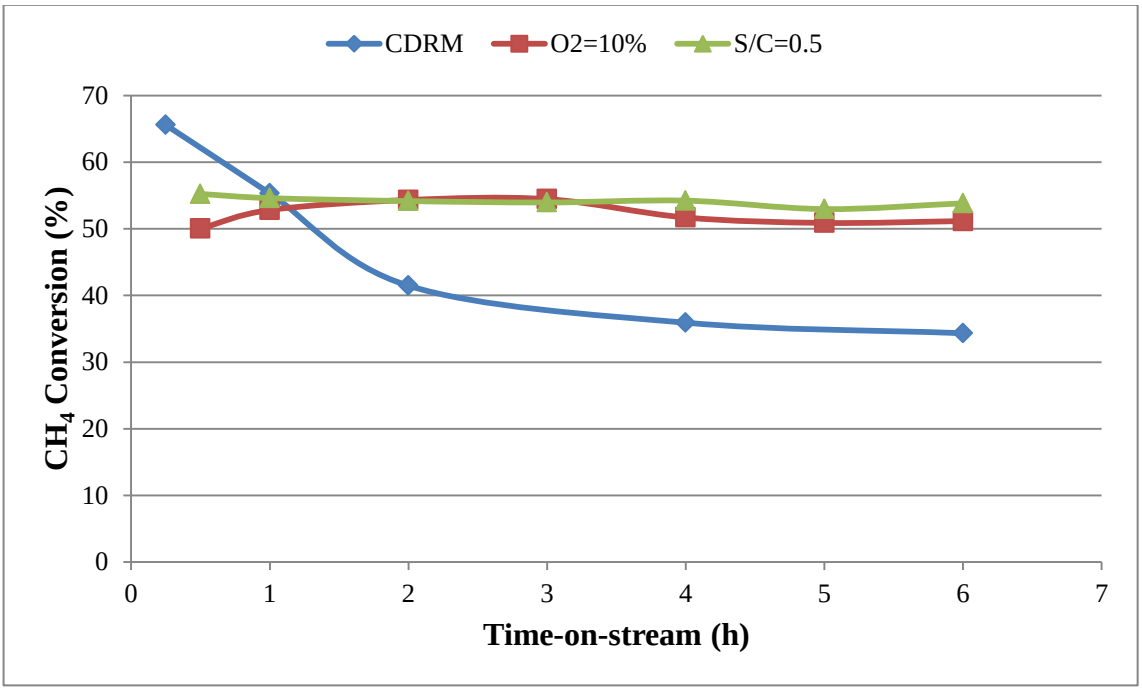

Figure 4.36. CH_4 TOS conversion values obtained for CH_4/CO_2 feed ratio of 2 at 923 K.

CO_2 conversion values were also obtained and compared both cases. CO_2 conversions for both additional oxygen sources decrease compared to CDRM-only process. It is expected as the surface utilizes the rich oxygen content sources better. In mixed reforming, TOS CH_4 activity values are very similar for both additional oxygen sources. Some slight changes in the CH_4 and CO_2 activity trends might occur due to temperature changes as SR activity is influenced by temperature significantly.

The most significant effect of type of additional oxygen source is on H_2/CO product ratio. In CDRM and POX, the only H_2 producing reactant is CH_4. In mixed reforming with SR, water is another hydrogen bearing reactant. Subsequently, with CDRM + SR mixed reforming, the H_2/CO ratios are higher than that obtained from both CDRM-only process and POX + CDRM mixed reforming. In all cases the selectivity values are stable

throughout the tests. The target H_2/CO ratio of 1 was approached better by oxygen addition than steam addition. These results are shown in following figures (Figures 4.40 and 4.41).

