AN EXPERIMENTAL STUDY ON DESIGN, DEVELOPMENT AND PERFORMANCE EVALUATION OF CATALYTIC DRY REFORMING OF METHANE CATALYSTS

by
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to my family

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ABSTRACT

AN EXPERIMENTAL STUDY ON DESIGN, DEVELOPMENT AND PERFORMANCE EVALUATION OF CATALYTIC DRY REFORMING OF METHANE CATALYSTS

The overall purpose of this research study is to design and develop effective non-noble catalysts having high and stable activity with suitable H_2/CO product selectivity for the production of synthesis gas via CO_2 reforming of methane (CDRM). In this context, bimetallic Co-La/ZrO_2, and trimetallic Co-Ni-La/ZrO_2 and Co-Ni-Ce/ZrO_2 catalysts were prepared, characterized and tested for their CDRM performance. The freshly reduced and spent samples were characterized by SEM-EDX. The reaction temperature, feed composition, space velocity, reaction time and nickel loading were the parameters used in activity and selectivity tests. In the catalysts, Co and promoter, i.e. La and Ce, loadings were kept fixed as 5 wt.% and 2 wt.%, respectively, while two Ni loading levels, 3 wt.% and 5 wt.%, was used in trimetallic samples. The results have shown that Co-La catalyst exhibited high stability, but only has moderate activity in CDRM. The introduction of nickel led to an increase in the activity which may be related with high dehydrogenation activity of Ni and strong and extensive Co-Ni surface interaction. The results show that Co:Ni loading ratio in the trimetallic catalyst has a significant effect on CDRM performance for the La promoted samples. There was no significant change in terms of activity and stability occur Co-Ni-Ce/ZrO_2 system in response change in Ni:Co ratio. Characterization of the catalysts indicated uniform distribution of metal on both Ce and La promoted trimetallic catalysts. The type of carbon deposited on trimetallic catalysts was all filamentous. It was also clearly observed that Ce-promoted catalyst have less carbon deposition than La-promoted one, remarking the effect of ceria on the stable activity of the catalysts through CeO_x redox cycle regulating surface oxygen transfer. On the basis of the performance test results, it was concluded that increasing temperature increased CH_4 and CO_2 conversions and H_2/CO product ratio. The results have shown that when the CH_4:CO_2 feed ratio is greater than 1.0, the lowest methane conversion, the highest carbon dioxide conversion and H_2/CO product ratio were observed for all catalysts. It was found out that increasing space velocity decreased the conversion values and H_2/CO product ratio.

ÖZET

METANIN KURU REFORMLAMASINDA KULLANILACAK ETKİLİ KATALİZÖRLERİN TASARIMI, GELİŞTİRİLMESİ VE PERFORMANS DEĞERLENDİRMESİ HAKKINDA DENEYSEL ÇALIŞMA

Bu çalışmanın amacı, metanın karbon dioksitle katalitik reformlaması yöntemiyle sentez gazı üretimini sağlayacak uygun H_2/CO ürün seçiciliğiyle birlikte yüksek ve kararlı aktiviteye sahip, soy metal içermeyen etkili katalizörler tasarlamak ve geliştirmektir. Bu bağlamda Co-La/ZrO_2, Co-Ni-La/ZrO_2 ve Co-Ni-Ce/ZrO_2 katalizörleri hazırlanarak karakterizasyonları yapılmış ve reaksiyon performansları test edilmiştir. İndirgenmiş ve kullanılmış katalizörlerin karakterizasyonu SEM-EDX ile yapılmıştır. Aktivite ve seçicilik testleri için parametreler olarak sıcaklık, besleme gazlarının oranı, besleme hızının katalizör miktarına oranı, reaksiyon süresi ve Ni yükleme miktarı seçilmiştir. Üç metalli katalizörlerde, kütlece %3 ve %5 Ni yüklemesi kullanılırken Co ve aktifleştiriciler (La, Ce) sırasıyla kütlece %5 ve %2 olarak sabit tutulmuştur. Sonuçlara göre Co-La katalizörü yüksek bir kararlılık, ancak orta dereceli bir aktivite göstermiştir. Nikel yüksek dehidrojenasyon aktivitesi, güçlü ve yaygın Co-Ni yüzey etkileşimi sayesinde katalitik etkinliği artırmıştır. Sonuçlar Co:Ni yükleme oranının La içerikli üç metalli katalizörlerin CDRM performanslarında önemli bir etkiye sahip olduğunu göstermektedir. Ni:Co oranındaki değişim Co-Ni-Ce/ZrO_2 sisteminde ise katalizör aktivite ve kararlığı açısından kayda değer bir değişim yaratmamıştır. Üç metalli katalizörlerin karakterizasyonu, tüm metal parçacıklarının homojen olarak dağıldığını göstermiştir. Bu katalizörlerin üzerinde biriken karbonun ipliksi yapıda olduğu belirtilmiştir. Ce içerikli katalizörlerin La içerikli olanlara göre daha düşük karbon birikimine sahip olması ve dolayısıyla daha yüksek aktivite göstermesi, Ce'nin yüzeydeki oksijeni CeO_x redoks döngüsü aracılığıyla taşıması ile açıklanır. Yapılan performans testlerine dayanarak, sıcaklık artışının hem CH_4 ve CO_2 dönüşüm yüzdelerini hem de H_2/CO ürün oranını arttırdığı görülmüştür. CH_4:CO_2 besleme oranının 1.0'den büyük olması, çalışılan tüm katalizör türleri için en düşük CH_4 dönüşümü sonuçlarını verirken, en yüksek CO_2 dönüşümü ve H_2/CO ürün oranını göstermiştir. Besleme hızının katalizör miktarına olan oranının arttırılmasının dönüşüm değerlerini ve H_2/CO ürün oranını azalttığı gözlemlenmiştir.

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LIST OF SYMBOLS

Al_2O_3	Aluminum oxide
Ce	Cerium
CH_4	Methane
Co	Cobalt
CO	Carbon monoxide
CO_2	Carbon dioxide
g-cat	Catalyst weight in grams
h	Hour
H_2	Hydrogen
La	Lanthanum
La_2O_3	Lanthanum oxide
MgO	Magnesium oxide
min	Minute
mL	Milliliter
Mo	Molybdenum
Ni	Nickel
Pt	Platinum

Rh	Rhodium
Ru	Ruthenium
SiO_2	Silicon dioxide
T	Temperature
W	Catalyst weight
$X(CH_4)$	Conversion of methane
ZrO_2	Zirconium oxide

LIST OF ACRONYMS/ABBREVIATIONS

C	Concentration
BOS	Birleşik Oksijen Sanayi
CDRM	Catalytic Dry Reforming of Methane
EDX	Energy Dispersive X-Ray Spectroscopy
F-T	Fischer Tropsch
GC	Gas Chromatography
HR-TEM	High-Resolution Transmission Electron Microscopy
RWGS	Reverse Water Gas Shift
SEM	Scanning Electron Microscopy
WGS	Water Gas Shift
XPS	X-Ray Photoelectron Microscopy
XRD	X-Ray Diffraction

1. INTRODUCTION

Global warming and rapidly depleting reserves due to the increase in the use of non-renewable fossil fuels, like petroleum and coal, have been an important incentive for the studies on alternative energy sources and minimization of greenhouse gases emission (Fan *et al.,* 2011; Al-Fatesh *et al.,* 2014). On this basis, natural gas, which consists of methane (between 70 and 98% depending on the location), CO_2 and a complex mixture of pollutant gases, is proposed as the fuel of the foreseeable future considering its worldwide reserves (Ross *et al.*, 1996; Pakhare *et al.*, 2013).

Most of the natural gas reserves, however, are situated in areas remote from the consumption centers thus, its compression, transportation and storage is costly. Since methane is the primary component of natural gas, its conversion to higher value products via an economically feasible way has become increasingly important (Mattos *et al.*, 2003; Pakhare *et al.*, 2013). There have been studies on direct oxidative conversion of methane into methanol, formaldehyde, benzene and other aromatics, and direct oxidative coupling of methane to ethane and ethylene but all have concluded with either low yield or high cost (Claridge *et al.*, 1998).

Currently, the use of methane as a feedstock involves its conversion to syngas, a mixture of carbon monoxide and hydrogen. Synthesis gas serves as the feedstock for further use in a variety of downstream chemical processes, such as methanol synthesis, Fischer–Tropsch synthesis for production of liquid hydrocarbons or ammonia synthesis (Cheng *et al.*, 2010).

The transformation of methane into synthesis gas can be performed by reforming process through three different ways: steam reforming, CO_2 reforming (or dry reforming) and partial oxidation. Carbon dioxide reforming of methane (CDRM) offers certain advantages over other processes. It allows the simultaneous conversion of two gases, CH_4 and CO_2, which have high global warming potential, into valuable syngas. The main advantage of syngas production from CO_2 reforming is a lower H_2/CO product ratio obtained, which is adequate for further synthesis of oxygenated hydrocarbons as well as its use as a feed to Fischer–Tropsch synthesis for production of higher hydrocarbons (Barroso-Quiroga *et al*., 2010; Fidalgo *et al*., 2010). CDRM is attractive process since it can be employed in fields where water is not available, and it can also be applied directly for utilization of natural gas which contains large amount of CO_2, without any pre-separation (Cheng *et al.*, 2010). Moreover, the higher operating pressures of steam reforming lead to higher operating expenses. Thus, lower operating pressures of the CDRM process would decrease both operating expenses and equipment costs, and improves plant safety as well. Ross et al. (1996) have shown that CDRM has the lowest operating costs, about 20% lower than any other reforming processes (Ross *et al.*, 1996).

The main drawback of dry reforming is high temperatures that are required to obtain high conversion levels owing to the highly endothermic nature of the process. These severe operating conditions cause deactivation by coke deposition and/or sintering of the metallic phase and support.

Different types of supported metal catalysts have been extensively studied to minimize coke deposition problem. Generally, carbon dioxide reforming is catalyzed by two main groups of catalysts, non-noble metals (e.g. Ni, Co, Fe) and noble metals (e.g. Ru, Rh, Pd, Pt, Ir). The former group is more favorable from an industrial point of view due to their low cost and abundance, but they are more rapidly deactivated via carbon deposition and/or metal sintering. On the other hand, catalysts containing noble metals such as Pt, Ru and Rh show high activity and selectivity in CDRM and they have high coke resistance. However, the high cost of PEM group metals and their low availability make them not economically competitive with other transition metal based materials.

The aim of this thesis is to design and develop effective non-noble catalysts having high and stable activity with suitable H_2/CO product selectivity for the production of synthesis gas via CO_2 reforming of methane (CDRM). In this context, Co-La/ZrO_2, Co-Ni-La/ZrO_2 and Co-Ni-Ce/ZrO_2 catalysts were prepared, characterized and tested for their CDRM performance where temperature, CH_4/CO_2 feed ratio, space velocity, reaction time and nickel loading are considered as the experimental parameters.

Chapter 2 involves a detailed literature survey on theorical background of carbon dioxide reforming of methane as well as the catalysts involved in the process and catalyst deactivation mechanisms. Chapter 3 contains the experimental work carried out. The results obtained in the experiments are discussed in Chapter 4 and the conclusions of the present study and recommendations for the future work are presented in Chapter 5.

2. LITERATURE SURVEY

2.1. Carbon Dioxide Reforming of Methane

The catalytic carbon dioxide reforming of methane (CDRM) [Equation 2.1] produces valuable synthesis gas, a mixture of CO and H_2, has gained renewed interest in recent years. CDRM is an advantageous reaction from both environmental and industrial perspective; it utilizes problematic greenhouse gases (CH_4 and CO_2) yielding H_2/CO product ratio of 1, which is suitable for production of useful hydrocarbons. CDRM is accompanied by some side reactions (Fan *et al.*, 2011; Ghelamallah *et al.*, 2012):

Carbon dioxide reforming of methane (CDRM): $CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$ (2.1)

Reverse water gas shift (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)

Steam reforming: $CH_4 + 2H_2O \leftrightarrow CO + 3H_2$ (2.4)

Carbon monoxide methanation: $3H_2 + CO \leftrightarrow CH_4 + H_2O$ (2.5)

Boudouard reaction: $2CO \leftrightarrow CO_2 + C$ (2.6)

Methane decomposition: $CH_4 \leftrightarrow C + 2H_2$ (2.7)

Coke asidification: $C + H_2O \leftrightarrow CO + H_2$ (2.8)

The products of the CDRM are mixture of carbon monoxide and hydrogen, which is also called syngas. The main advantage of syngas production from CO_2 reforming over other processes, e.g. steam reforming [Equation 2.9] or partial oxidation [Equation 2.10] is its lower H_2/CO product ratio, 1/1 or less, which makes CDRM an industrially advantageous process.

$$CH_4 + H_2O \rightarrow 3H_2 + CO \qquad H_2/CO = 3/1 \qquad \Delta H^0_{298} = 206\ kJmol^{-1} \qquad (2.9)$$

$$2CH_4 + O_2 \rightarrow 4H_2 + 2CO \qquad H_2/CO = 2/1 \qquad \Delta H^0_{298} = -36\ kJmol^{-1} \qquad (2.10)$$

The syngas H_2/CO ratio of unity makes it a feedstock for further use in a variety of downstream chemical processes, such as methanol synthesis [Equation 2.11], Fischer–Tropsch synthesis for production of long-chain hydrocarbons with selectivity towards olefins [Equation2.12] or dimethyl ether synthesis, all of which need lower H_2/CO ratios than that can be obtained by conventional steam reforming (Barroso-Quiroga *et al.*, 2010; Fidalgo *et al.*, 2010; Cheng *et al.*, 2010; Pakhare *et al.*, 2013).

$$CO + 2H_2 \rightarrow CH_3OH \qquad H_2/CO = 2 \qquad (2.11)$$

$$nCO + 2nH_2 \rightarrow \text{-}(CH_2)_n\text{-} + nH_2O \qquad H_2/CO = 2 \qquad (2.12)$$

CDRM offers other certain advantages over alternative reforming processes; the reactants of CDRM are available at low, or even at negative, prices. Natural gas reservoirs contain between 70 and 98% of methane mixed with CO_2 for a maximum of 15% depending on the location from where it is produced. Evaluations of economically feasible production conclude that CO_2 reforming process has the lowest operating costs, about 20% lower than the others, mainly due to the relatively lower feedstock requirement [Ross *et al.*, 1996; Pakhare *et al.*, 2013]. CDRM can be employed in fields where water is not available and can also be applied directly for utilization of natural gas which contains large amount of CO_2, without any pre-separation (Cheng *et al.*, 2010).

As CDRM is a strongly endothermic process, it requires high temperatures to reach high conversion levels. These conditions lead to some drawbacks such as rapid coke deposition that causes catalyst deactivation, catalyst destruction, reactor blockage, and sintering of the metallic phase and/or the support (Ozkara-Aydınoglu *et al.*, 2010; Al-Fatesh *et al.*, 2011). Among the side reactions, the reverse water-gas shift or RWGS [Equation 2.2], methane decomposition [Equation 2.7], and Boudouard [Equation 2.6], reaction seem to be the most significant ones and determine the selectivity of the global process. Coke formation mainly originates from methane decomposition and the Boudouard reaction (i.e. carbon monoxide disproportion) (Barroso-Quiroga *et al.*, 2010). The former is an endothermic reaction which is favored at higher temperatures and lower pressures, whereas the latter is an exothermic reaction, which is favored at lower temperatures and higher pressures (Al-Fatesh *et al.*, 2011).

The research efforts on design and development of effective CDRM catalysts have been primarily concentrated on developing systems that minimize the coke deposition even when methane dehydrogenation rate is high.

2.2. Catalysts for CO_2 Reforming of Methane

Many studies on CDRM were conducted over different types of catalysts composed of transition metal carbides and sulfides, perovskite-type mixed oxides, unsupported metals and supported group VIII metals. In order to achieve high CDRM performance, obtaining catalysts that show both high activity and good stability towards synthesis gas production, which are resistant to coking and allowing the minimization of the energy requirement, is of great interest in recent years. Numerous supported metal catalysts have been prepared and tested (Cheng *et al.,* 2010; Kumar *et al*., 2007). Both non-noble metals (e.g. Ni, Co, Fe) and noble metals (e.g. Ru, Rh, Pd, Pt, Ir) were found to be catalytically active in CDRM. The former group is more favorable from an industrial standpoint due to low cost and the abundance of their active metals. However, the important problems for non-noble metal based catalysts involve significant coke formation, sintering effect that is reasoned by high reaction temperature, and metal oxidation, all of which hinder their practical application in the industry (Fan *et al.,* 2010). Catalysts containing noble metals such as Pt, Ru and Rh show high activity and selectivity in CDRM reaction in addition to good stability against coke deposition. However, their high cost and low availability make them not economically competitive with other transition metal based materials. Among non-precious transition metals, nickel and cobalt supported on various oxide systems show promising performances (Luisetto *et al*., 2012).

