

AN EXPERIMENTAL ANALYSIS ON CATALYTIC DRY REFORMING OF
METHANE (CDRM) PERFORMANCE OF Ni/SBA-15 SYSTEM

by
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ABSTRACT

An Experimental Analysis on Catalytic Dry Reforming Of Methane (CDRM) Performance of Ni/SBA-15 System

The main objective of this study is to design and develop an efficient Ni based and SBA-15 supported mono metallic catalyst in order to produce a high yield synthesis gas via catalytic dry reforming of methane. The priority was given to the inhibition of the coke deposition. In this context, first of all, the effect of the catalyst preparation & pre-treatment (i.e. impregnation technique, calcination and reduction temperatures) and reaction conditions (i.e. reaction temperature) was investigated on the reference catalyst, 10% Ni/SBA-15. Secondly, effect of the modifications (i.e. metal loadings as 7.5 and 15%, addition of CTAB and TMB to SBA-15, drying temperature) on the catalyst were investigated. During these tests, the activity and selectivity was determined in terms of CH₄ and CO₂ conversions, and of H₂/CO ratio, respectively. The results of the performance tests suggested that the catalytic performance is highly dependent on the preparation route. It was seen that incipient wetness impregnation method favors catalytic performance in terms of both activity and selectivity. Additionally, higher calcination and reduction temperatures found to have a positive effect on the catalytic performance. Changing the metal loading (7.5 and 15%) led to an inverse impact in both activity and stability; whereas lower drying temperatures increased the catalytic activity and stability. Although modification of the SBA-15 by addition of CTAB and TMB enhanced the properties of the supporting material, Ni/CTAB_SBA-15 and Ni/TMB_SBA-15 catalysts showed lower reactant conversions with higher stabilities. Characterizations on the chosen samples indicated coke formation over the surface of the catalysts and the coke deposition could be suppressed with an appropriate preparation route. All in all, the results of the performance tests and characterization techniques suggested that 10% Ni/SBA-15 catalyst which was impregnated with the incipient wetness impregnation method and calcined at 750 °C for 6 hours with 2 °C/min ramping rate in air was the most promising CDRM catalyst. This idea was also supported by the stability test conducted at 750 °C for 72 hours.

ÖZET

Ni/SBA-15 Sisteminin Metanın Katalitik Kuru Reformlaması Reaksiyonu Performansı Üzerine Deneysel Çalışma

Bu çalışmanın ana amacı, metanın katalitik kuru Reformlaması yöntemi ile yüksek verimli sentez gazı üretebilecek Ni bazlı ve SBA-15 destekli tek metalli bir katalizör tasarlamak ve geliştirmektir. Çalışmada öncelik karbon birikiminin önlenmesine verilmiştir. Bu içerikte, ilk olarak katalizör hazırlama ve ön muamelesinin (impregnasyon teknikleri, kalsinasyon ve indirgeme sıcaklığı) ve tepkime koşullarının (tepkime sıcaklığı) etkisi referans katalizörü olan 10% Ni/SBA-15 üzerinde incelendi. İkinci olarak, katalizör üzerinde bazı değişikliklerin (7.5 ve 15% olan metal yüklemeleri, SBA-15 üzerinde CTAB ve TMB eklenmesi, kurutma sıcaklığı) etkisi incelendi. Bu testler esnasınca, katalizörün aktivitesi ve seçiciliği CH_4 ve CO_2 dönüşümü ve H_2/CO oranı cinsinden belirlendi. Performans testleri sonucunda, katalizörün etkinliğinin hazırlanma koşulları ile sıkıca bağlantılı olduğu bulundu. Nemli emdirme metodunun katalizör performansını arttırdığı, yüksek kalsinasyon ve indirgeme sıcaklığının olumlu bir etkisi olduğu gözlemlendi. Metal yüklemesinin 7.5 ve 15%'ye değiştirilmesinin hem aktivite hem de kararlılıkta ters bir etkisi olduğu; ancak kurutma sıcaklığının düşürülmesinin bu performansı yükselttiği bulundu. CTAB ve TMB eklemesi SBA-15'in özelliklerini geliştirse bile, Ni/TMB_SBA-15 ve Ni/CTAB_SBA-15 katalizörleri düşük reaktan dönüşümü, yüksek kararlılık gösterdi. Seçilen bazı katalizör örnekleri üzerinde uygulanan karakterizasyon teknikleri katalizör üzerinde karbon oluşumu olduğunu gösterdi. Ayrıca, karbon birikiminin katalizör hazırlama yöntemleri ile azaltılabileceği bulundu. Yapılan performans testleri ve incelenen katalizör örnekleri sonucunda, en iyi sonuç veren katalizörün, IWI yöntemi kullanılarak impregne edilmiş olan ve 750 °C'de 6 saat süresince dakikada 2 °C sıcaklık artışı ile kalsine edilmiş olan 10% Ni/SBA-15 katalizörü olduğu belirlendi. Bu düşünce, katalizör ile yapılan 72 saatlik kararlılık testi ile desteklendi.

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LIST OF SYMBOLS/ABBREVIATIONS

ΔH	Enthalpy of the Reaction
BET	Brunauer Emmett Teller
BOS	Birleşik Oksijen Sanayi
CCUS	Carbon Capture Utilization Storage
CDRM	Carbon Dioxide Reforming of Methane
EDX	Energy Dispersive X-Ray
IWI	Incipient Wetness Impregnation
MS	Mass Spectrometer
POX	Partial Oxidation
PSD	Pore Size Distribution
RWGS	Reverse Water Gas Shift
SEM	Scanning Electron Microscope
SRM	Steam Reforming of Methane
TPV	Total Pore Volume
TSA	Total Surface Area
TSI	Two Solvent Impregnation
UNFCC	United Nation Framework Convention on Climate Change
XPS	X-Ray Photoelectron Spectrometry
XRD	X-Ray Diffraction

1. INTRODUCTION

Rapid rise in global population and demand for improved quality of life lead to an increase in energy need. Despite of the technological developments, fossil based fuels such as natural gas, crude oil and coal still dominates the primary energy mix (Abdullah *et al.*, 2017), and reliable forecasts suggest the decrease in their share will be very gradual in short- and medium-term perspectives. The excessive usage of these fossil fuels causes an increase in the concentration of the certain gaseous products in the atmosphere, known as the greenhouse gases (GHG), such as methane, carbon dioxide and nitrous oxides. The accumulation of GHG causes unprecedented rise in global average temperature, decrease in arctic ice, rise of the sea level, and increase in the acidity of the oceans (Jang *et al.*, 2019), all are the parts of today's well known problem, the global warming, which is one of the most serious threats to environmental prosperity and security.

Among all greenhouse gases, CO₂ is the primary and the most abundant greenhouse gas owing to its thermodynamic stability, and the most viable CO₂ mitigation routes are Carbon Capture, Utilization and Storage (CCUS) technologies (Aramouni *et al.*, 2018). As there are environmental and financial concerns about the CO₂ storage techniques, CO₂ utilization has been widely assessed as a more efficient and reliable way owing to its long time sustainability and safety. CO₂ utilization can be achieved by either using it directly in different areas (i.e. oil recovery by flooding, solvent applications, agriculture, food industry) or using it as a reactant in several chemical reactions, such as photocatalytic reactions, electrochemical conversions, carboxylation reactions and dry reforming reactions (Abdulrasheed *et al.*, 2019).

Although there are several ways to utilize CO₂, catalytic dry reforming of methane, also known as the carbon dioxide reforming of methane (CDRM) is the most environmentally friendly approach which utilizes not only CO₂ but also CH₄ -*the most dangerous GHG owing to its more potent heat absorbing capacity*- and generates synthesis gas, a mixture of H₂ and CO (Lavoie, 2014). Besides, CDRM produces syngas with a H₂/CO molar ratio close to 1, which is a convenient ratio for the production of valuable hydrocarbons and olefins by further via Fischer Tropsch Synthesis (FTS). The

corresponding chemical reaction of the catalytic dry reforming of methane and its standard enthalpy value are given below (Equation 1.1).



Although CDRM is a promising research area attracting attention for almost 30 years as a plausible CO₂ utilization route, it is still not a mature process for the chemical industry due to its major drawbacks. Carbon dioxide reforming of methane (CDRM) is a highly endothermic reaction which operates at extremely high temperatures, generally over 800 °C, in order to achieve higher reactant conversions with better product selectivity. However, after a certain temperature level, possible metal sintering and coke formation over the catalyst surface, *resulted mainly by the methane decomposition as it becomes thermodynamically impossible to prevent*, eventually lead deactivation of the catalyst (Abdullah *et al.*, 2017). Therefore, in order to eliminate these drawbacks, a thermally stable CDRM catalyst is needed.

Despite the downsides of CDRM, recent studies show that coke formation can be inhibited if (i) the reaction rates of carbon formation reactions and carbon oxidation reactions (i.e. CO gasification) are really close to each other and/or (ii) the formed carbon is forced to be dispersed over the catalyst surface rather than blocking the active sites of the catalytic surface (Aziz *et al.*, 2019). The research suggest that the former can be achieved via enhancing the molecular interaction between the supporting material and the active metal of the catalysts; while the latter can be attained via using a supporting material having a large surface area (Abdulrasheed *et al.*, 2019).

The main objective of this research is to design and develop (a) high performance Ni based CDRM catalyst(s) supported on mesoporous SBA-15. In this context, the main priority was given to suppression of carbon formation while maintaining the activity close to thermodynamic limit in order to achieve high and sustainable performance.

In the study, Chapter 2 consists of a detailed literature survey on CDRM and the catalysts used in the reaction and Chapter 3 illustrates the experimental work and setup. Results of the experiments and the characterization of the catalyst samples are presented and discussed in Chapter 4. Finally, the study is summarized and concluded in Chapter 5.

2. LITERATURE SURVEY

2.1. Carbon Dioxide Reforming Of Methane

Carbon dioxide reforming of methane (CDRM) is a more environmentally friendly utilization strategy to cope with the increasing GHG exploitation which has increased drastically in recent years. Unlike steam reforming of methane (SRM) and partial oxidation of methane (POX) which uses only CH₄, CDRM utilizes both CH₄ and CO₂ which are two of the most abundant and dangerous GHG to produce a safer fuel, hydrogen. The chemical reaction of CDRM is given below (Singh *et al.*, 2020).



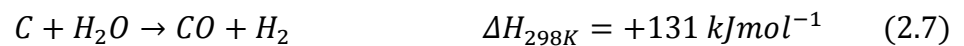
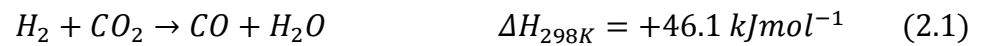
The products of the CDRM are hydrogen and carbon monoxide, which is called as the synthesis gas (syngas). Syngas generated by CDRM has a molar ratio of 1, different than SRM (ratio of 3) and POX (ratio of 2), which is appropriate to generate more valuable liquid hydrocarbons such as methanol, dimethyl ether and long-chain hydrocarbons via Fischer Tropsch Synthesis (FTS), oxo-synthesis and hydroformylation without requiring any purification (Park *et al.*, 2018).

Although syngas is a highly valuable product for generating valuable chemicals, hydrogen alone is one of the most vital components of the energy industry and it has attained increasing attention for the last century. Hydrogen can be used in numerous areas such Haber-Bosch ammonia process in fixation of nitrogen from the air, hydrogenation of fats and oils, methanol synthesis, welding and rocket fuels (Das *et al.*, 2019). However, in order to obtain pure hydrogen from the syngas stream, a purification process is needed.

Despite its advantages over SRM and POX, CDRM is not a widely used technology till this date in the industry. This is mainly caused by its long list of side reactions which are caused by its operation conditions. CDRM is a highly endothermic reaction which requires high energy input to operate with higher reactant conversions. CDRM operates at high temperatures over 600 °C, generally around 800 °C, and 1 atm pressure. One of the

drawbacks of the CDRM is metal sintering which is caused by exceeding Tamman temperature levels during the reaction in order to obtain higher conversions. Moreover, at this level, methane decomposition reaction (one of the side reactions of CDRM) occurs and creates a carbon layer over the active metal sites of the catalyst which blocks the feed to connect with the active sites and decreases the catalytic activity. Unfortunately, it is thermodynamically impossible to avoid carbon formation since it is favored at high temperatures (Abdulrasheed *et al.*, 2019).

The side reactions of CDRM can be listed as reverse water gas shift (RWGS, Eq. 2.1), carbon dioxide methanation (Eq. 2.2), steam reforming of methane (SRM, Eq. 2.3), carbon monoxide methanation (Eq. 2.4), CO disproportionation/Boudouard reaction (Eq. 2.5), methane decomposition (Eq. 2.6), coke acidification (Eq. 2.7), CO₂ hydrogenation (Eq. 2.8) and CO hydrogenation (Eq. 2.9).



According to the side reactions given above, there are different ways to end up with carbon deposition as well as loss of catalytic activity. Although carbon formation is inevitable for high temperatures, studies showed that coke formation can be limited by achieving high metal dispersion on the support surface. Hence, in order to commercialize the CDRM, a highly dispersed catalyst with high stability and activity for the CDRM is needed.

2.2. Catalysts Used for CDRM

In any chemical reactions, the bonds holding the reactants together must be broken in order to form another compound, called as the product. The minimum energy needed for breaking the bonds is called as the activation energy of the reaction, which is unique for every reaction.

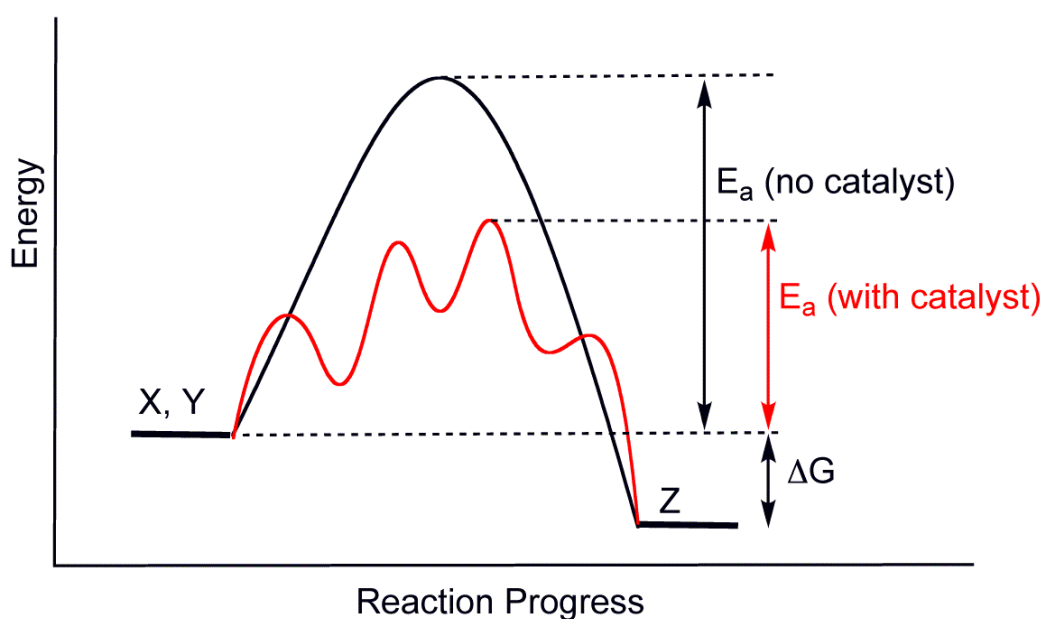


Figure 2.1. An Example for the Effect of Catalyst on the Minimum Energy

In the presence of a catalyst, one of the reactants undergoes a reaction with the catalyst and form a new product, different than the aimed one, called as the intermediate product. After the intermediate product is formed, it reacts with the other reactant and generates the desired product. Generally, this path has lower activation energy than

converting reactants directly. Hence, a catalyst is a substance that accelerates the reaction by decreasing the activation energy needed for the reaction (see Figure 2.1.). By using an appropriate catalyst, a reaction which may take years or decades to proceed can be handled within seconds.

Catalyst can be introduced either homogeneous or heterogeneous depending on the reaction. If a catalyst is in the same phase with both reactants and products, it is called as homogeneous catalyst. If not, then it is called as the heterogeneous catalyst. A catalyst is composed of 2 main parts; namely supporting materials and active metals. However, depending on requirements, a new component called as promoters can be added to the catalyst to improve its performance.

In the following sections catalysts that can be used in CDRM will be examined.

2.2.1. Active Metals and Promoters Used for CDRM

Although CDRM is a highly potent for carbon formation over the solid catalyst surface due to its endothermic nature, it is one of the essential processes for the chemical industry with its environmentally friendly ways to produce syngas.

On the other hand, from the industrial point of view, CDRM which operates at extremely high temperatures is not a cheap process. Hence, it is desired to operate lower temperatures than optimum reaction conditions. However, since carbon formation is thermodynamically inevitable above a certain level, known as the Tammann temperature level, couple of the carbon formation reactions such as Boudouard reaction and carbon dioxide hydrogenation is predominant at lower temperatures than optimum reaction temperature of CDRM. Hence the selection of the active metal for the catalyst is vital for activity and stability of the catalyst by limiting the reaction rate for the carbon formation.

In general, the active metal of the catalysts is preferred from the noble, precious metallic elements that are located in d-block of the periodic table. These metals are known to be platinum group elements (PGM) such as platinum, ruthenium, palladium, iridium and rhodium. These metals show high dispersion over the support surface which shows great

stability over the catalyst deactivation by limiting carbon formation. On the other hand cerium, zirconium, lanthanum and samarium are used as promoters in order to enhance the catalytic performance of the targeted catalysts.

The noble metals and their corresponding promoters are investigated in the subsection below.

2.2.1.1. Noble Metal Based Catalysts for CDRM

One of the widely studied noble metals is Ruthenium (Ru) (Pakhare *et al.*, 2013). studied the influence of the reaction temperature, varying from 525, 575 and 625 °C, on the activity of Ru and Pt based and La_2ZrO_7 supported mono metallic catalysts. Ru/ La_2ZrO_7 catalyst presented higher CH_4 and CO_2 conversion due to its lower activation energy and better metal dispersion over the catalyst surface. Furthermore, increased metal concentration over the La_2ZrO_7 support led a decrease in the coke formation rate. On the other hand, bimetallic Ru-Pt catalysts exhibited even higher stability but lower reactant conversions over the dry reforming reaction at 800 °C due to increased metal growth size caused by the Pt-Ru alloy (Singh & Madras, 2016).

Ru loading, varying from 0.75, 1.125 and 1.5% in weight, over the Co/SBA-15 catalyst at 790 °C reaction temperatures were studied in order to investigate the impact of the Ru amount to the catalytic performance (Jabbour *et al.*, 2014). It was stated that 1.125% Ru loaded catalyst showed the best performance for DRM by leading a decrease in the reduction temperature of the catalyst. Although it was highly stable for the first 20 hours, dramatic decrease in the activity occurred due to the coke deposition over the catalyst surface.

The effect of the Ru particle size on dispersion and catalytic activity was tested on $\text{ZrO}_2\text{-SiO}_2$ mixed oxide supported CDRM catalyst at high temperatures. It was found that smaller the Ru particles led higher the support-metal interaction and greater metal dispersions. Therefore, negligible coke formations and high catalytic activities were reported even with high reactant velocities (Li *et al.*, 2017).

In the means of Ru based catalysts, Shariatinia *et al.* (2016), showed the most promising results for CDRM with 3% Ru/CeZr_{0.5}GdO₄. The catalyst exhibited no carbon formation for 30 hours due to acidity of the supporting material and the influence of Zr addition which improved the CO₂ adsorption and thermal stability. Hence, the catalyst was completely stable for 30 hours.

Another study conducted by Khani *et al.* (2016), on the effect of Zr on Ru. Among Ni, Pt and Ru on the Zr doped LaAlO₄, Ru impregnated catalysts showed greater results in activity, stability and carbon resistance, even at high temperatures around 800 °C, due to the synergy between Zn and Ru.

Similar to ruthenium, rhodium (Rh) is also widely studied for CDRM. The study which investigated the catalytic activity of Rh on Zr grafted Al concluded that due to the high oxygen mobility led by Rh caused higher conversion and syngas yields along with good activity at moderate temperatures (Li *et al.*, 2017).

Another study was performed on Rh supported by alumina by Cimino *et al.* (2017), in order to see the effect of the addition of La₂O₃ as a promoter. It was stated that the addition of La improved the Rh dispersion over the alumina support and the interaction of Rh and La created a force that preserves the original basicity of the catalysts. Hence, additional basic sites were formed and favored the CO₂ activation that increased the conversion.

Rh and Pt based catalysts on La₂O₃ (L) and Al₂O₃-La₂O₃ (AL) supports were prepared and experimented in order to compare the performances of different noble metals on different supports. The best performance was shown by Rh/AL catalyst due to limited carbon formation caused by the nature of the noble metal. Moreover, although Pt-Ru/AL bimetallic catalyst showed increased reactivity, Rh-Pt interaction was weakened the stability over the carbon formation and caused metal sintering. The worst activity and stability was observed on Pt/L catalyst due to the lower dispersion of Pt over the support caused by weak interaction of La with Pt (Wu *et al.*, 2014). Additionally, Beltrán *et al.* (2017) showed a similar trend for Rh and Pt relation by testing Rh, Pt and Ru on different perovskites. It was concluded that Rh showed greater performance than both Ru and Pt due

to its high potential in dispersion over the catalyst support. Plus, all samples demonstrated minor activity losses over 65 hours due to the strong molecular structure of perovskites that minimizes the coke formation.

Platinum (Pt), one of the most expensive active metals, was analyzed to understand its effect on CDRM by using single oxide MgO, ZrO₂, CeO₂ and La₂O₃ metal supports. It was discovered that Pt disperses well on binary oxides, especially the combination of CeO₂ and La₂O₃, which increases the stability over coke formation and prevents it for the first 24 hours (Oliveira *et al.*, 2014). In order to see its influence over the bimetallic DRM catalysts, Li *et al.* (2015) conducted a study on Ni-Pt catalysts over different supports. Pt addition inhibited the coke formation and promoted the activity of catalyst even at extremely high temperatures, around 900 °C, since it favors CH oxidation and blocks carbon oxidation. This phenomenon is thought to be mainly caused by the alloy formed between Pt and Ni atoms.

Yentekakis *et al.* (2015) investigated the impact of different iridium (Ir) loadings, varying from 1 to 3 %, on CDRM with Al₂O₃, (A) Y₂O₃ doped ZrO₂ (YSZ) and CdO₃ doped CeO₂ (GDC) supports at 850 °C. It was exhibited that Ir loadings had no significant effect on the performance of the catalysts since Ir is highly active and stable. The best performance in syngas yield was observed in Ir/A whereby the best performance in stability is observed in Ir/GDC due to its higher surface mobility than A and YSZ supports. Additionally, another study was performed to understand the effect of La₂O₃ addition as a promoter to Ir/CeO₂ catalyst at temperatures between 500 and 800 °C. It was expressed that the addition of La promoter improved the oxygen storage capacity and created new active sites over the catalyst surface. Therefore, better Ir dispersion and strong thermal stability at were observed in the whole temperature range (Wang *et al.*, 2017).

Another supportive research was conducted for palladium (Pd) for low temperature CDRM with Pd over CeO₂ support at 350 °C. It was evinced that even at those low temperatures; methane conversion around 3.5% can be obtained due to good metal dispersion of small Pd particles and strong metal-support interaction (Singha *et al.*, 2017).

Different impregnation techniques for Pd based and Hydroxyapatite (HAP) supported CDRM catalysts at 650 °C were conducted to see their impact on metal dispersion. The catalyst impregnated with ion exchange method (IE) showed better results than incipient wetness method (IWI) due to the better metal dispersion over the catalyst support. Furthermore, the alkaline nature of HAP (pH value around 10) led one of best methane conversion levels up to 97% (Kamieniak *et al.*, 2017).

Gold (Au), one of the rarest and most expensive metals on earth, has a limited usage in catalyst world. However, Gao *et al.* (2017) investigated tri-metallic Ni-Au-Pt catalysts on 3 different supports as Al, Al-MgO and Al-Ce. The alloy formed by the tri-metallic structure strongly dominated the energy layer over the catalyst surface, caused well dispersed metal particles and increased the performance of all 3 catalysts. It was strongly stated that due to the alloy formation, the change in supporting material had no influence on the catalytic activity of the Au based dry reforming catalysts.

As it was mentioned above, these noble metals (Au, Pt, Rh, Ru, Ir and Pd) are very popular due to their high stability and activity; however, these metals are very expensive and rare. This is why non-PGM metals such as nickel and cobalt are preferred as the active metal of the CDRM catalyst in most cases. In the subsection below, Ni based catalyst and their corresponding promoters are examined.

2.2.1.2. Ni Based Catalysts for CDRM

Nickel (Ni) is the one of the most widely used active metal for CDRM catalyst owing to its high availability, low cost and high selectivity. Furthermore, due to its appropriate redox properties, Ni has high activity over dry reforming reaction. However Ni is highly prone to carbon deposition which results in a carbon layer covering the active sites of the catalyst causing dramatic activity loss and metal sintering. Moreover, additional coke deposition expands the catalyst bed significantly and causes severe operational problems during the reaction. Therefore, Ni based catalysts need to be improved to prevent carbon deposition (Kaydouh *et al.*, 2016).

Mono metallic Ni-Co and bimetallic Ni-Co based catalysts were studied at 700 °C, over oleyamine (Oam) and oleic acid silica supports. It was observed that the bimetallic catalyst has higher conversion and stability due to the alloy formed between Ni and Co particles which increase the metal dispersion over the catalyst support and prevent Ni from metal sintering and metal size growth. Hence, the catalyst performed a great stability for 30 hours with 79% CH₄ conversion (Kaydouh *et al.*, 2016). This study is assisted by another research, which conducted the same performance test with similar metal loading over mesoporous SBA-15 supports. Supportively, Ni-Co alloy formation and limited metal size growth were noted (Erdogan *et al.*, 2018).

Gaillard *et al.* (2017) investigated the performance of Ni based Al₂O₃ catalysts at extremely high temperatures, around 800 °C. The catalysts with different metal loadings showed significant activity, however after 30 hours, methane conversion decreased enormously to 40% due to metal sintering. Addition of molybdenum (Mo) decreased the reduction temperature and improved thermal stability. Furthermore, a separation between 2 metallic states which created an interatomic force to improved mechanical strength against the high volumetric flow rates was observed.

Ni was also tested in mixed metal oxide supports, to understand the influence of the metal-support interaction on oxidation routes of CDRM. Ni/MgO-SiO₂ and Ni/MgO-ZrO₂ catalysts were prepared and tested at 850 °C in similar reactant flow rated in different research groups. It was mentioned that MgO was incorporated in the inner walls of the both SiO₂ and ZrO₂ oxides, increasing strength against thermal and mechanical issues. Due to the interaction between Ni with SiO₂ and Ni with ZrO₂, resistance to carbon formation gained to prevent metal sintering. Both catalysts performed high stability for 40 hours with 80% and 97% methane conversions respectively (Titus *et al.*, 2016; Xu *et al.*, 2017).