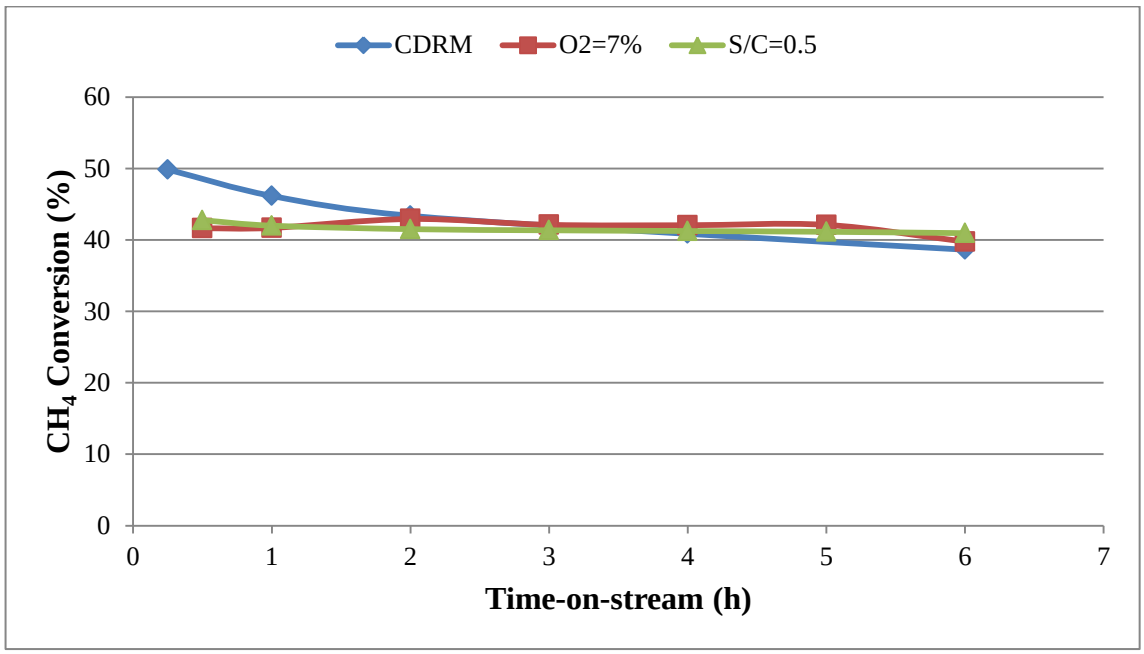

Figure 4.37. CH_4 TOS conversion values obtained for CH_4/CO_2 feed ratio of 1 at 873 K.