2.2.1. Ni-based Catalysts

It has been reported that performance of supported metallic catalysts for CDRM reaction depends on numerous factors, such as the nature of the metal(s), the support type, the parameters involved in each stage of preparation and pretreatment procedures, introduction of promoters into the catalyst formulation and modification by small amounts of noble metals (Fidalgo *et al*., 2010; Ozkara-Aydinoglu *et al.,* 2009; Sousa *et al.,* 2012).

The redox properties, wide availability, activity and selectivity of nickel catalysts make them desirable for the CDRM. Ni has mainly been preferred as a catalyst because it is more economical than precious metals such as Pt, Rh, and Ru, even though it is more sensitive to carbon deposition.

The deposited carbon can have different structural order, morphology and reactivity depending on both the reaction conditions and the structure of the catalyst. There are three types of carbon, namely, amorphous (polymeric), filamentous, and graphitic, can be formed on the surface of Ni-based catalysts. In the study by Xu *et al.* (2009), the carbon deposited on the surface of La_2O_3 modified Ni/Al_2O_3 during CDRM was analyzed. Results exhibited that the size of Ni particles have an effect on the formation and morphology of filamentous carbon. Metallic Ni particles less than 15 nm suppressed the formation and deposition of carbon filaments, decreased the amount of carbon deposition, and produced more active C_α species, resulting in a better activity and higher stability (Xu *et al.*, 2009).

Several studies focused on suppressing coke deposition have been performed. It is found that coke deposition decreases when Ni is impregnated on supports that present marked Lewis alkalinity/acidity and have improved thermal stability, such as ZrO_2 and La_2O_3. Kumar *et al.* (2007) studied CDRM over a variety of ZrO_2-, ceria-doped ZrO_2-, and CeO_2–ZrO_2-supported Ni catalysts. In their work, the objective was to evaluate how manipulating the size of the ensembles of the nickel on the surface can inhibit the coke formation during low-temperature CDRM and to show how the stability can be affected by preparation methods of both ZrO_2 and CeO_2–ZrO_2 supports. For low-temperature CDRM, the use of ceria–zirconia ($Ce_xZr_{1-x}O_2$) solid solution prepared by using a surfactant as a support led to the most stable performance compared to zirconia and ceria-doped zirconia. Temperature-programmed oxidation (TPO) experiments indicated excellent resistance toward carbon formation for Ni supported on $Ce_xZr_{1-x}O_2$ compared to other catalysts studied. Among the catalysts studied, 5% Ni $Ce_{0.6}Zr_{0.4}O_2$ was found to have the highest activity which was stable for up to 100 h at 650 and 700°C. At 800°C, the catalyst activity remained stable for more than 200 h (Kumar *et al.*, 2007).

The studies on CDRM over supported Ni catalysts have demonstrated that support may have remarkable role in the activity and carbon deposition resistance. The modified supports have been studied in order to improve the stability and the carbon resistance of nickel catalysts.

Soloviev *et al.* (2011) studied CDRM over Ni/Al_2O_3-based composites supported on cordierite monoliths. It was reported that these are highly efficient catalysts for CDRM, surpassing essentially the conventional granulated ones, owing to greater utilization of their active components. The effects of alkali and rare-earth metal oxides as modifying additives on the catalytic properties of these structured systems were investigated. By adjusting the surface acid-base properties of catalysts via introduction of alkali metal (Na, K) oxides, the surface carbonization was inhibited and as a result, the operational stability of these catalysts was enhanced. On $Ni\text{-}La_2O_3/Al_2O_3$/cordierite catalyst, an additional route for the CO_2 activation is displayed which increases methane conversion under excess oxidant (Soloviev *et al.*, 2011).

The interest on the use of activated carbon based supports has grown in recent years owing to their low cost, high mechanical strength, high surface area, the possibility of adjusting the pore size distribution, and well reductive properties (Fidalgo *et al.*, 2010). Recently, Fidalgo *et al.* (2010) prepared a series of carbon-based nickel (Ni) catalysts in their work. Their objective was to examine the influence of the drying method, the temperature of the reduction stage on the Ni particle size and the surface chemistry of the activated carbons used as support. In order to investigate the role of the surface chemistry, the active carbon was tested as received and in its oxidized forms. Although a better Ni dispersion was acquired over the oxidized support, lower conversions were obtained. Results indicate that oxidation of the carbon support allows enhanced interaction between Ni particles and carbon surface, and therefore increases Ni dispersion. It was also observed that the microwave drying offers various advantages over conventional drying; the operating time is greatly reduced, smaller Ni particle sizes are obtained and the influence of the surface chemistry on the Ni particle size is minimized (Fidalgo *et al.*, 2010).

In the study conducted by Yang *et al.*, a series of supported $Ni/\gamma\text{-}Al_2O_3$ catalysts and La_2O_3–CeO_2 binary promoted Ni-based catalysts were synthesized via impregnation method. The carbon deposition and stability of catalysts were particularly, investigated. The results showed that the activity of the 10 wt.% $Ni/\gamma\text{-}Al_2O_3$ catalyst was higher than those of catalysts having other Ni loadings. However, the Ni/γ-Al_2O_3 catalyst was not found stable because large amount of carbon was deposited on its surface. Although the activity of Ni/γ-Al_2O_3 catalyst was not obviously increased with the La_2O_3 promotion, carbon deposition on 10%Ni/3%La_2O_3–γ-Al_2O_3 catalyst decreased to one-third of that on 10%Ni/γ-Al_2O_3 catalyst under the same reaction conditions because of the alkaline functionality and the enhanced Ni dispersion led by La_2O_3. In addition, the activity was improved slightly on Ni/γ-Al_2O_3 with the La_2O_3–CeO_2 binary promoters. Due to both suppression of the sintering of Ni particles and the formation of the reactive filamentous carbon on the Ni-based catalyst that promoted by La_2O_3 and CeO_2, 10%Ni/3%CeO_2–3%La_2O_3–γ-Al_2O_3 catalyst presented stable activity (Yang *et al.,* 2010).

It has been found that certain supports are able to suppress carbon deposition by providing oxygen to the metal during the reaction. Thus, oxides with high oxygen exchange capacity and mobility are seemed to be good candidates as supports for the CDRM reaction (Ozkara-Aydinoglu *et al.,* 2009).

Barroso-Quiroga *et al*., (2010) worked on Ni-based CDRM catalysts supported on different ceramic oxides (Al_2O_3, CeO_2, La_2O_3, ZrO_2) prepared by wet impregnation. The effect of the addition of lithium and potassium oxides as activity modifiers on the Ni/CeO_2 catalyst was also studied. High and stable catalytic activity was obtained on Ni/ZrO_2 catalyst; it displayed no deactivation during the reaction period. The catalyst supported on CeO_2 has a relatively good activity, but exhibits signs of deactivation after a certain time during the reaction. Its performance was studied after the addition of 0.5 wt% Li and K as activity modifiers. The introduction of the alkaline metals results a reduction of the catalytic activity but a better stability (Barroso-Quiroga *et al.,* 2010).

The modification of Ni-based catalysts by a very little amount of noble metal can be a way of obtaining both high activity and low carbon formation over an inexpensive supported bimetallic system. One important aspect of modifying the Ni-based bimetallic catalyst is the range of nickel loading. Ozkara-Aydinoglu *et al.* (2011) prepared a set of δ-Al_2O_3 supported Pt–Ni bimetallic catalysts, having Ni/Pt molar ratio between 110 and 250, and tested in carbon dioxide reforming of methane with the aim of determining an effective catalyst with optimum Ni/Pt metal ratio assuring high activity and stability. It was found that the catalytic performance of bimetallic Pt–Ni samples strongly depended on the metal loadings and Ni/Pt loading ratio. Among all the catalysts, 0.3%Pt–10%Ni/Al_2O_3, which has the lowest Ni/Pt ratio, showed the highest catalytic activity and stability. This sample led to a relatively easy reduction of nickel oxide species and to smaller nano-sized nickel particles providing a better dispersion, both of which result from the intimate interaction between Pt and Ni sites (Ozkara-Aydınoglu *et al.*, 2011).

Promoters such as ceria or other rare earth metal oxides can enhance the performance of Ni- based catalysts since they provide a higher oxygen storage capacity and therefore the inhibition of carbon formation can be achieved. In the study, which was performed by Al-Fatesh *et al.* (2011), the catalytic performance of the Ca, Zr, and Ce-promoted 3%Ni/γ-Al_2O_3 was investigated. The influence of Ca, Ce and Zr promoters on catalyst stability and coke deposition were studied. It was found that 3%Ni/γ-Al_2O_3 promoted with 0.15% Ce and 0.05% Ca exhibited the best performance with low coke formation. Their work showed that the presence of small quantities of Ca in the Ni/γ-Al_2O_3 catalyst improved catalyst activity and stability; however, the methane decomposition reaction is favored at a higher Ca content. Ce was found to be the best promoter yielding stable performance for the 3%Ni/γ-Al_2O_3 catalyst. The addition of Ca and Ce oxides to the catalyst enhanced its Lewis basicity contributing to an advanced absorption of CO_2 that give higher stability and lower carbon deposition (Al-Fatesh *et al.*, 2011).

Among the reported promoters, CeO_2 has been stated as an effective promoter for Ni catalysts. In the study by N. Laosiripojana *et al.* (2005), doping of CeO_2 as a promoter on Ni/Al_2O_3 was investigated. It was found that the catalyst provides higher reforming reactivity and resistance toward deactivation from carbon deposition compared to conventional Ni/Al_2O_3. CeO_2 doped Ni/Al_2O_3 with 8% ceria content gave the best reforming activity among those with the ceria content between 0 and 14%. Increasing Ce content showed decreased amount of carbon formation; however it was also noted that when more than 10% of ceria was doped, oxidation of Ni occurs which could reduce the reforming reactivity (Laosiripojana *et al.*, 2005).

It has also been reported that the addition of cobalt to nickel catalysts may sometimes led to superior activity, selectivity and deactivation resistance compared to those of the monometallic ones. In their work, Luisetto *et al*. (2012) investigated bimetallic the CDRM performance of Co–Ni/CeO_2 catalyst and compared with those of monometallic Ni/CeO_2 and Co/CeO_2 systems in order to understand the effect of the supported metal on the catalytic activity and carbon deposition. Co/CeO_2 (Co 7.5 wt.%), Ni/CeO_2 (Ni 7.5 wt.%) and Co–Ni/CeO_2 (Co 3.75 wt.%, Ni 3.75 wt.%) catalysts were prepared by surfactant assisted co-precipitation method. The bimetallic Co–Ni/CeO_2 catalyst exhibited higher CH_4 conversion compared to monometallic systems in the whole temperature range, being 50% at 600 $^{\circ}$C and 97% at 800 $^{\circ}$C. H_2/CO selectivity decreased in the following order: Co-Ni/CeO_2 > Ni/CeO_2 > Co/CeO_2. Due to the combination of the high activity of nickel with the high resistance of cobalt against carbon deposition, bimetallic Co–Ni/CeO_2 seems to be a very promising system, having high activity, selectivity and stability in syngas production by CDRM (Luisetto *et al.*, 2012).

In the preparation of most of the heterogeneous catalysts, the calcination step is required for decomposition of the metal precursor whereas the reduction step is needed to achieve the catalytically active metal, and these treatments affects the final properties of the catalysts.

The effect of treatments on the properties and CDRM performance of Ni/Al_2O_3 catalysts has been studied by Juan-Juan *et al.* (2009). The performed pretreatment methodologies are: i-calcination followed by hydrogen reduction, ii-direct hydrogen reduction, iii- heat treatment up to the reaction temperature under inert atmosphere. According to the results, pronounced influence the pretreatment carried out on the amount of deposited coke has been observed In addition, it was found that the pretreatments affect significantly the size and the structure of nickel particles. The experimental findings, in general terms showed that the higher the mean particle size the higher the amount of deposited carbon. The catalyst reduced at 973 K, without calcination, led an active catalyst with the lowest carbon deposition (Juan-Juan *et al.*, 2009).

2.2.2. Co-based Catalysts

Compared with nickel, cobalt is another material of interest for the researchers, as it generally presents better behavior towards the suppression of carbon deposition and thus better stability under reaction conditions (Luisetto *et al*., 2012).

Ruckenstein *et al.* (2000) worked on the CDRM over Co supported on an alkaline earth metal oxide (MgO, CaO, SrO, or BaO) as well as on γ-Al_2O_3 and on SiO_2. It was searched out that MgO provided the high and stable activity with 93% CO and 90% H_2 yield at high space velocity with the stability up to 50 h time-on-stream. Among the supports, γ-Al_2O_3 showed initially a high CO yield, which then rapidly decayed. All the other supports gave low CO yields, and CaO and SiO_2 also showed low stabilities. As the oxygen atoms are shared by both Mg and Co and their interactions with Mg are strong, the solid solution of CoO and MgO, which was identified by XRD, becomes less reducible than the pure CoO. Small clusters of metallic Co are obtained, which are more stable to sintering than the usual ones; the small Co cluster size does not favor coke formation as being small. It was mentioned that the suppression of carbon deposition and the resistance to sintering of Co/MgO catalyst are induced by the fact that CoO and MgO form the solid solution. For these reasons, the catalyst exhibits high and stable activity for the CO_2-reforming of CH_4 (Ruckenstein *et al.*, 2000).

The influence of support on the performance of different Co-containing metal oxide catalysts (e.g. CoO–MgO, CoO–CeO_2 or ZrO_2, etc.) in the CO_2 reforming was investigated by Mondal *et al.* (2007). Catalytically inactive CoO_x–MgO presents high reforming activity and selectivity in CDRM when it is deposited on a commercial low surface-area macro-porous silica–alumina support (SA-5205) or when CoO_x is deposited on the support precoated with MgO. In order to obtain better catalytic performance, the choice of the metal oxide used for precoating is in the following order: MgO > Z-ZrO_2 > CeO_2 > Y_2O_3 > ThO_2. It is observed that when the support or the accompanied metal oxide is absent, the CoO_x catalyst presents very poor activity with higher coking rate in the CDRM. The CoO_x–MgO/SA-5205 and CoO_x/MgO/SA-5205 are found as highly active and selective catalysts, having negligibly small coking rate. The CoO_x/ZrO_2(or CeO_2)/SA-5205, is considered as a next promising CDRM catalyst choice (Mondal *et al.*, 2007).

In Omata *et.al* (2004) study, Co catalysts in combination with oxides or carbonates of basic metal, such as Sr, Ca, Ce and La, were prepared and compared by their CDRM activity in reaction tests conducted at 1 MPa pressure. As a result, cobalt catalyst supported on strontium carbonate ($Co/SrCO_3$) catalyst was found to show a steady activity, and small amount of carbon deposition was observed in contrast to that observed on Co/MgO. It is indicated that cobalt supported on strontium carbonate by impregnation method has high tolerance to oxidative atmosphere under reaction conditions compared to that of cobalt in Co–MgO catalyst (Omata *et.al*, 2004).

In the case of Co catalysts, another research is carried out by Ozkara-Aydınoglu *et al.* (2010) with the purpose of investigating and developing stable and effective Co-based DR catalysts supported on zirconia. In order to improve the performance of the Co-based catalysts and increase their resistance to coking, the effect of addition of metal additives, namely lanthanum, cerium, manganese, potassium and magnesium, was studied. Scanning electron microscopy studies and different activity levels of the catalysts indicate that the metal dispersion properties and catalytic performances of Co/ZrO_2 catalysts are mainly affected by the characteristics of the promoter. Results showed that monometallic Co/ZrO_2 had high initial activity, but severe carbon deposition formed during CDRM was the significant problem. La-modified catalyst, on the other hand, displayed high stability without severe coke deposition, but they have moderate activity. Ce-doped Co/ZrO_2 exhibited the highest activity among all the catalysts prepared and had a very limited activity loss in time-on-stream tests (Ozkara-Aydınoglu *et al*., 2010).