These studies are assisted with another research, which strongly evinced that MgO decreased the carbon formation and increased stability up to 12 hours at 700 °C. However, all of these researches exhibited undesired H₂/CO molar ratio, lower than 1, approximately 0.60 (Ghods *et al.*, 2016).

As another support, ceria supported catalysts are also conducted in order to see the effect of the surface morphology. Ni/CeO₂ showed a great stability at 700 °C for 40 hours; however the methane conversion was lower as 70%. Addition of Gd provided a better dispersion of Ni particles by the interaction of Gd and Ni particles. Therefore, thermal stability of the catalyst increased up to 100 hours and methane conversion increased up to 78% (Gurav *et al.*, 2017).

Similarly, the impact of Ag addition was performed to enhance the performance of the Ni based DRM catalysts. It was stated that Ag addition inhibited the coke formation (both in whiskers and graphite forms) and promoted the coke gasification to form CO₂ on the catalyst surface. Although the bimetallic catalyst was stable over 100 hours, the activity of the catalyst was not great since H₂/CO ratio was 0.46 at 760 °C (Yu *et al.*, 2015).

2.2.1.3. Promoters Used for CDRM Catalysts

Besides using bimetallic catalysts for CDRM, another research area has gained an increasing attention in catalyst promoters. Ni based catalysts were tested on perovskites with using La as promoter at 800 °C. It was found that the catalyst was more active any stable due to the strong interaction between Ni and La. Plus, the catalyst showed minor activity losses during the process for 70 hours with 70% methane conversion and 0.95 H₂/CO ratio (Zubenko *et al.*, 2017). Similarly, La was used as a promoter for Al₂O₃ supported Ni catalyst at 750 °C. Enhancement of medium strength basicity and generation of Ni⁺² ions which is the most active form of Ni on the catalyst surface was observed. Therefore, the performance of the La promoted catalyst increased both conversion and stability considerably (Zhang *et al.*, 2017).

Samarium promoted Ni/SBA-15 catalysts were investigated with different Sm:Ni ratios at 700 °C. Samarium promotion improved the particle distribution size and increases the Ni dispersion over the mesoporous SBA-15 support. Due to the strong support-metal interaction, the activity of the promoted catalyst increased to 58% CH₄ conversion and stability for 12 hours. However, Sm promotion had no important effect on syngas yield with a 0.78 H₂/CO ratio (Taherian *et al.*, 2017).

Ceria, one of the most widely used catalyst promoters for CDRM, was tested on Ni based and alumina supported catalysts with different Ce loading at 700 °C. It was found that the optimum Ce loading was 5%, and Ce was tend to locate itself into the weaker sides of the support and increased both stability and activity of the catalysts by creating new active sites for the reaction. However, ratio of 0.99 for H₂/CO was obtained with 70% CH₄ conversion (Movasati *et al.*, 2017).

One of the most promising results for the low temperature methane dry reforming reaction was found by Yao *et al.* (2016) using Zr as a promoter to Ni based and SiO₂ supported CDRM catalyst at 450 °C. Although mono metallic Ni/SiO₂ catalyst showed no activity at 450 °C, introduction of Zr as a promoter improved the catalytic activity up to 6.5% methane conversion with a H₂/CO ratio of 0.6. This research created a new area for low temperature dry reforming studies.

2.2.2. Supports Used for CDRM

As it is strongly influenced by the active metal and promoters, the catalytic activity is also affected by the supporting material chosen. Owing to their physical and chemical properties such as oxygen vacancy, acidity and pore volume; supports contribute to active metal dispersions over the surface and the metal-support interaction. In general, supports are not chemically active materials; however, by introducing active sites, they can be used in chemical reaction (Aziz *et al.*, 2019).

For CDRM, there are various types of support has been tried till this date, categorized as single metal oxide supports such as SiO₂, Al₂O₃, MgO, ZrO₂, TiO₂, La₂O₃; mixed metal oxide supports such as La₂O₃-ZrO₂, CeO₂-ZrO₂, CeO₂-Al₂O₃, MgO-Al₂O₃, CaO-ZrO₂, ZrO₂-Al₂O₃; ordered mesoporous or microporous silica supports such as SBA-15, SBA-16, MCM-41, MSN, HMS, MFI and Y; and clay-type supports such as natural clay, synthetic clay and active carbon.

For the sake of comparison, Ni based mono metallic catalysts without any promotes are chosen to investigate the effect of the supporting material over the catalyst performance in the means of catalytic activity and stability under similar reaction conditions.

Throughout the history of dry reforming reactions, metal oxide type Ni based catalysts are studied due to their unique physicochemical properties. In order to understand the differences between the certain single metallic oxides, including SiO_2 , Al_2O_3 , MgO , ZrO_2 and TiO_2 , the series of NiO based catalysts were synthesized and experimented under atmospheric pressure and at 800 °C. The results showed encouraging activities in both Ni/ Al_2O_3 with 63% CH_4 conversion and Ni/ MgO with 50% CH_4 conversion which was presumably caused by their alkaline properties which increased their CO_2 adsorption potential. On the other hand, Ni/ TiO_2 catalyst resulted in a much poorer CH_4 conversion, around 5% at 800 °C, which was mainly caused by the surface area of the support being extremely lower than other causing an impotent metal-support interaction and metal dispersion over the catalyst surface (Han *et al.*, 2017). Another study was conducted by Zhang *et al.* (2015), concluding with better performance on NiO based catalyst on MgO modified Al_2O_3 support with methane conversion higher than 85%. The study indicated that due to its convenient surface morphology and interaction with the active metal, Al_2O_3 led better NiO dispersion and stabilization on CDRM reaction route. Additionally, for NiO/ TiO_2 samples, greater metal growth was observed due to the weaker metal-support interaction between TiO_2 and Ni.

Although some of the single metal oxides show remarkable activity, there are large number of oxide those cannot reach desirable levels. By combining them with each other, it is possible obtain a high-performance mixed oxide supports that can be used in CDRM systems. The mixed oxide La_2O_3 - ZrO_2 supported Ni catalysts evinced more exclusive results as 51.25% of CH_4 conversion at 750 °C, than both of its single oxide components as 40% and 35% methane conversions respectively. Similarly, Ni/ CeO_2 - ZrO_2 catalyst exhibited better stability than both of the single oxide supported ones, up to 28 hours at 750 °C owing to the formation of alloy that increases the ion exchange rate leading a better metal dispersion over the catalyst surface (Goula *et al.*, 2017). Furthermore, in the low temperature dry reforming case, Ni/ ZnO - Al_2O_3 catalyst were prepared with varying from 0.09 to 1.78 Zr/Al ratios and tested at 400 °C both of which had superior catalytic performance over their single metal oxide supported catalysts. It was stated that a catalyst with a Zr/Al ratio greater than 1 showed higher catalytic activity than those with a ratio lower than 1 due to the rapid formation of Zr-Al alloy which has higher oxygen vacancy. However, those have a Zr/Al ration lower than one exhibited a higher stability, reaching up

to 120 hours, since Zn rich samples were prone to rapid sintering due to coke formation over its active sites while Al rich samples not (Sokolov *et al.*, 2017).

Besides metal oxide type supports, numerous studies have been conducted on zeolites, especially ordered microporous and mesoporous silica because of their surface morphologies such as high surface area and ordered pore size distributions. Furthermore, the textural properties of zeolites can easily be reshaped by using various additives which makes them one of the best alternative catalyst supports for CDRM. To compare zeolites with single oxides, Drobná *et al.* (2017) conducted a research on Ni based catalyst over SBA-15, MCM-41 and Al₂O₃ supported catalysts towards dry. The experiments exhibited that the support type had significant impact on the catalytic performance, both in activity and stability. The study concluded that along with MCM-41, SBA-15 showed extremely higher conversions, around 85%, than Al₂O₃ supported catalysts at 750 °C due to their higher surface areas which leads greater Ni dispersions over the catalyst surface. However, both of the mesoporous silica supports suffered from deactivation, due to the carbon formation over the active sites and increasing Ni growth both of which decreases the metal support interaction.

In order to eliminate the performance issues of the mesoporous silica supports, various studies have been focused on reducing the particle size. Mourhly *et al.* (2020) reported the advantages of mesoporous silica nanoparticles (MSN) by using Ni/MSN on CDRM. MSN exhibited more favorable textural properties, owing to its higher porosity which enables to increase the surface area and pore volume of the mesoporous material. Furthermore, Ni/MSN showed promising performance, around 92% methane conversion at 750 °C. However, similar to SBA-15 and MCM-41, MSN was not stable for long time due to weaker metal-support interaction.

As in the active metal selection, supporting materials including all those are synthesized chemically are expensive. However, some of those materials can be found in nature, easier than thought, such as clay-type supports. Natural clays can be attributed as an interesting option for catalyst supports, owing to its naturally availability, lower cost and specific physical and chemical properties. Although natural clay supported catalysts were not catalytically active, they showed promising activity at higher temperatures. At

800 °C, due to its convenient physicochemical properties, Ni/clay successfully initiated the DRM with 78% and 67% carbon dioxide and methane conversions respectively. Since clay has inadequate electrochemical properties, Ni/clay catalysts exhibited worse stability than zeolites and metal oxides. Hence, natural clay supported catalysts requires additives, such as promoters (Liu & Zhang, 2018).

Furthermore, clay-type supports can be synthesized with desired properties especially surface area, pore size, pore volume and intrinsic basicity, known as the synthetic clays which can enhance the catalytic performance in a long temperature range. For example, the surface area of the natural clay is generally around 55 m²/g, whereas synthetic clays approximately have 600 m²/g surface areas. Most of the research that are aimed at synthetic clays consists of 2 types of synthetic clays, namely hydrotalcite-like compound (HTLC) and layered double hydroxides (LDH). Both of the synthetic clay showed promising results, especially in methane conversion reaching up to 85% and stability over 320 hours, owing to their adjusted physicochemical properties (Lin et al., 2015). Additionally, activated carbon (AC) is also one of most widely used catalyst supports owing to its higher surface areas, generally over than 800 m²/g, high porosity and low price. Although activated carbon is strongly resistance to coke formation and metal sintering, at higher temperatures, Ni/AC catalyst showed no remarkable conversion values and syngas yield (García *et al.*, 2015).

3. EXPERIMENTAL WORK

In this study, the experimental setup can be divided into 3 main groups, which can be listed as catalyst preparation systems, catalyst characterization systems and the performance test system.

Catalyst preparation systems can be classified in 2 different parts. These are impregnation system on which the desired amount of active metal injected on the supporting material, also known as the incipient wetness impregnation method, and the water bath system on which the first part of the synthesis of the supporting material initiated. After starting the mesoporous silica preparation, the preparation process continues with autoclave reactor, filtration and calcination steps.

Among numerous catalyst characterization methods, scanning electron microscopic imaging (SEM), X-ray diffraction (XRD), Raman spectrometry, X-Ray Photoelectron Spectroscopy (XPS) and Brunauer-Emmet-Teller (BET) methods are performed in order to investigate different properties of the catalyst such as surface morphology, crystalline structure, surface area, pore volume, pore size distribution, elemental analysis and coke formation on the surface.

These characterization methods help concluding the experimental results and compare them with each other to obtain the superior catalyst that is the most suitable for catalytic dry reforming of methane reaction.

The performance test system is composed of three main components as feed section where the inlet stream is mixed with the desired ratios, reaction section where gaseous products go through a reaction on the selected catalysts and analysis section where the composition of the outlet stream is measured by a mass spectrometer.

3.1. Experimental Setup

Three components of the experimental setup used in the scope of thesis are examined in detail in the following section.

3.1.1. Catalyst Preparation System

The catalyst impregnation system is composed of two different blocks which are used in impregnation steps for catalyst preparations and synthesis of supporting materials, mesoporous silica sieve SBA-15.

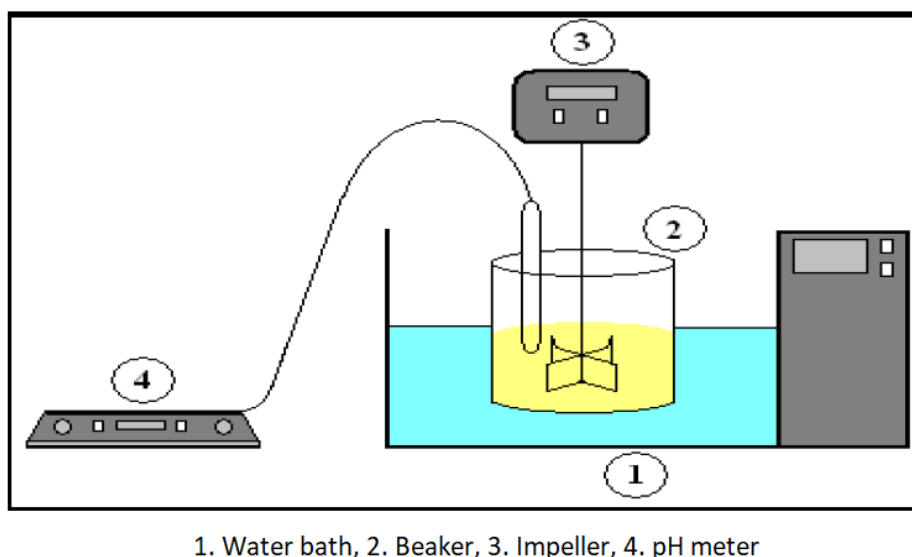
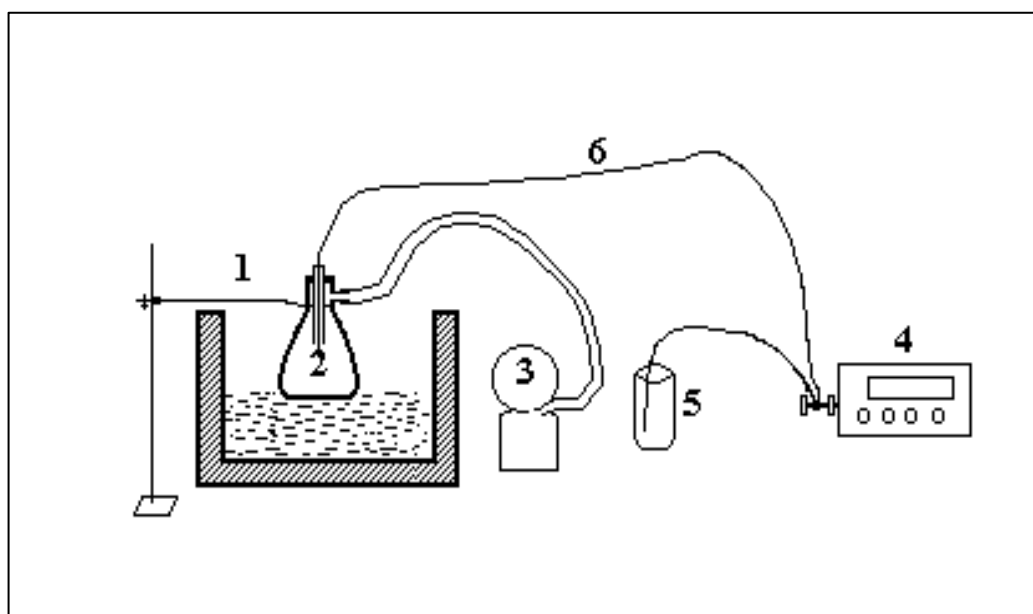


Figure 3.1. Reaction system for SBA-15 synthesis

The catalyst preparation processes start with the synthesis of the supporting material, which is performed in the water bath system shown in Figure 3.1.

Water bath system consist of a water bath filled with distilled water, a stainless steel impeller, a beaker as a reactor and pH meter and it is used to initiate a reaction in order to synthesize SBA-15 supporting materials. After using water bath system, synthesized SBA-15 materials are treated with heat in an autoclave reactor.



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

Figure 3.2. The impregnation system used for catalyst preparation

The second part of the catalyst preparation system is the impregnation system on which the desired amount of metal is loaded inside the pores of the supporting material which can be seen on Figure 3.2.

The impregnation system is for incipient-wetness impregnation (IWI) method, consisting of an ultrasonic mixer, a Buchner erlen, a vacuum pump, a peristaltic pump, a small tank that is filled precursor solution and silicon tubing for connection. The same system is used for all the catalysts that are prepared with incipient-wetness impregnation method.

3.1.2. Catalyst Characterization Systems

In the scope of this thesis, multiple different characterization techniques such as scanning electron microscopic imaging (SEM), X-ray diffraction (XRD), Raman spectrometry, X-Ray Photoelectron Spectroscopy (XPS) and Brunauer-Emmet-Teller (BET) are used.

X-Ray Diffraction (XRD): The crystalline structures of all of the synthesized SBA-15 batches were investigated by using XRD equipment (Rigaku DMAX) before the impregnation and pre-treatment processes. The main reason of XRD analysis was to compare the synthesized SBA-15 materials with the ones used in the literature as well as to compare them with each other.

Brunauer-Emmett-Teller (BET) Analysis: All of the synthesized SBA-15 batches were analyzed in BET in order to obtain their textural properties such as surface area, pore volume, pore size distribution and wall thickness. When the most suitable route was set for the SBA-15 synthesis, BET analysis assured that all of the synthesized batches have similar properties with each other. Furthermore, the analysis enabled to compare the effects of the additives which were used to arrange the surface morphology of the molecular sieves.

Raman Spectrometry: The carbon depositions over the surface of all the catalysts and freshly reduced sample of different catalysts were analyzed by using the Raman Spectrometry (Renishaw inVia Microscope). The results were used in the explanation of the catalyst deactivations in the experiments by metal sintering.

Scanning Electron Microscope (SEM) Imaging: The carbon formations over the surfaces of the spent catalysts as well as the surface morphology of the different SBA-15 samples were investigated by using SEM imaging technique in order to understand the influence of the additives that were used to increase the pore volume and homogenize the pore size distributions.

X-Ray Photoelectron Spectroscopy (XPS): The elemental analysis over the chosen catalyst samples (both freshly reduced and spent samples) and analysis of the chemical states of the present elements were conducted via XPS. Therefore, loss of the active phase of the catalyst surface and generation route for the carbon deposition were analyzed and compared with each other.

All of the characterizations methods were performed at the Advanced Technologies Research and Development Center of Boğaziçi University.

3.1.3. Performance Test System

The catalytic methane dry reforming system was designed and constructed at Boğaziçi University Chemical Engineering Department. Although CDRM system has 2 different furnaces that enable performing 2 sets of reactions both in parallel and series mode, the system was modified to work with only one of the furnaces to perform CDRM.

The reaction system consists of 3 main parts; namely feed section, reaction section and product analysis section all of which are connected to each other by stainless steel tubes with diameters of 1/4, 1/8 and 1/16 inches.

The feed section is mainly composed of gas tubes of CO₂, CH₄, CO, H₂, He and N₂, which take place either in reaction or calibration. All of the tubes are connected to their corresponding mass flow controller devices (MFCs) independently with 1/16 inch tubing materials which are made of either copper (for CO, H₂, He and N₂) or stainless steel (for CO₂ and CH₄ which may be used in higher pressures). All of the mass flow controllers are fixed on a rectangular prism shape box made of plexiglass with on-off valves attached to them. With this way, it is easier to control flows of gases and to prevent back flows.

The gas flow can be directed on a soap bubble in order to calculate the total volumetric flow rate of the flow for double checking or calibration purposes. Before the flow enters the furnace, the tubing is modified to a certain spiral-shape in order to develop a well-mixing area by decreasing the tube diameter from 1/4 inch to first 1/8 and then 1/16 inches gradually. This mixing area is required to obtain a homogeneous gaseous mixture inlet. Lastly, the inlet gaseous flow goes through a heating area which is heated by heating bands, checked by thermocouples and insulated by glass wool and aluminum foil. After the pre-heating process is done, the flow can either be sent directly to the reactor or it can be bypassed and sent to analysis in order to see its gas composition or volumetric flow rate.

The second part of the CDRM system is called as the reaction system which is composed of a furnace with an upper limit of 1300 °C and a micro reactor. The furnace is one of the typical heating tube furnaces made by Protherm, which stands vertically. The

furnace has its own thermocouple which can adjust temperature with ± 0.1 K standard deviation.

The micro reactor is made of quartz glass, which is strongly resistant to heat, with 10 mm inner diameter and 780 mm length. There is a small notch which divides the reactor into 2 pieces with 350 mm and 430 mm in length. The notch is used to fix 10 mm of height quartz wool on which the catalyst is put which is known as the catalyst bed.

In order to connect the quartz reactor and stainless steel tubing at both ends, a stainless steel fitting is constructed with CNC machines and welded to 1/4 inch tubing. Both fittings have 10.5 mm inner diameter, 50 mm outer diameter and 30 mm height. In order to seal the reactor, O-ring made of viton is put inside the fittings. Both ends of the furnace are insulated with cylindrical-disk shaped insulators in order to prevent the heat loss which could affect the temperature profile of the reactor.

After the reaction, the outlet gas low flow is directly sent to a cold trap unit which is designed to catch the H₂O flow if there is any. H₂O may condense and plug the tubing or it may go the analyzer and jeopardize the results. Therefore, although there is no H₂O pumped to the reaction system, cold traps are required.

The outlet flow, also referred as the product flow, can be conveyed to soap bubble or to the analyzer, the mass spectrometer (MS). If the flow is sent to the soap bubble, it is directed to the exhaust pipes after its total volumetric flow is measured. Otherwise, the outlet stream goes to the mass spectrometer.

The mass spectrometer (Hiden Analytical HPR-200) is equipped with a Faraday detector and an 8-way manifold system which is connected to a computer with the required software. The mass spectrometer is used to measure concentrations of all the gases in the product stream (or the inlet stream if needed) on line.

The flowsheet of the whole system is shown in Figure 3.3.

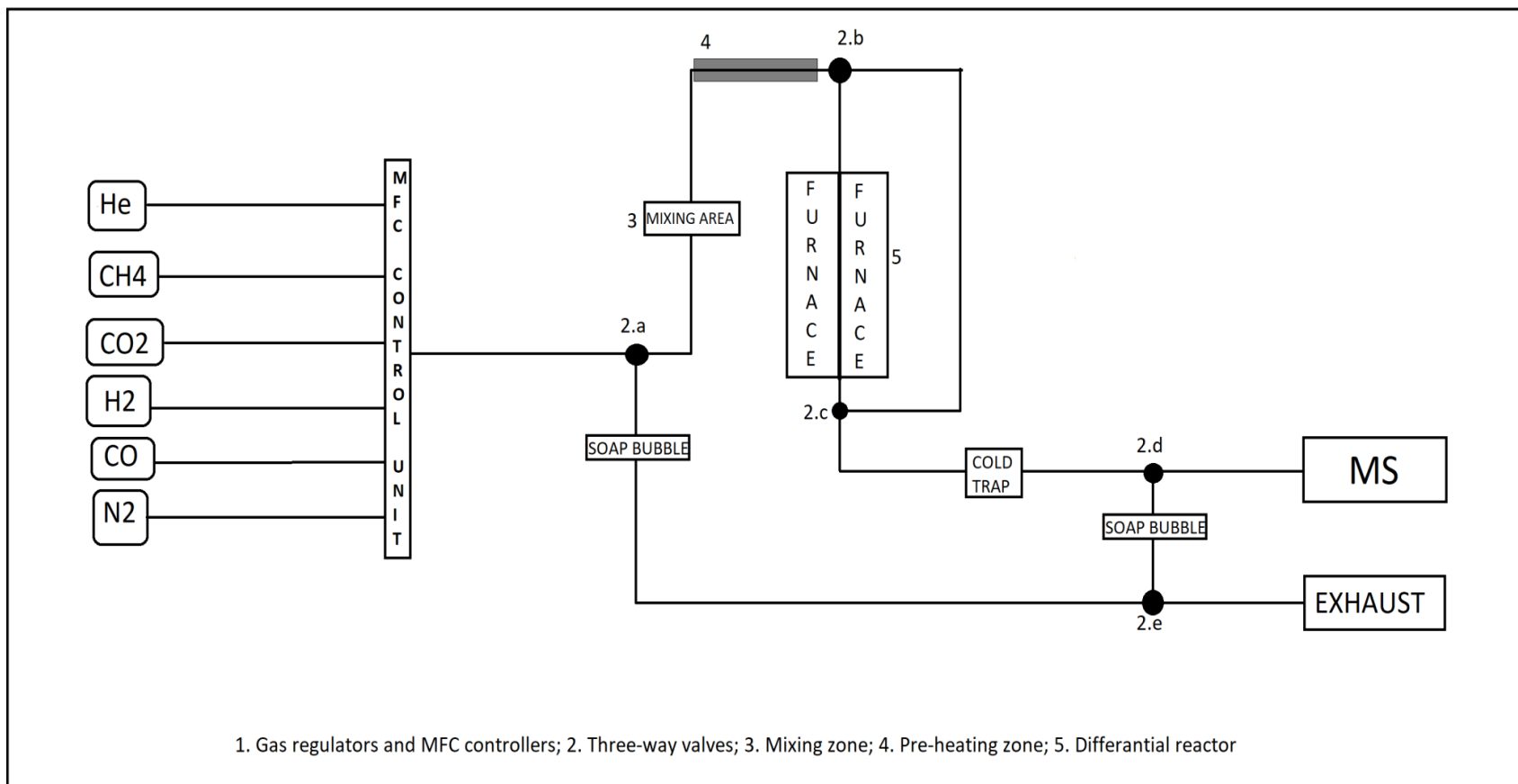


Figure 3.3. The flow sheet of the CDRM reaction system

3.2. Catalyst Preparation

3.2.1. Materials

All of the chemicals and gases that are used in scope of this study are given in the tables below (Tables 3.1-3.3) with their specifications and application areas.

Table 3.1. Chemicals used in SBA-15 synthesis

Chemicals	Formula	Phase	Source
Deionized Water	H ₂ O	Liquid	In-house
Hydrochloric Acid	HCl	Liquid	Alfa Aesar
Pluronic (P123) Acid	(EO) ₂₀ (PO) ₇₀ (EO) ₂₀	Solid	Merck
Tetraethyl Ortho-Silicate	Si(OC ₂ H ₅) ₄	Liquid	Alfa Aesar
Cetyl Trimethyl Ammonium Bromide	C ₁₉ H ₄₂ BrN	Solid	BSH
1,3,5-trimethyl benzene	C ₉ H ₁₂	Liquid	Alfa Aesar
Ethanol	C ₂ H ₅ OH	Liquid	Merck

Table 3.2. Chemicals used in catalyst preparation

Chemicals	Formula	Phase	Source
Deionized Water	H ₂ O	Liquid	In-house
Nickel (II) Nitrate Hexahydrate	Ni(NO ₃) ₂ ·6H ₂ O	Solid	Merck

Table 3.3. Gases that are used in the reaction system

Gases	Specification	Application
Methane	99.5 % BOS	Reactant, MS Calibration
Carbon dioxide	99.995 % BOS	Reactant, MS Calibration
Hydrogen	99.99 % BOS	Reduction, MS Calibration
Carbon monoxide	99.999 % BOS	MS Calibration
Helium	99.999 % BOS	Inert, MS Calibration
Nitrogen	99.998 % BOS	Calcination, MS Calibration

3.2.2. Synthesis of the Supporting Material

SBA-15 is one of the porous materials used as the supporting material for various catalytic reactions such as selective oxidation, hydrodesulphurization and biomass transformation. Along with MCMs, SBA-15 is located in the mesoporous subsection of the porous materials owing to its pore size ranging from 2 to 50 nanometers.