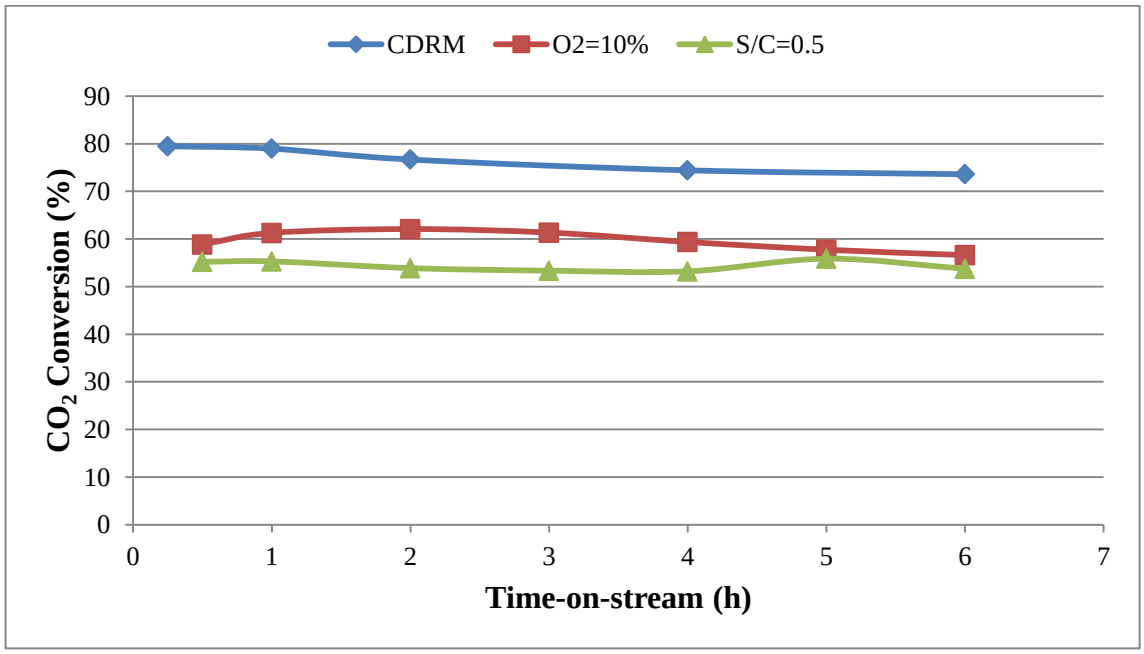

Figure 4.38. CO_2 TOS conversion values obtained for CH_4/CO_2 feed ratio of 2 at 923 K.

As a conclusion, the additional oxygen source doesn't have a significant effect on CH_4 and CO_2 conversion values as long as the coke deposition is removed. The H_2/CO product selectivity is closer to unity in CDRM + POX mixed reforming.

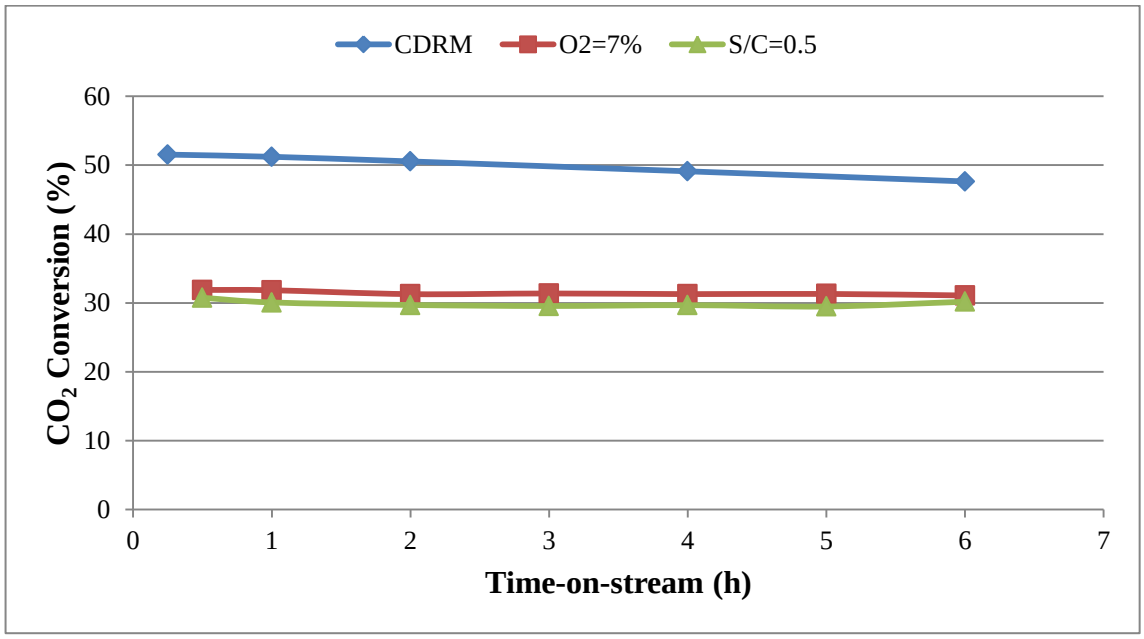

Figure 4.39. CO_2 TOS conversion values obtained for CH_4/CO_2 feed ratio of 1 at 873 K.