Nagaoka *et al.* (2004) evaluated the influences of an addition of trace amounts of Pt (Pt/Co= 0.005–0.05 in atomic ratio) or Ru (Ru/Co= 0.01–0.05) on Co/TiO_2 and of replacement of cobalt by nickel (Ni:Co= 1:99–100:0) for CDRM conducted at 2 MPa. It is found that the addition of noble metals (Pt or Ru) to Co/TiO_2 improved the catalytic stability and reducibility of cobalt oxide. The replacement of Co by small amounts of Ni in Co/TiO_2 also enhanced the catalytic stability by inhibiting the oxidation of metallic Co, but replacement by an excess amount of Ni caused in a decrease of stability due to serious coke deposition. $CoNi/TiO_2$ with an optimum Co:Ni ratio of 10:90 showed high stability without a significant amount of coke deposition under a reaction condition where highly favorable coke deposition present (Nagaoka *et al.*, 2004).

In the content of bimetallic catalysts, alumina supported Ni, Co and bimetallic Ni–Co catalysts (with 9 wt.% metal content) have been prepared, characterized and tested for the CDRM by Jose-Alonso *et al.,* (2009). They mentioned that among the studied catalysts, those with the highest cobalt content, Co (9) and NiCo (1–8) catalysts, are the most active and stable ones for methane dry reforming, but they suffered from large amount of carbon deposition. It is indicated that cobalt rich catalysts displayed higher activity, which is related with high activity of this metal for methane decomposition, and they have remarkable stability because of the production of non-deactivating carbon deposits (Jose-Alonso *et al.,* 2009).

2.2.3. Noble Metal Catalysts

Carbon dioxide reforming of methane has been extensively studied using noble metal catalysts as they show good activity and their high resistance to the deactivation by carbon deposition (Hou *et al.*, 2006; Ballarini *et al.*, 2012; Miguel *et al.*, 2012).

Research efforts have been primarily concentrated on the additive effects of noble metals on the catalytic performance. In order to develop a catalyst that has high resistance toward carbon deposition and high catalytic activity, small amounts of noble metals (Pt, Pd, Rh, Ru,etc.) are added to Ni-catalyst in the study conducted by Dalin Li *et al.* (2011). It is observed that both Pt and Pd modification promote the Ni reduction while Pt provides resistance to coke deposition and Pd suppress the hot spot formation of Ni catalyst. High reforming activity and high resistance to hot spot formation was obtained by small amount of Rh addition. The effect of Ru modification is proposed to be similar to that of Rh. Other noble metals, such as Ir and Au, were also effective in promoting the catalyst reducibility; however, the effect is not so remarkable as those of Pt, Pd, Rh, and Ru (Dalin Li *et al.,* 2011).

Methane reforming reaction has also been investigated over supported catalysts involving Group VIII metals (e.g. Ni, Co, Ru, Rh, Pd, Pt) in various academic research. The work of Ghelamallah *et al.* (2012), in which monometallic platinum and rhodium based catalysts supported on α-Al_2O_3 doped with La_2O_3 and BaO, is one of them. It is indicated that Pt and Rh incorporation leads to different types of interactions with La and

Ba-modified α-Al_2O_3. Pt would preferentially interact with Ba leading loss of activity through a significant increase in the apparent activation energy. On the other hand, the preferential interaction of Rh with lanthanum oxide after Ba incorporation led no remarkable change in catalyst activity (Ghelamallah *et al.*, 2012).

In CDRM, a series of noble metal (Ru, Rh, Pt and Ir) catalysts supported on alumina-stabilized magnesia (Spinel) showed excellent coke resistance that directly enhances CDRM activity and stability. The results showed a high degree of activity and stability for Ru, Rh and Pt catalysts. The TPO analysis showed that Ru and Rh catalysts have the higher activity and stability due to the formation of highly reactive surface carbon (C_α) compared to the other catalysts. It is also mentioned that due to both formation of less reactive surface carbon and sintering of the catalyst during reaction, Pd catalyst displayed lower activity and stability (Rezaei *et al.*, 2006).

It is expected that bimetallic catalysts involving Pt display more stable performance at longer reaction times compared to those of monometallic ones (Miguel *et al.*, 2012; García-Diéguez *et al*., 2012). Bimetallic Ni(10%)Pt(0.5%)/Al_2O_3 showed a higher and stable catalytic activity compared with the Ni(10%)/Al_2O_3 catalyst during 6500 min reaction time and has lower amount of carbon deposited. Characterization techniques reveal that the presence of platinum makes the reduction of NiO species easier in the bimetallic catalyst since nickel and platinum are in close contact during the simultaneous reduction of the two oxide precursors (Miguel *et al.*, 2012).

Ozkara-Aydinoglu *et al.* (2009) studied CDRM over Ce promoted Pt/ZrO_2 catalysts for different temperatures and feed compositions. The principal aim of this study was to obtain an effective Pt-based DR catalyst supported on zirconia. In their work, impregnation strategy, cerium amount, reaction temperature and CH_4/CO_2 feed ratio were chosen as experimental parameters. The results show that introduction of 1 wt.% Ce to the Pt/ZrO_2 catalyst by co-impregnation method led to the highest catalytic activity and stability. 1 wt.%Ce–1 wt.%Pt/ZrO_2 catalyst prepared by sequential impregnation displayed inferior CH_4 and CO_2 conversion performances with lowest H_2/CO production ratios. 1 wt.%Ce–1 wt.%Pt/ZrO_2 catalyst prepared by co-impregnation showed the highest activity even for the feed with high CH_4/CO_2 ratio. It was also mentioned that under normal reaction conditions, increasing the loading of Ce from 1 wt.% to 5 wt.% caused a decrease in the catalytic activity of catalysts at high reaction temperatures (Ozkara-Aydinoglu *et al.,* 2009).

The combination of the endothermic dry reforming (DR) and exothermic catalytic partial oxidation (CPO), mixed reforming has been gaining more interest as a promising energy effective route. In their work, Ballarini *et al.* studied combined dry reforming and partial oxidation of methane to produce synthesis gas over Pt supported on alkaline and alkaline-earth metal-doped γ-Al_2O_3. Considering cost impact of the noble metal, Na-, K- and Mg-doped Al_2O_3 samples containing different Pt loadings (0.1 and 0.5wt%) were studied aiming to develop catalysts with high Pt dispersion, thermal stability and coke resistance. It is observed that the better catalytic performances are obtained when the higher Pt loading was applied. In DR tests, the Mg-doped catalyst also performed better when the Pt loading is 0.1wt%. For higher Pt loadings, the K-doped catalyst shows a higher conversion and selectivity (Ballarini *et al.*, 2012).

Nematollahi *et al.* (2011) has also studied CO_2 reforming combined with partial oxidation of methane to syngas over noble metal catalysts (Rh, Ru, Pt, Pd, Ir) supported on alumina-stabilized magnesia. The BET measurements revealed that for the Ru, Rh, and Pd catalysts have higher specific surface area compared to those of Ir and Pt catalysts. It is observed that all the catalysts displayed a high stability during the three reactions (DR, POM and CR) yielding methane conversion. The results showed the degree of activities for the catalysts are in the following order : Rh > Ru > Ir > Pt > Pd (Nematollahi *et al.,* 2011).

2.3. Deactivation of Catalytic Processes

Catalyst deactivation, the loss of catalytic activity and/or selectivity over time, is an important issue due to its effects on the performance of a given type of reactor or on the economics of a certain process in the chemical industries. Catalyst deactivation can be caused by (i) a decrease of the number of active sites; (ii) a reduction of the quality of the active sites; and (iii) a degradation in accessibility of the pore space (Moulijn *et al.*, 2001). Deactivation of the catalysts can occur by three major mechanisms defined as fouling in terms of deposits of coke, poisoning and thermal degradation (sintering). In Fig. 2.1, the deactivation mechanisms of catalysts are illustrated (Sie, 2001).

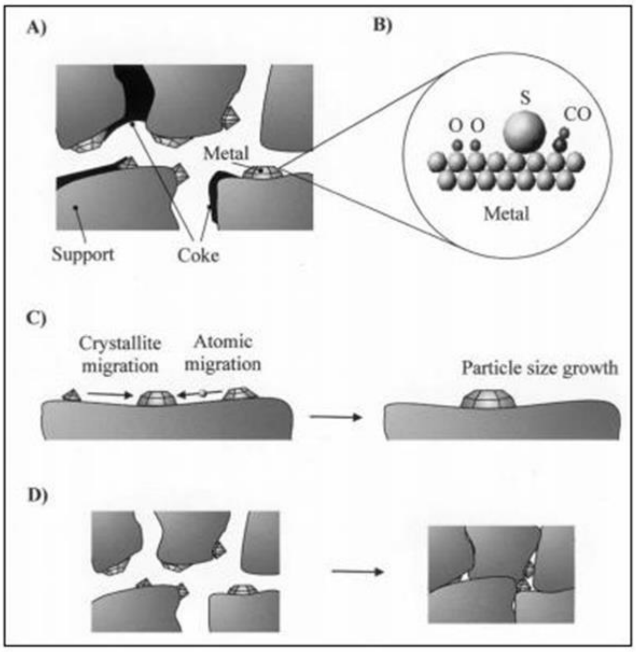


Figure 2.1. Deactivation mechanisms: A) Coke formation, B) Poisoning, C) Sintering of the active metal particles, and D) Sintering and solid-solid phase transitions of the washcoat and encapsulation of active metal particles (Sie, 2011).

Fouling is the physical blockage of surface and/or pores usually by carbon, formed as a side product during reaction, which results in activity loss. Carbon may i) block access of reactants to metal surface sites, ii) completely enclose a metal particle and deactivate that particle, iii) plug micro- and mesopores such that access of reactants is rejected to many crystallites inside these pores (Bartholomew *et al.*, 2001). Poisoning is the loss of activity due to the strong chemisorption of reactants, products or impurities present in the feed stream. A poison can act as a geometric effect via blocking an active site or as an electronic effect via changing the adsorption properties of the active surface (Forzatti *et al.*, 1999). Sintering, on the other hand, is thermally induced loss of catalytic surface area due to crystallite growth of either the bulk material, ie. support, or the active phase (Moulijn *et al.*, 2001).

Catalyst deactivation is caused by mainly sintering and fouling by carbon during CDRM. A number of studies indicate that the coke may deposit itself on the nickel catalyst in various forms, including i) C_α,adsorbed atomic carbon (dispersed, surface carbide), ii) C_β,polymeric films and filaments (amorphous), iii) C_v,polymeric films and filaments (amorphous), iv) C_γ,nickel carbide (bulk), v) C_c,graphitic platelets and films (crystalline). It has been reported that under CDRM conditions C_v and C_c may be the forms of coke formed on the catalyst surface. The C_v or whisker carbons are graphitic and in general has the same diameter as the metal crystal. Due to the presence of a dissolved carbon concentration gradient in the crystal, whiskers are formed in tubular shape. On the other hand, the C_c graphitic films diffuse across the Ni particle surface and thereby ordered graphite layers parallel to the metal-carbon interface are developed (Ginsburg *et al.*, 2005; Forzatti *et al.*, 1999).

Coke is typically a product of two reactions, methane decomposition [Eq. (2.7)] and carbon monoxide disproportionation [Eq. (2.6)]. The former is an endothermic reaction and favored at higher temperatures and lower pressures whereas the latter is exothermic and favored at lower temperatures and higher pressures (Corthals *et al.*, 2008). The reactions are reversible and it is possible to minimize coke formation by adjusting operating conditions. Catalyst structure, including metal type, metal crystallite size, promoter, and catalyst support are primary parameters that determine the rate of a carbon or coke accumulation under given reaction conditions. A dynamic balance between carbon formation and its oxidation guaranteeing high and stable CDRM activity can be obtained via optimization of reaction conditions, including temperature, CH_4/CO_2 ratio, catalyst type and structure (Bartholomew *et al.*, 2001).

Sintering, as illustrated in Figures 2.1 c and 2.1 d, relates to the loss of active surface via structural modification of the catalyst. The underlying mechanism of sintering of small metal particles is the surface diffusion, or at higher temperatures, the mobility of larger agglomerates. Promoters or impurities have an impact on sintering and redispersion by either increasing (e.g. chlorine and sulfur) or decreasing (e.g. oxygen, calcium and cesium) metal atom mobility on the support. Sintering is strongly temperature dependent and its rates increases with increasing temperature. Water vapor also increases the sintering rate. As a result, in the case of dry reforming conditions, the high temperature window and the formation of water by the reverse water gas shift reaction, expressed in Equation (2.2), make the catalysts sensitive to metal sintering (Bartholomew *et al.*, 2001; Forzatti *et al.*, 1999).

3. EXPERIMENTAL WORK

3.1. Materials

3.1.1. Chemicals

The chemicals used in catalyst preparation are presented in Table 3.1.

Table 3.1. Chemicals used in catalyst preparation (all specifications: research grade).

Chemicals	Formula	Source	Molecular Weight (g/mol)
Cerium(III) nitrate hexahydrate	$Ce(NO_3)_3.6H_2O$	Merck	434.23
Nickel (II) nitrate hexahydrate	$Ni(NO_3)_2.6H_2O$	Merck	290.81
Lanthanum nitrate hexahydrate	$La(NO_3)_3.6H_2O$	Merck	433.02
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

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

Table 3.2. Specifications and applications of the liquids used.

Liquid	Specification	Application
Water	Distilled	Aqueous solution

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

Gas/Standard	Specification	Application
Methane	99.5 % BOS	Reactant, GC Calibration
Carbon dioxide	99.995 % BOS	Reactant, GC Calibration
Carbon monoxide	99.999 % BOS	GC Calibration
Hydrogen	99.99 % BOS	Reduction, GC Calibration
Argon	99.998 % BOS	GC Carrier Gas
Dry air	99.998 % Linde	Calcination, GC 6-way pneumatic valve
Nitrogen	99.99 % Linde	Inert, GC Calibration

3.2. Experimental Systems

The experimental systems used can be described in four main groups.

- Catalyst Preparation Systems: This group of experimental systems included the set-up for preparing catalysts by incipient-to-wetness impregnation technique.

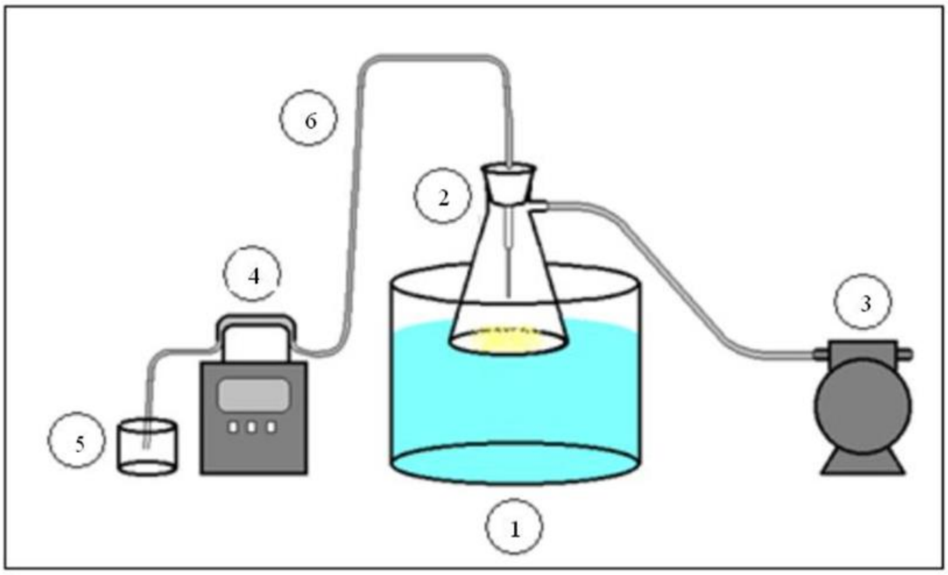
- Catalyst Characterization Systems: Different analytical and spectroscopic systems which were used to characterize the physical, microstructural and electronic properties of the catalyst samples prepared and to analyse any carbonaceous deposits formed on the spent samples are included in this group of systems.

- Catalytic Reaction System: This is a continuous flow microreactor system, involving mass flow controllers, a temperature controlled oven, and a reaction chamber, feed and product sampling sections, that was used for determining the catalytic activity, selectivity and stability.

- Product Analysis System: A gas chromatograph connected on-line to the microreactor flow system is used for the quantitative determination of the composition of the species both in the reactor effluent and feed stream.

3.2.1. Catalyst Preparation Systems

The system used for preparing catalysts by incipient-to-wetness impregnation technique (Figure 3.1) included a Retsch UR1 ultrasonic mixer, a vacuum pump, a Buchner flask and a MasterFlex computerized-drive peristaltic pump.