In this study, 3 different types of SBA-15 were synthesized, impregnated and tested for CDRM under different reaction conditions. All of the mesoporous SBA-15 materials used in this study were synthesized by the hydrothermal method which firstly suggested by Zhao *et al.* (1998).

After numerous trials, it was discovered that in order to synthesize the SBA-15 molecular sieves, a strongly acidic media especially with a pH value of 1 or less is required. A pH value between 2 and 7, despite of its acidity, inhibited SBA-15 synthesis and led disordered molecular sieves.

To synthesize mesoporous SBA-15, one of the varieties of the pluronic acid, also known as nonionic pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) was used as the structure-directing agent along with tetraethoxysilane ($\text{SiC}_8\text{H}_{20}\text{O}_4$) which was used as the silica source for the mesoporous silica.

The acidic media was created by using 60 grams of hydrochloric acid (HCl, 2M) and 30 grams of deionized water, which was used to dissolve 4 grams of pluronic acid in a beaker. However, P123 could not be dissolved easily in the acidic solution; hence an impeller was used with 500 rpm. The dissolution process took around 2 hours, depending on the room temperature. It was observed that an increase in the temperature of the solution (i.e. putting the beaker in the water bath) aided the dissolution process, however, it is not suggested because rapid dissolution in the acidic solution decreases the yield of SBA-15 synthesized.

After approximately 2 hours of mixing, the solution was checked with blue light to observe if the P123 was dissolved completely. If there was an indication of bright reflections from the solution, the stirring process was continued, if not, the beaker was put in the water bath at 35 °C and 8.5 grams of TEOS was added to the solution drop by drop. During the TEOS addition, the solution kept being stirred with 500 rpm. After TEOS was added, the solution was stirred for 20-24 hours. Note that it is highly important to add TEOS drop by drop because it was observed that pouring TEOS at once caused spherical bulk TEOS formations insulated from the P123 solution by a gel-like layer. Since TEOS was not able to interact with P123, the synthesis could not be initiated.

When the 20 hours stirring was finished, the pre-SBA-15 solution mixture was taken from the water bath and put to rest for approximately 20 minutes until the color separation in the mixture occurs. On the top of the solution with the lighter density, bubble formation was observed. The resting process also helped the bubbles to pop and obtain SBA-15 particles easily.

After the color separation occurred, the mixture was poured into the Teflon autoclave which is supported by stainless steel outside. The autoclave was sealed by an O-ring made of viton to prevent material loss which could cause rusting of the autoclave. The autoclave was put in a furnace at 90 °C for 48 hours, leading the second phase of the reaction between P123 and TEOS under higher pressures.

Since the autoclave was hot, it was put to rest for couple of hours to cool down before it was opened. Reaction in autoclave generated SBA-15 particles with larger sizes

inside the dark green solution. In order to get rid of the green solution, a filtration system composed of a vacuum pump, a filter paper, a funnel and a dust-catching beaker was set. The solution was poured on the filter paper, and washed with plenty of deionized water and ethanol until the green color of solution was gone, around 12 times each. It was observed that the deionized water was the main element to remove the green solution, whereas ethanol inhibited the bubble formation by influencing the surface tension. Hence, starting filtration with deionized water was a better option.

The filtrated SBA-15 residue was again put in the furnace at 80 °C for overnight (for approximately 12 hours). Then, it was separated from the filter paper and smashed with a spoon to break its lump structure. Lastly, it was calcined in a muffle furnace at 550 °C with a ramping rate for 1 °C/min for 6 hours. The calcination process was chosen among numerous trials which were thought to be the best for dry reforming of methane reaction. The samples synthesized with this main synthesis route were denoted as SBA-15 to prevent any confusion in the experiments.

Additionally, as it was mentioned above, by modifying the main SBA-15 synthesis method, 2 different types of SBA-15 sieves were synthesized in scope of this thesis. The first modification was aimed to increase the pore sizes and mechanical strength by enhancing the wall thickness of the mesoporous silicas with the addition of 6.5 grams 1,3,5-tri methyl benzene (TMB) as a swelling agent to the mixture, just before the TEOS was injected to the solution. The rest of the procedure remained the same. The supports synthesized by this method were denoted as TMB_SBA-15.

Similar to the previous one, the second modification was targeted to enhance the porous structure of the mesoporous silica, favoring generation of uniformly-sized hexagonal shaped pores (see Figure 3.4.) as in the synthesis of MCM-41 case, with the addition of 10 grams cetyl-trimethyl ammonium bromide (CTAB) as a co-surfactant before the TEOS injection procedure. Other parameters of the synthesis route remained the same. The supports synthesized with this method were denoted as CTA_SBA-15.

The impacts of the different SBA-15 types on the performance of Ni catalyst for the carbon dioxide reforming of methane reaction are investigated in the discussion part.

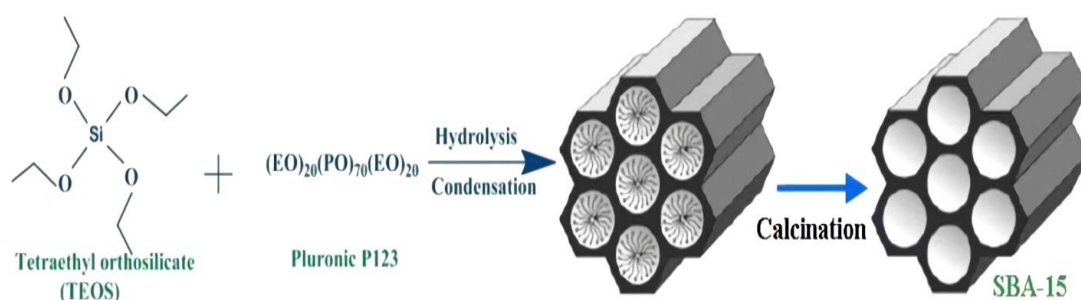


Figure 3.4. The synthesis route of SBA-15 (Chaudhary & Sharma, 2017)

3.2.3. Preparation of the Catalysts

All the catalysts designed and prepared for this study were prepared by 2 different impregnation methods, namely incipient wetness impregnation method (IWI) and two-solvent impregnation method (TSI).

The incipient wetness method was performed in the impregnation system given in the Section 3, Figure 3.1. For all the impregnation runs, approximately 1 gram of calcined SBA-15 was weighed and put in a Buchner erlen. The Buchner erlen was fixed on the top of the water inside the ultrasound mixer, and mixed for 30 minutes under high vacuum in order to empty the pores of the support filled with air. During this process, appropriate amount of Nickel precursor, for 7.5, 10 and 15 mass percent nickel, Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), dissolved in a certain amount of water which is slightly enough to wet the support. The precursor solution was impregnated on to the support with a peristaltic pump supported injector with a flow rate of 0.4 mL per second. After the impregnation was complete, the impregnated sample was kept on the ultrasonic mixer and vacuumed for another 90 minutes and then the impregnation process was stopped. At the end, the Buchner erlen was put in the furnace at 110 °C, in order to vaporize the excessive water. Then the dried sample was sent to calcination in a muffle furnace or to the system (if calcination under nitrogen flow was needed) with varying temperatures, ramping rates and calcination durations.

For some of the catalysts, two solvent impregnation methods was used to understand the influence of the impregnation technique on the CDRM performance of the Ni based catalysts. Two solvent impregnation method did not require a special system,

since it was performed by using simple erlens. First of all, 3 grams of calcined SBA-15 was weighed and dissolved in 10 mL of deionized water by using a magnetic stirrer. The stirring process took around 24 hours since the SBA-15 particles dissolved in water completely. Similar to dissolution of calcined SBA-15, the desired amount of Nickel precursor was dissolved in ethanol in order to prepare Ni based catalysts with 7.5, 10 and 15 mass percent. Then the Nickel solution was injected to the SBA-15 solution drop by drop while stirring. After the injection, the impregnated sample was mixed for another 24 hours at the room temperature then it was put in a furnace at 110 °C for overnight. Finally, the dried sample was sent to calcination in a muffle furnace.

The prepared catalysts were tested and the results of their performance tests along with their characterizations are discussed in the discussion part.

3.2.4. Pretreatments for the Catalysts

All of the catalysts were calcined after the impregnation either in-situ in the air with a gas flow rate of 10 mL/min or under the nitrogen flow in the reaction system with a gas flow rate of 10 °C. The calcination temperatures were 650, 700, 750 and 800 °C depending on the experiments and the reaction temperature. Similar to calcination process, all of the catalysts were reduced in hydrogen flow with a gas flow rate of 50 mL/min. Reduction in hydrogen flow was performed in situ right before the reaction, at different temperatures (650, 700, 750, 800 °C) with a ramping rate of 10 °C/min. After the reduction procedure, the hydrogen gas was wiped out from the reaction system with helium gas before the reaction initiated. The properties of all the catalysts that are tested, such as calcination and reduction temperatures, are given in Table 3.4.

3.3. Reaction Tests

3.3.1. Blank Test

After system was constructed, a blank test was conducted without using a catalyst to understand if the quartz micro reactor and the quartz wool used for fixing the catalyst bed would affect the outcome. At the end of the blank test, the results indicated that the

quartz part of the CDRM reaction system was inert, even at extremely high temperatures; hence the experiments could start safely.

3.3.2. Performance Tests

Ni/SBA-15 catalysts were prepared and treated in order to understand the effect of metal loading of the catalyst, calcination procedure including calcination temperature, ramp, gas and duration, reduction, reaction and overnight temperature, support additives and impregnation method. For all the performance tests, reduction was performed under hydrogen flow for 2 hours with 90 milligrams of catalyst. Furthermore, the inlet volumetric flow rate was set to 60 milliliters per minute with 1:1 methane to carbon dioxide ratio (15 mL/min methane, 15 mL/min carbon dioxide, 30 mL/min helium).

Table 3.4. Performance Tests with Corresponding Catalyst Preparation Routes, Reaction and Reduction Conditions

Exp	Catalyst	Calcination Procedure for the Catalyst	Reduction Temp. (°C)	Reaction Temp. (°C)
1	10% Ni/SBA-15 (Impregnated with IWI Method)	750°C for 6 hours with 2 °C/min ramping rate in air	750	750
2	10% Ni/SBA-15 (Impregnated with TSI Method)	750°C for 6 hours with 2 °C/min ramping rate in air	750	750
3	10% Ni/SBA-15 (Impregnated with IWI Method)	750 °C for 6 hours without any ramping rate in air	750	750
4	10% Ni/SBA-15 (Impregnated with TSI Method)	750 °C for 6 hours without any ramping rate in air	750	750

Table 3.4. Performance Tests with Corresponding Catalyst Preparation Routes, Reaction and Reduction Conditions (cont.)

Exp	Catalyst	Calcination Procedure for the Catalyst	Reduction Temp. (°C)	Reaction Temp. (°C)
5	10% Ni/SBA-15 (Impregnated with IWI Method)	550 °C for 6 hours without any ramping rate in air	750	750
6	10% Ni/SBA-15 (Impregnated with IWI Method)	650 °C for 6 hour with 2 °C/min ramping rate in N ₂ flow	750	750
7	10% Ni/SBA-15 (Impregnated with IWI Method)	700 °C for 6 hours with 2 °C/min ramping rate in air	750	750
8	10% Ni/SBA-15 (Impregnated with IWI Method)	750 °C for 2 hours with 2°C/min ramping rate in air	750	750
9	10% Ni/SBA-15 (Impregnated with IWI Method)	750 °C for 6 hours with 2°C/min ramping rate in N ₂ flow	750	750
10	10% Ni/SBA-15 (Impregnated with IWI Method)	750 °C for 6 hours with 2 °C/min ramping rate in air	700	750
11	10% Ni/SBA-15 (Impregnated with IWI Method)	750°C for 6 hours with 2 °C/min ramping rate in air	650	750
12	10% Ni/SBA-15 (Impregnated with IWI Method)	750°C for 6 hours with 2°C/min ramping rate in air	750	700

Table 3.4. Performance Tests with Corresponding Catalyst Preparation Routes, Reaction and Reduction Conditions (cont.)

Exp	Catalyst	Calcination Procedure for the Catalyst	Reduction Temp. (°C)	Reaction Temp. (°C)
13	10% Ni/SBA-15 (Impregnated with IWI Method)	750°C for 6 hours with 2°C/min ramping rate in air	700	700
14	10% Ni/SBA-15 (Impregnated with IWI Method)	750°C for 6 hours with 2°C/min ramping rate in air	750	650
15	10% Ni/SBA-15 (Impregnated with IWI Method)	750°C for 6 hours with 2°C/min ramping rate in air	750	800
16	15% Ni/SBA-15 (Impregnated with IWI Method)	750°C for 6 hours with 2 °C/min ramping rate in air	750	750
17	7.5% Ni/SBA-15 (Impregnated with IWI Method)	750°C for 6 hours with 2 °C/min ramping rate in air	750	750
18	15% Ni/SBA-15 (Impregnated with IWI Method)	750 °C for 6 hours without any ramping rate in air	750	750
19	7.5% Ni/SBA-15 (Impregnated with IWI Method)	750 °C for 6 hours without any ramping rate in air	750	750
20	15% Ni/TMB_SBA-15 (Impregnated with IWI Method)	750°C for 6 hours with 2 °C/min ramping rate in air	750	750

Table 3.4. Performance Tests with Corresponding Catalyst Preparation Routes, Reaction and Reduction Conditions (cont.)

Exp	Catalyst	Calcination Procedure for the Catalyst	Reduction Temp. (°C)	Reaction Temp. (°C)
21	15% Ni/CTAB_SBA-15 (Impregnated with IWI Method)	750°C for 6 hours with 2 °C/min ramping rate in air	750	750
22	7.5% Ni/TMB_SBA-15 (Impregnated with IWI Method)	750°C for 6 hours with 2 °C/min ramping rate in air	750	750
23	7.5% Ni/CTAB_SBA-15 (Impregnated with IWI Method)	750°C for 6 hours with 2 °C/min ramping rate in air	750	750
24	10% Ni/SBA-15 (Impregnated with IWI Method, Dried at 80 °C)	550 °C for 6 hours without any ramping rate in air	750	750
25	10% Ni/SBA-15 (Impregnated with IWI Method, Dried at 50 °C)	550 °C for 6 hours without any ramping rate in air	750	750

4. RESULTS AND DISCUSSION

Carbon dioxide Reforming of Methane (CDRM), which utilizes CO_2 as the oxygen source, is an environmentally sound route of reforming owing to the facts that it converts two greenhouse gasses to valuable $\text{CO}+\text{H}_2$ mixture having $\text{CO}:\text{H}_2$ ratio ca. 1, and it does not need (*and consume*) water as well. On the downside, it needs high temperature levels for acceptable activity due to its thermodynamically stable reactants. Additionally, its catalysts can be prone to carbon deposition as at conditions leading high activity, the inhibition of carbon formation could be achieved only if carbon formation rate on the active metal sites producing hydrogen is balanced with oxidation rate of deposited carbon. For a monometallic catalyst, this can be accomplished when the combination of support chemistry, surface structure, metal type and loading, and catalyst preparation method applied leads to a highly dispersed active sites, *which increase C-H activation rate of the catalyst*, and enhances both CO_2 splitting and transfer of yielded surface oxygen, *which cleans carbon formed*, to active metal sites to the same extent.

The main objective of this research is to design and develop (a) high performance Ni based CDRM catalyst(s) supported on mesoporous SBA-15. In this context, the main priority was given to suppression of carbon formation while maintaining the activity close to thermodynamic limit in order to achieve high and sustainable performance.

In the current study, conditions (and methods) used in the preparation of support materials and catalysts were parametrically changed in order to optimize the molecular interaction between the supporting material, SBA-15, and the active metal, Ni, such as to reach targeted high and stable CDRM activity. In this context; use and type of co-solvent in support preparation; the Ni-loading level, calcination temperature, impregnation method, and reduction temperature in catalyst preparation; and reaction temperature in performance tests were used as the experimental parameters. The evaluations and comparative analyses presented in the following sections are based on micro-structural and surface-chemical properties of the supports and catalysts prepared, and the CDRM performance characteristics of the catalysts. As the number of parameters is high, the effect of experimental parameters on CDRM performance were studied in two parts: first, the

effects of catalyst preparation and pretreatment (*i.e. impregnation strategy, calcination temperature, reduction temperature*) and reaction condition (*i.e. reaction temperature*) were studied over 10 %Ni loaded catalysts prepared on our reference support, SBA-15. In the second part, the effects of modification in SBA-15 preparation method *through the use of co-surfactants* on the performance of 10% Ni-loaded catalysts prepared on them; the effect of metal loading level, between 7.5 to 15%, on the performance of the catalysts prepared on reference SBA-15, and lastly effect of drying temperature on the performance of 10 %Ni/SBA-15, were evaluated to form a basis for further works. The stability test was conducted over the catalysts showing the best performance.

Prior to performance and stability tests, the reduction duration was kept fixed at 90 minutes. In the performance tests, the composition of feed mixture and its flow rate were kept fixed (*feed mixture: 15 mL/min of CH₄, 15 mL/min CO₂ and 30 mL/min of He*). During the performance and stability tests, CH₄ conversion and H₂/CO product ratio, which are used as indicators of activity and selectivity, respectively, were measured and used in comparative performance and stability analysis of the samples. The supports and catalysts were characterized by XRD, BET, SEM-EDX and XPS to analyze textural and morphological properties, such as surface area, pore volume, pore size distribution, as well as crystal structure and surface composition of SBA supports, and oxidation states of the active sites formed on the SBA supported catalysts prepared. The type and extent of coke formation over the surface of the spent catalysts were analyzed by RAMAN and XPS.

4.1. Characterization of SBA-15 Supports

A series of mesoporous SBA-15 were synthesized as supports for Ni/SBA-15 CDRM catalysts. The support samples were analyzed by their crystal structure with X-ray diffraction and by their micro-structural properties with BET. The results of those characterization tests were used to establish a relation between preparation parameters and support properties, as well as to compare the properties of the prepared samples with those reported in the literature.

The XRD result of the first SBA-15 batch (Figure 4.1) showed that the characteristic crystalline peak of the mesoporous silica was obtained at around 1.75 and

1.98, which are almost identical with the literature (Abbaspour *et al.*, 2012). When other batches were analyzed, only slightly different results were obtained, indicating that the synthesis route of the SBA-15 was reproducible.

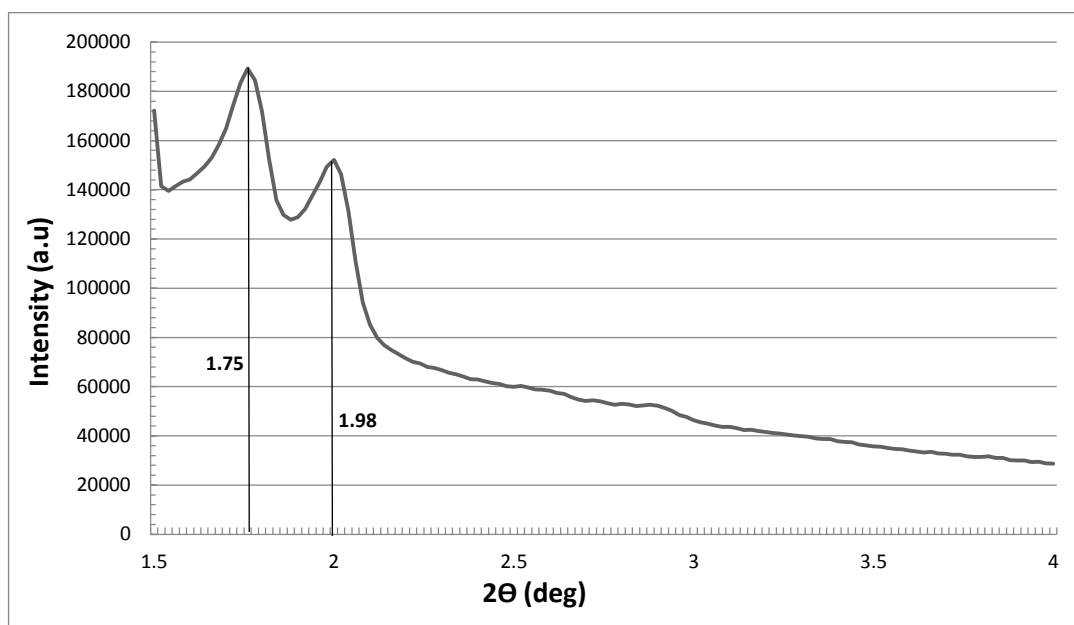


Figure 4.1. XRD Pattern of Mesoporous SBA-15

As it was mentioned in the previous chapters, the surface morphology and the textural properties of the SBA-15 was aimed to be manipulated by using different additives, TMB and CTAB, in order to observe their effect on the properties of the catalysts prepared on them and their performance. Those co-solvents added to the synthesis solution fill the pores of the mesoporous SBA-15 samples, and provide mechanical strength through preventing pores from collapse. However, due to their high volatility, TMB and CTAB evaporated during the calcination at high temperatures. Therefore, as expected, no notable change is observed in the XRD patterns of the different SBA-15 samples.

Although the characteristic XRD peaks of TMB_SBA-15, which are at 1.71 and 1.94, have a shift to left compared to those of the other mesoporous silica samples, as seen in Figure 4.2, it could be said that they are still located on the safe zone for SBA described

in the literature (Abbaspour *et al.*, 2012). On the other hand, upon the addition of CTAB, the peaks were not as sharp as those observed for the other batches due to the strong repulsion between CTA^+ and Si^+ ions, as mentioned in the literature (Yasmin & Müller, 2011). Accordingly, the intermolecular force between those ions changed the crystalline structure of the mesoporous silica as soon as it was set, even though CTA^+ ion was not permanent in the porous structure.

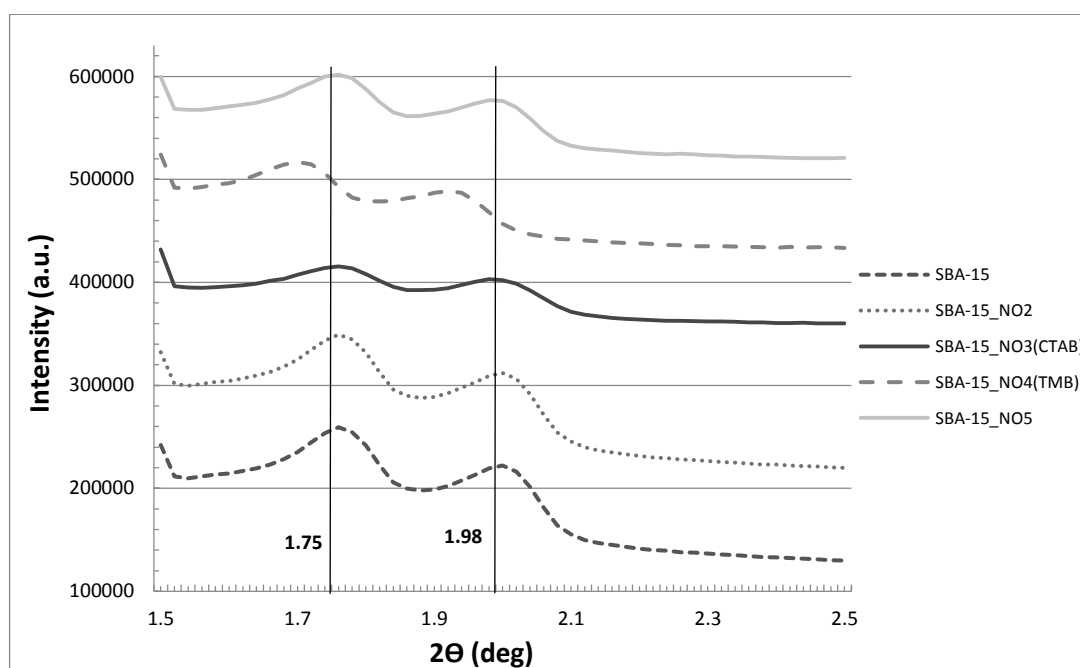


Figure 4.2. XRD Results of Different Mesoporous SBA-15 Materials

The physical properties of SBA-15 samples were furtherly analyzed by N_2 -adsorption. As in the XRD case, the ranges of BET surface area (TSA), Total Pore Volume (TPV) and average pore size values given in Table 4.1 support that the main method used as SBA-15 synthesis route was convenient, while the addition of surfactants led to changes in the physical structure of the synthesized products.

Table 4.1. Results of BET Analysis of Different Mesoporous SBA-15 Materials

Sample	BET Surface Area (m²/g)	Pore Volume (cm³)	Pore Size (nm)
SBA-15	945.32	1.24	5.25
SBA-15_NO2	916.88	1.27	5.55
CTAB_SBA-15_NO3	764.41	2.59	8.75
TMB_SBA-15_NO4	815.41	2.42	9.85
SBA-15_NO5	932.21	1.23	5.29

The BET analysis of different SBA-15 samples showed that introduction of additives has a strong influence on TSA, TPV and average pore size, confirmed by a pronounced increase in the pore size and TPV, while a decrease in TSA. Hence, it can be concluded that the addition of CTAB and TMB reshaped the physical structure of SBA-15 samples as was aimed.

Further analysis was performed to understand the pore size distributions (PSD) of the modified SBA-15 samples (Figure 4.3). The results show that introduction of TMB and CTAB addition led to significant impacts on PSD of the analyzed SBA-15 samples, resulting in PSD peaks at larger pore size and higher TPVs compared to those of SBA-15.