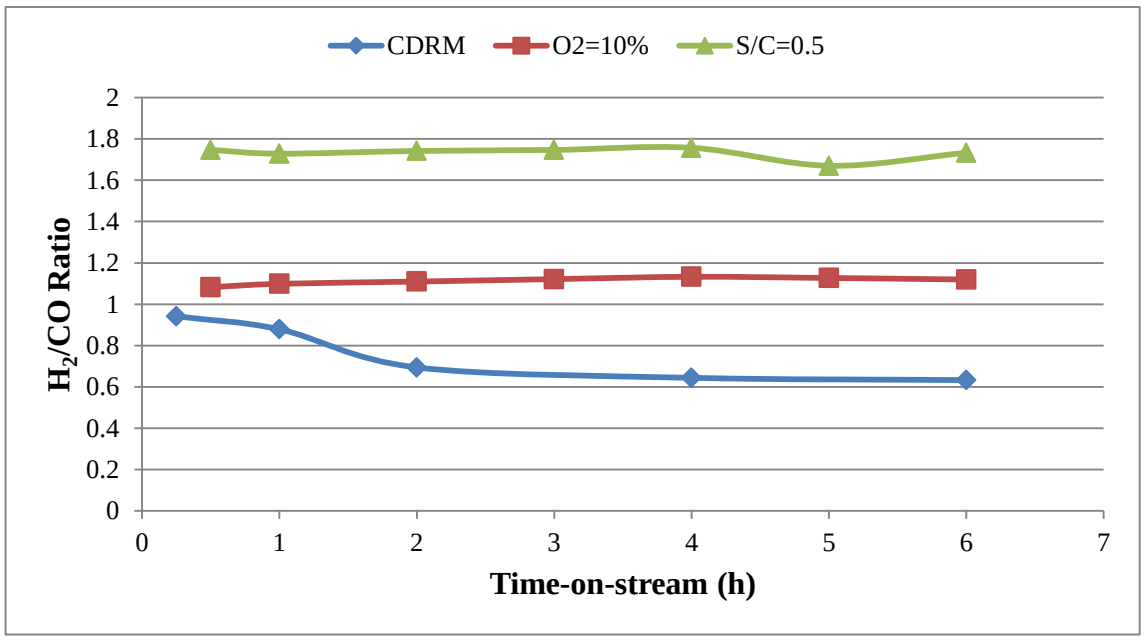

Figure 4.40. H_2/CO TOS ratio values obtained for CH_4/CO_2 feed ratio of 2 at 923 K.