1.Ultrasonic mixer, 2.Buchner flask, 3.Vacuum pump, 4.Peristaltic pump, 5.Reactant storage tank, 6.Silicone tubing

Figure 3.1. Schematic diagram of the impregnation system.

3.2.2. Catalyst Characterization Systems

3.2.2.1. Scanning Electron Microscopy (SEM). Micrograph of the freshly reduced and used samples (Co-Ni-La/ZrO2 and Co-Ni-Ce/ZrO2 catalyst samples) after reaction were characterized by SEM and SEM-EDX (Energy Dispersive X-Ray) to analyse their microstructure and metal dispersion, and to observe morphology of the deposited carbon that formed on the surface during CDRM performance tests. The tests were conducted in a Philips XL 30 ESEM-FEG system, having a maximum resolution of 2 nm. The experiments were performed at the Advanced Technologies Research and Development Center of Boğaziçi University.

3.2.3. Catalytic Reaction System

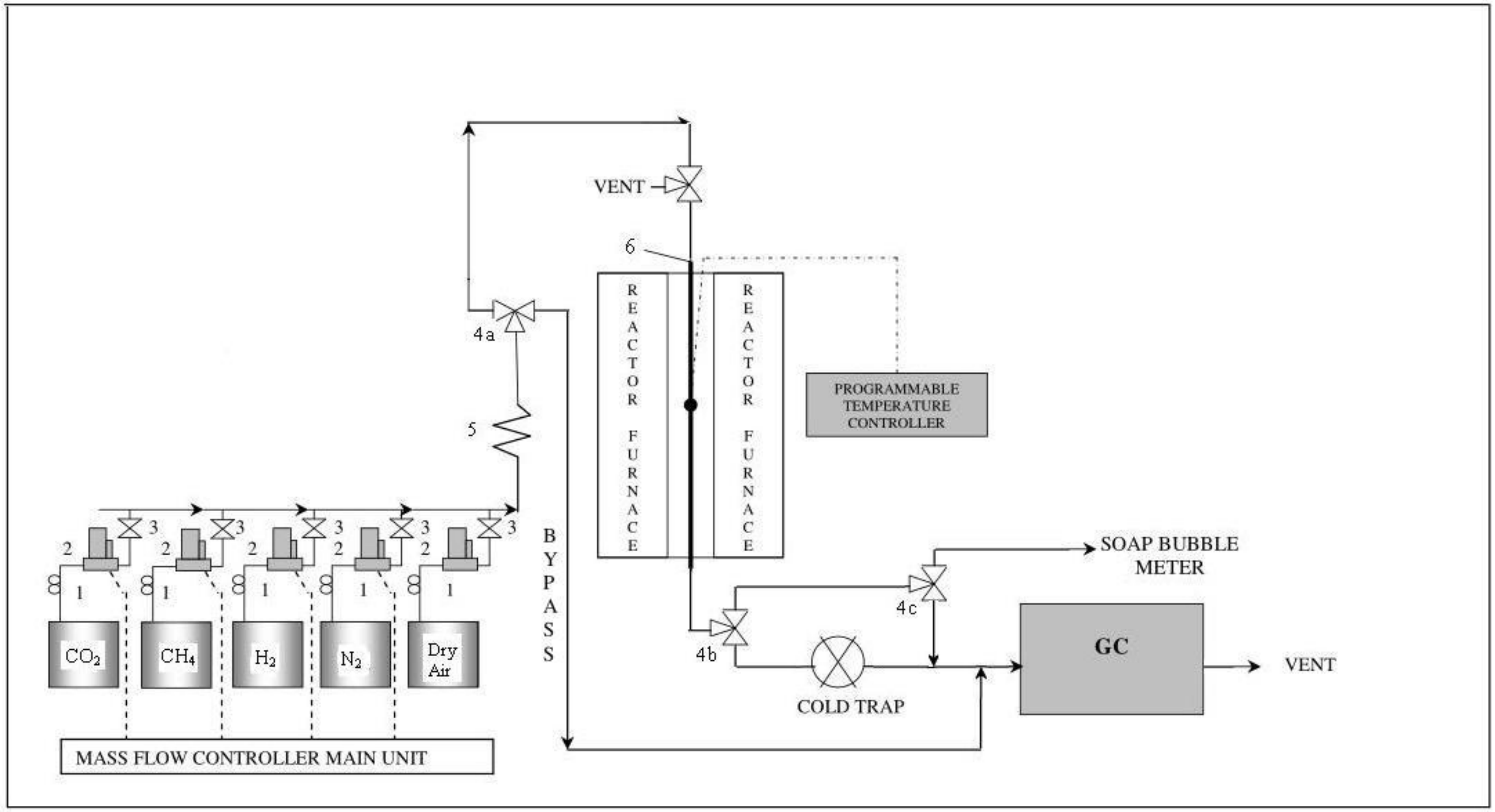
The catalytic reaction system which was designed and constructed in the Catalysis and Reaction Engineering Laboratory of Chemical Engineering Department, Boğaziçi University, involves three characteristic sections:

- Feed section
- Reaction section
- Product analysis section

The feed section includes mass flow control systems, 1/4", 1/8" and 1/16" stainless steel tubes and fittings for feeding gaseous species, i.e. methane, carbon dioxide, nitrogen, hidrogen and dry air at desired quantities accurately. The gases that were supplied by pressurized tubes were passed through the gas flow regulators (items 1 in Figure 3.2) and the flow rates of the gases were regulated by calibrated Brooks Instrument mass flow controllers. The flow rate values were adjusted by the Brooks Instrument 0254 series control box for all gases. To avoid from possible back-pressure fluctuations, on-off valves (items 3 in Figure 3.2) were placed in front of the mass flow controllers. It was possible to meter the flow of individual species and adjust desired feed ratios since each gas was fed from its independent line. The gases were then introduced to a primary mixing zone (zone 5 in Figure 3.2) in order to obtain the flow of homogenous reactant gas mixture directed the reactor. The system configuration allows to divert the feed gases to a bypass line before entering the reactor by using a three way valve (item 4a in Figure 3.2) which provides an opportunity for determination of the feed composition using gas chromatograph whenever necessary.

The mixed reactants in the feed section were allowed to pass through the reaction section. This is the section that was consisted of a 45 cm × 20 cm × 20 cm furnace controlled by a Shimaden FP23 programmable temperature controller with ±0.1 K precision connected to a K type sheathed thermocouple, which involves a 12 mm ID, 75 cm long quartz down-flow microreactor. To connect the quartz reactor to the system from both ends of the ractor, stainless steel fittings that were welded to 1/4" stainless steel tubes were designed and constructed. Identical fittings with 12 mm inner diameter, 24 mm outer diameter and 50 mm height prevented any gas leak. Quartz wool, which was placed on the center of the quartz microreactor, was used to hold the catalyst bed in a fixed position. In order to prevent heat loss, ceramic glass wool insulations were placed on top and bottom ends of the reactor furnace.

The steam existing in the product stream during reaction was removed by placing two ice cold traps before GC inlet to avoid any condensation.



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

Figure 3.2. Schematic diagram of the microreactor flow system.

3.2.4. Product Analysis System

Agilent Technologies 6850 gas chromatograph (GC) equipped with a Thermal Conductivity Detector (TCD) and a HayeSep D column was used to detect feed and product stream. Analysis conditions are given in Table 3.4 below.

Table 3.4. Reactant and product gas analysis conditions.

GC Parameter	Agilent Technologies 6850
Detector type	TCD
Column temperature,K	313
Injector temperature,K	373
Detector temperature,K	423
Carrier Gas	Argon
Carrier Gas flow rate, mL/min	25
Column packing material	Hayesep D
Column tubing material	Stainless steel
Column length & ID	3m x 3 mm
Sample loop	1 ml

Before performing the experiments, the gas chromatograph was calibrated by injecting known concentration of the gases to be analyzed under the conditions given in Table 3.4. This procedure enables the construction of “volume versus peak area” curves for each gas and the corresponding calibration factors were determined by linear regression.

3.3. Catalyst Preparation and Pretreatment

In this study, three sets of catalysts were prepared:

- Co-La/ZrO_2 bimetallic catalyst
- Co-Ni-La/ZrO_2 catalysts with different Co:Ni loading ratio
- Co-Ni-Ce/ZrO_2 catalysts with different Co:Ni loading ratio

The list of the catalysts are presented in Table 3.5.

Table 3.5. List of catalysts studied.

Denotation	Co wt%	Ni wt%	La wt%	Ce wt%	Preparation procedure
5Co2La	5	-	2	-	sequential impregnation
5Co5Ni2La	5	5	2	-	co-impregnation
5Co3Ni2La	5	3	2	-	co-impregnation
5Co5Ni2Ce	5	5	-	2	co-impregnation
5Co3Ni2Ce	5	3	-	2	co-impregnation

3.3.1. Support Preparation

High temperature levels are required to perform CDRM tests due to endothermic nature of the reaction. Therefore, the catalyst support should provide high thermal stabilities beside its high surface area, and should possess mechanical strength as well. For this matter, zirconia was used as the support. The support was first meshed to 45-60 mesh size and then calcined at 1073 K for 4 h in muffle furnace prior to addition of the metals.

3.3.2. Preparation of Catalysts

The experimental set-up, which was shown schematically in Figure 3.1, was used used in catalyst preparation by the incipient-to-wetness impregnation, consists of three parts:

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

For all catalysts, five grams of support was placed in the Buchner erlen and kept under vacuum both before and during the addition of precursor solutions. Vacuum pump was used to give a uniform distribution of the active component and to remove the trapped air. Before impregnating the solution, the support material was mixed with ultrasonic mixer under vacuum for 30 min.

For incipient wetness impregnation, a Masterflex computerized-drive peristaltic pump was used to feed the precursor solution (ca. 0.6 mL/g support) to the vacuum flask at a rate of 5 mL/min via silicone tubing. In order to maintain uniform distribution of the precursor solutions, the slurry was mixed by an ultrasound mixer during the impregnation. After the precursor solution was added, the slurry was ultrasonically mixed for additional 90 min. The thick slurry obtained was dried at 388 K overnight at each impregnation step.

3.3.2.1. Co-La/ZrO2 Catalyst. Bimetallic Co-La catalyst was prepared by sequential impregnation of aqueous lanthanum nitrate solution was followed by heat treatment at 773 K for 4h in muffle furnace and then by impregnation of aqueous cobalt nitrate solution. Each impregnation step was performed under vacuum. After the impregnation step, the sample was dried overnight at 388 K.

3.3.2.2. Co-Ni-La/ZrO2 Catalysts. Threemetallic Co-Ni-La catalyst was prepared by co-impregnation, in which impregnation of aqueous lanthanum nitrate solution was followed by impregnation of aqueous precursor solutions of Co (cobalt nitrate) and Ni (nickel nitrate) together onto La-ZrO_2 with defined concentrations in order to obtain desired loading ratios. In this thesis, catalysts that have a Co loading level of 5 wt. per cent, a La loading level of 2 wt. per cent and Ni loading levels of 3 and 5 wt. per cent were prepared. Each impregnation step was performed under vacuum. The resulting slurries were dried overnight at 388 K and finally calcined at 773 K for 4h.

3.3.2.3. Co-Ni-Ce/ZrO_2 Catalysts. In threemetallic Co-Ni-Ce catalyst preparation, co-impregnation method was used. In order to obtain fixed Co load of 5 wt. per cent, Ce load of 2 wt. per cent and Ni loads of 3 and 5 wt. per cent, impregnation of aqueous cerium(III) nitrate hexahydrate solution was followed by impregnation of aqueous cobalt(II) nitrate hexahydrate and nickel(II) nitrate hexahydrate solutions together onto Ce-ZrO_2 with defined concentrations. Each impregnation step was performed under vacuum. After the impregnation steps, resulting samples were dried overnight at 388 K and finally calcined at 773 K for 4h.

3.3.3. Pretreatment

The catalysts were calcined *in situ* in dry air (30 mL/min) for 4 h at 773 K and subsequently reduced *in situ* in H_2 (50 mL/min) for 2 h at the same temperature. Before calcination, the temperature was raised to 773 K under nitrogen flow (25 mL/min) with temperature increase of 10 K/min. In order to prevent the mixing of dry air and hydrogen, nitrogen flow was also introduced between calcination and reduction periods for 30 minutes. After reduction, the nitrogen flow was adjusted to 5 mL/min and the system was left overnight prior to the reaction tests.

3.4. Reaction Tests

3.4.1. Blank Tests

Blank tests were performed to ensure that the material of construction, quartz disc and the reactor did not interfere with the reaction test outputs. The results indicated that quartz disc and the reactor were inert under the conditions used in the reaction experiments.

3.4.2. Carbon dioxide reforming of methane over catalysts

The CDRM reaction has been studied over Co-La/ZrO_2, Co-Ni-La/ZrO_2 and Co-Ni-Ce/ZrO_2 catalysts to evaluate the effects of temperature, CH_4/CO_2 ratio, promoter loading ratio and space velocity. After changing the nitrogen flow from 5 mL/min to 25 mL/min, the temperature of furnace was ramped with rate of 10 K/min. Meanwhile, the GC operation procedure was followed. After both the GC and the system temperature were ready, the reactions were performed at the temperatures within the interval of 873-973 K with CH_4/CO_2 ratios of 1/1, 2/1 and space velocities of 20000 and 60000 mL/h g-catalyst. Data for every 30 minutes up to 6 hour were obtained. Then, data for feed analysis were obtained after waiting for 30 minutes for the feed gases to mix completely in the bypass line. Experiments performed in this study are shown at Table 3.6 in detail.

Table 3.6. Summary of the experimental conditions used in this study.

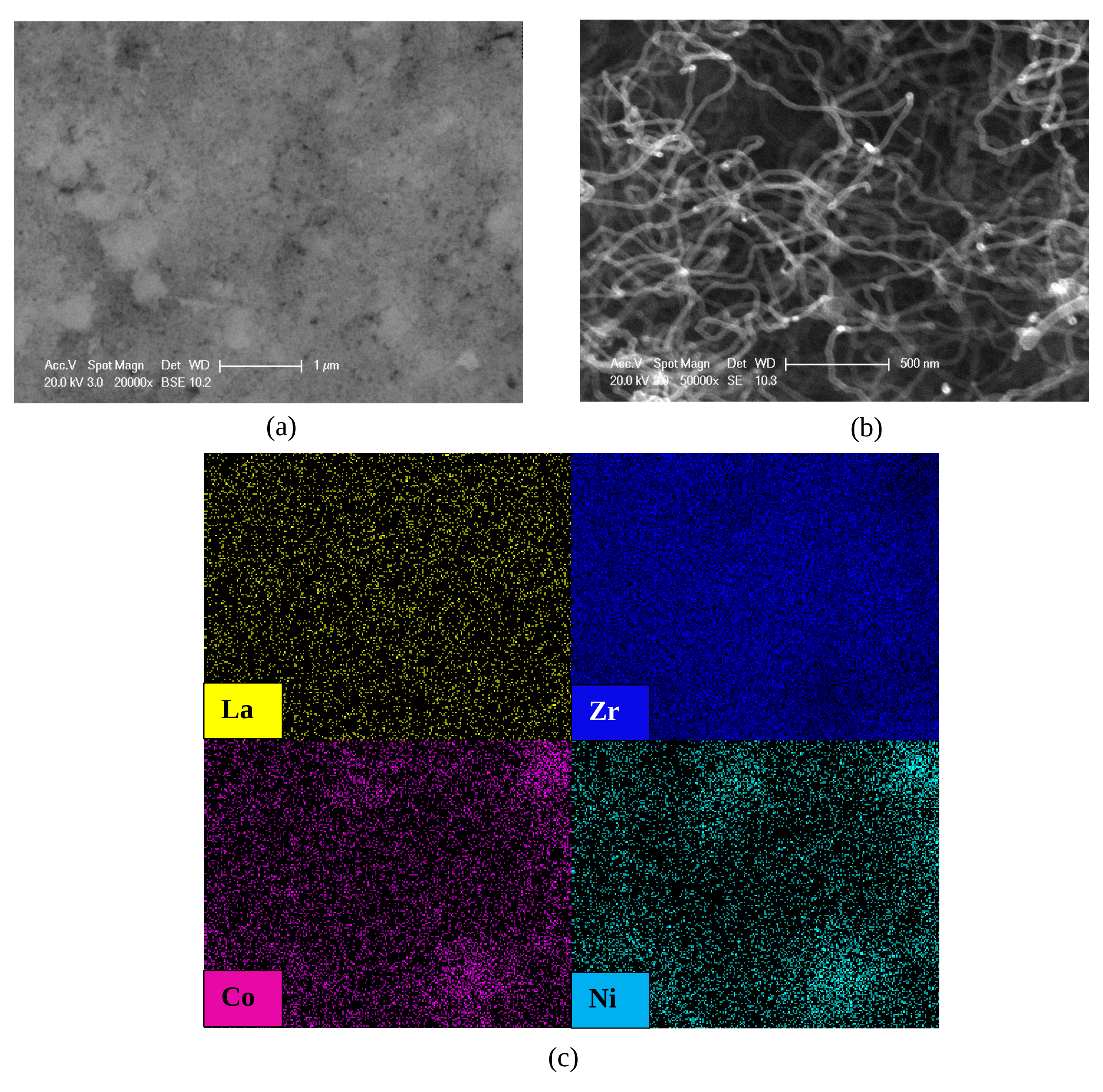
Experiment No	Catalyst	Space Velocity (mL/hg-catalyst)	CH_4/CO_2 Ratio	Temperature (K)
1	$5Co2La/ZrO_2$	60000	1/1	973
2	$5Co2La/ZrO_2$	60000	1/1	923
3	$5Co2La/ZrO_2$	60000	1/1	873
4	$5Co5Ni2La/ZrO_2$	60000	1/1	973
5	$5Co5Ni2La/ZrO_2$	60000	1/1	923
6	$5Co5Ni2La/ZrO_2$	60000	1/1	873
7	$5Co5Ni2Ce/ZrO_2$	60000	1/1	973
8	$5Co5Ni2Ce/ZrO_2$	60000	1/1	923
9	$5Co5Ni2Ce/ZrO_2$	60000	1/1	873
10	$5Co2La/ZrO_2$	60000	2/1	923
11	$5Co5Ni2La/ZrO_2$	60000	2/1	923
12	$5Co5Ni2Ce/ZrO_2$	60000	2/1	923
13	$5Co2La/ZrO_2$	20000	1/1	923
14	$5Co5Ni2La/ZrO_2$	20000	1/1	923
15	$5Co5Ni2Ce/ZrO_2$	20000	1/1	923
16	$5Co3Ni2La/ZrO_2$	60000	2/1	923
17	$5Co3Ni2Ce/ZrO_2$	60000	2/1	923