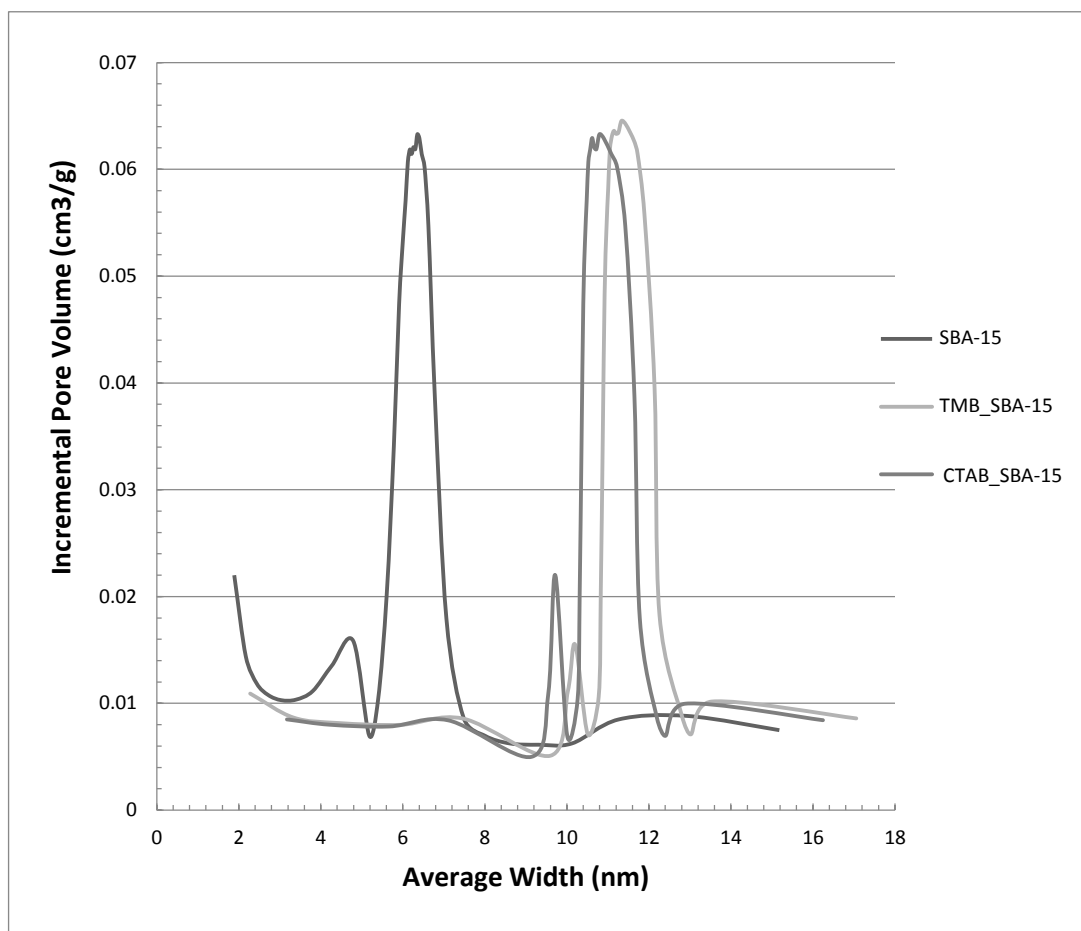


Figure 4.3. Pore Size Distributions of Different Mesoporous SBA-15 Materials

SEM imaging was used to investigate the surface morphology of SBA-15 samples further. Figure 4.4 shows that mesoporous SBA-15 is mostly formed by bundles of prismatic (hexagonal) tube-shaped silica chains laterally attached with each other by strong interaction between SBA-15 formations. *(Note that the hexagonal structure of the prismatic tubes is confirmed by Figure 4.7 acquired at higher magnification)*

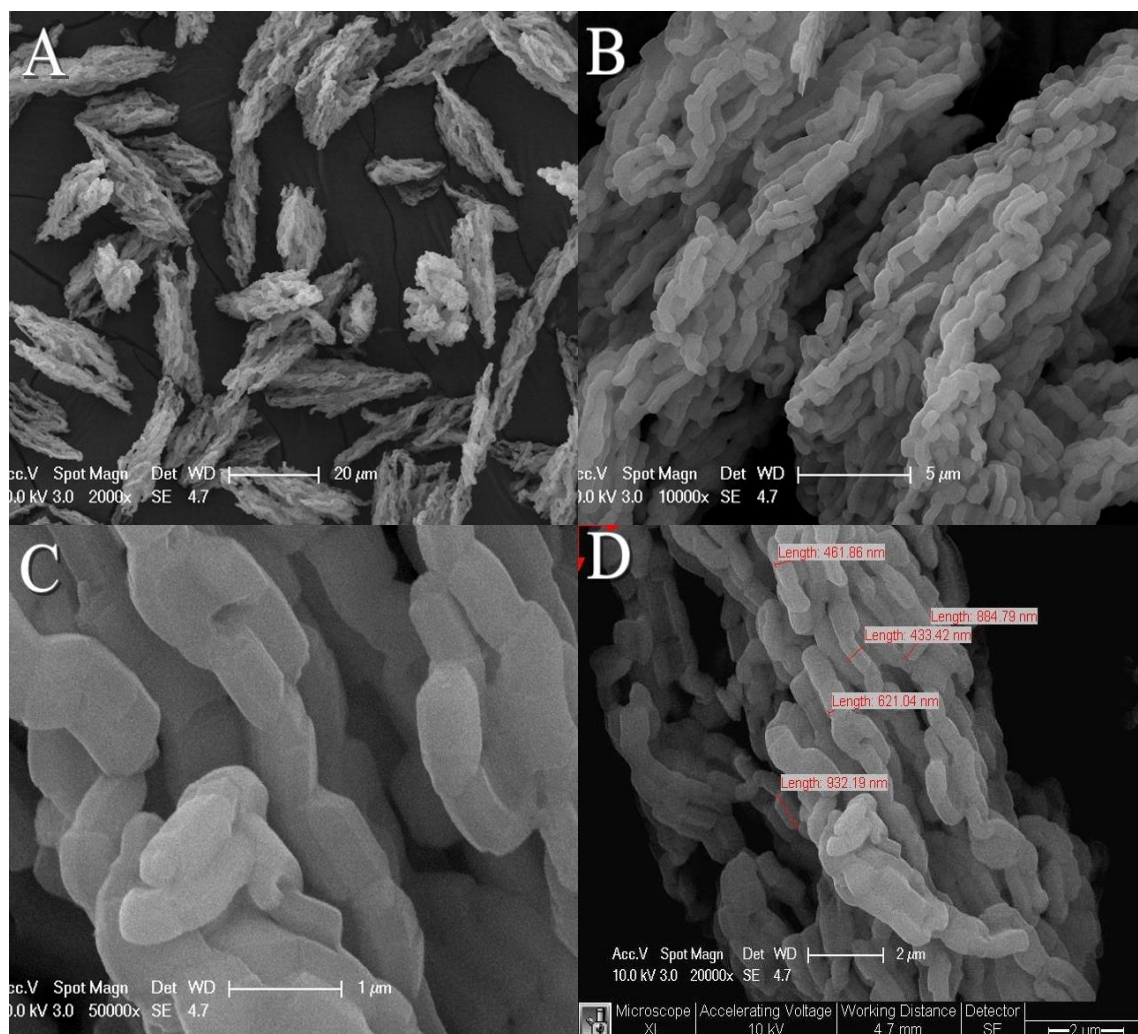


Figure 4.4. SEM Images of Mesoporous SBA-15 in 2000x (A), 10000x (B), 50000x (C) and 20000x (D)

It can be also seen from Figure 4.4 that some of the chains tend to form curved (or spheroidal) shapes rather than straight formations. Although prismatic tubes are not homogeneously formed, the length and width of SBA-15 formations are similar to each other having ca. 450 nm width and 900 nm length.

Figure 4.5 shows the effect of TMB addition as a co-surfactant on the micro-structural surface properties of SBA-15. In general, the images indicate that TMB addition does not change the formation of SBA-15 chains, which is in accordance with the literature (Chen *et al.*, 2011). On the other hand, as TMB is reported to fill the pores of the SBA-15 formations and increase not only their strength against mechanical stress but also the

molecular interaction between them (Zhao et al., 1998; Zhou et al., 2019), the SBA-15 chains in TMB_SBA-15 case (Figure 4.5) are longer and bigger than those of pure SBA-15 samples (Figure 4.4). Moreover, the same phenomenon is the main reason of longer and thinner hexagonal shaped SBA-15 formations, which are 1000 nm in length and 340 nm in width. Similar results were obtained for the CTAB addition case, as it can be seen from Figure 4.6.

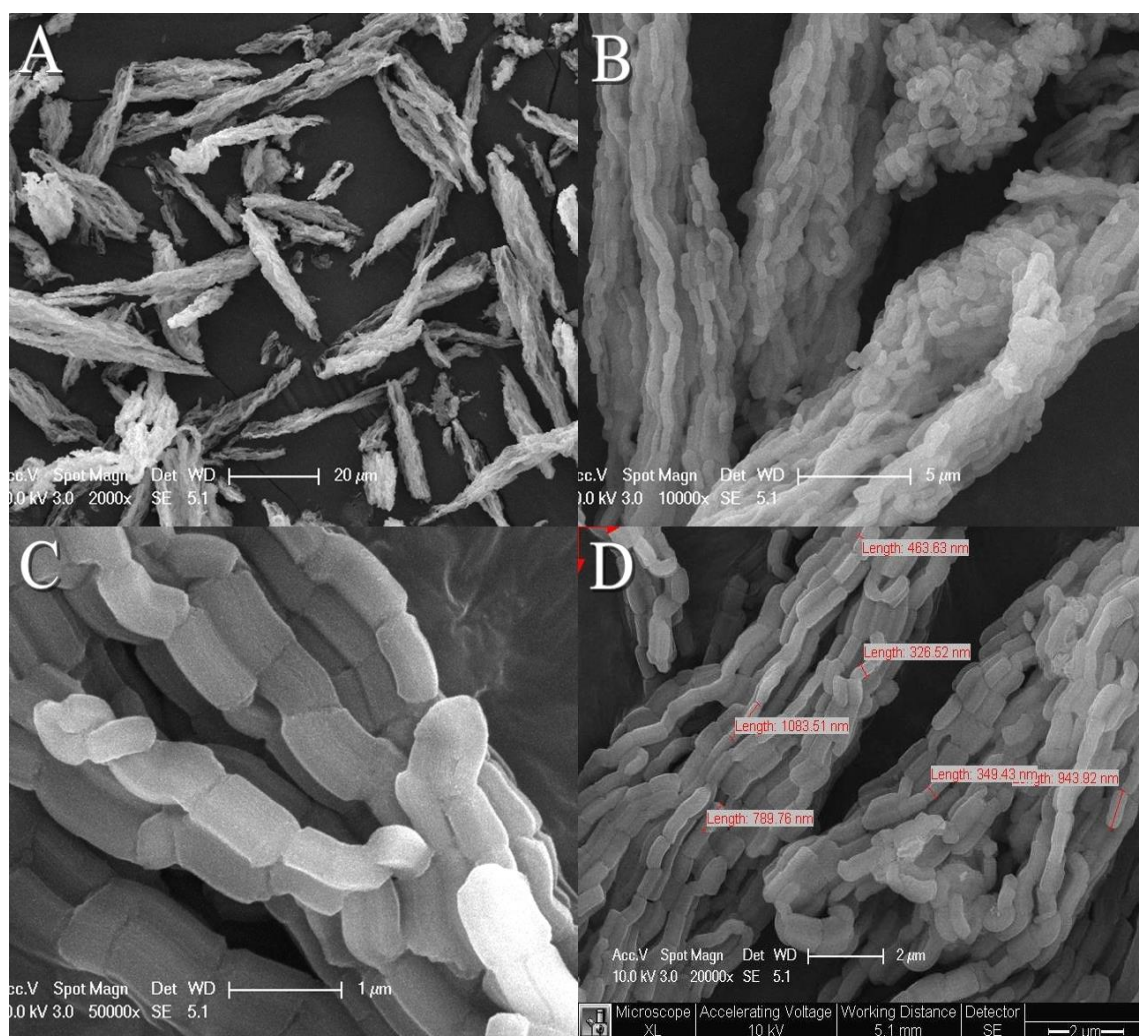


Figure 4.5. SEM Images of Mesoporous TMB_SBA-15 in 2000x (A), 10000x (B), 50000x (C) and 20000x (D)

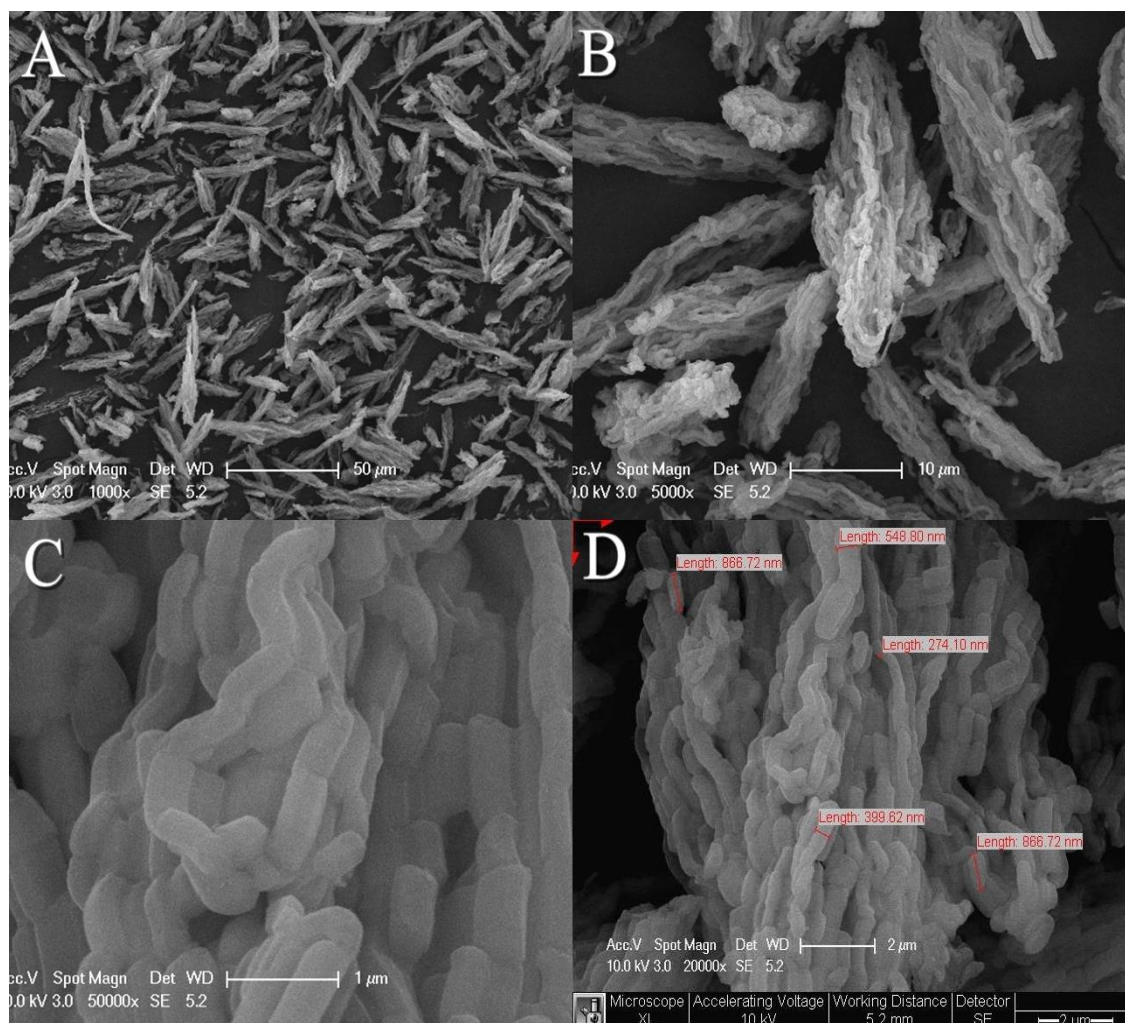


Figure 4.6. SEM Images of Mesoporous CTAB_SBA-15 in 1000x (A), 5000x (B), 50000x (C) and 20000x (D)

Despite the similarities in the morphological properties of the mesoporous silica samples in SEM images, CTAB added SBA-15 sample exhibits a difference in the silica formation, which can be easily seen on Figure 4.7. The SEM images show that some of the SBA-15 formations are gathered to form laterally bound bundles of hollow rod like chain structures, which increases the uniformity and homogeneity of the synthesized silica materials. The plausible reason of those formations is the increased electrostatic forces led by dissolution of CTAB into its cation (CTA^+) and anion (B^-) in the synthesis solution (Yasmin & Müller, 2011).

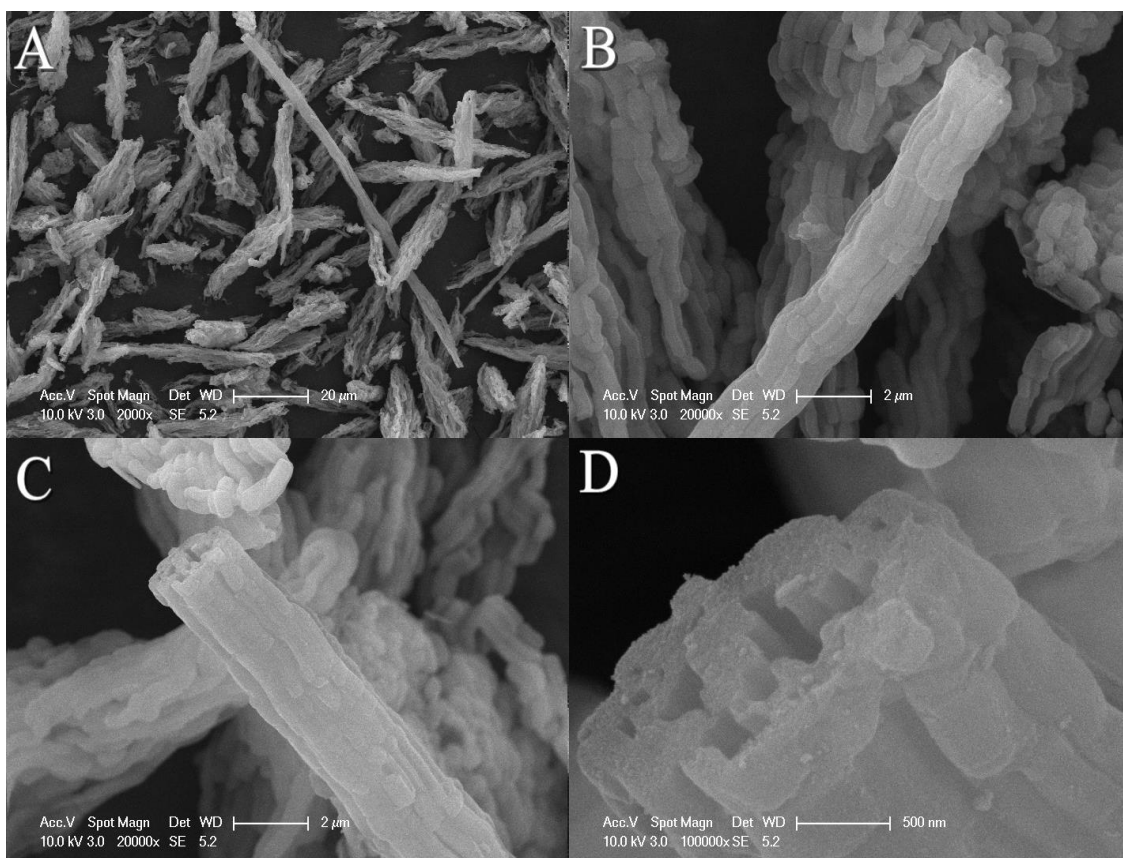


Figure 4.7. SEM Images of Hexagonal Shaped Mesoporous CTAB_SBA-15 Materials in 2000x (A), 20000x (B and C) and 100000 (D)

Though this phenomenon might have a positive impact on impregnation and metal dispersion over the SBA-15 type supports, only a small fraction of the prepared sample has this shape. Furthermore, as shown in Figure 4.8, there are some irregularities in the formations. Hence, CTAB addition in SBA-15 synthesis should be investigated widely.

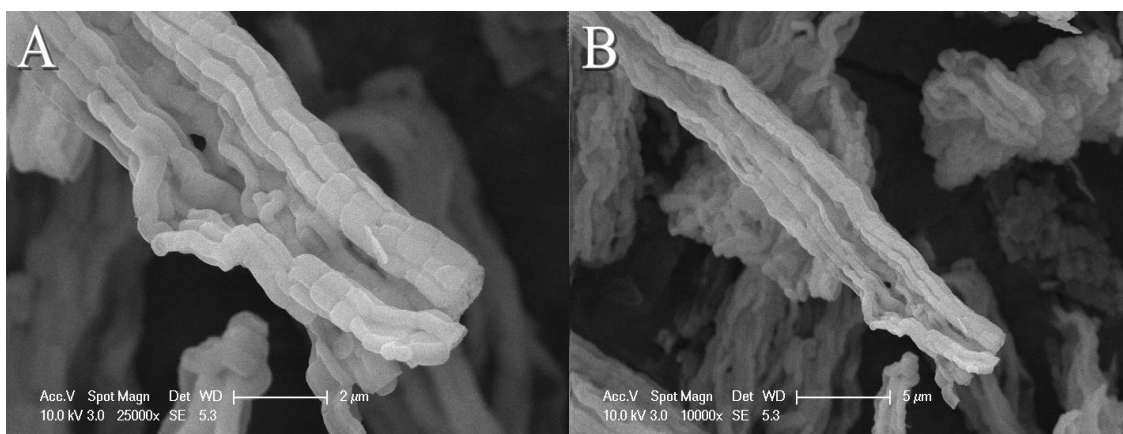


Figure 4.8. SEM Images of Unformed Hexagonal Mesoporous CTAB_SBA-15 Materials in 25000x (A) and 10000x (B)

In order to understand the influence of the co-solvent addition over the elemental composition of the mesoporous silica support surface, the samples were furtherly analyzed by X-Ray Photoelectron Spectroscopy (XPS).

Although different characterization methods showed sharp differences in pore volumes, pore size distributions, BET surface areas and morphological properties; as it can be seen from Figure 4.9, all 3 types of the mesoporous silica samples (i.e. SBA-15, TMB_SBA-15 and CTAB_SBA-15) yielded almost identical XPS profiles, with peaks at ca. 103 and 154 eV for silica 2p, and at 538 eV for oxygen 1s orbitals.

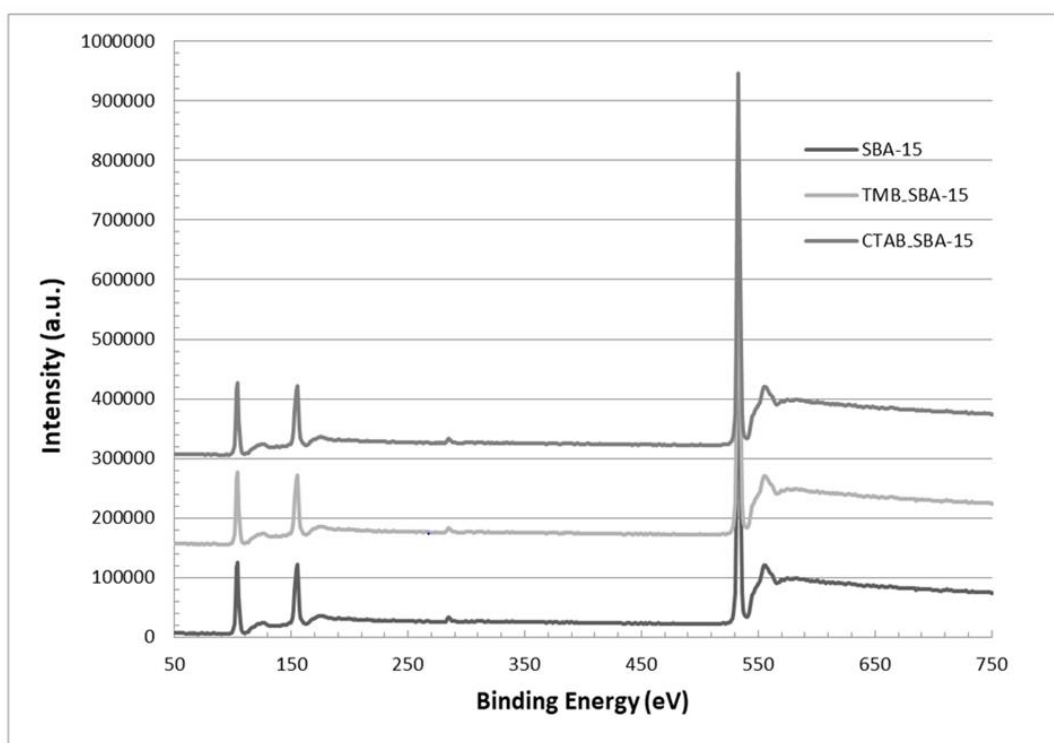


Figure 4.9. XPS Results of Different Mesoporous SBA-15 Materials

Elemental compositions for the same samples were calculated based on XPS data. As it was expected, similar elemental compositions, with Si:O wt ratio of ca. 1:3 were obtained. (See Table 4.2)

Table 4.2. Elemental Compositions of Different SBA-15 Materials

	SBA-15	TMB_SBA-15	CTAB_SBA-15
Si Weight %	24.65	24.42	24.86
O Weight %	75.35	75.58	75.14

Overall evaluation of characterization results reveals that mesoporous SBA-15 supports can be reshaped in terms of their textural and morphological properties via addition of CTAB and TMB as co-solvents; whereas co-solvent addition does not lead any change on their elemental surface composition.

4.2. CDRM Performance Tests over Ni/SBA-15 System

A series of CDRM performance tests over monometallic Ni catalysts supported on pure and modified SBA-15 samples were conducted in order to understand the effect of the method (*i.e. absence/presence and type of additive used*) used in preparation of SBA-15 type supports, Ni loading level of the catalysts, and type of impregnation method used and parameters (*i.e. calcination and reduction temperature*) applied in preparation of catalysts, and reaction temperature on the CDRM performance characteristics.

As the number of parameters is high, the effect of experimental parameters on CDRM performance were studied in two parts: first, the effects of catalyst preparation and pretreatment (*i.e. impregnation strategy, calcination temperature, reduction temperature*) and reaction condition (*i.e. reaction temperature*) were studied over 10 %Ni loaded catalysts prepared on our reference support, SBA-15. In the second part, the effects of modification in SBA-15 preparation method *through the use of co-surfactants* on the performance of 10% Ni-loaded catalysts prepared on them; the effect of metal loading level, between 7.5 to 15%, on the performance of the catalysts prepared on reference SBA-15, and lastly effect of drying temperature on the performance of 10 %Ni/SBA-15 were evaluated to form a basis for further works. The stability test was conducted over the catalysts showing best performance.

4.2.1. Effect of the Catalyst Preparation, Pretreatment and Reaction Conditions

4.2.1.1. Effect of the Impregnation Method

Recently the studies on the catalyst technology revealed that the catalytic performance of the chosen catalyst is strongly dependent on the intermolecular forces between the supporting material and the active metal(s) of the catalyst (Wu *et al.*, 2014). Moreover, this metal-support interaction can be enhanced by modifying the catalyst preparation process. In this context, 10% Ni/SBA-15 catalysts were prepared by using different impregnation techniques and they were tested at 750 °C.

Most of the catalysts used in this study were impregnated with the incipient wetness impregnation method although there were only few of examples of incipient wetness impregnation (IWI) in the literature for dry reforming of methane (Gaillard *et al.*, 2017; Gao *et al.*, 2017; Li *et al.*, 2017). To compare the effect of the impregnation technique on CDRM performance of the catalysts, 2 other sets of 10% Ni loaded catalysts were prepared by two-solvent impregnation (TSI) method.

For this purpose, the most promising calcination route (calcination at 750 °C for 6 hours with a ramping rate of 2 °C/min in air) was chosen for Exp 1 (IWI method) and Exp 2 (TSI method). In order to compare the results, another set of catalysts were prepared with calcination at 750 °C for 6 hours without any ramping rate in air, and they were used in Exp 3 (IWI method) and Exp 4 (TSI method).