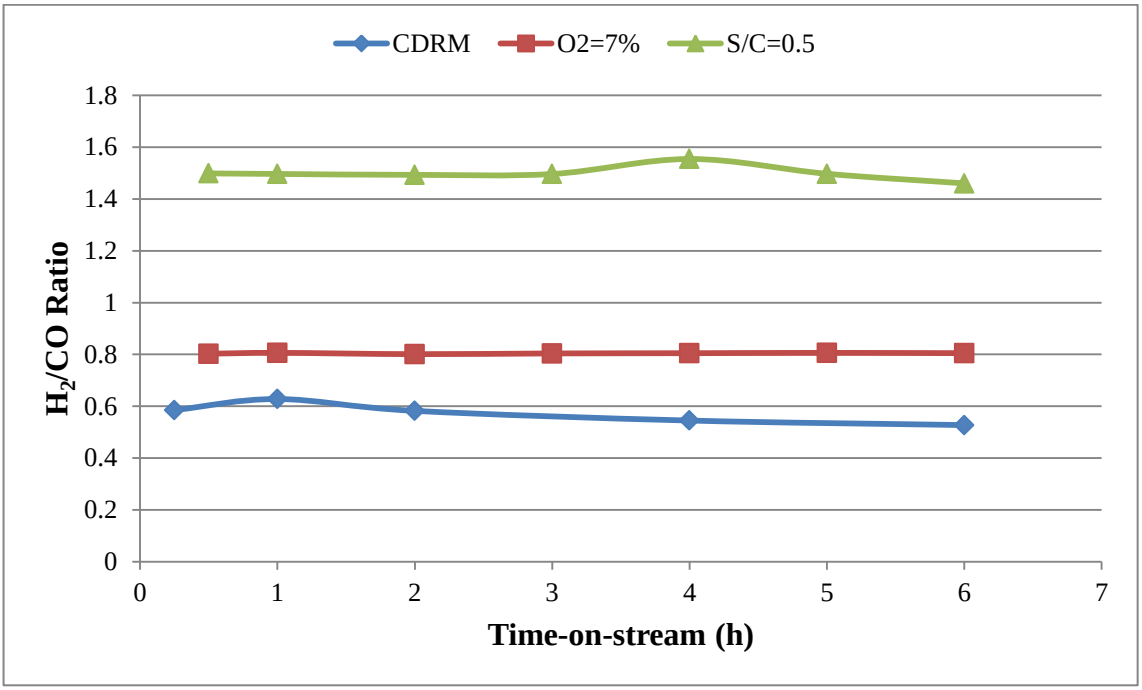

Figure 4.41. H_2/CO TOS ratio values obtained for CH_4/CO_2 feed ratio of 1 at 873 K.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The purpose of this study is to investigate the mixed reforming, both CDRM + SR and CDRM + POX, activity of the Co-Ce/ZrO_2 system. 10 wt.%Co-2 wt.%Ce/ZrO_2 was designed and tested to determine the optimal mixture of the oxygen sources for the improved catalytic performance. The major conclusions that can be drawn from this study can be given as follows:

- It was clearly observed that mixed reforming, CDRM + SR, activity (CH_4 conversion) and CDRM activity (CO_2 conversion) are increased with increasing temperature. The H_2/CO product ratio is pushed close to unity at high temperatures.
- The addition of steam has improved overall performance and stability in mixed reforming compared to those in individual CDRM. The results show that H_2/CO product ratio can be controlled.
- Lowering CH_4/CO_2 feed ratio in mixed reforming decreases CH_4 conversion, increases CO_2 conversion and suppresses H_2/CO product ratio.
- The results have shown that mixed reforming, CDRM + POX, activity (CH_4 and CO_2 conversions) increase with an increase in temperature. The H_2/CO product ratio is constant and close to unity in temperature range of 873-973 K.
- Stable activity can be achieved and H_2/CO product ratio can be controlled by changing O_2 concentration in the feed. Coke deposition in reactor is decreased immensely with increasing O_2 concentration in the feed.
- The additional oxygen source, steam or oxygen, doesn't have a significant effect on activity (CH_4 and CO_2 conversion values). In CDRM + POX mixed reforming, the H_2/CO product selectivity is more closer to unity than that in CDRM + SR mixed reforming.
- According to XPS analysis, the mixed reforming conditions yielding high surface Co^{2+}/Co^{3+} ratio leads to high H_2/CO ratio, and affects CO_2 conversion posivitely. The results have indicated that in CDRM+POX mixed reforming, Ce^{3+}/Ce^{4+} ratio

decreases at higher conversion values due to high utilization of oxygen on active sites.

5.2. Recommendations

According to the results of the current study, the following points are recommended to be investigated in future studies:

- The CDRM catalysts, with different active metals, supports and promoters, suffering from severe coke deposition can be experimentally tested in mixed reforming conditions to improve their catalytic activity, stability and selectivity.
- Wider range of temperatures, CH_4/CO_2 feed ratios and additional oxygen concentrations should be investigated to determine the optimal conditions for Co-Ce/ZrO_2 mixed reforming activity.
- The effect of impregnation strategy can be investigated.
- The mixed reforming kinetics can be studied over Co-Ce/ZrO_2 catalyst.
- The effect of pretreatment conditions on mixed reforming activity and selectivity can be studied by changing calcination and reduction temperatures.
- The micro-structural characteristics of spent Co-Ce/ZrO_2 catalysts in mixed reforming process can be studied.

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