4. RESULTS AND DISCUSSION

The purpose of the current work is to design and develop a non-noble CDRM catalyst yielding high and stable activity with suitable H_2/CO product selectivity. In this context, one of the main intentions was to increase the resistance of catalysts to coking even when the noble metal is replaced by less costly, non-noble metals, like Co. In the current work, zirconia supported Co-based bimetallic and trimetallic catalysts were prepared. Aiming to enhance the performance of the catalysts, first lanthanum was added to investigate the effect of metal additive on the CDRM performance of the catalysts. As the improvement of the performance was limited after La addition, in order to increase the activity of La-modified catalyst further, Ni was also added to catalyst formulation, and three metallic Co-Ni-La system was prepared. It has been proved by our group that Ce plays a direct role in surface carbon removal formed during CDRM through regulating transfer of surface oxygen. Thus, as an alternative trimetallic system having improved coke deposition resistance, Co-Ni-Ce catalysts were also prepared and tested. To determine optimal combination of reaction conditions and catalyst composition leading to superior productivity and selectivity; reaction temperature, feed composition (i.e. CH_4/CO_2 ratio in the feed), space velocity and catalyst composition were used as the parameters. SEM and EDX tests were performed in order to obtain information on the micro-structural properties of the freshly calcined and reduced forms of the catalysts, and on the extent and kind of carbonaceous deposits formed on the catalyst surface during the reaction. The catalysts characterized and tested in this part of the work are given in Table 3.5 in Experimental Section.

4.1. Catalyst Characterization Tests

Freshly calcined and reduced Co-Ni-La and Co-Ni-Ce catalysts prepared by co-impregnation method were characterized by using SEM-EDX to obtain information on their microstructural and metal dispersion properties, and the amount of carbon deposit formed on their surface during CDRM. Metal mapping studies were performed to understand the dispersion of metals and whether the agglomeration of metals occurs on the support surface during reaction. For each of the sample, a representative set of SEM-EDX test results, including bright area images of freshly reduced and spent samples, and metal mappings on their surface are given in Figures 4.1 and 4.2.



(a) (b)

(c)

Figure 4.1. 5 wt.%Co-5 wt.%Ni-2 wt.%La/ZrO_2 catalyst (a) SEM bright area image of freshly calcined and reduced catalyst (b) SEM bright area image of the spent catalyst for CH_4/CO_2 feed ratio of 1/1 T=973K (c) Co-Ni-La-Zr mapping of freshly reduced catalyst.

It is seen from the SEM area image given in Figure 4.1 that the particles were uniformly distributed on the catalyst surface except the relatively high populated areas with similar metal particle size (Figures 4.1a and 4.1c). In particular; Co-Ni-La-Zr mapping in Figure 4.1c of the freshly reduced catalyst clearly show that La is well and homogeneously dispersed over the surface of 5 wt.%Co-5 wt.%Ni-2 wt.%La/ZrO_2 catalyst.

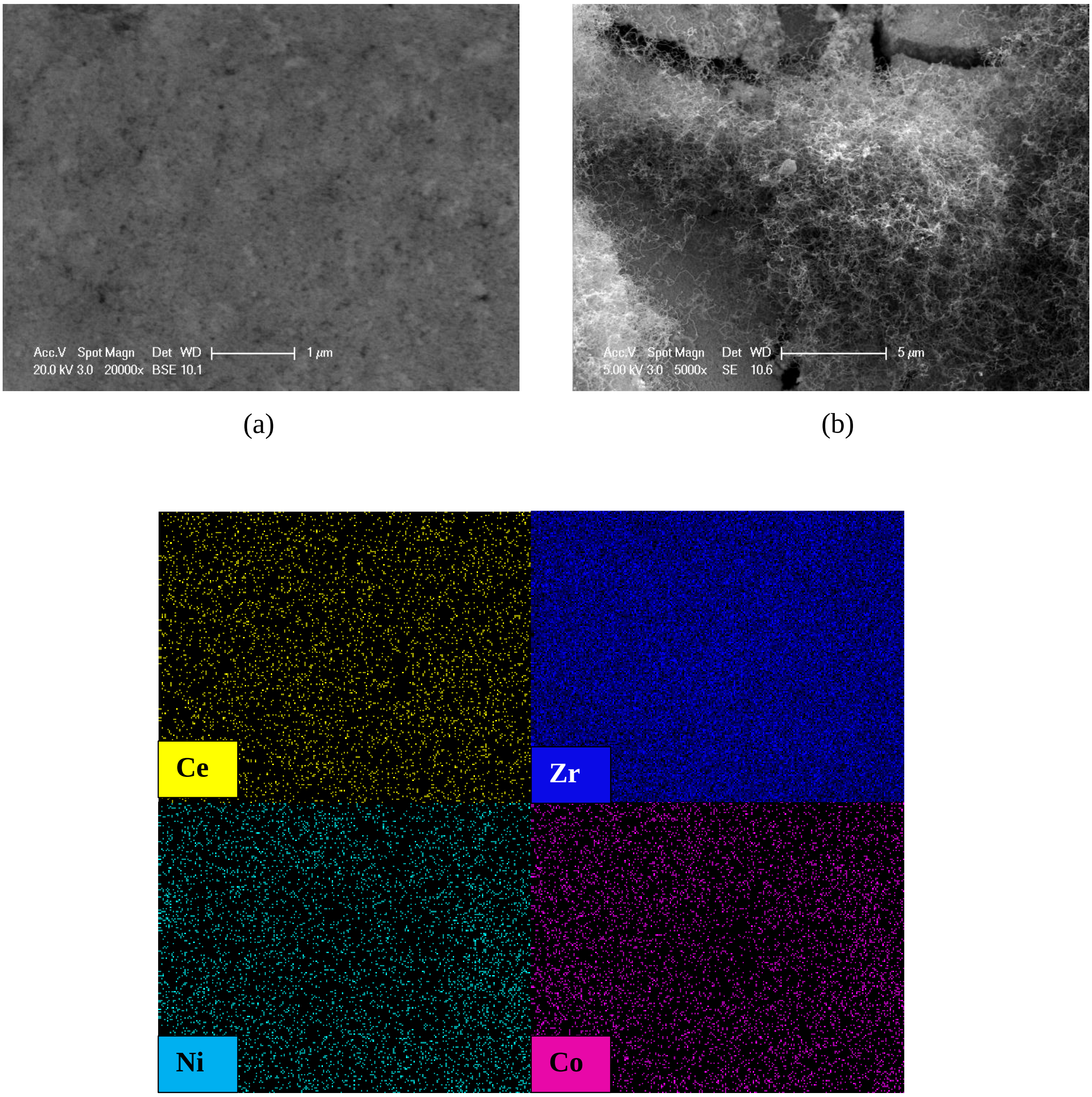
It is very well known that the type of carbon deposit on the catalyst during the CDRM reaction is an important factor affecting activity and stability. In order to get a deeper insight on the morphology and structure of the carbon deposits formed on the surface of used (spent) catalysts, 5 wt.%Co-5 wt.%Ni-2 wt.%La/ZrO_2 sample used in CDRM test conducted at 973 K with CH_4:CO_2=1/1 feed ratio at the end of 6 h TOS was investigated by SEM. Figure 4.1b clearly show filamentous carbon whiskers formed during reaction and it can be observed that the formed carbon nanofibers seem almost identical. Due to the presence of a dissolved carbon concentration gradient, whiskers are formed tubular in shape, and carbon filaments formed on the active metal removed and carried tiny metal formations with them.

The SEM micrograph of 5 wt.% Co-5 wt.%Ni-2 wt.%Ce/ZrO_2 catalyst sample is shown in Figure 4.2. It is seen that all particles were uniformly distributed over the surface. The metal mappings of the Co, Ni, Ce and Zr (Figure 4.2c) confirm the well dispersion of Co, Ni and Ce with a good homogeneity on freshly reduced sample. Figure 4.2b shows that the carbon formation is filamentous, and is very similar to that observed on Co-Ni-La sample. Results indicate that such morphology is typical of supported nickel catalysts, in which nickel crystallites serve as the catalysts for the growth of carbon filaments. However; over the surface of 5 wt.%Co-5 wt.%Ni-2 wt.%Ce/ZrO_2 catalyst, amount of carbon deposit is lower compared to that formed on 5 wt.%Co-5 wt.%Ni-2 wt.%La/ZrO_2 catalyst, which is confirmed by the SEM/EDX analyses (Table 4.1). It is known that during CDRM, two processes occur simultaneously on the surface of the ZrO_2 supported catalyst in general regardless of the difference in the detailed mechanism of the reaction; those are (i) production of hydrogen through methane/methyl dehydrogenation producing surface carbon on the primary active metal sites, i.e. Co or Ni in the current case, as the side product, and (ii) dissociative adsorption of CO_2 on ZrO_2 producing surface oxygen, which is transferred to active sites and used in cleaning of carbon deposit through oxidation forming CO. CO formed as the result of carbon oxidation on the metal sites, and CO_2 disproportionation on the ZrO_2 surface desorb directly to the gas phase. Most probably, the high resistance of the Ce-promoted catalyst against carbon deposition comes from the very high oxygen utilization activity stemming both from redox property of surface CeO_x regulating surface oxygen transfer during reaction, which is more pronounced compared to that of La species, and the very well dispersion of Ce all over the catalyst surface.

Table 4.1. SEM-EDX analysis results for all catalyst samples.

Catalyst	Co wt.%	Ni wt.%	Ce wt.%	La wt.%	C wt.%
5Co5Ni2La (fresh)	5.47	5.62	-	2.44	-
5Co5Ni2La (spent)	3.74	3.96	-	1.72	30.89
5Co5Ni2Ce (fresh)	4.76	4.46	2.15	-	-
5Co5Ni2Ce (spent)	4.37	3.63	3.35	-	14.01

The results revealed that the presence of Ce on the surface provided an additional storage capacity for oxygen coming from ZrO_2 support. Ce centers went through continuous reduction/oxidation cycle during the reaction acting as a buffer for surface oxygen and enhanced the oxygen transfer leading high coke resistance.



(a)

(b)

(c)

Figure 4.2. 5 wt.%Co-5 wt.%Ni-2 wt.%Ce/ZrO_2 catalyst (a) SEM bright area image of freshly reduced catalyst (b) SEM bright area image of the spent catalyst for CH_4/CO_2 feed ratio of 1/1 T=973K (c) Co-Ni-Ce-Zr mapping of freshly reduced catalyst.

4.2. Performance Tests

The performance tests of the catalysts were performed and evaluated considering the "activity, selectivity and stability" as the primary set of criteria in deciding the direction of experimental tests. The reaction conditions used during the performance tests listed in Table 3.6. The CH_4 and CO_2 conversions and H_2/CO ratio in the product stream were calculated by using the formulas below:

$$\text{Conversion }\% = \frac{C_{in} - C_{out}}{C_{in}} \text{x}100 \tag{4.1}$$

$$\frac{H_2}{CO} = \frac{C_{H_2}}{C_{CO}} \tag{4.2}$$

In the evaluation of the performance test results, CH_4 and CO_2 conversion values were used as measure of activity while H_2/CO ratio in the product stream was considered as the measure of selectivity. It should be noted that obtaining H_2/CO product selectivity as close to 1 is widely accepted as a desired criteria considering the fact that it is a suitable feed ratio for production of olefinic hydrocarbons through Fischer–Tropsch synthesis.

4.2.1. The Effect of Temperature

The catalysts were tested in CO_2 reforming of methane at 873-973 K temperature range by using 60,000 mL/h g-catalyst space velocity with CH_4:CO_2 feed ratio as 1:1. Figures 4.3 - 4.5 show the CH_4 conversion, CO_2 conversion and H_2/CO ratio obtained over Co-La, Co-Ni-La and Co-Ni-Ce catalysts, as a function of reaction temperature. In comparing activity and selectivity of the samples, 6 h TOS data, guaranteeing well established concentrations of the species on the surface, were used. According to the performance tests, it was seen that increasing temperature increases the CH_4 and CO_2 conversions due to the endothermic nature of CDRM. The H_2/CO ratios for the catalysts were found in 0.5-0.6 region. The different activity levels of the catalysts clearly indicate the effects of different promoters used on Co-based, ZrO_2 supported catalysts. A comparative analysis of CH_4 conversion values obtained during the tests over 5 wt.%Co-5 wt.%Ni-2 wt.%La/ZrO_2 (5Co5Ni2La) and 5 wt.%Co-5 wt.%Ni-2 wt.%Ce/ZrO_2

(5Co5Ni2Ce) clearly show that Co-La has the inferior activity between the catalysts tested; Ni addition to Co-La leads to an improved activity and, for the Co-Ni/ZrO_2 system, Ce is a better promoter compared to La especially at the mid temperature tested, i.e. 923 K. The increase of activity resulted from Ni addition to Co-La/ZrO_2 via co-impregnation method may be related with the intimate contact between Ni and Co when they are both impregnated on ZrO_2 support that present a marked Lewis alkalinity/acidity. It can be noted that co-impregnation of Ni and Co together onto ZrO_2 surface and subsequent high temperature thermal treatment (calcination and reduction at 773 K) can led to a strong and extensive Co-Ni surface interaction.