Both of the impregnation techniques aim to evacuate air trapped inside the pores of the catalysts by using an ultrasound mixer in order to obtain a well active metal dispersion over the surface of the supporting material. IWI method was performed under high vacuum which contributes the evacuation process. However, the presence of aqueous water and ethanol solutions in TSI method decreased the contact rate of the supporting material and the active metal, which may limit dispersion of active metal. The performance test results presented in Figure 4.10 reveal that both catalysts prepared by TSI showed lower catalytic performance in terms of CDRM activity and stability.

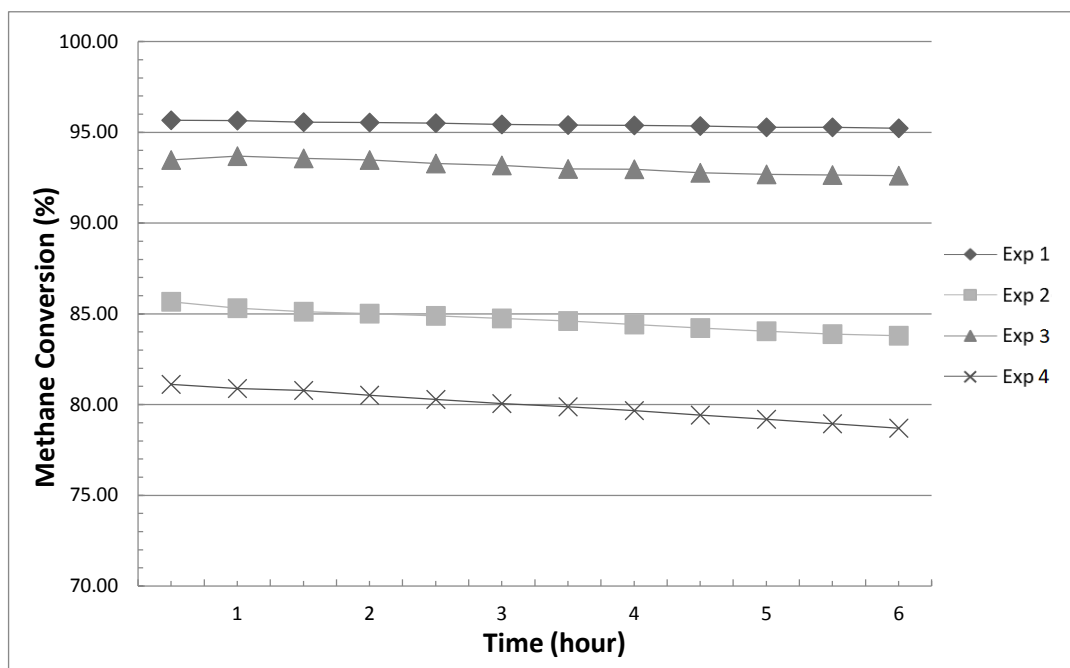


Figure 4.10. The Effect of Impregnation Method on the Catalytic Performance (Exp 1: IWI method with ramping in calcination step; Exp 2: TSI method without ramping in Calcination step; Exp 3: IWI method with ramping in calcination step; Exp 4: TSI method without ramping in calcination step)

Although H_2/CO ratio, which is used as a measure of selectivity, obtained over catalysts prepared by IWI were really close to 1, as shown in Figure 4.11, it was lower, ca.0.85, over the samples prepared by TSI. The results indicated that H_2/CO ratio of the syngas produced is highly dependent on the impregnation method used, which can directly influences the interaction between support and active metal. Consequently, unless an improvement in the two solvent impregnation method is made, the results suggest the use of IWI.

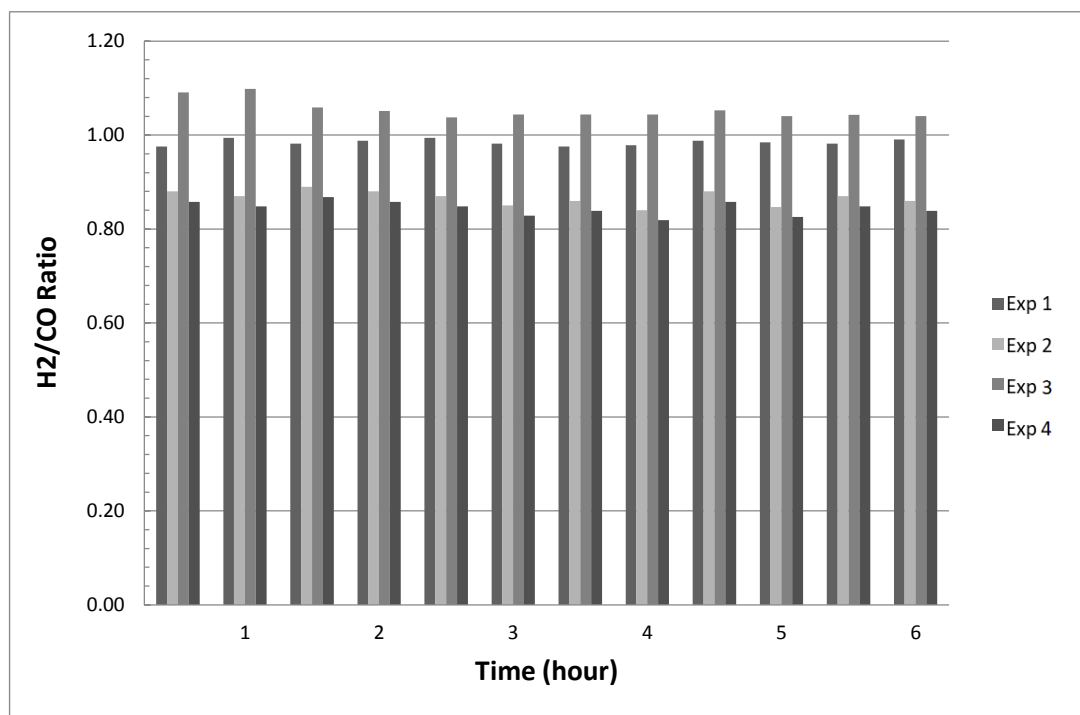


Figure 4.11. The Effect of Impregnation Method on the H_2/CO Ratio (Exp 1: IWI method with ramping in calcination step; Exp 2: TSI method without ramping in calcination step; Exp 3: IWI method with ramping in calcination step; Exp 4: TSI method without ramping in calcination step)

4.2.1.2. Effect of the Calcination Temperature

As it is well known that calcination has a pronounced effect on active metal dispersion, dispersion stability during reaction and catalyst performance; different calcination procedures were applied while all the other parameters were kept fixed. In the performance tests, conducted at 750 °C, 1 atm, the ratio of the reactants at the inlet was used as $CH_4:CO_2:He$ was set to 1:1:2.

The results of the experiments, presented in Figure 4.12, showed that the optimum calcination procedure for the Ni/SBA-15 was calcination at 750 °C for 6 hours *with a ramping rate of 2 °C/min from room T to calcination temperature* (Exp 1). The results suggest that the use of calcination temperature lower than 750 °C resulted in lower catalytic activities with relatively limited performance stabilities.

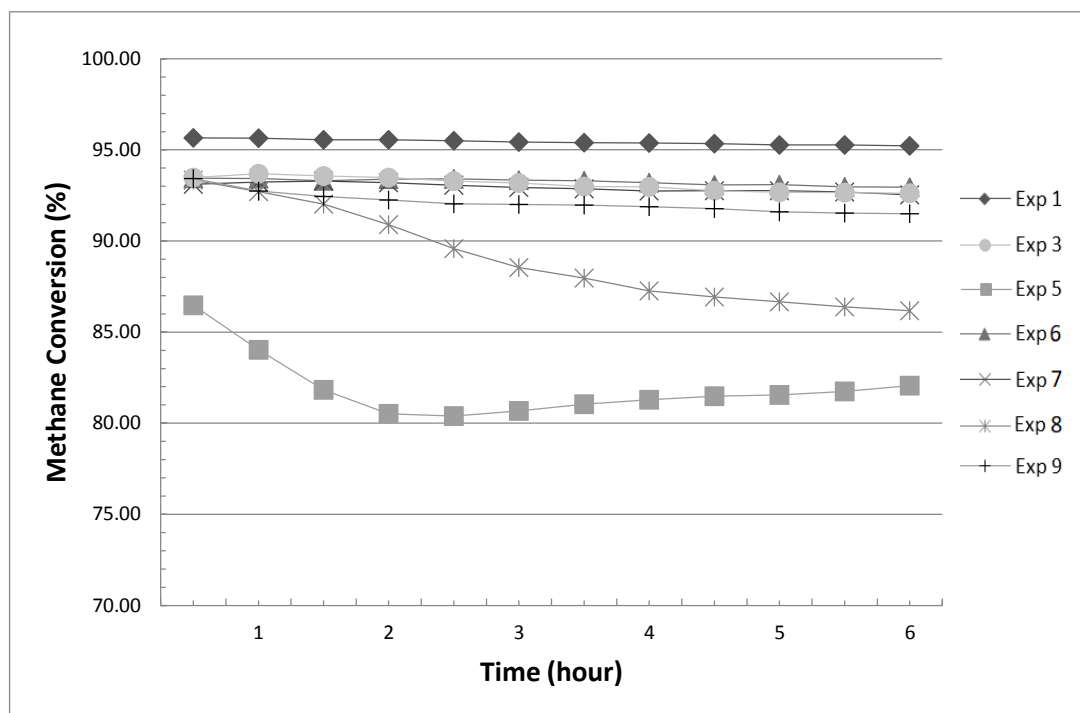


Figure 4.12. The Effect of Calcination Process on the Catalytic Performance (Exp 1: 750 °C for 6 hours with 2 °C/min ramp in air; Exp 3: 750°C for 6 hours without any ramp in air; Exp 5: 550°C for 6 hours without any ramp in air; Exp 6: 650°C for 6 hours with 2°C/min ramping rate in N₂; Exp 7: 700°C for 6 hours with 2°C/min ramping rate in air; Exp 8: 750°C for 2 hours with 2°C/min ramping rate in air; Exp 9: 750°C for 6 hours with 2°C/min ramp in N₂)

It seems that Ni particles need at least 6 hours to be stabilized over the SBA-15 surface. Furthermore, since the surface structure of SBA-15 is highly affected by the rapid temperature changes (Usman *et al.*, 2015), calcination without controlled ramping rate caused instability over the structural properties of SBA-15, which may decrease the dispersion of Ni on the catalyst surface. However, the adverse effects of rapid temperature change could be compensated for the first 4 hours of calcination at 750 °C. Most probably, this was the main reason why the stabilities of the experiments 5 (calcination at 550 °C for 6 hours without ramp in air) and Exp 8 (calcination at 750°C for 2 hours with 2°C/min ramping rate in air) were lower than the others’.

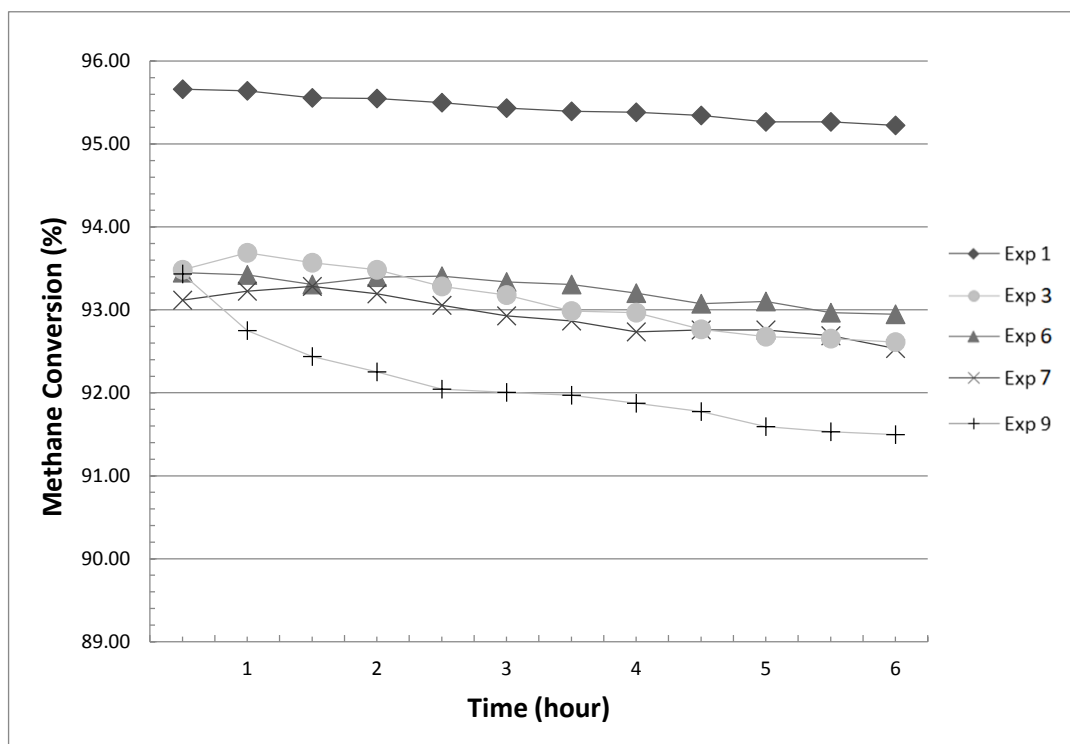


Figure 4.13. A Closer Look in the Effect of Calcination Process (Exp 1: 750 °C for 6 hours with 2 °C/min ramp in air; Exp 3: 750°C for 6 hours without any ramp in air; Exp 6: 650°C for 6 hours with 2°C/min ramping rate in N₂; Exp 7: 700°C for 6 hours with 2°C/min ramping rate in air; Exp 9: 750°C for 6 hours with 2°C/min ramp in N₂)

The effect of calcination under inert atmosphere on catalyst performance was also studied. The results of the Exp 6 showed that the catalyst calcined under nitrogen at 650 °C showed similar activities compared to those measured over the samples calcined at 650 and 700 °C under air flow. Though similar initial activity level was obtained in Exp 9 over the sample calcined under nitrogen flow at 750 °C, there observed a slight lost in its TOS stability most probably owing to the reported increase in the radical behavior of nitrogen at high temperatures that may negatively affect nickel stabilization on the catalyst surface. (Kikhtyanin *et al.*, 2018; Zeng *et al.*, 2017)

The H₂/CO ratio of 1, which is the ratio desired for olefin selectivity in Fischer Tropsch Synthesis, was obtained for almost all the cases (except for Exp 5), verifying Ni/SBA-15 systems are feasible for CDRM leading syngas yield.

As an overall evaluation, the results suggest that the use of calcination temperature lower than 750 °C, calcination performed in inert atmosphere and/or conducted for shorter than 6-hrs resulted in lower catalytic activities with relatively limited performance stabilities.

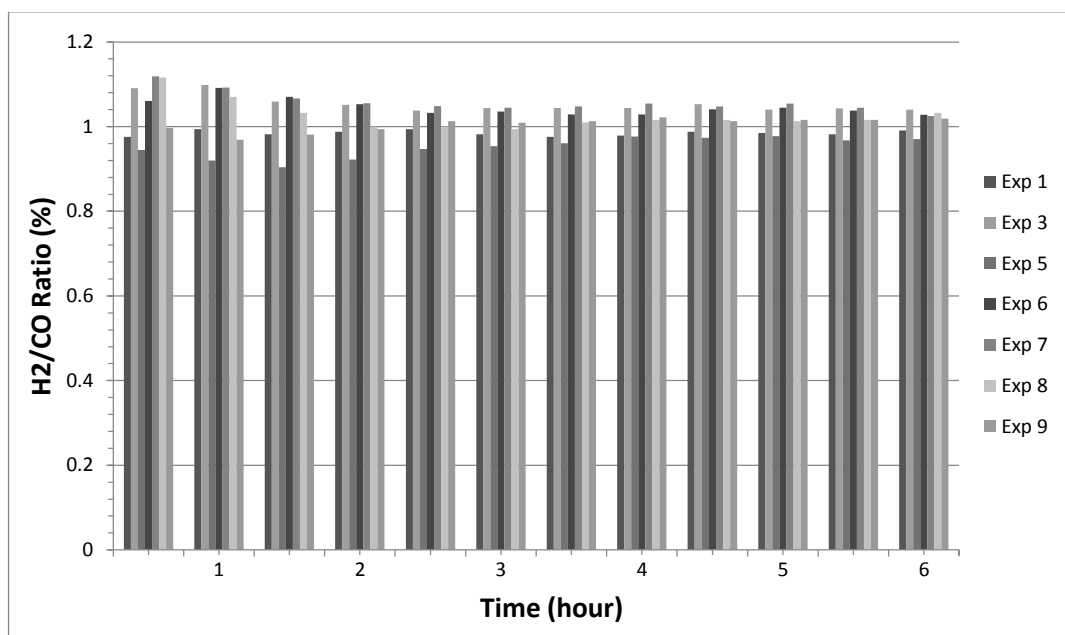


Figure 4.14. The Effect of Calcination Process on the Catalytic Performance (Exp 1: 750 °C for 6 hours with 2 °C/min ramp in air; Exp 3: 750°C for 6 hours without any ramp in air; Exp 5: 550°C for 6 hours without any ramp in air; Exp 6: 650°C for 6 hours with 2°C/min ramping rate in N₂; Exp 7: 700°C for 6 hours with 2°C/min ramping rate in air; Exp 8: 750°C for 2 hours with 2°C/min ramping rate in air; Exp 9: 750°C for 6 hours with 2°C/min ramp in N₂)

4.2.1.3. Effect of the Reduction Temperature

Reduction is one of the vital steps of catalyst pretreatment during which the catalysts are activated. All of the catalysts prepared were reduced in 30 mL/min hydrogen flow. In order to understand the impact of the reduction over the catalytic performance, a series of catalysts were reduced at different temperatures (Exp 11: 650 °C, Exp 10: 700 °C

and Exp 1: 750 °C) with the same W/F for 2 hours, then their CDRM performance was tested under the same reaction conditions.

The results presented in Figure 4.15 suggest that higher reduction temperatures led higher methane conversion levels. Although Exp 11 showed that reduction at 650 °C led dramatic loss of activity, reduction at 700 °C did not. Hence, it was deduced that the reduction must be performed around the reaction temperature, and the lower reduction temperatures applied cannot be compensated by possible activation during reaction. Furthermore, the results in Exp 10 and Exp 11 also exhibited that the activity losses were 0.85 and 1.36 % respectively; whereas the activity loss in Exp 1 was 0.45 % during the reaction. Therefore, it is suggested that the decrease in the reduction temperature slightly decreases the catalytic stability as well.

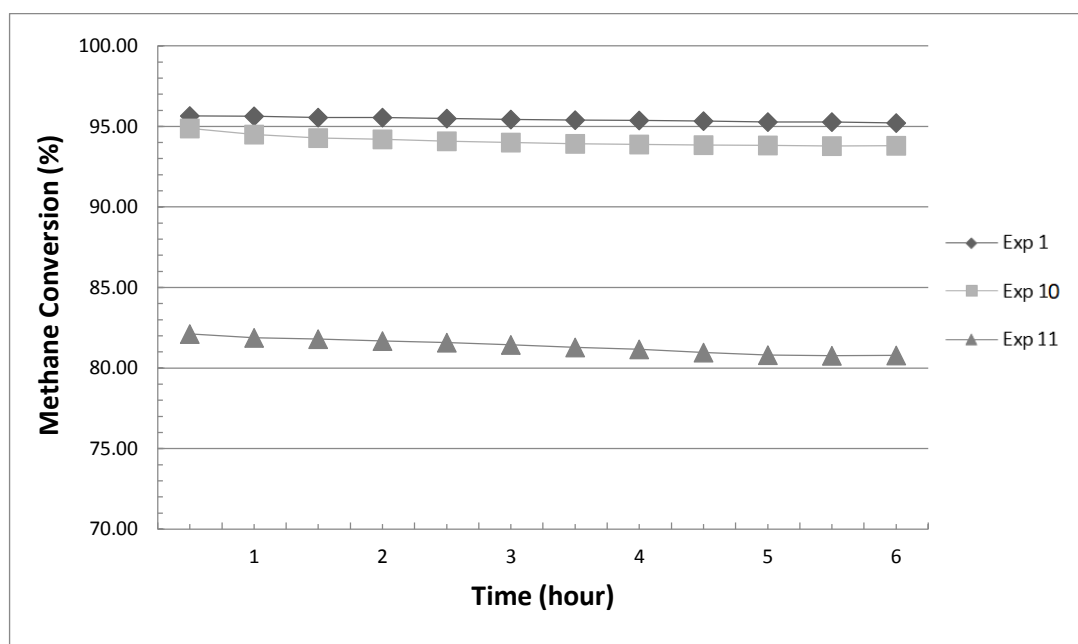


Figure 4.15. Effect of Lower Reduction Temperature on the Catalytic Performance (Exp 1: Reduction at 750 °C; Exp 10: Reduction at 700 °C; Exp 11: Reduction at 650 °C)

In addition to the tests conducted at 750 °C, an additional series of performance tests were performed at 700 °C, aiming to see whether similar performance can be obtained at a lower reaction temperature (Figure 4.16). As it was suggested for the previous case,

results of Exp 12 (Reduction at 750 °C) and Exp 13 (Reduction at 700 °C) also evinced that higher reduction temperatures increase methane conversion. In the tests, the activity losses at 6 h TOS were observed as 1.56 and 1.76 % for Exp 12 and Exp 13, respectively.

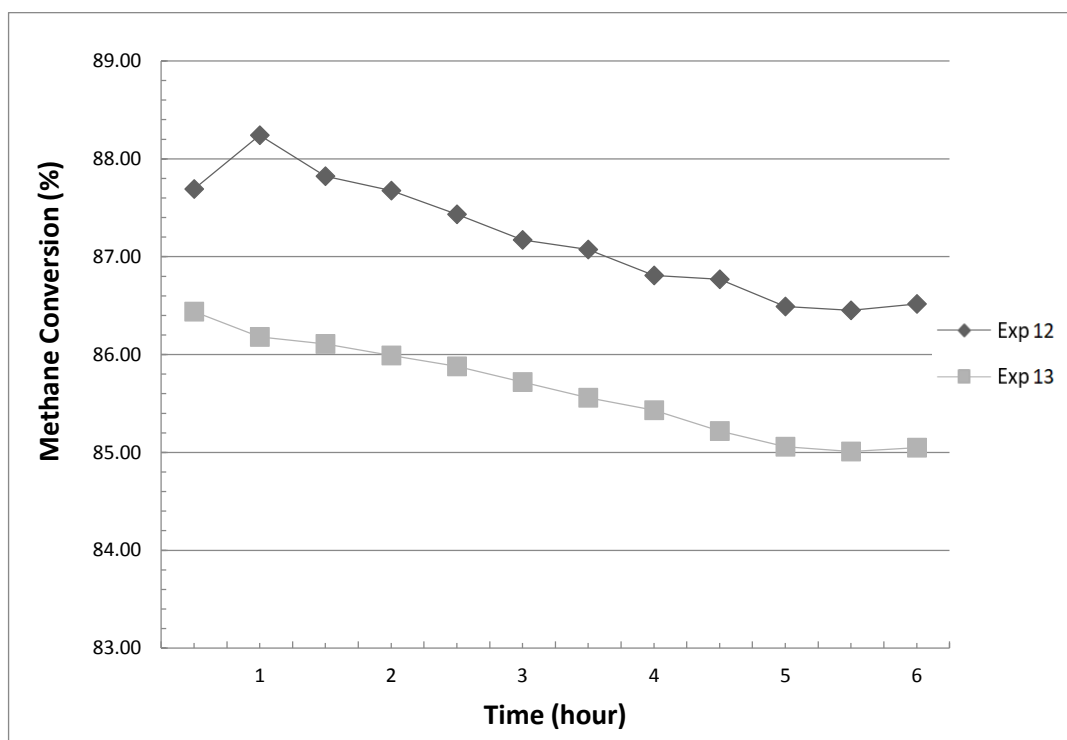


Figure 4.16. Effect of Higher Reduction Temperature on the Catalytic Performance (Exp 12: Reduction at 750 °C; Exp 13: Reduction at 700 °C)

Although the performance tests conducted at both 700 and 750 °C showed that the catalytic activity was highly influenced by the changes in the reduction temperature; Figures 4.17 and 4.18 evinced that the changes in the reduction temperature had no direct influence on H_2/CO product ratio, which is a measure of selectivity; the ratio is close to 1 for all experiments.