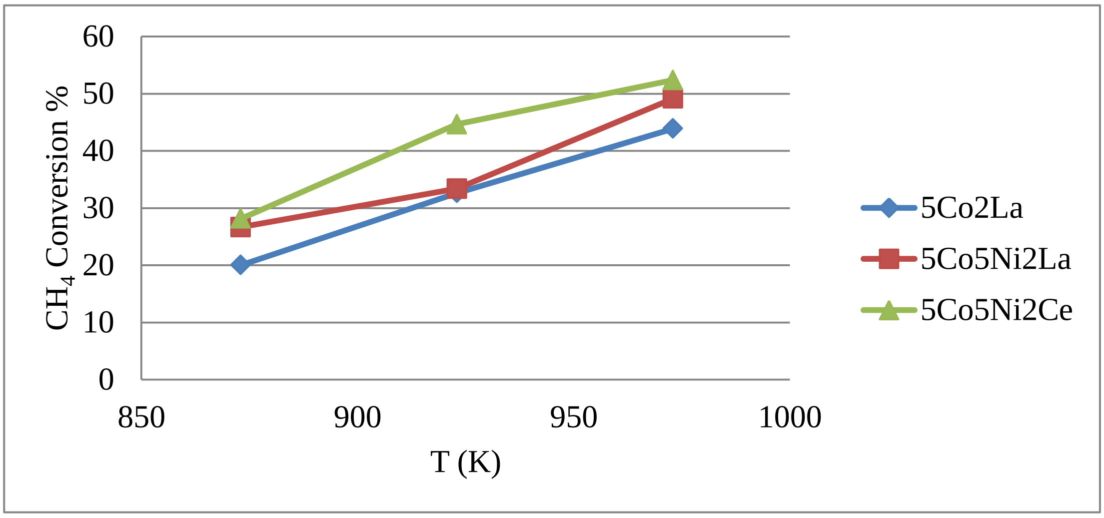


Figure 4.3. CH_4 conversions for the different catalysts in the CDRM as a function of the reaction temperature. Conversion values measured at the end of 6 h on stream. CH_4/CO_2= 1/1. Space velocity = 60,000 mL/h.g-cat.

It is noteworthy from Figures 4.3-4.5 that addition of cerium instead of lanthanum via co-impregnation method assures a superior catalytic performance. High CH_4 conversions were obtained over 5Co5Ni2Ce catalyst over the whole temperature range investigated: the CH_4 conversion ranged from 28.1% at 873 K to 52.3% at 973 K. Results assured that Ce is a better promoter than La in Co-based CDRM catalysts. Addition of cerium enhances and regulates the amount and transfer of surface oxygen through reduction/oxidation cycle of CeO_x, and, most probably, the reducibility of the oxide support; this combined effect favors the increase in the long-term activity and stability of the catalyst.

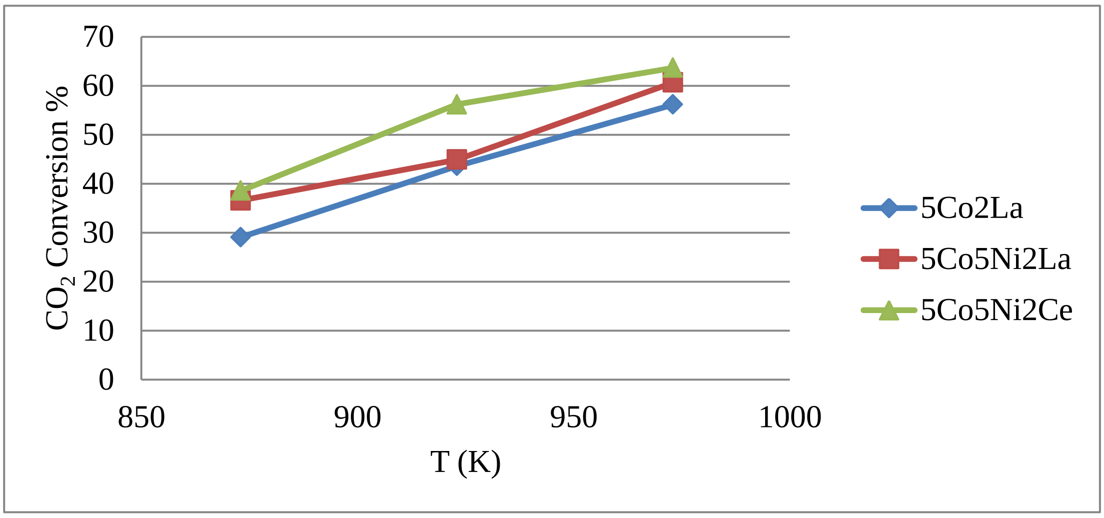


Figure 4.4. CO$_2$ conversions for the different catalysts in the CDRM as a function of the reaction temperature. Conversion values measured at the end of 6 h on stream. CH$_4$/CO$_2$= 1/1. Space velocity = 60,000 mL/h.g-cat.

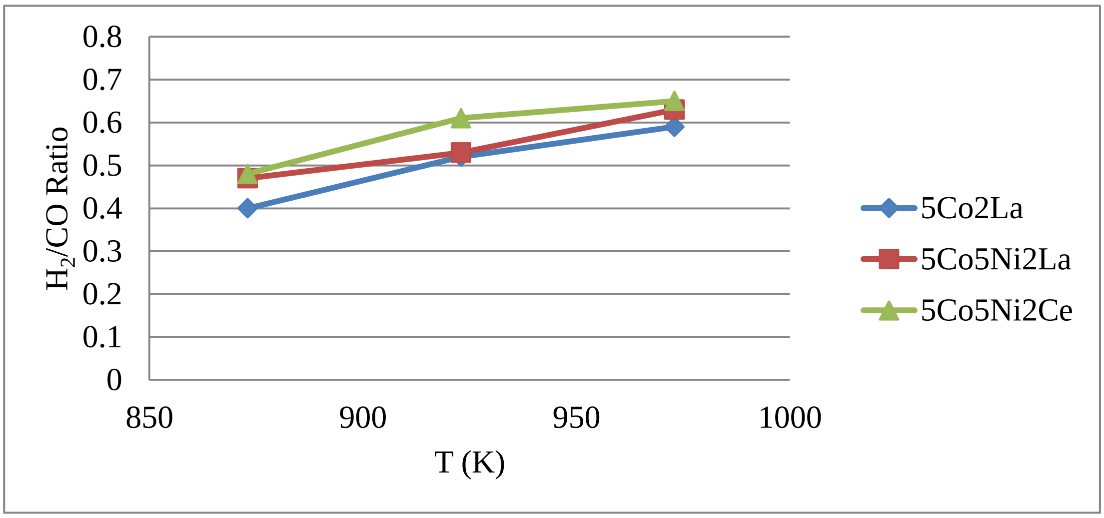


Figure 4.5. H$_2$/CO molar ratio in the CDRM product stream as a function of the reaction temperature. Conversion values measured at the end of 6 h on stream. CH$_4$/CO$_2$= 1/1. Space velocity = 60,000 mL/h.g-cat.

In the performance test results obtained for CH$_4$/CO$_2$ feed ratio of 1/1, CO$_2$ conversion levels have always been found to be higher than the CH$_4$ conversions, which is most probably due to the reverse water-gas shift (RWGS) reaction [Equation 2.2], which is favored at high temperatures occurs simultaneously with CDRM. As RWGS reaction consumes some of H$_2$ produced by CDRM, H$_2$/CO ratio values become lower than unity as shown in Figure 4.3. At higher temperatures, DR activity dominates and H_2/CO molar ratio in the product stream tends to be unity.

4.2.2. Time-On-Stream (TOS) Activity Profiles Of The Catalysts

Time-on-stream activity tests were performed at 973K for a fixed space velocity (60000 mL/h.g-cat) by using CH_4:CO_2 ratio of 1:1 in the feed, where the highest conversions were obtained, for all three catalysts. 6 h TOS data are used in the comparative analysis. Figures 4.6-4.8 show the CH_4 and CO_2 conversions and the H_2/CO molar ratio in the product stream as a function of the reaction time, respectively. At the end of 6th hour TOS, the 5 wt.%Co-2 wt.%La/ZrO_2 (5Co2La) catalyst prepared by sequential impregnation showed lower activity compared to other samples and lost 13.2% of its initial CH_4 activity, whereas both Ni-included catalysts prepared by co-impregnation method, 5Co5Ni2La and 5Co5Ni2Ce, reached higher activities and lost 18.2% and 15.6% of their initial CH_4 activity at the end of 6 h TOS, respectively. The results indicate two important effects of Ni addition on CDRM performance; Ni leads high CDRM activity but, at the same time, decreases the coke resistance of the samples most probably due to its very high dehydrogenation activity, which led carbon formation.

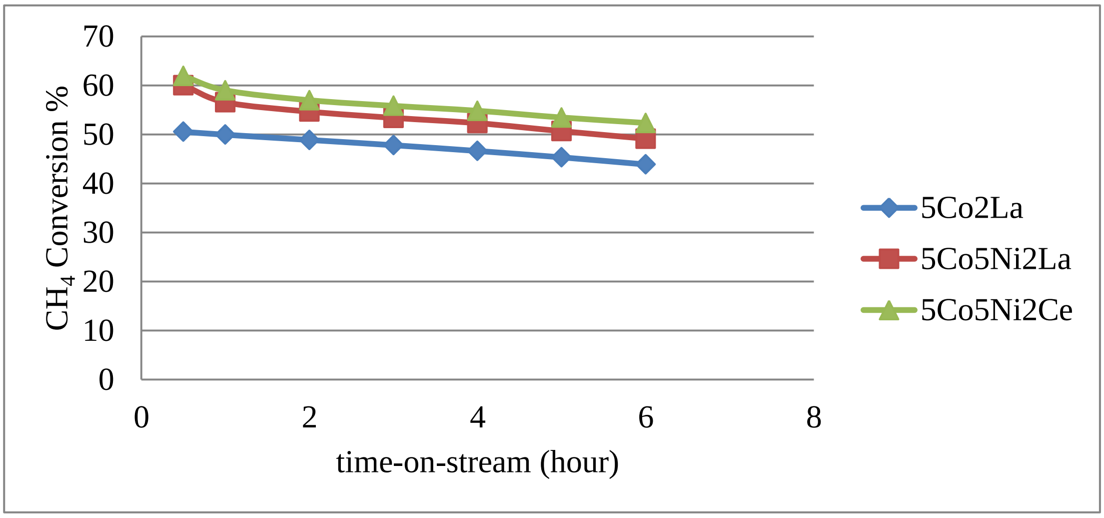


Figure 4.6. CH_4 conversions for the different catalysts in the CDRM as a function of the reaction time. Reaction Temperature= 973 K. CH_4/CO_2= 1/1. Space velocity = 60,000 mL/h.g-cat.

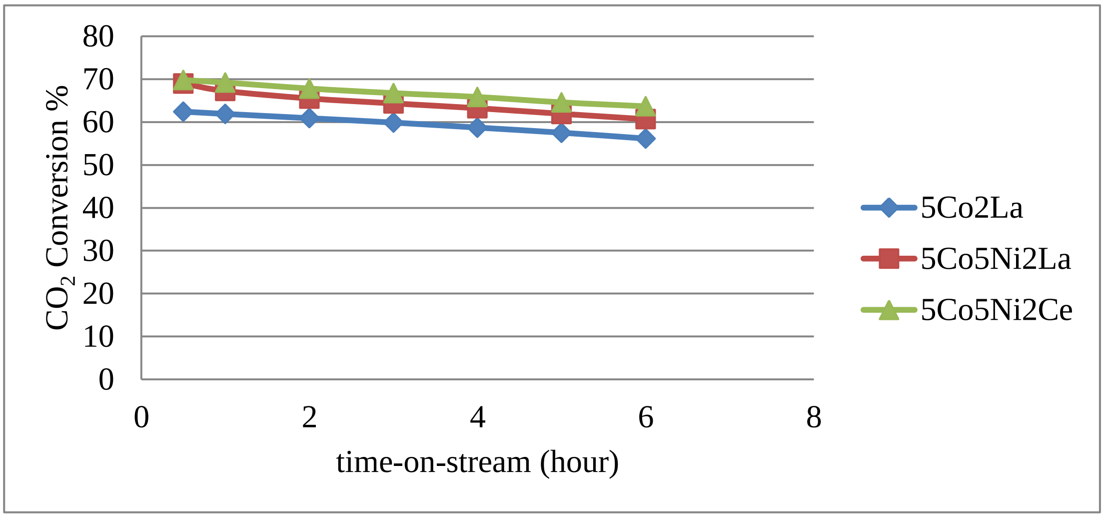


Figure 4.7. CO_2 conversions for the different catalysts in the CDRM as a function of the reaction time. Reaction Temperature= 973 K. CH_4/CO_2= 1/1. Space velocity = 60,000 mL/h.g-cat.

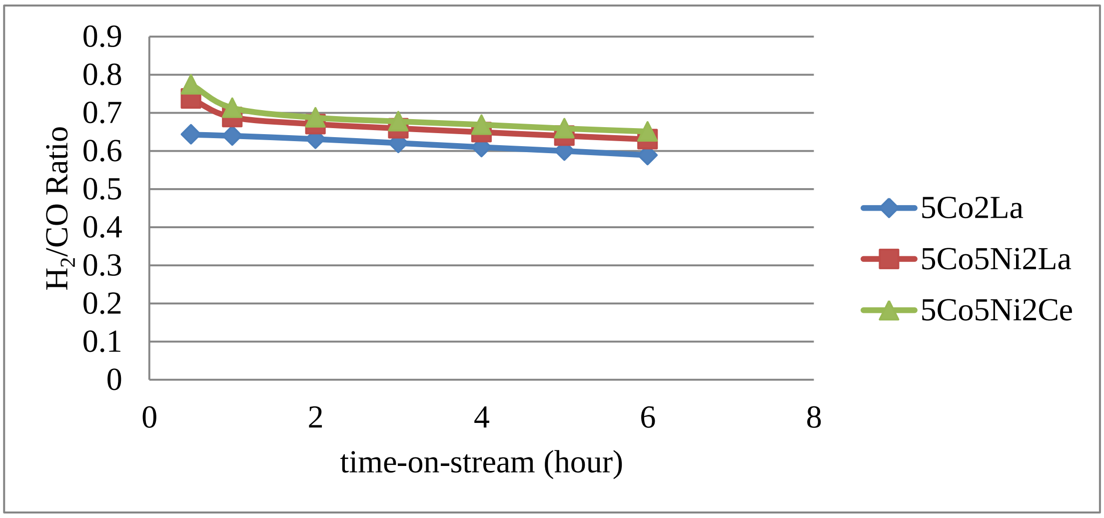


Figure 4.8. H_2/CO molar ratio for the different catalysts in the CDRM product stream as a function of the reaction time. Reaction Temperature= 973 K. CH_4/CO_2= 1/1. Space velocity = 60,000 mL/h.g-cat.

Based on the results of the experiments carried out, high methane and carbon dioxide conversions were obtained again on 5Co5Ni2Ce catalyst at 973 K. Among the trimetallic catalysts, the activity loss of Ce-promoted catalyst was lower than that observed over La-promoted one. It is confirmed previously by our group for Pt-Ce system that Ce enhances transfer of surface oxygen, which is produced on ZrO_2 support, by creating an additional oxygen storage capacity which makes primary metal and the catalyst more carbon deposition resistant. The increase in the amount of surface oxygen causes an improved capability of cleaning carbon which accumulates on the metal sites during CH_4 dehydrogenation. Moreover, as explained in previous section, addition of Ce improved the reducibility of the oxide support which results in an increase in the number of oxygen vacancies. This situation led to an increase in the ability of dissociative adsorption of CO_2. Increase in both the dissociation ability and carbon cleaning capacity resulted in enhanced activity and stability of Ce-promoted CDRM catalysts.

4.2.3. Effect of CH_4/CO_2 Ratio in the Feed

All three catalysts were tested in CDRM at 923K for a fixed space velocity (60000 mL/h.g-cat) by using $CH_4:CO_2$ ratio of 1:1 and 2:1 in the feed stream. For different $CH_4:CO_2$ feed ratios, 6 hour time-on-stream data were used for the comparative analysis of activity and selectivity. Figures 4.9-4.11 show CH_4 conversion, CO_2 conversion and H_2/CO product ratio values obtained over the catalysts as a function of $CH_4:CO_2$ feed ratio, respectively.

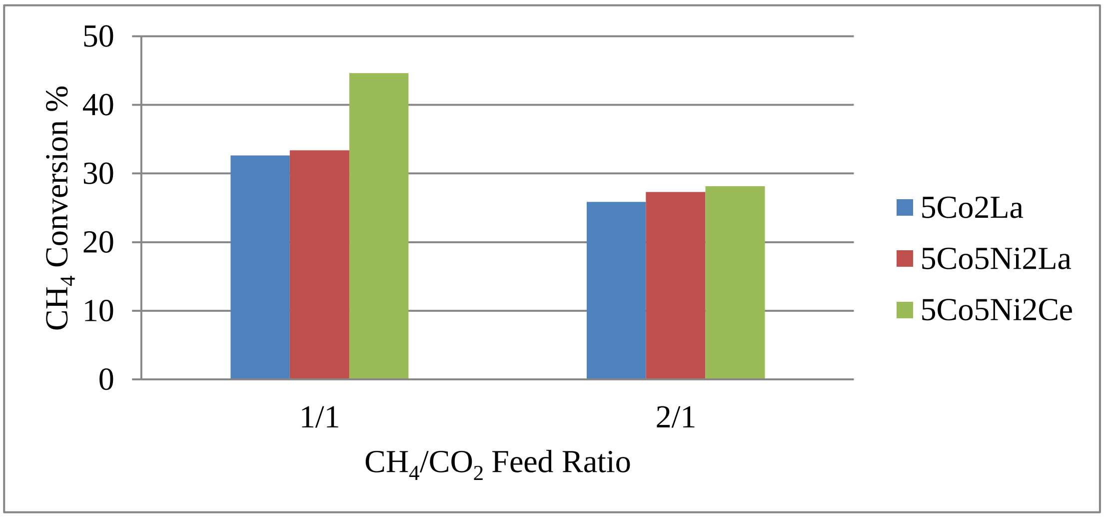


Figure 4.9. CH_4 conversions for the different catalysts in the CDRM as a function of the feed ratio. Reaction Temperature= 923 K. Space velocity = 60,000 mL/h.g-cat.

The stoichiometry of reactants, CO_2 and CH_4, in CDRM reaction is 1. A high CH_4/CO_2 feed ratio (>1.0) is considered as a severe condition for CDRM; when the ratio is greater than 1.0, methane becomes excess and the carbon formed upon its decomposition on the active sites may not find enough mobile oxygen to be cleaned out. Carbon, that is produced by the methane decomposition reaction [Equation 2.7], may deposit on the surface of the catalyst, and deactivates the catalyst through blocking the active sites. As shown in Figures 4.7-4.9, CH_4/CO_2 feed ratio of 1/1 yielded the highest methane conversion with the lowest carbon dioxide conversion and H_2/CO product ratio. Under the severe condition (CH_4/CO_2 feed ratio of 2/1), there was a decrease in methane conversion for all catalysts. It is observed that carbon dioxide conversion and H_2/CO product ratio is higher for all catalysts when $CH_4:CO_2$ feed ratio is increased to 2 except those for Ce-promoted sample whose CO_2 conversion decreases while H_2/CO product ratio stays similar. This shows that activity loss in methane conversion could be related to the higher carbon deposition led by high feeding rate of carbon source, CH_4, compared to the feeding rate of oxygen source, CO_2. The cleaning of coke formed becomes difficult for the catalysts when feed ratio is increased to 2:1. At the end of 6 hours of reaction, methane conversions were evaluated as 28.2%, 27.3% and 25.9% for 5Co5Ni2Ce, 5Co5Ni2La, and 5Co2La catalysts, respectively whereas these values were observed as 44.6%, 33.4%, and 32.6% for the feed ratio of 1:1.

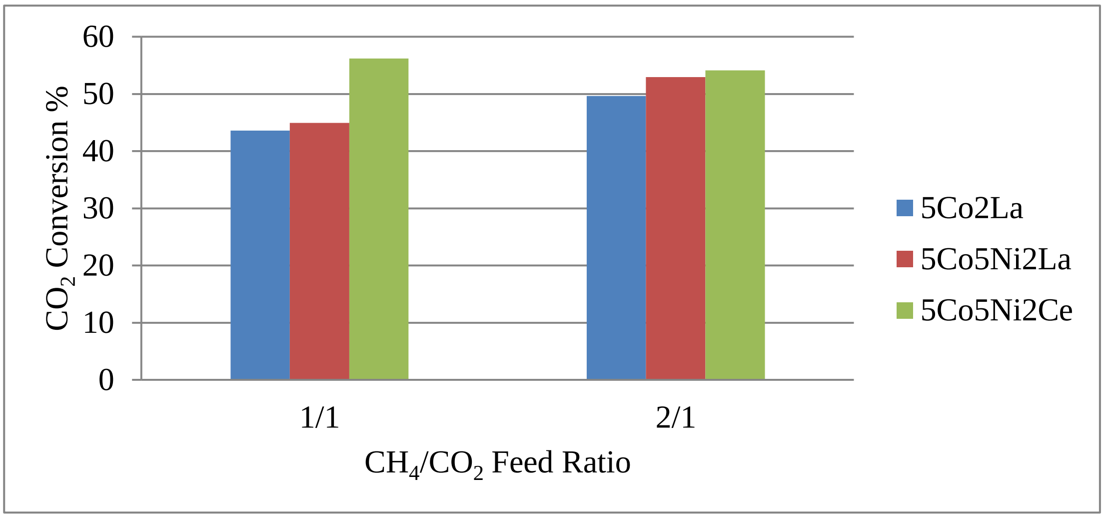


Figure 4.10. CO_2 conversions for the different catalysts in the CDRM as a function of the feed ratio. Reaction Temperature= 923 K. Space velocity = 60,000 mL/h.g-cat.

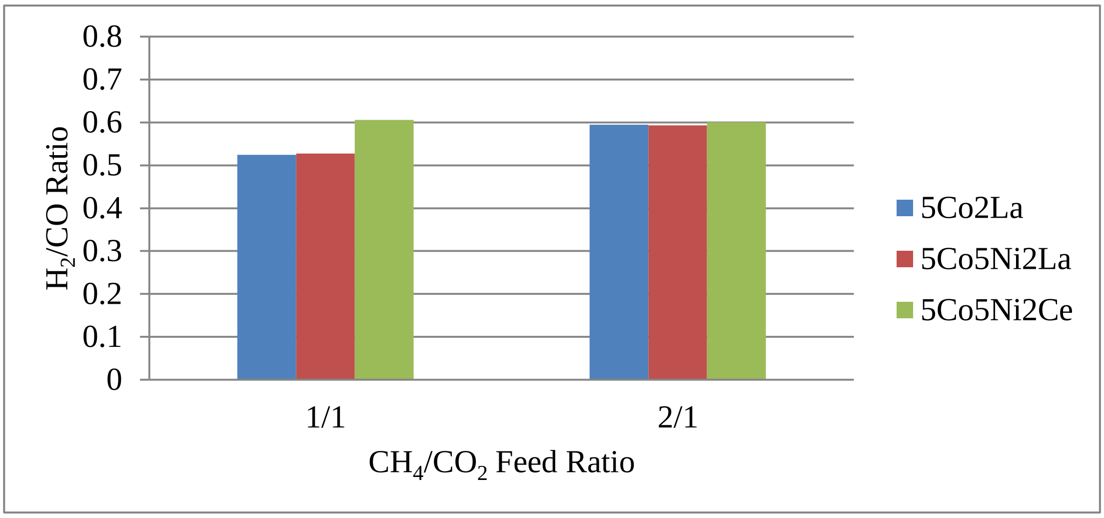


Figure 4.11. H_2/CO molar ratio for the different catalysts in the CDRM product stream as a function of the feed ratio. Reaction Temperature= 923 K. Space velocity = 60,000 mL/h.g-cat.

Carbon dioxide conversions were higher than methane conversion values and were recorded as 43.6%, 44.9% and 56.2% at 1:1 feed ratio for 5Co2La, 5Co5Ni2La, and 5Co5Ni2Ce catalysts, respectively. An increase of approximately 15% in carbon dioxide conversion was observed for Co-La and Co-Ni-La catalysts when feed ratio is increased to 2:1. The highest decrease in methane conversion accompanied with slight CO_2 conversion decrease with an increase in CH_4:CO_2 ratio for Ce-promoted sample points out that surface oxygen transfer regulation function of Ce is severely affected when carbon deposition rate exceeds surface oxygen transfer rate.

4.2.4. The Effect of Space Velocity

Aiming to understand the performance characteristics, i.e. activity and selectivity (H_2/CO ratio) of the catalysts at higher space velocity, space velocity was decreased to 20000 mL/h-g.cat at 923 K with CH_4:CO_2 feed ratio as 1:1. For different space velocities, 6 hour time-on-stream data were used for the comparative analysis of activity and selectivity. Figures 4.12 - 4.14 show the CH_4 conversion, CO_2 conversion and H_2/CO ratio obtained over the catalysts in CDRM, respectively, as a function of space velocity.

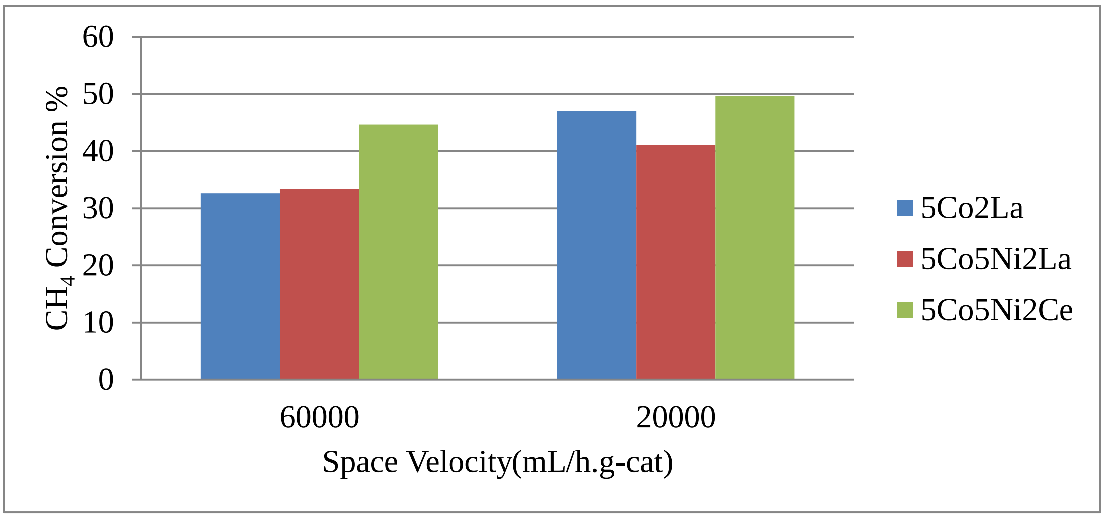


Figure 4.12. Effect of space velocity on CH_4 conversion for the different catalysts in the CDRM. Conversion values measured at the end of 6 h on stream.

Reaction Temperature = 923 K. $CH_4/CO_2=1/1$.

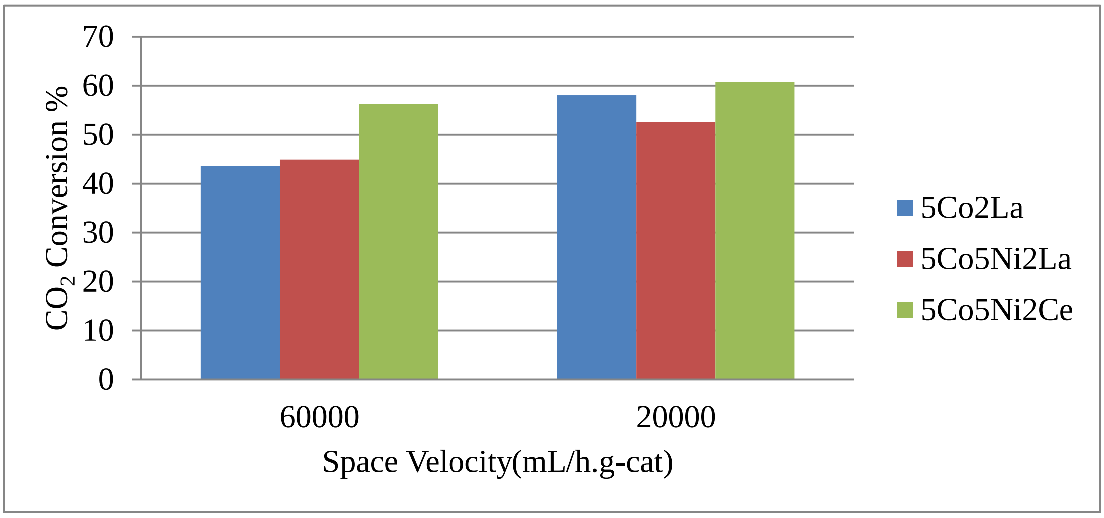


Figure 4.13. Effect of space velocity on CO_2 conversion for the different catalysts in the CDRM. Conversion values measured at the end of 6 h on stream.

Reaction Temperature = 923 K. $CH_4/CO_2=1/1$.

As expected; CH_4 and CO_2 conversions increased with the decrease in space velocity for all catalysts. A decrease in space velocity means a considerable increase in the average time that the reactants spend on the catalyst surface, which leads to significant increase in both CH_4 and CO_2 conversion values. The increase in methane conversions were calculated as 44%, 23%, and 11% for 5Co2La, 5Co5Ni2La, and 5Co5Ni2Ce catalysts, respectively.

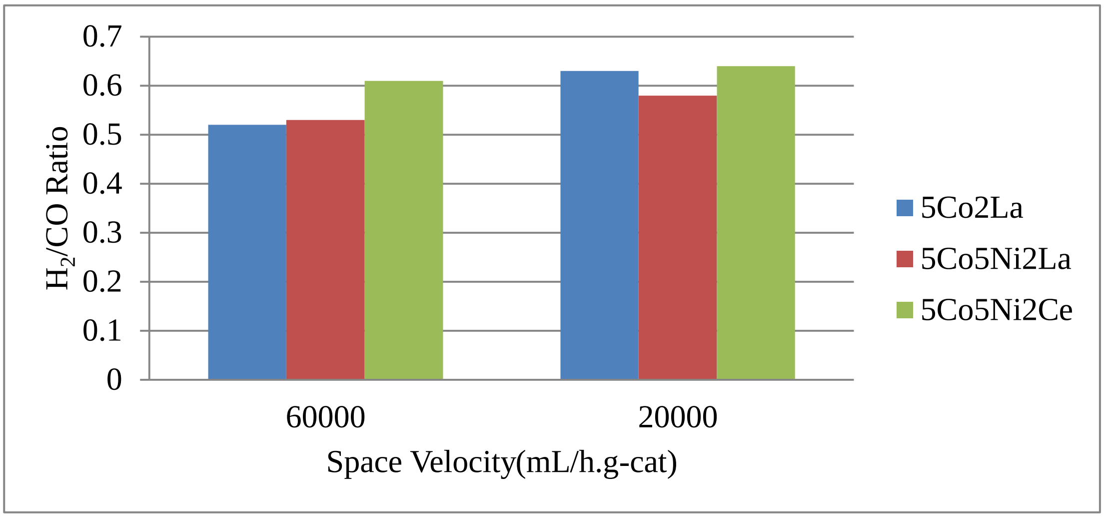


Figure 4.14. H_2/CO molar ratio for the different catalysts in the CDRM product stream as a function of the space velocity. Reaction Temperature= 923 K. CH_4/CO_2=1/1.

H_2/CO ratio in the product stream profiles for all catalysts, given in Figure 4.14, showed that CO production rate, in other words combined rates of CO_2 dissociation and carbon cleaning, is relatively more suppressed compared to that of H_2 production, i.e. methane dehydrogenation, when the average contact time decreases.

4.2.5. The effect of Ni-loading

Considering their higher activity levels led by strong and extensive Co-Ni surface interactions, Co-Ni-La and Co-Ni-Ce systems were tested further. It is very well known, and confirmed by the results of the current study, that methane dehydrogenation activity of Ni is higher than that of Co. Additionally, quantum mechanical simulation studies that had been performed by our group show that Ni lacks the ability of CO_2 disproportionation and consequent surface O-generation, but, although limited, Co has an ability of CO_2 activation producing surface O. Thus, in order to obtain a catalyst with high and stable CDRM activity, catalysts with a lower Ni:Co ratio were prepared and their performance is compared with that of 5Co5Ni systems.

Figures 4.15 – 4.17 show the effect of nickel amount on CH_4 conversion, CO_2 conversion and H_2/CO ratio of Co-Ni-La system, respectively. For the Co-Ni-Ce system, effect of nickel loading on CH_4 conversion, CO_2 conversion and H_2/CO ratio was given in Figures 4.18 - 4.20.