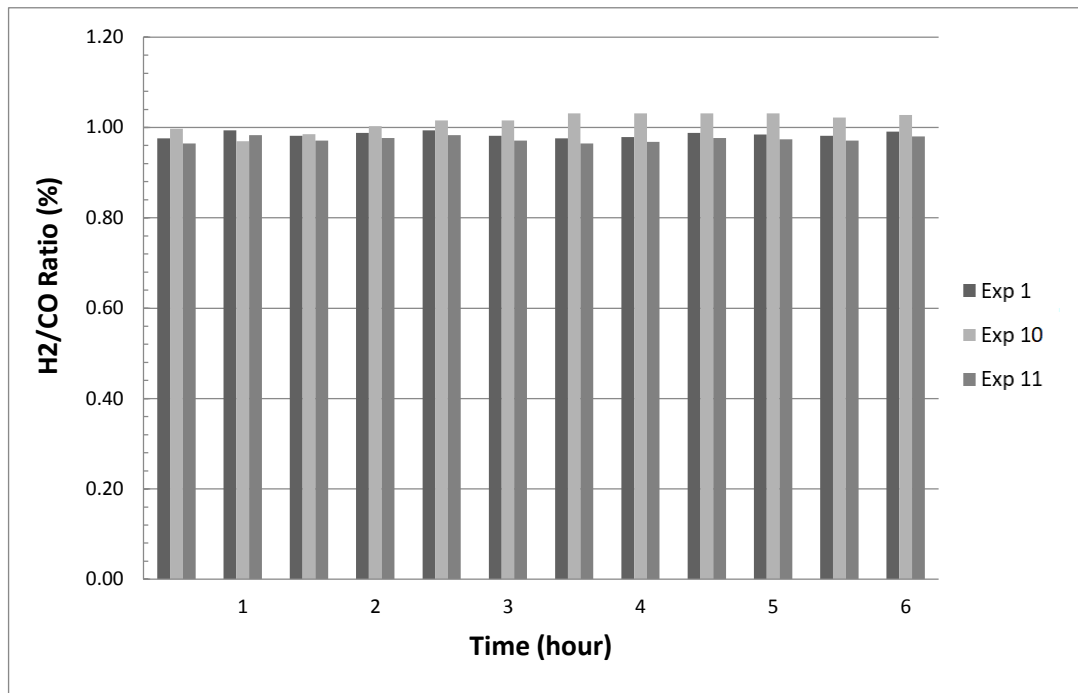


Figure 4.17. Effect of Reduction Temperature on H₂/CO Ratio at 750 °C (Exp 1: Reduction at 750 °C; Exp 10: Reduction at 700 °C; Exp 11: Reduction at 650 °C)

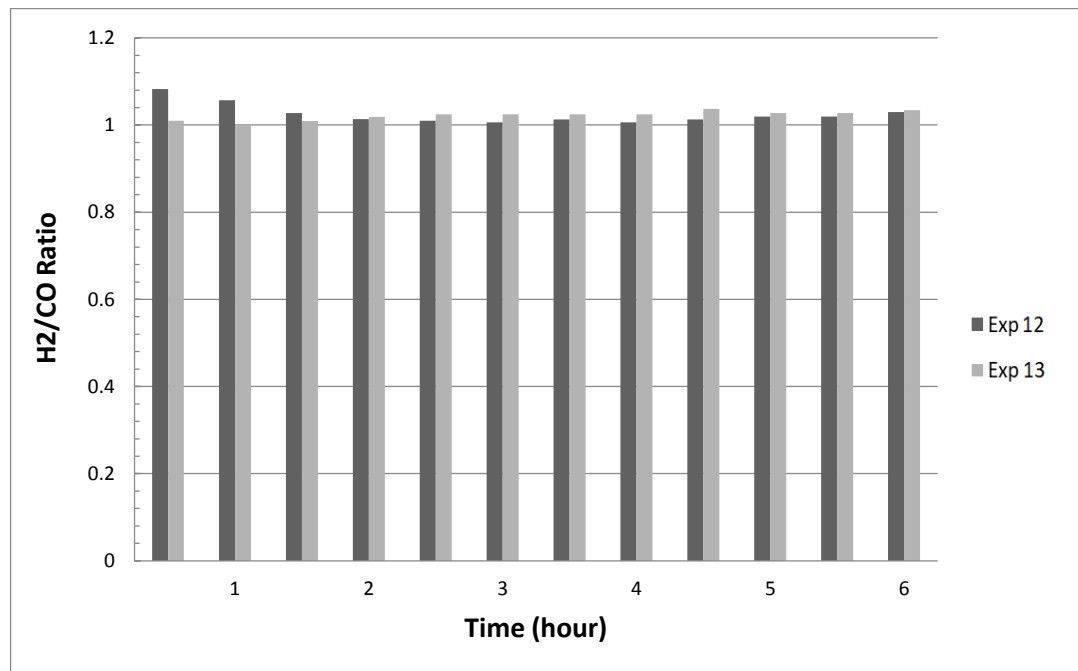


Figure 4.18. Effect of Reduction Temperature on the H₂/CO Ratio at 700 °C (Exp 12: Reduction at 750 °C; Exp 13: Reduction at 700 °C)

4.2.1.4. Effect of the Reaction Temperature

A series of 10%Ni/SBA-15 catalysts were prepared and treated at 750 °C for 6 hours with a ramping rate of 2 °C/min in air, which had been found as the most appropriate calcination route, and then reduced at 750 °C under hydrogen flow. The catalysts were tested for their CDRM performance at different temperatures 650, 700, 750 and 800 °C. As expected, increase in reaction temperature causes an increase in methane.

As it can be seen from the Figure 4.19, the rise in methane conversion in response to temperature increase becomes less significant as the conversion rate comes close to thermodynamic limit.

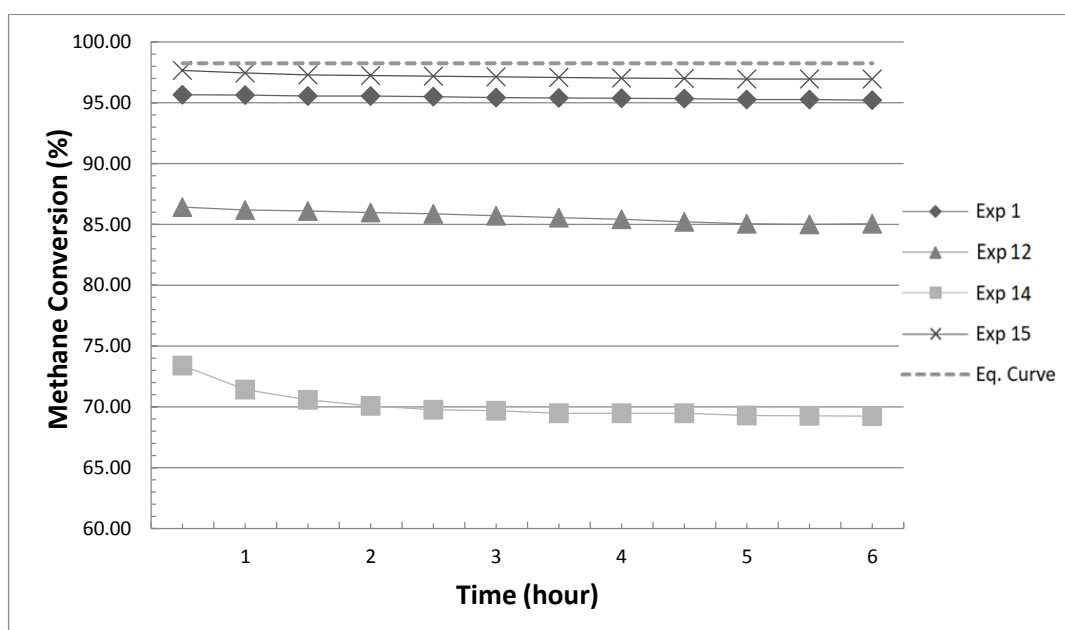


Figure 4.19. Effect of Reaction Temperature over the Catalytic Performance (All samples were calcined at 750 °C for 6 hours with 2 °C/min ramping rate in air; Exp 1: 750 °C; Exp 12: 700 °C; Exp 14: 650 °C; Exp 15: 800 °C)

Although nickel is prone to coke deposition (Bracciale *et al.*, 2019), 3 of the catalysts tested showed stable activity under CDRM conditions for 6 hours, even at high temperatures, suggesting that coke formation over the catalyst surface was insignificant.

The results also suggest that metal sintering was inhibited. However, when the result of Exp 14 was examined, a relatively higher activity loss was observed for the first two hours TOS suggesting that lower reaction temperatures is not beneficial for stable CDRM activity.

Moreover, H_2/CO ratios (Figure 4.20) obtained at the end of all experiments was really close to 1, except for Exp 14 which was conducted at 650 °C. Hence, the results suggest that even very high, close to equilibrium, activity did not lead any change in H_2/CO product selectivity.

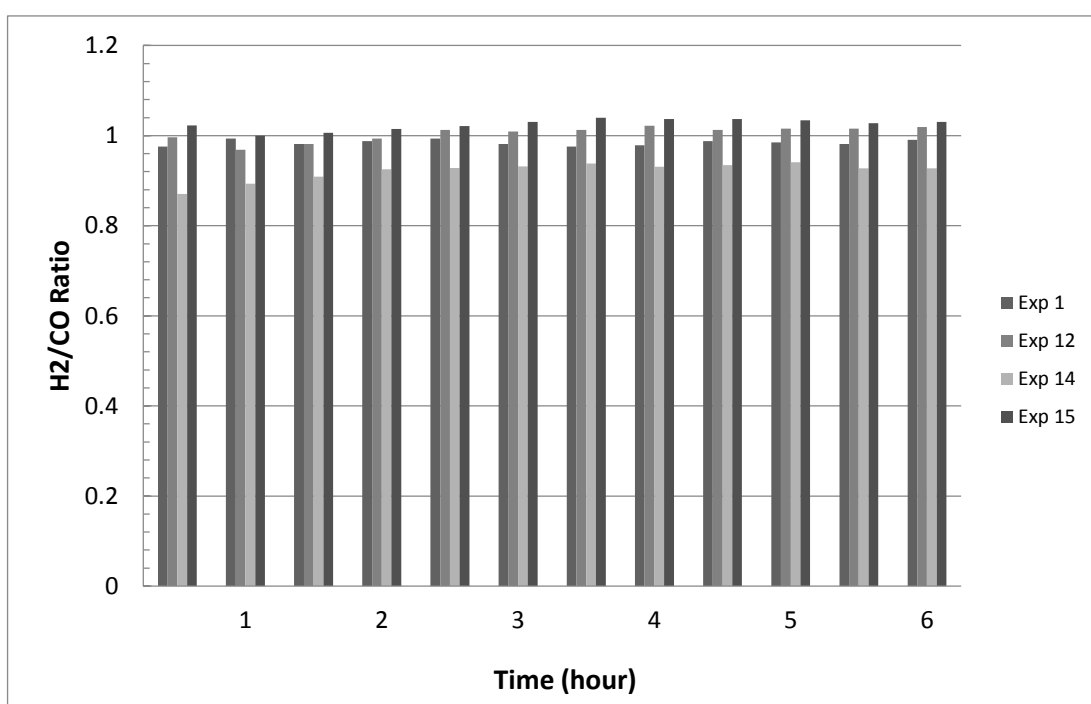


Figure 4.20. The Effect of Reaction Temperature on H_2/CO Ratio (All samples were calcined at 750 °C for 6 hours with 2 °C/min ramping rate in air; Exp 1: 750 °C; Exp 12: 700 °C; Exp 14: 650 °C; Exp 15: 800 °C)

4.2.2. Effect of the Modifications on the Reference Catalysts

4.2.2.1. Effect of the Active Metal Loading

In order to investigate the effect of active metal loading on the catalytic performance of the SBA-15 supported catalysts, the best performing catalyst (10% Ni/SBA-15, calcined at 750 °C for 6 hours with a ramping rate of 2 °C/min) was synthesized again with different Ni metal loadings (7.5% for Exp 17 and 15% for Exp 16) and tested for CDRM performance at 750 °C

As can be seen from Figure 4.21, 10% Ni/SBA-15 catalyst showed the best CDRM performance in terms of both activity and stability. However, the results revealed that when Ni loading is lowered down to 7.5%, the activity is decreased with a loss in stability.

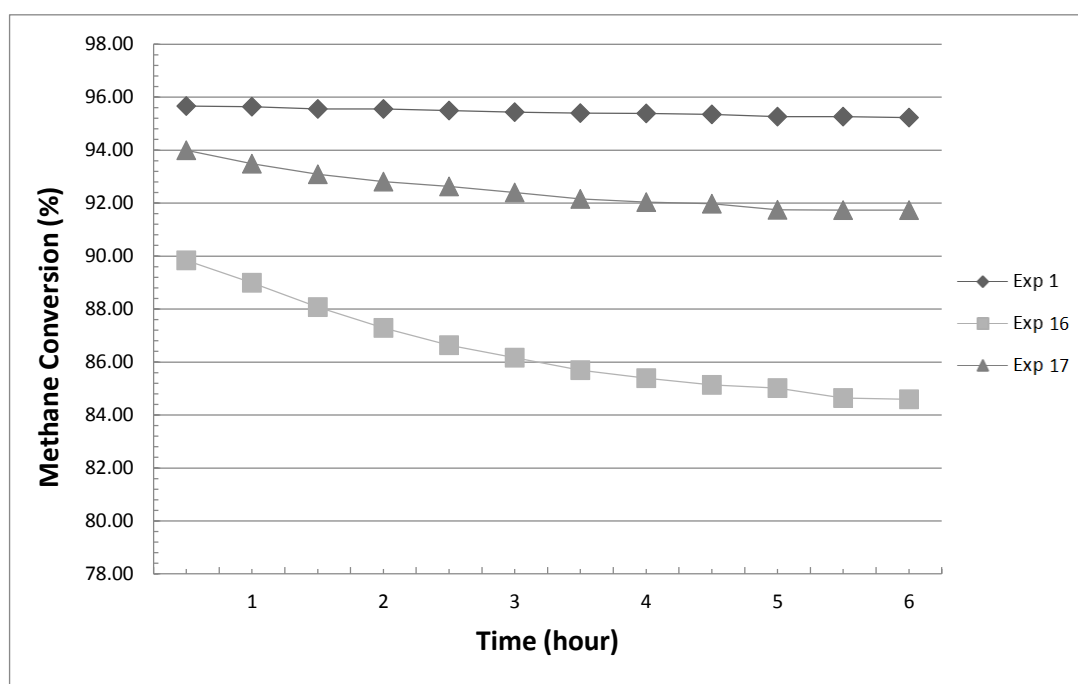


Figure 4.21. The Effect of Ni Loading on the Catalytic Performance (Exp 1: 10% Ni/SBA-15; Exp 16: 15% Ni/SBA-15; Exp 17: 7.5% Ni/SBA-15)

On the other hand, 15% Ni/SBA-15 showed the worst activity owing to larger amount of nickel impregnated on its surface, which may lead to agglomeration of Ni to form larger clusters and hence a loss in Ni dispersion.

Another set of catalysts with different metal loadings (7.5, 10 and 15 %) was prepared on SBA-15 for which calcination at 750 °C for 6 hours without any ramp was applied. Results in Figure 4.22 showed that although 10% nickel loaded sample showed the best stability over the 6 hours TOS, methane conversion values were converged and become essentially the same for all of the samples tested.

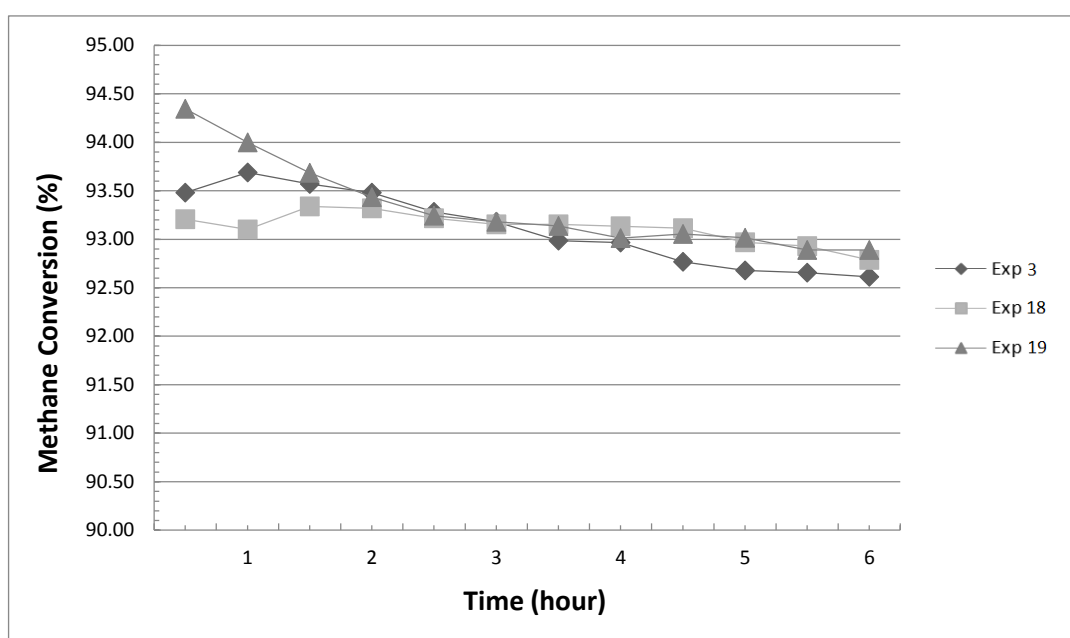


Figure 4.22. Another Example for the Effect of Ni Loading on the Catalytic Performance (Exp 3: 10% Ni/SBA-15; Exp 18: 15% Ni/SBA-15; Exp 19: 7.5% Ni/SBA-15)

An overall evaluation indicates that 10% Ni/SBA-15 catalyst is the best choice to obtain high catalytic performance under the applied reaction conditions.

It should be noted that the H_2/CO selectivity ratio at the end of the experiments did not differ significantly (Figure 4.23 and Figure 4.24), indicating that it is not affected by the active metal loadings for the metal loading range tested.

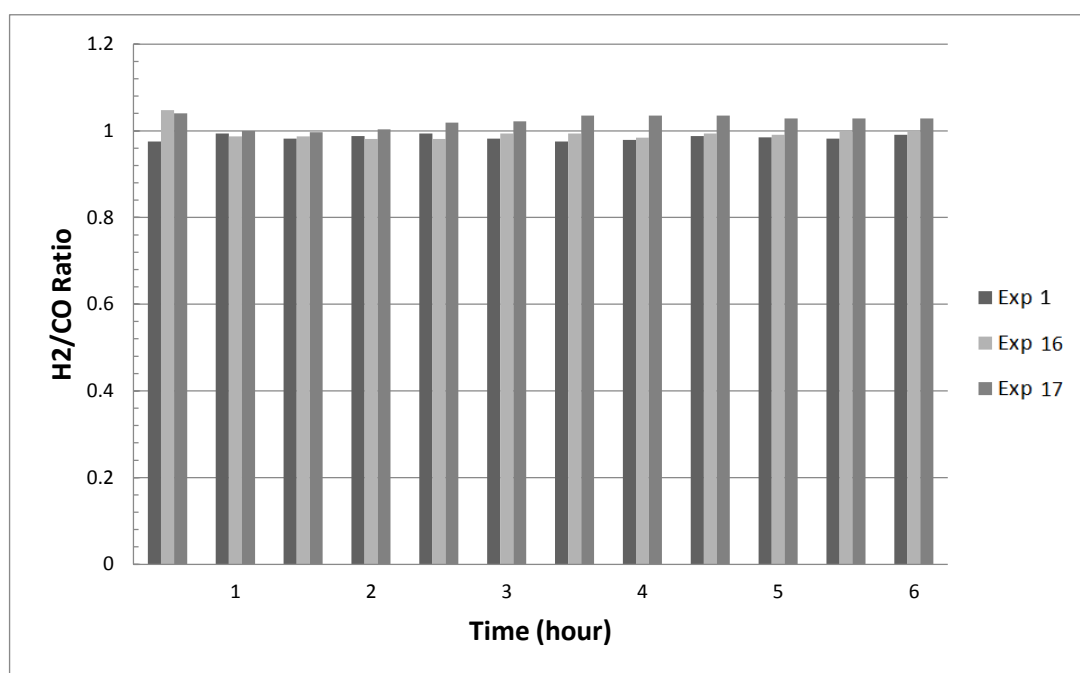


Figure 4.23. The Effect of Ni Loading on H₂/CO Ratio (Exp 1: 10% Ni/SBA-15; Exp 16: 15% Ni/SBA-15; Exp 17: 7.5% Ni/SBA-15)

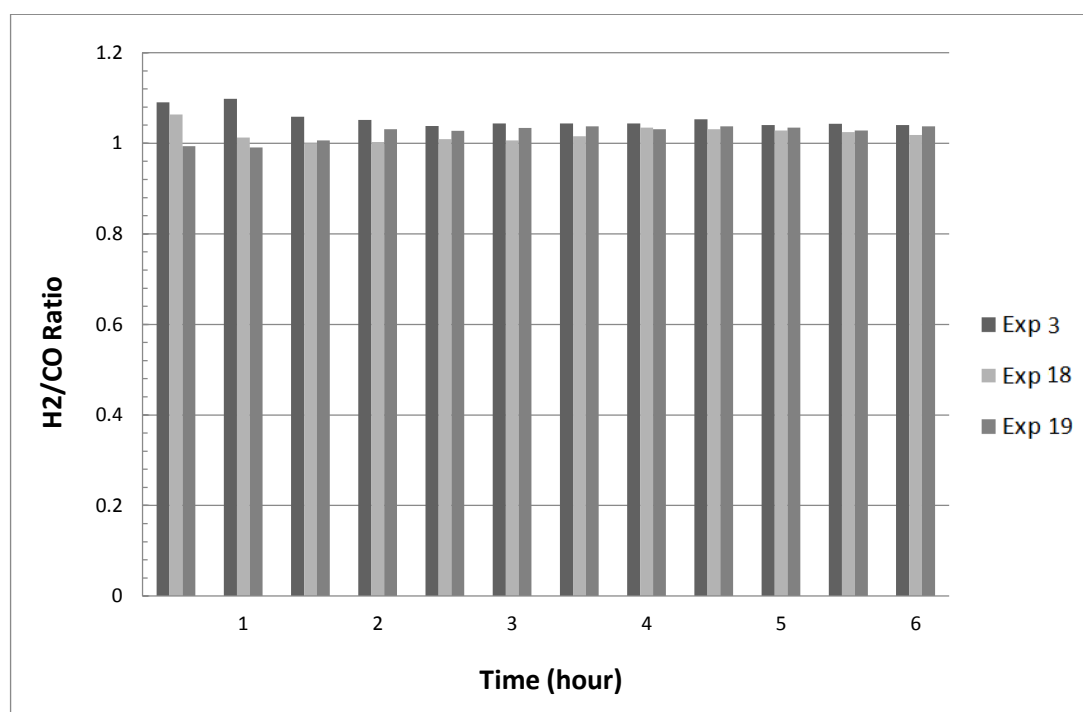


Figure 4.24. Another Example for the Effect of Ni Loading on H₂/CO Ratio (Exp 3: 10% Ni/SBA-15; Exp 18: 15% Ni/SBA-15; Exp 19: 7.5% Ni/SBA-15)

4.2.2.2. Effect of the Supporting Material

It is known that the use of various additives, such as 1, 3, 5-tri methyl benzene (TMB) as a co-solvent and cetyl-trimethyl ammonium bromide (CTAB) as a surfactant, during SBA preparation may re-shape the structural properties of the mesoporous silica and hence increase the catalytic performance of the catalysts (Yasmin & Müller, 2011). Both TMB and CTAB addition aimed to increase the pore size and volume of the homogeneously distributed porous SBA structures.

In this section, 15% and 7.5% Ni loaded catalysts, which exhibited relatively lower CDRM performances when supported on SBA-15, were prepared on modified SBA-15 samples to observe the influence of the different types of mesoporous SBA-15 on activity. 15% Ni loaded catalysts prepared on both modified SBA-15 samples exhibited lower activities with high stabilities. The sharp activity loss observed on Figure 4.25 for 15% Ni/SBA-15 was prevented for both 15% Ni/TMB_SBA-15 and 15% Ni/CTA_SBA-15, most probably owing to the enhanced metal-SBA interaction led by the use of additives during preparation.

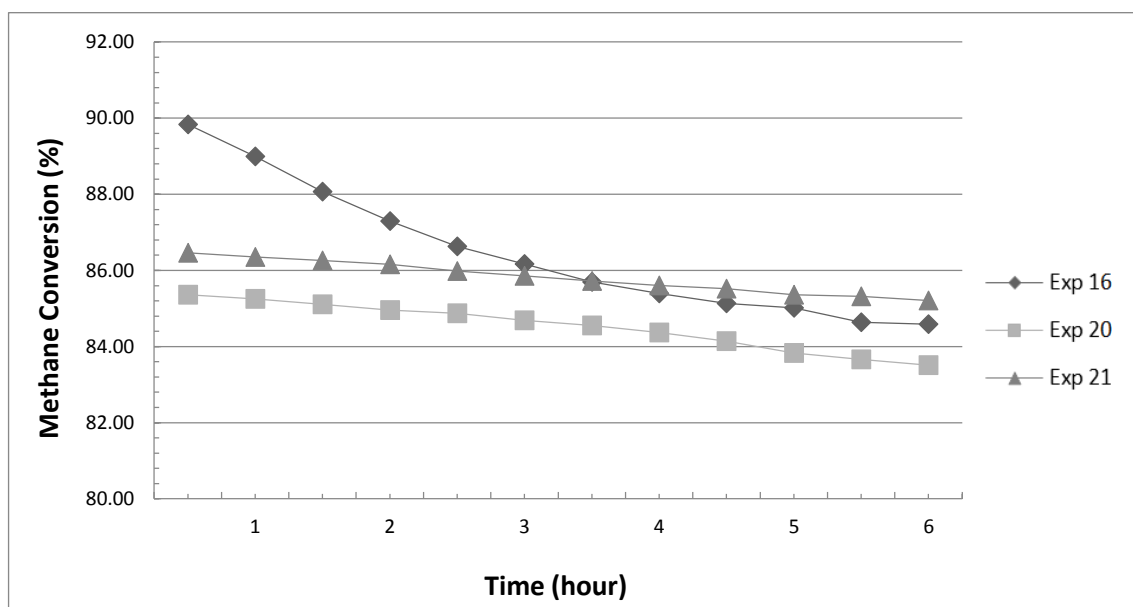


Figure 4.25. Effect of the Supporting Material on the Catalytic Performance of 15% Ni/SBA-15 Catalysts (Exp 16: 15% Ni/SBA-15; Exp 20: 15% Ni/TMB_SBA-15; Exp 21: 15% Ni/CTAB_SBA-15)

It seems that increased pore sizes and pore volumes (*please see Table 4.1*) led active metals to be dispersed easier on the catalyst surface, which in turn enhanced the resistance to carbon formation and deposition over the active metals and prevented metal sintering. Furthermore, CTAB_SBA-15 was more stable than TMB_SBA-15 most probably due to reported strong intermolecular repulsion forces present between Ni^+ and CTA^+ (Renuka *et al.*, 2013). Similar results were obtained over 7.5% Ni loaded catalysts and shown in Figure 4.26.

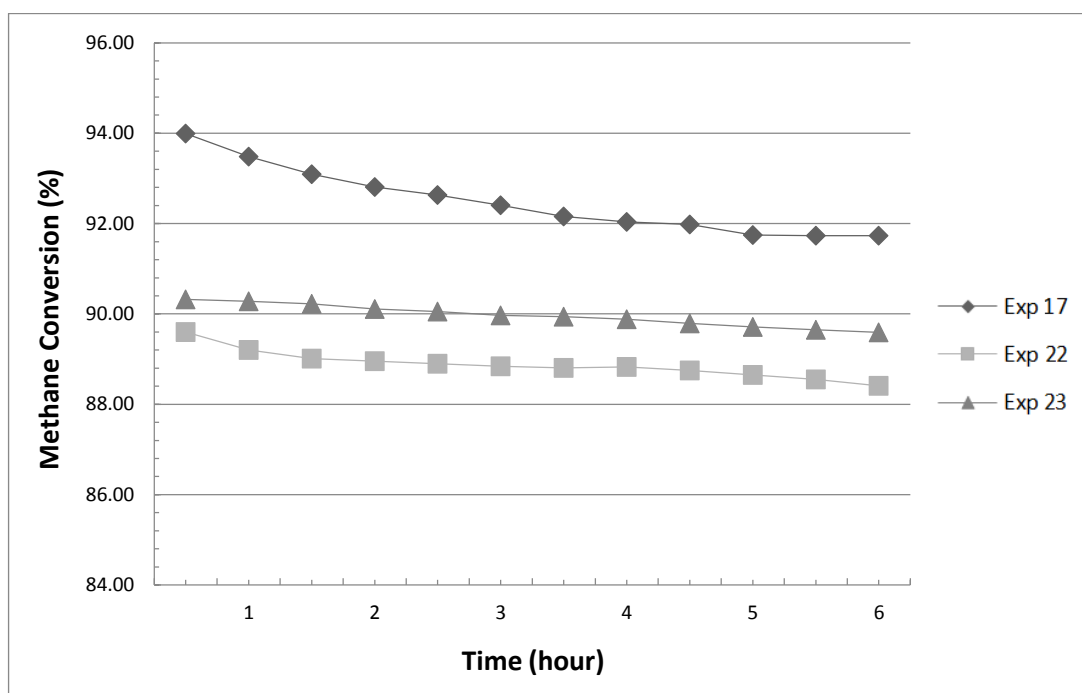


Figure 4.26. Effect of the Supporting Material on the Catalytic Performance of 7.5% Ni/SBA-15 Catalysts (Exp 17: 7.5% Ni/SBA-15; Exp 22: 7.5% Ni/TMB_SBA-15; Exp 23: 7.5% Ni/CTAB_SBA-15)

On the other hand, despite of their increased pore sizes and volumes, the catalytic activities of the modified supported catalysts were slightly lower than those supported on SBA-15, especially during the first 3 hours of the reaction, for both of 7.5% and 15% Ni loading levels. However, as both 7.5% and 15% Ni loaded samples prepared on modified SBA-15 showed greater stability during the reaction, the initial gaps in conversion levels diminished in time, especially for 15% Ni/SBA-15 case.

All the H_2/CO ratios obtained in the performance tests were close to 1 (shown in Figure 4.27 and Figure 4.28) which proved that the modification of the mesoporous silica support had no significant effect on selectivity.

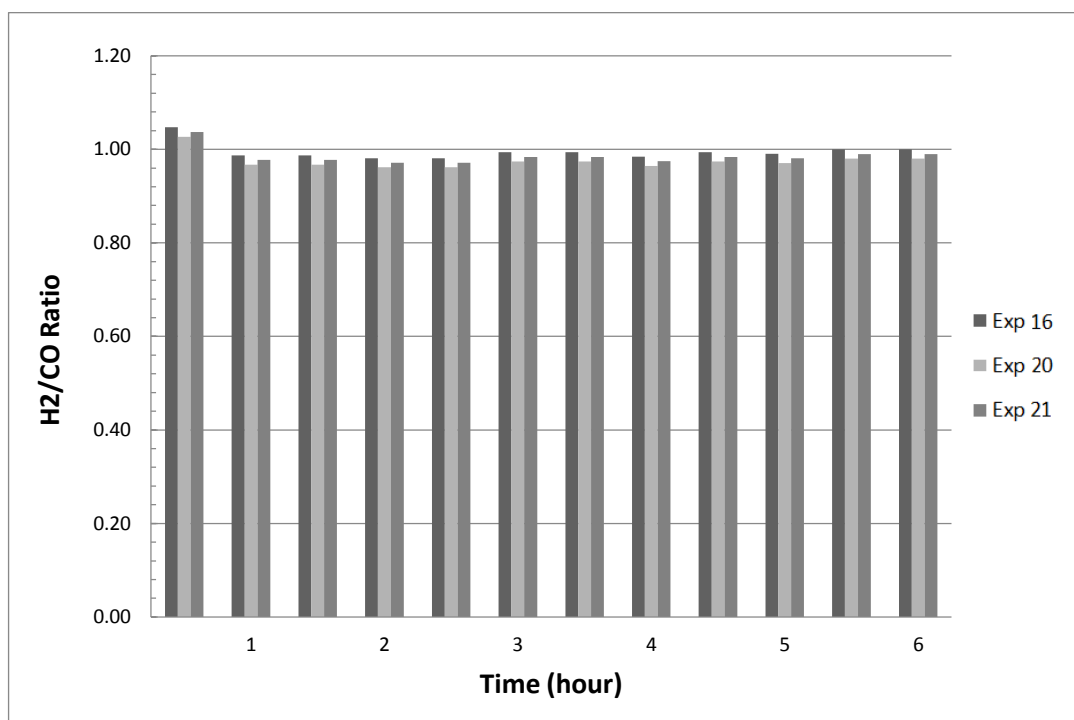


Figure 4.27. Effect of the Supporting Material on H_2/CO Ratio of 15% Ni Based Catalyst Samples (Exp 16: 15% Ni/SBA-15; Exp 20: 15% Ni/TMB_SBA-15; Exp 21: 15% Ni/CTAB_SBA-15)

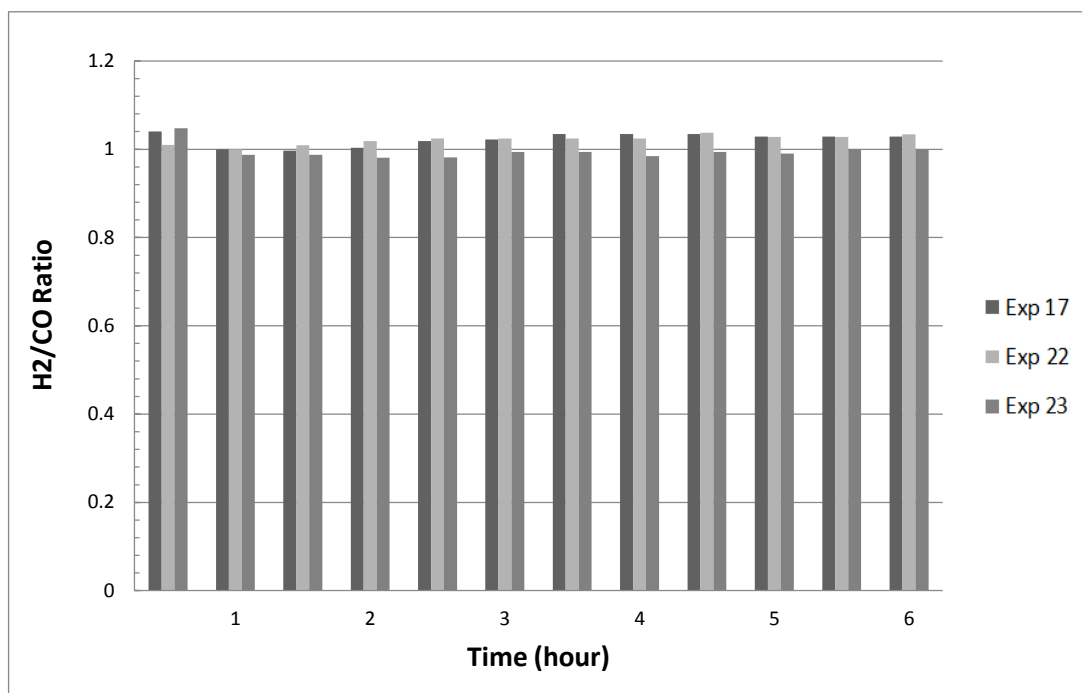


Figure 4.28. Effect of the Supporting Material on H₂/CO Ratio of 7.5%Ni Based Catalyst Samples (Exp 17: 7.5% Ni/SBA-15; Exp 22: 7.5% Ni/TMB_SBA-15; Exp 23: 7.5% Ni/CTAB_SBA-15)

4.2.2.3. Effect of the Drying Temperature

After the studies were conducted on the effects of different impregnation techniques, it was concluded that the impregnation and post-impregnation steps might be strongly effective on the catalytic performances of the CDRM catalysts as they were suggested by the recent studies on catalyst technologies. In this part of the thesis, the influence of the drying temperature applied following impregnation was investigated.

In order to observe the effect of the drying temperature, the catalyst calcined at 550 °C for 6 hours without any ramping rate, which exhibited one of the worst catalytic performances, was chosen and three different drying temperatures, 50 °C 80 °C, and 110 °C were applied.

Although the drying was not thought as one of the most significant parts of the catalysts preparation, the results of the conducted experiments evinced that the decrease in the overnight temperature strongly affected the catalytic performance, favored both catalytic activity and stability over CDRM as it can be seen on Figure 4.29.

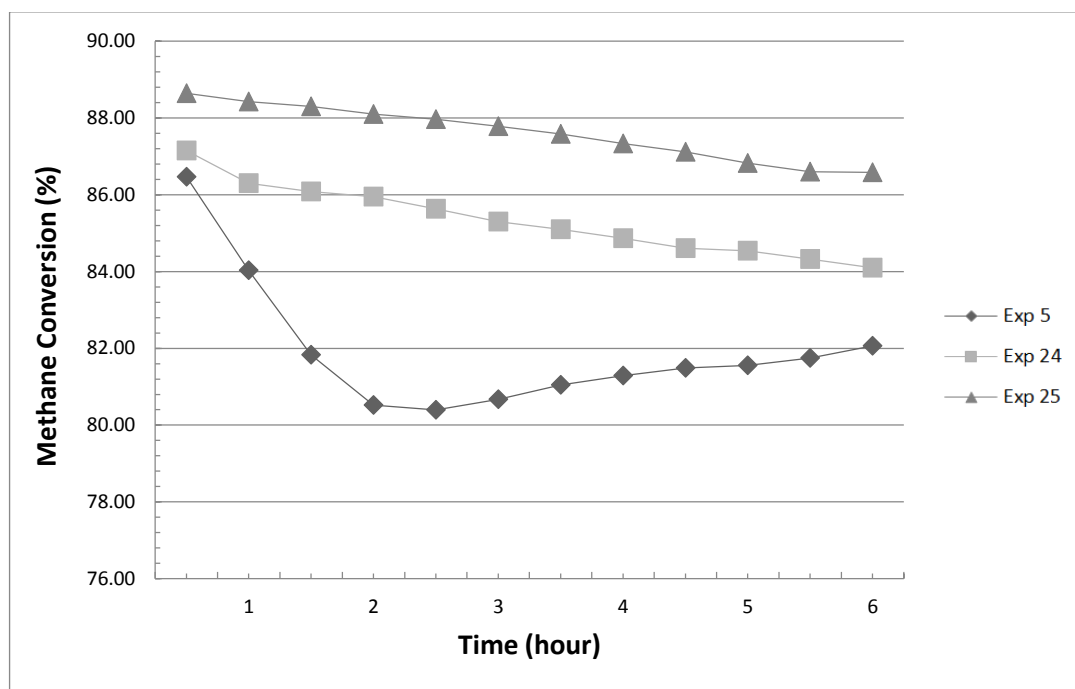


Figure 4.29. The effect of Overnight Temperature on Catalytic Performance (All experiments were conducted at 750 °C on 10% Ni/SBA-15 samples calcined at 550 °C for 6 hours without any ramping rate in air; Exp 5: drying at 110 °C; Exp 24: drying at 80 °C; Exp 25: drying at 50 °C)

During drying step, not only the precursor solution on the upper surface but also the solution penetrated inside the catalysts' pores is evaporated. As the rate of evaporation is strongly dependent on the temperature of the medium, these results confirm the importance of the step on performance, and suggest the necessity of detailed testing in the following studies.

Most probably, high temperature, i.e. 110 °C, favors the fast evaporation of the solution inside the pores and the pressure gradient formed pushed the liquid outside the pore. On the other hand, when the evaporation rate is low at 50 °C and 80 °C, and does not

lead to a pressure gradient along the pore; the solution is slowly evaporated and active metal precursor remain inside the pores. It should be noted that the effect of drying temperature on the H_2/CO ratio was found insignificant (Figure 4.30).

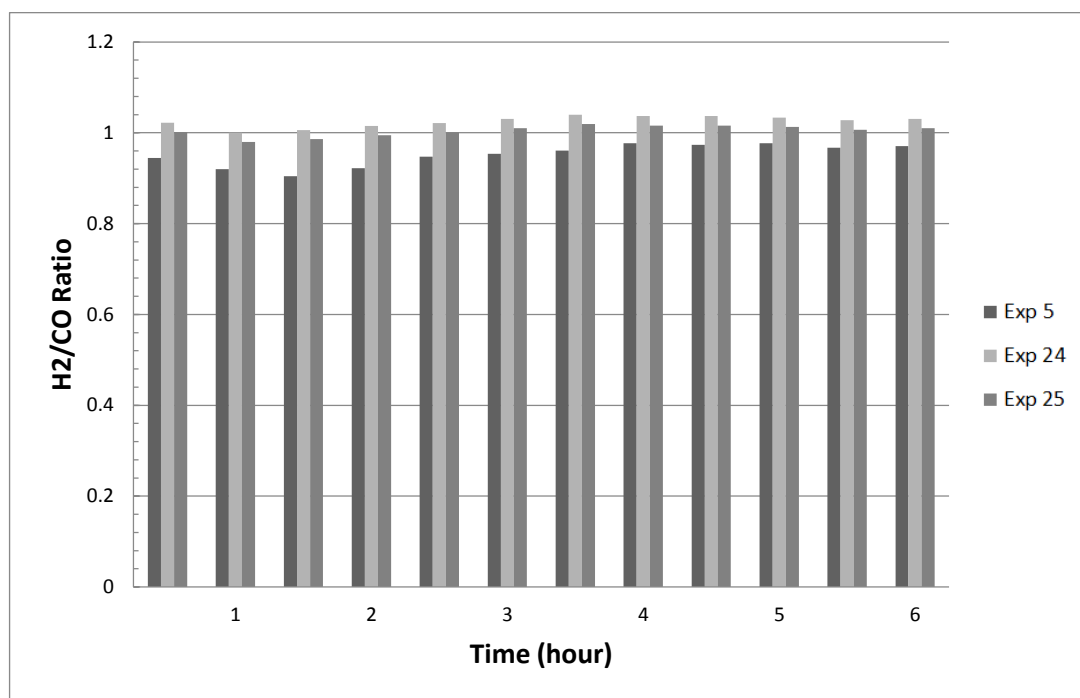


Figure 4.30. The Effect of Overnight Temperature on H_2/CO Ratio (All experiments were conducted at 750 °C on 10% Ni/SBA-15 samples calcined at 550 °C for 6 hours without any ramping rate in air; Exp 5: drying at 110 °C; Exp 24: drying at 80 °C; Exp 25: drying at 50 °C)

4.3. Stability Test for the Best Performing Catalyst

CDRM performance stability test was conducted over 10% Ni /SBA-15, which had showed the highest performance, for 72 hours at 800 °C. The catalyst was calcined at 750 °C for 6 hours with a ramping rate of 2°C/min. The stability test evinced that the methane conversion was around 97% with an insignificant activity loss of 1.28% at the end of 72 hr TOS (Figures 4.31 and 4.32).

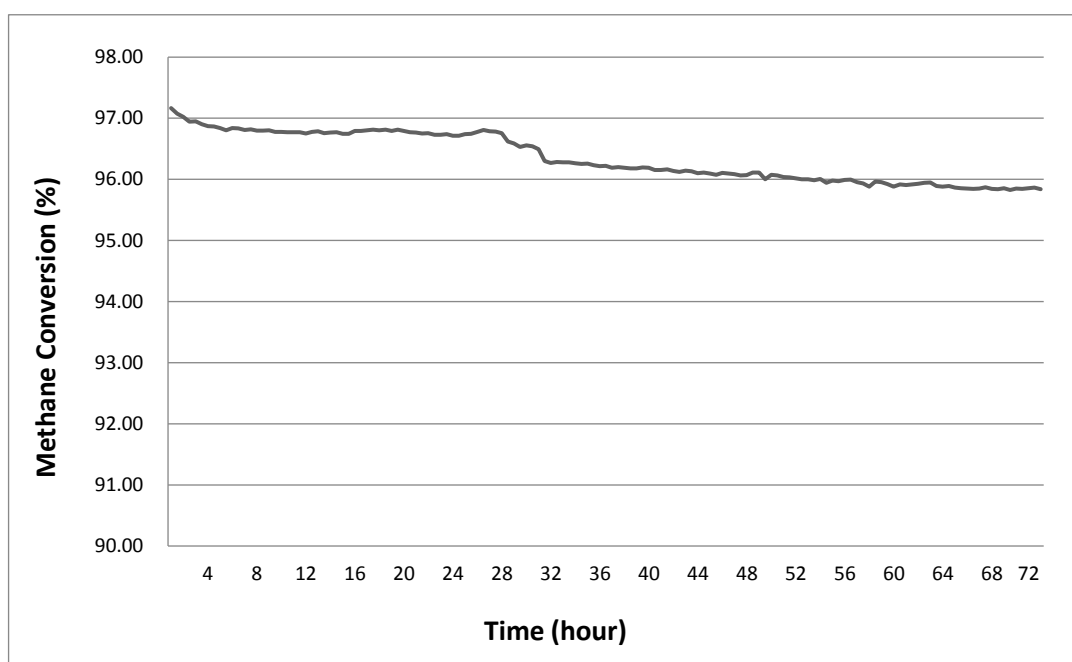


Figure 4.31. CH₄ Conversion Data of the Stability Test for 72 Hours

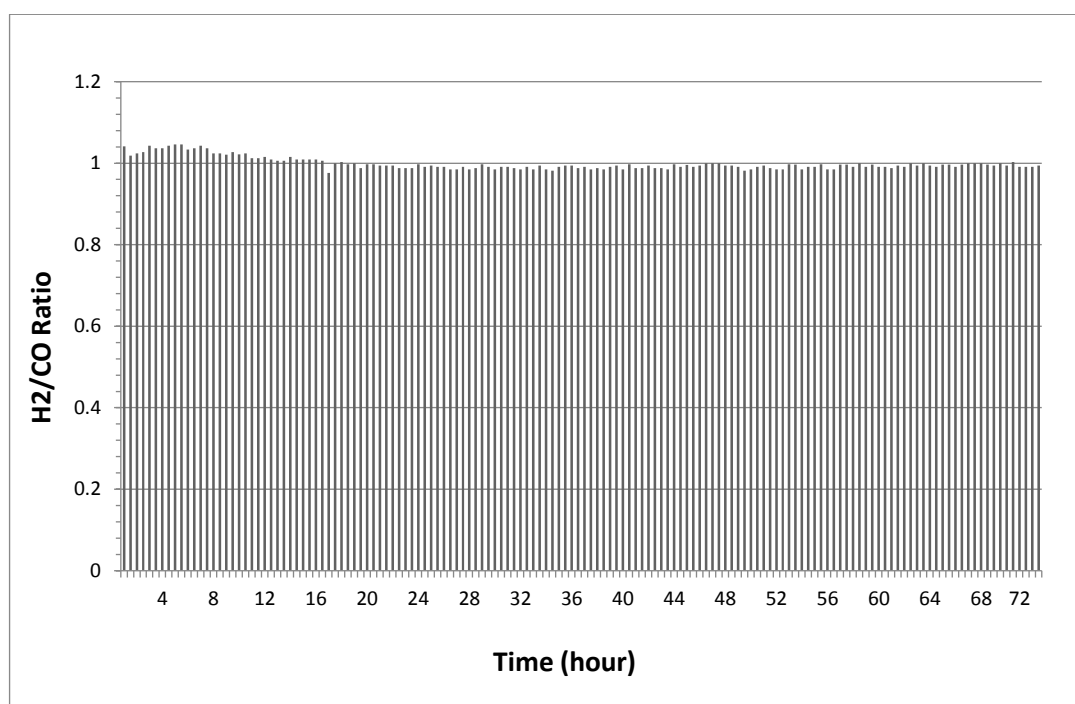


Figure 4.32. H₂/CO Data of the Stability Test for 72 Hours

4.4. Active Metal Dispersion on SBA-15

The performance test results confirm that most of the Ni based SBA-15 catalysts had high and significantly promising catalytic performances. It is known that metal dispersion is one of the most crucial parameters that affect catalyst performance. In this section, freshly reduced and spent forms of the most promising 10% Ni/SBA-15 catalyst were analyzed by using SEM in order to examine whether the interaction between active metal and supporting material leads high and stable dispersion. The fresh sample was prepared with IWI, calcined at 750 °C for 6 hours with a ramping rate of 2 °C/min in air, and the spent form was used in performance test conducted at 750 °C for 6 hours.

It can easily be seen in Figure 4.33 that Ni particles of the freshly reduced sample are well dispersed over the mesoporous SBA-15 indicating the effectiveness of preparation method.

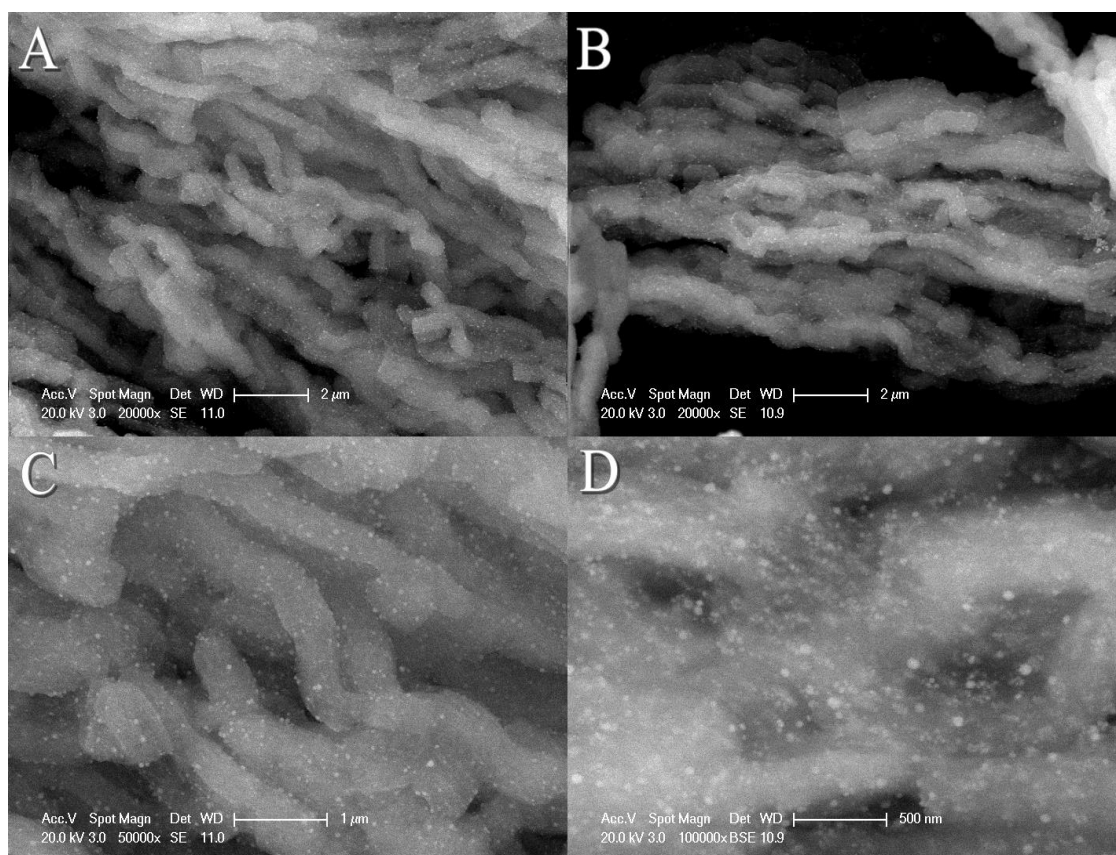


Figure 4.33. SEM Images for Ni Dispersion over Freshly Reduced Catalyst Samples in 20000x (A) and (B), 50000x (C) and 100000x (D)

The SEM images of the spent sample reveal that in most of the areas, the metal dispersion remained essentially constant, as it can be seen in Figure 4.34, and metal dispersion obtained on SBA-15 was highly stable at CDRM condition hinting strong active metal and support interaction.

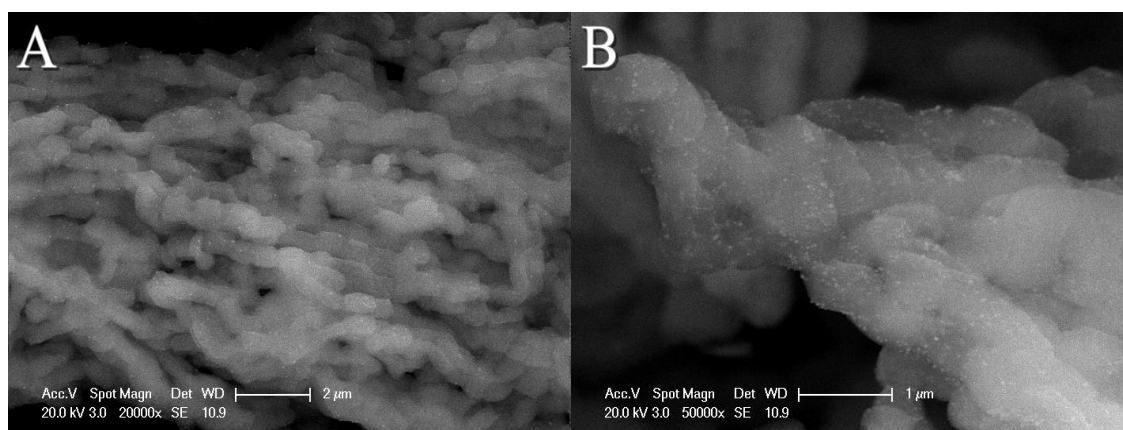


Figure 4.34. SEM Images for Ni Dispersion over Spent Catalyst Samples in 20000x (A) and 50000x (B)

However, it should be noted that in some limited number of areas, metal size growth were observed, as it can be seen Figure 4.35. The catalytic activity and stability was not dramatically affected most probably because these areas are low in number.

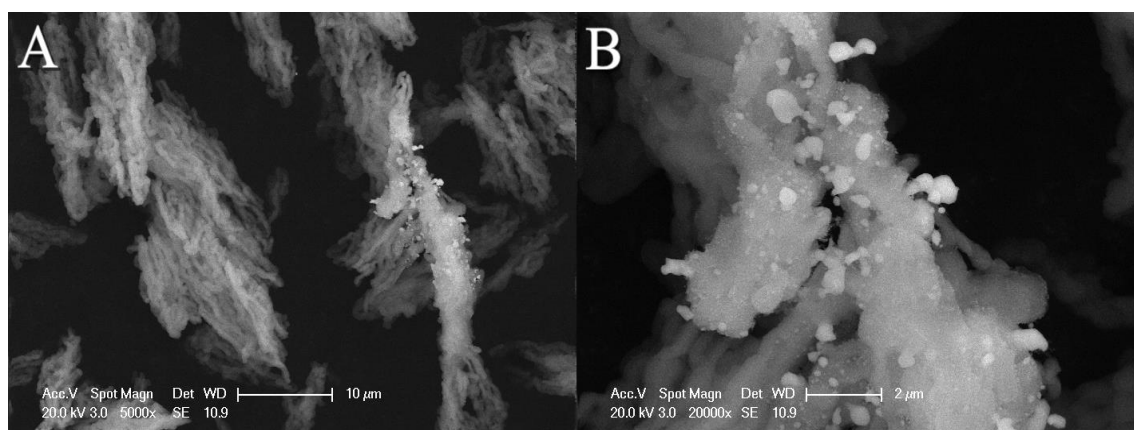


Figure 4.35. SEM Images for Ni Growth on Spent Samples in 5000x (A) and 20000x (B)

4.5. XPS Analysis on Catalyst Samples

The freshly reduced and spent forms of the catalyst samples mentioned in experiments #1, 5, 8 and 16, were analyzed by XPS aiming to observe whether changes happened during the reaction for given reaction conditions. The freshly reduced and spent samples were denoted with FR_X and SP_X (where X is number of the exp) respectively.

In CDRM over Ni-based catalysts, elemental form of nickel, also known as Ni^0 , is the active form; it is known that the reaction occurs on Ni^0 particles rather than its oxide form, Ni^{+2} (González-Elipe *et al.*, 1992).