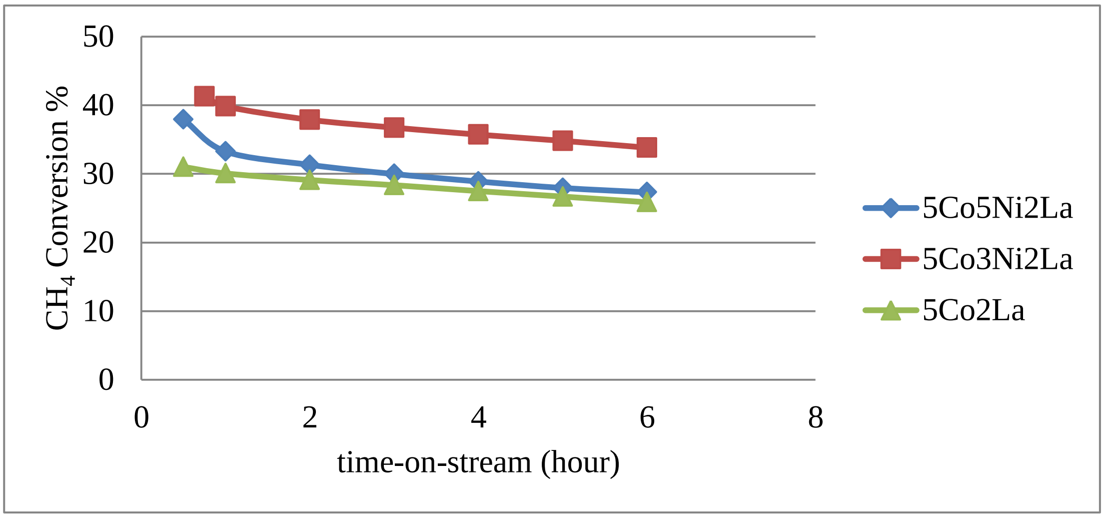


Figure 4.15. Catalyst: Co-Ni-La /ZrO_2 Effect of Ni-loading on CH_4 conversion in the CDRM as a function of the reaction time. Reaction Temperature= 923 K. CH_4/CO_2= 2/1 Space velocity = 60,000 mL/h.g-cat.

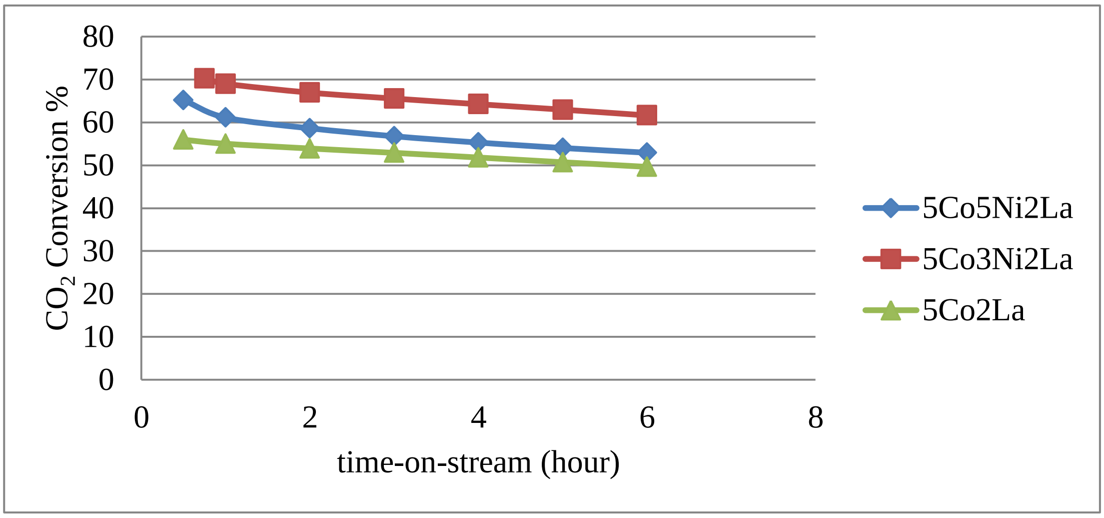


Figure 4.16. Catalyst: Co-Ni-La /ZrO_2 Effect of Ni-loading on CO_2 conversion in the CDRM as a function of the reaction time. Reaction Temperature= 923 K. CH_4/CO_2= 2/1 Space velocity = 60,000 mL/h.g-cat.

The results clearly show the beneficial effect of decreasing Ni:Co ratio by lowering Ni loading to 3 wt.%; higher CH_4 and CO_2 conversion values were obtained on 5 wt.%Co-3 wt.%Ni-2 wt.%La/ZrO_2 (5Co3Ni2La) catalyst prepared by co-impregnation method over the whole time-on-stream test. It is clear that lowering Ni suppressed the coke formation, as expected. Additionally, lower Ni loading may led to an enhancement in metal dispersion with a limited accumulation of metals on each other while keeping metal-metal interface allowing beneficial Ni-Co interaction which may yield relatively easy reduction of NiO_x species.

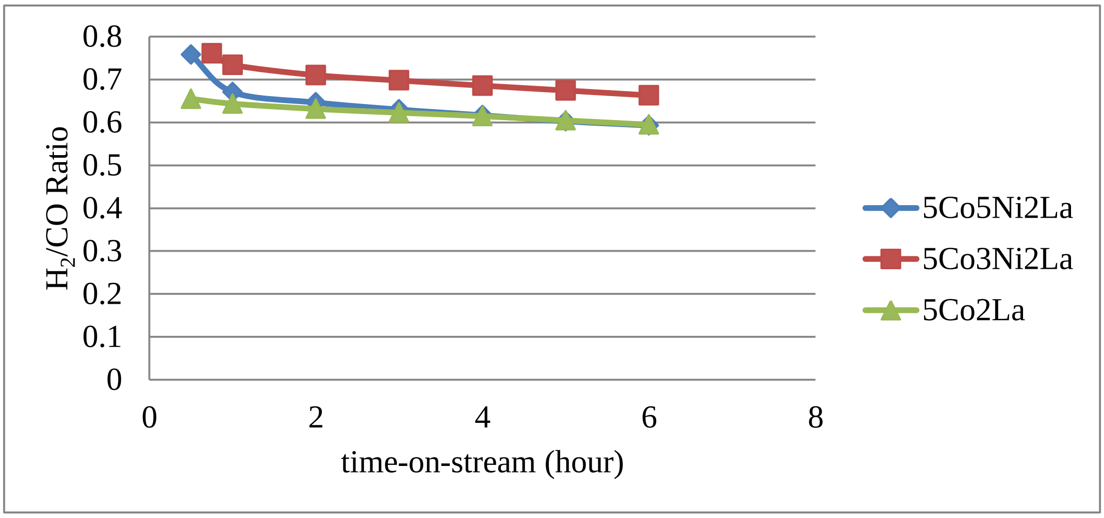


Figure 4.17. Catalyst: Co-Ni-La /ZrO_2 Effect of Ni-loading on H_2/CO ratio in the CDRM as a function of the reaction time. Reaction Temperature= 923 K. CH_4/CO_2= 2/1. Space velocity = 60,000 mL/h.g-cat.

The results showed that high Ni loading resulted in a decrase in the overall stability of the Co-Ni-La/ZrO_2 catalyst. At the end of 6th hour of TOS, higher Ni containing catalyst (5Co5Ni2La) lost 18% of its initial CH_4 activity whereas the CH_4 conversion of low-loaded Ni catalyst (5Co3Ni2La) decreased continuously by almost 15% during the reaction period. As it can be seen from Figures 4.15 and 4.16, between the Co-Ni-La/ZrO_2 catalysts, the one with the lower Ni loading, 5Co3Ni2La, displayed a relatively favorable stability profile.

Unlike the results obtained for La-promoted catalyst, the performance test results are very close for Ce-promoted samples having different Ni:Co loading ratio.

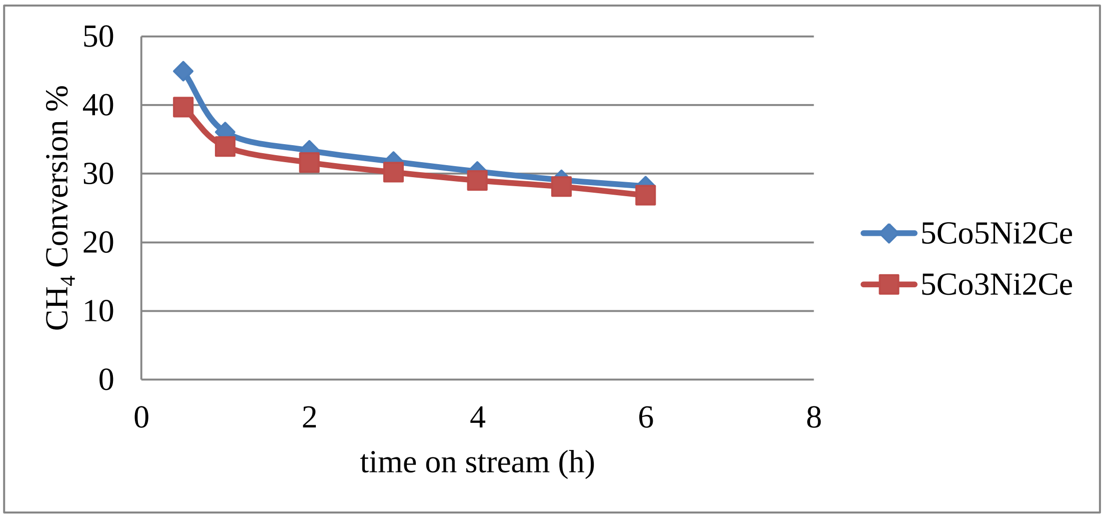


Figure 4.18. Catalyst: Co-Ni-Ce /ZrO_2 Effect of Ni-loading on CH_4 conversion in the CDRM as a function of the reaction time. Reaction Temperature= 923 K. CH_4/CO_2= 2/1. Space velocity = 60,000 mL/h.g-cat.

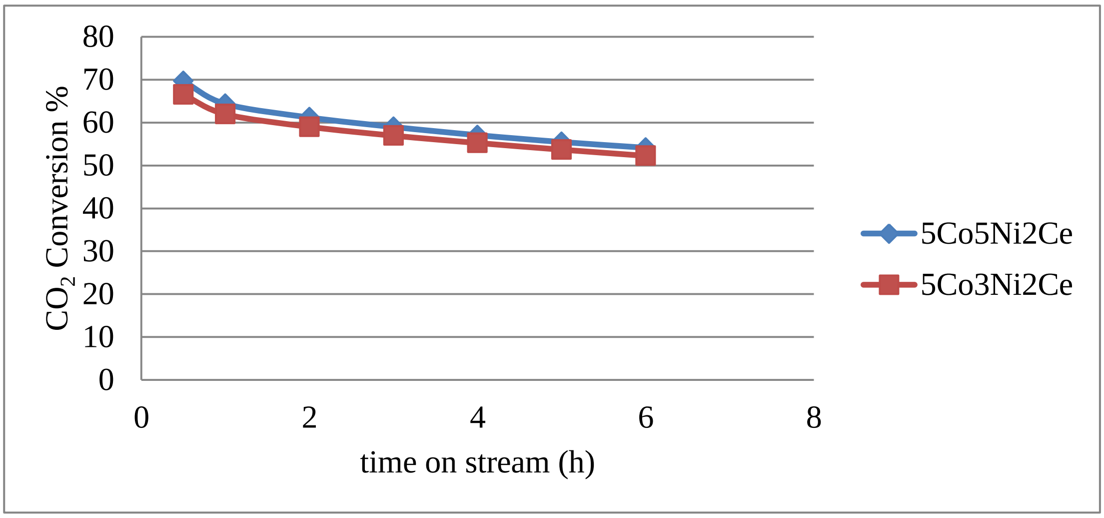


Figure 4.19. Catalyst: Co-Ni-Ce /ZrO_2 Effect of Ni-loading on CO_2 conversion in the CDRM as a function of the reaction time. Reaction Temperature= 923 K. CH_4/CO_2= 2/1. Space velocity = 60,000 mL/h.g-cat

As it is seen from Figures 4.18- 4.20, results indicate that the effect of the amount of Ni on Co-Ce catalyst performance and activity is very similar. Carbon dioxide conversions for both catalysts, in Figure 4.19, were higher than that of methane with values of approximately 53%.

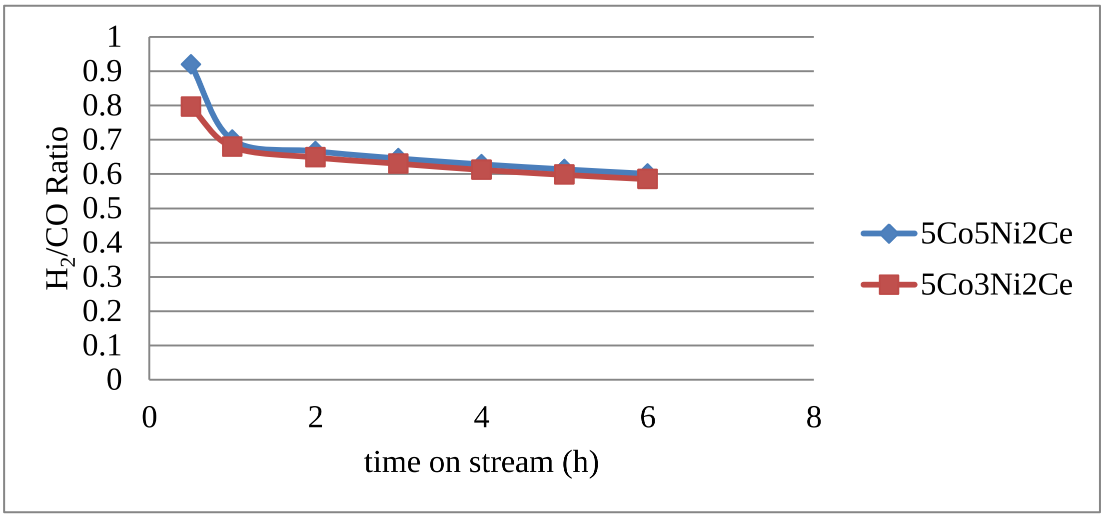


Figure 4.20. Catalyst: Co-Ni-Ce /ZrO_2 Effect of Ni-loading on H_2/CO ratio in the CDRM as a function of the reaction time. Reaction Temperature= 923 K. CH_4/CO_2= 2/1. Space velocity = 60,000 mL/h.g-cat.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

Co-La/ZrO_2, Co-Ni-La/ZrO_2 and Co-Ni-Ce/ZrO_2 catalysts were prepared, characterized and tested for their CDRM performance. In the catalysts, Co and promoter, i.e. La and Ce, loadings were kept fixed as 5 wt. % and 2 wt. %, respectively, while two Ni loading levels, 3 wt. % and 5 wt.%, was used in trimetallic samples. The major conclusions that can be drawn from current study can be given as follows:

- The different activity levels of the catalysts clearly show that the catalytic performances of the Co/ZrO_2 based samples strongly depended on the type of the promoters used.

- Ni addition has two important effects on CDRM performance of the trimetallic samples; it leads high CDRM activity but, at the same time, decreases the coke resistance of the samples. Decreasing the amount of nickel to 3 wt% from 5 wt% led to a significant increase in the activity of the Co-Ni-La/ZrO_2 catalyst. On the other hand, change in Ni:Co ratio did not yield any significant change in Ce-promoted CDRM catalysts.

- SEM images of the spent catalysts indicated that the type of carbon deposited on Ni-based catalysts was all filamentous.

- Use of cerium was found to be beneficial for CDRM activity through regulating transfer of surface oxygen. Among all the catalysts, Co-Ni-Ce/ZrO_2 catalysts exhibited the highest catalytic activity over the whole TOS tests in CDRM reaction. Results indicated the effect of La addition is limited.

- For all catalysts, increasing temperature increased both CH_4 and CO_2 conversions and H_2/CO ratio. The feed ratio of 2/1 gave the lowest results for methane conversion but the highest values for carbon dioxide conversion and H_2/CO ratio. Increasing space velocity decreased the conversion values and H_2/CO ratio.

5.2. Recommendations

Considering the resulst of the experimental study, following ideas are thought to be beneficial for future studies on CDRM:

- To prevent carbon deposition, modified support or binary support can be designed and developed for the CDRM performance.

- Different Co:Ce and/or Co:La loadings of the catalysts can be studied aiming to find an optimum ratios. Increasing Ce amount might result in better catalytic activity than La based catalyst.

- The kinetic studies can be performed over Co-based ZrO_2 catalysts.

- Ni-included catalysts, Co-Ni-La/ZrO_2 and Co-Ni-La/$ZrO_{2,}$ can also be prepared by sequential impregnation method to investigate the effect of impregnation strategy on the reforming performance.

- Different analytical and spectroscopic systems (HRTEM, XPS, etc.) can also be used to characterize the physical, microstructural and electronic properties of the catalyst samples.

- The effect of calcination and reduction temperature on the reforming activity can be investigated.

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