In figure 4.36, it can be seen that regardless of its preparation process, all of the freshly reduced samples showed no differences in terms of peaks' binding energies. All of the freshly reduced samples had two different peaks at 852.4 for Ni^0 and 855.7 for Ni^{+2} (Biesinger *et al.*, 2012). As reduction reduces the oxidized Ni particles in calcined sample; Ni^{+2} peaks were much lower than the active Ni^0 form.

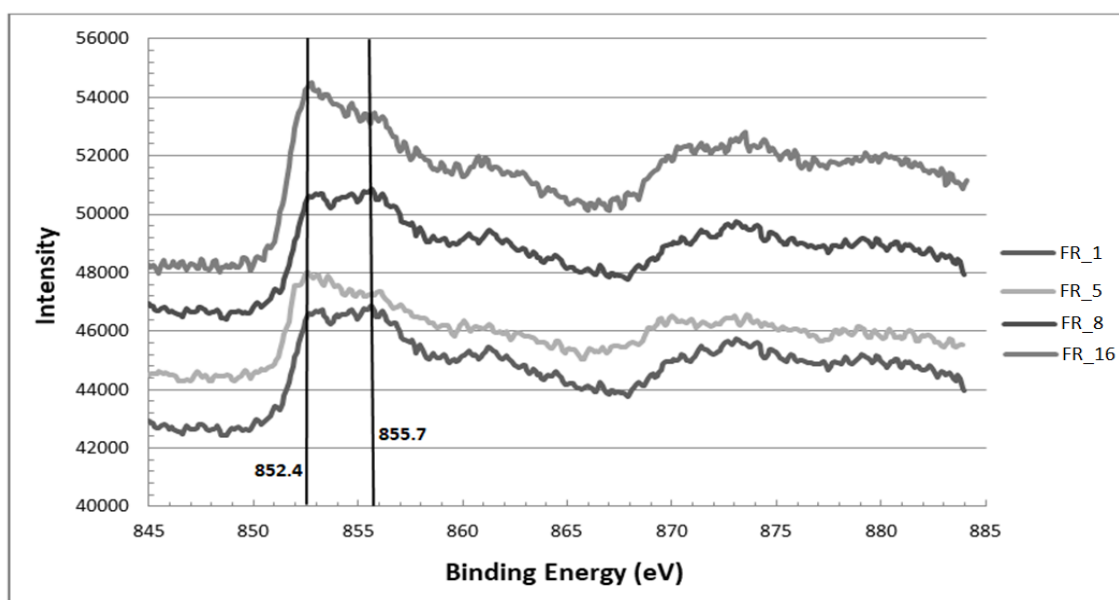


Figure 4.36. XPS Results of Nickel for Freshly Reduced Samples (FR_1: 10% Ni/SBA-15 calcined at 750 °C for 6 hours with 2 °C/min ramping rate in air; FR_5: 10% Ni/SBA-15 calcined at 550 °C without any ramping for 6 hours in air; FR_8: 10% Ni/SBA-15 calcined at 750 °C for 2 hours with 2 °C/min ramping rate in air; FR_16: 15% Ni/SBA-15 calcined at 750 °C for 6 hours with 2 °C/min ramping rate in air)

When the XPS profiles of the spent forms of the same catalysts were examined (Figure 4.37), although the trends in terms of nickel peaks were similar, an increase in the intensity of the Ni^{+2} form was observed for each sample indicating the oxidation of some zero valent active metal sites during CDRM.

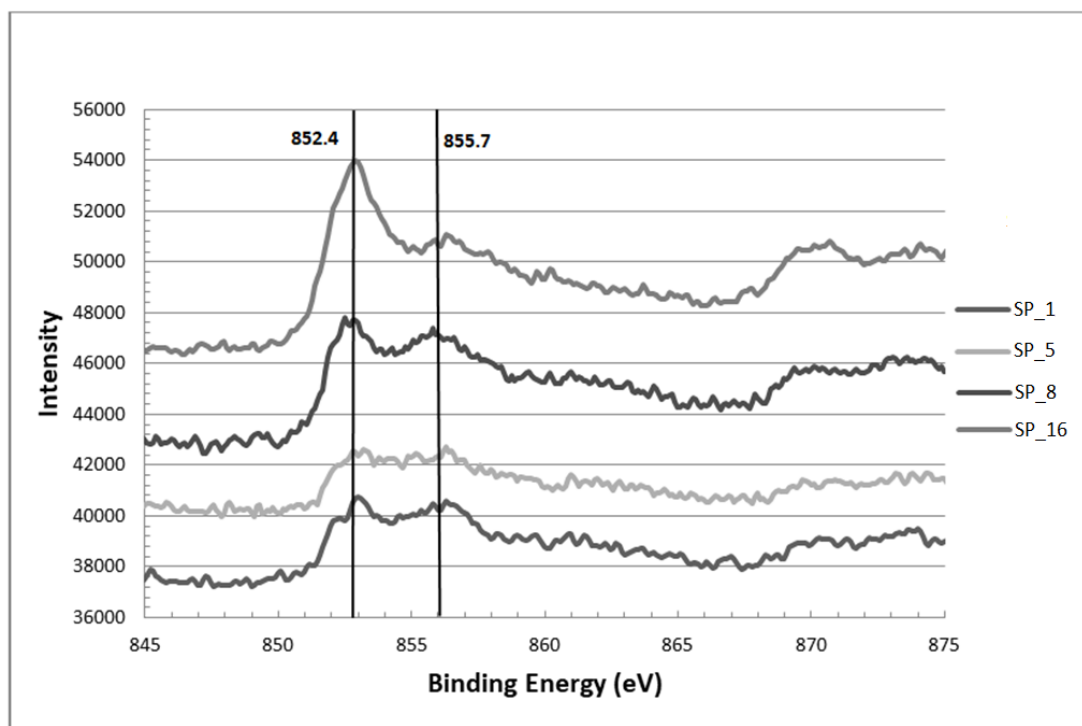


Figure 4.37. XPS Results of Nickel for Spent Samples after Reaction at 750 °C for 6 hours (SP_1: 10% Ni/SBA-15 calcined at 750 °C for 6 hours with 2 °C/min ramping rate in air; SP_5: 10% Ni/SBA-15 calcined at 550 °C without any ramping for 6 hours in air; SP_8: 10% Ni/SBA-15 calcined at 750 °C for 2 hours with 2 °C/min ramping rate in air; SP_16: 15% Ni/SBA-15 calcined at 750 °C for 6 hours with 2 °C/min ramping rate in air)

Further analysis of XPS data was conducted in order to understand the loss of active form of the nickel metal to its oxidized form by examining the weight percentages of nickel metal. As suggested by Zhao *et al.* (2020), first of all, the corresponding peaks of the $\text{Ni } 2p_{3/2}$ orbital of Ni/SBA-15 samples were determined and the areas under them were calculated by using the symmetrical properties of the Gaussian-Lorentzian shapes of the Ni 2p orbitals. For example, as it is shown in Figure 4.38, for the spent form of the catalyst used in Exp 5, peak at 852.4 eV represents the Ni^0 species whereas peak at 855.7 eV

represents the Ni^{+2} species (Biesinger *et al.*, 2012). The areas under the corresponding deconvolution curves were calculated as 10453.23 for Ni^0 and 16701.55 for Ni^{+2} species. By dividing these areas to each other and normalizing the values, Ni^0 and Ni^{+2} weight percentages were obtained, and these values were presented in Table 4.3. Similar calculation route was followed for the other catalyst samples.

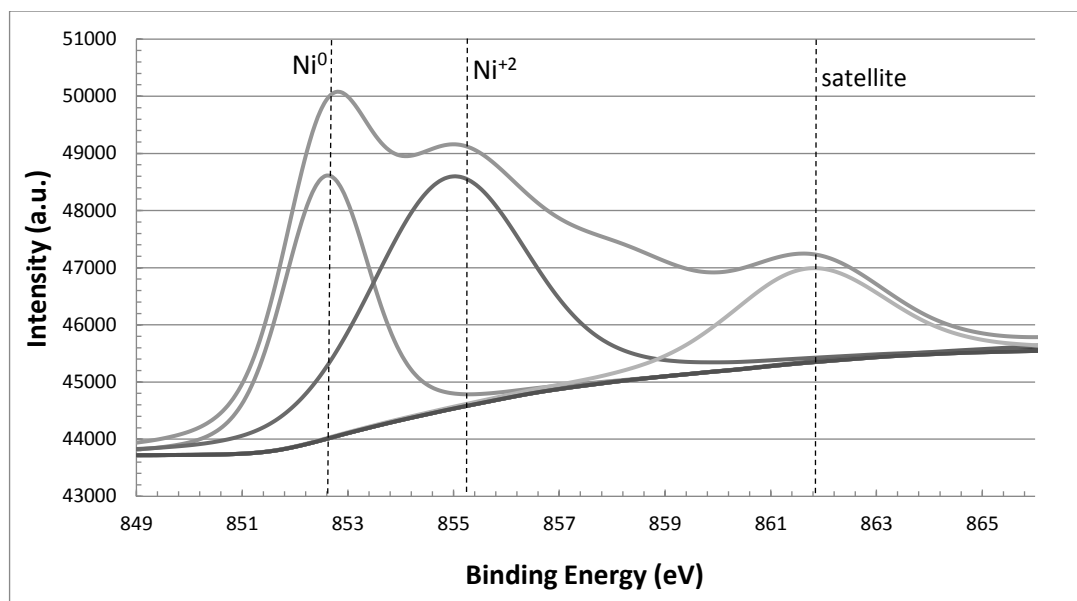


Figure 4.38. Ni 2p Scan of Spent Catalyst Sample of Exp 5 (SP_5: 10% Ni/SBA-15 calcined at 550 °C without any ramping for 6 hours in air)

Table 4.3. Elemental Analysis of Nickel for Freshly Reduced and Spent Samples

Catalyst	$\text{Ni}^0/\text{Ni}^{+2}$	Ni^0 %	Ni^{+2} %
FR_1	0.811	44.8	55.2
FR_5	0.906	47.5	52.5
FR_8	2.162	68.4	31.6
FR_16	0.885	46.9	53.1
SP_1	0.756	43.1	56.9
SP_5	0.626	38.5	61.5
SP_8	1.395	58.2	41.8
SP_16	0.701	41.2	58.8

It was seen that for all freshly reduced samples tested except FR_8, Ni⁰ percentages were similar to each other, at around 47%; whereas FR_8 had much higher Ni⁰ percentage around 68%. This was mainly caused by the calcination route of the catalyst, which was calcined for only 2 hours while others were calcined for 6 hours. It seems that as the calcination duration was shorter for FR_5, nickel atoms could not find enough time to be oxidized in greater extent, and the sample become richer in Ni⁰ upon reduction.

When the percent loss of Ni⁰ was measured and tabulated (Table 4.4), it is seen that the best performing catalyst showed a slight decrease, around 3.8 %, whereas others showed more than 12%. Hence, the results clearly show that loss of Ni⁰ sites was a dominant parameter determining the stability of the catalysts.

Table 4.4. Ni⁰ Loss of Freshly Reduced Samples

Catalyst	Ni ⁰ Loss (%)
FR_1	3.8
FR_5	19.0
FR_8	14.8
FR_16	12.2

Ni⁰ loss during CDRM was supported by the comparative analysis of XPS profiles of the freshly reduced and spent forms of the catalyst used in Exp 16. The XPS results shown in Figure 4.39 reveal a clear formation of a second peak in the XP spectrum of the spent catalyst sample around 856 eV, which signifies the formation Ni⁺².

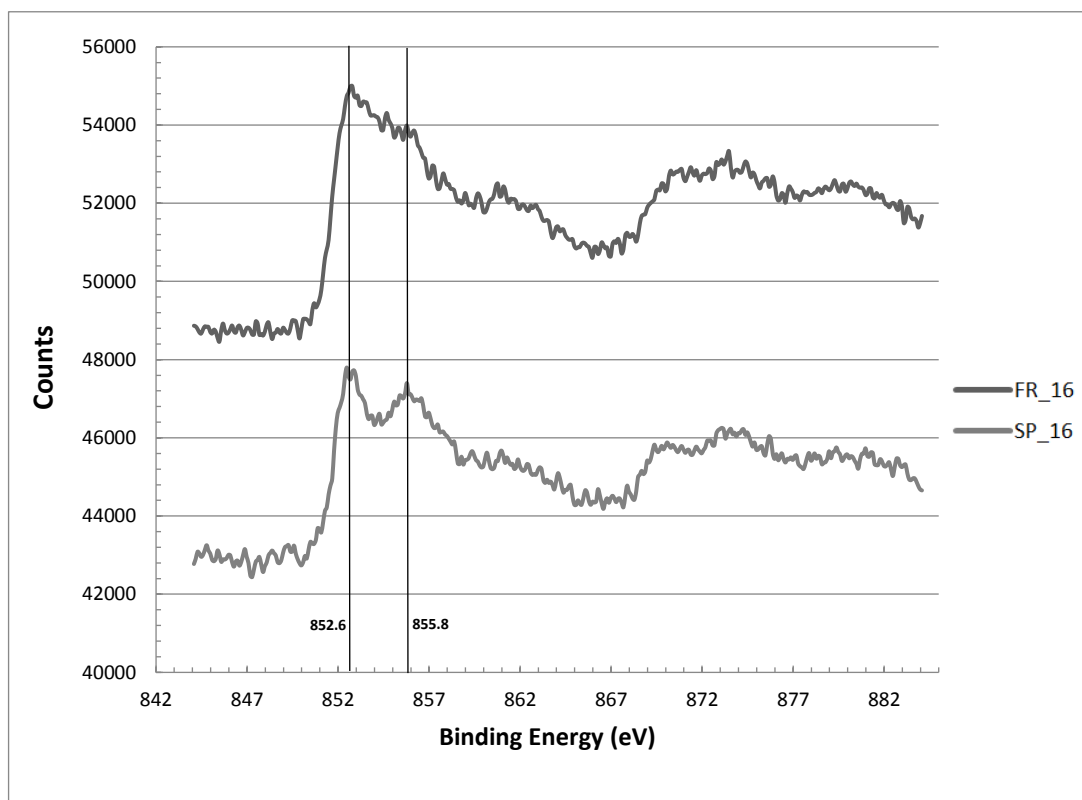


Figure 4.39. XPS Results of Nickel for Freshly Reduced and Spent Sample of Exp 16 (FR_16 & SP_16: 15% Ni/SBA-15 calcined at 750 °C for 6 hours with 2 °C/min ramping rate in air; SP_16: Reaction at 750 °C for 6 hours)

In order to understand the impact of the reaction on the surface of mesoporous silica support, the elemental analyses by XPS were also conducted on oxygen and silica. For this purpose, the freshly reduced and spent samples of Exp 1 (FR_1 & SP_1: 10% Ni/SBA-15 calcined at 750 °C for 6 hours with 2 °C/min ramping rate in air; SP_1: Reaction at 750 °C for 6 hours) and Exp 5 (FR_5 & SP_5: 10% Ni/SBA-15 calcined at 550 °C for 6 hours without any ramping rate in air; SP_5 Reaction at 750 °C for 6 hours) were comparatively analyzed.

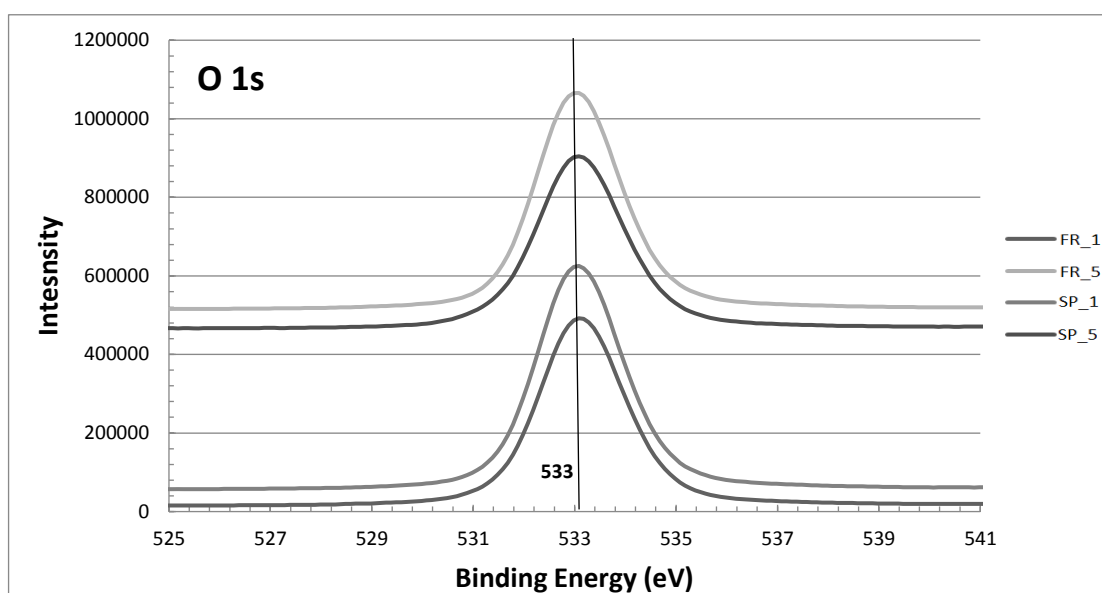


Figure 4.40. XPS Results of Oxygen for Freshly Reduced and Spent Samples (FR_1 & SP_1: 10% Ni/SBA-15 calcined at 750 °C for 6 hours with 2 °C/min ramping rate in air; SP_1: Reaction at 750 °C for 6 hours; FR_5 & SP_5: 10% Ni/SBA-15 calcined at 550 °C for 6 hours without any ramping rate in air; SP_5: Reaction at 750 °C for 6 hours)

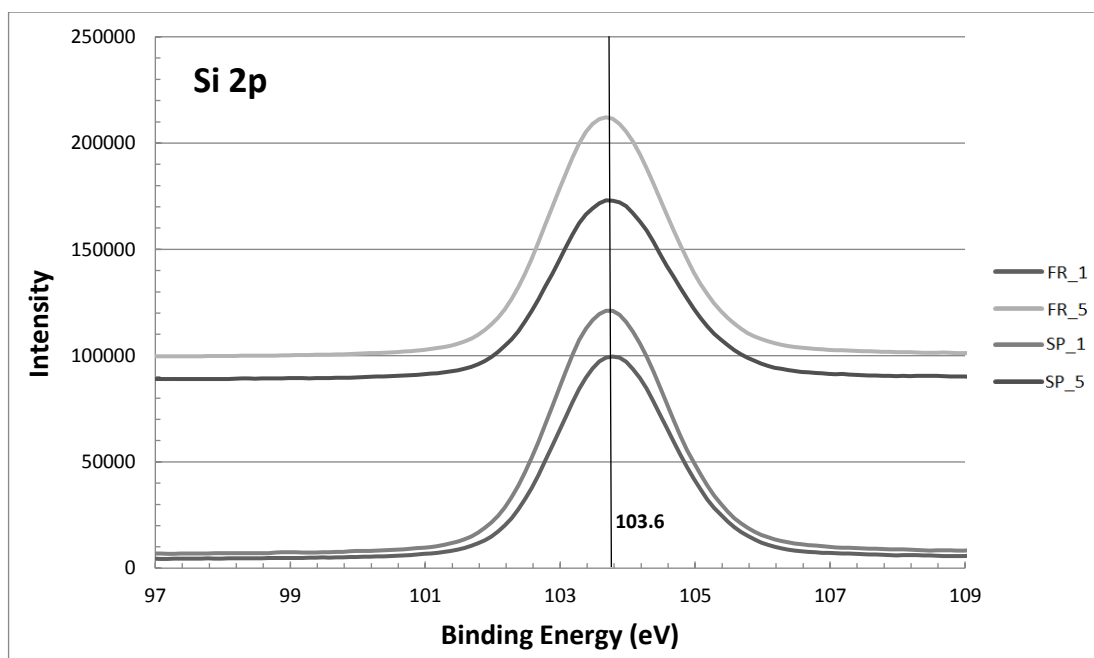


Figure 4.41. XPS Results of Silica for Freshly Reduced and Spent Samples (FR_1 & SP_1: 10% Ni/SBA-15 calcined at 750 °C for 6 hours with 2 °C/min ramping rate in air; SP_1: Reaction at 750 °C for 6 hours; FR_5 & SP_5: 10% Ni/SBA-15 calcined at 550 °C for 6 hours without any ramping rate in air; SP_5: Reaction at 750 °C for 6 hours)

For both of freshly reduced and spent samples of Experiment 1 and 5, oxygen had a peak at 533 eV, which represents the presence of O^{-2} species (Figure 4.40) whereas silica had a peak around 103.6 eV, which are attributed to the Si^{+2} species (Figure 4.41)(Gomez-Bolivar *et al.*, 2019). Therefore, since the elemental binding energies have exactly the same values, and the deconvolution results give the same areas for freshly reduced and spent catalysts' spectra, the results confirm that the reaction did not cause any changes on the surface elemental properties of the supporting material.

4.6. Coke Formation on the Catalyst

Coke deposition is one of the main reasons of activity loss during CDRM. The inhibition of carbon formation could be achieved only if carbon formation rate on the active metal sites producing hydrogen is balanced with oxidation rate of deposited carbon. Carbon deposition over a catalyst can easily be analyzed by Raman spectroscopy. In Raman spectrum, mainly on 2 different areas known also as D-band and G-band. D-band exhibits the disordered structure of the diamond like amorphous carbon caused by the defects such as impurities or holes on the supporting material; whereas G-band indicates the presence of graphite like crystalline carbon structures which is mainly caused by the C-C bond stretching mode of the sp^2 hybridization due to the honeycomb structure of the samples. Approximately, G band has a peak around 1550 cm^{-1} and D band has a peak around 1360 cm^{-1} on the Raman shift curves (Silva *et al.*, 2018).

Raman spectroscopy was conducted on 6 different samples, including the freshly reduced catalysts of experiment 1 and 8 (FR_1 and FR_8 respectively), spent catalysts of experiment 1, 5 and 8 (SP_1, SP_5 and SP_8 respectively) and the stability test (STAB), in order to study the relation between coke deposition and catalytic performance. *The preparation routes of the catalysts were; calcination at 750 °C for 6 hours with a ramping rate of 2 °C/min in air for Exp 1 and stability test; calcination at 550 °C for 6 hours without any ramping rate in air for Exp 5; calcination at 750 °C for 2 hours with 2 °C/min ramping rate in air for Exp 8. All of these catalyst samples were reduced in H_2 flow at 750 °C for 2 hours. Exp 1, Exp 5 and Exp 8 were conducted at 750 °C for 6 hours; whereas the reaction took place at 800 °C for 72 hours for during stability test.*

Although structural properties of the formed carbons can be determined by the Raman shifts, these results could be supported by another significant parameter, called as the degree of graphitization, which is the extent of transformation to graphite-like carbons (Lin et al., 2017). When Figure 4.42 is examined, it was seen that the freshly reduced samples of experiments 1 and 8 had degree of graphitization (I_G/I_D) of 1.013 and 0.985 respectively. Additionally, they showed no sharp peaks located at D-band or G-band. On the same graph, spent form catalyst having best performance (SP_1) showed a low peak around D-band and even a lower peak on the G-band with I_G/I_D of 0.97, meaning that there was insignificant amount of carbon deposition in the graphite form. Furthermore, higher peak around D-band suggested the formation of disordered form of carbon with structural defects rather than the graphite form, also known as high crystalline form, of carbon. The results confirm the stable performance the catalyst.

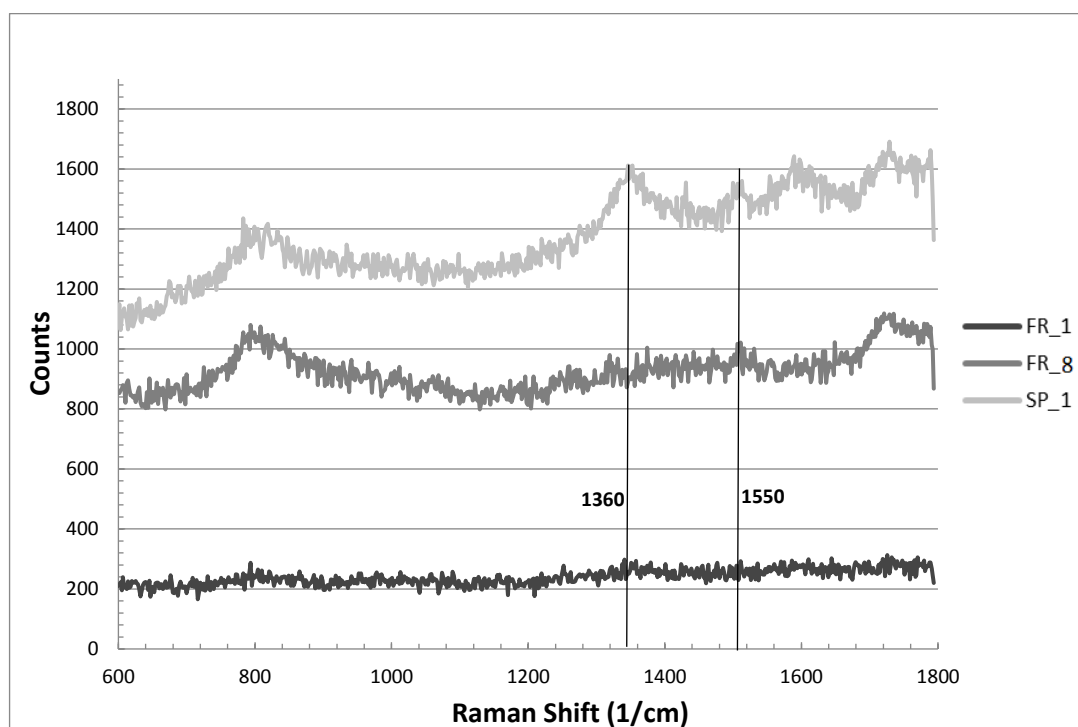


Figure 4.42. Raman Spectra of FR_1 and SP_1 (Calcination at 750 °C for 6 hours with 2 °C/min ramping rate in air), FR_8: Calcination at 750 °C for 2 hours with 2 °C/min ramping rate in air) and SP_1 (Calcination at 750 °C for 6 hours with 2 °C/min ramping rate in air, reaction at 750 °C for 6 hours)

On the other hand, Figure 4.43 showed that spent samples of experiment 5 and experiment 8, two of the catalyst samples faced with the highest catalyst deactivation during the reaction, showed sharper peaks on both D-band and G-band with I_G/I_D ratios of 1.326 and 1.208 respectively. Therefore, the graphite-like carbon formations over the catalyst support were significant for experiments 5 and 8.

Contrary to spent sample of experiment 1, both samples of experiment 5 and experiment 8 showed higher peaks on G-band meaning that the deposited carbon on the catalyst samples had higher crystallinity with larger nanoparticle sizes. The rapid deactivation on the catalyst samples observed during performance tests are in accordance with these findings, similar results were obtained for the catalyst that was used for the stability test over 72 hours with I_G/I_D ratio of 1.124. However, lower peak sizes suggested limited total of carbon deposition over the catalyst surface; this result explains the very limited, ca.1.28%, activity loss of the catalyst at the end of 72 h TOS stability test.

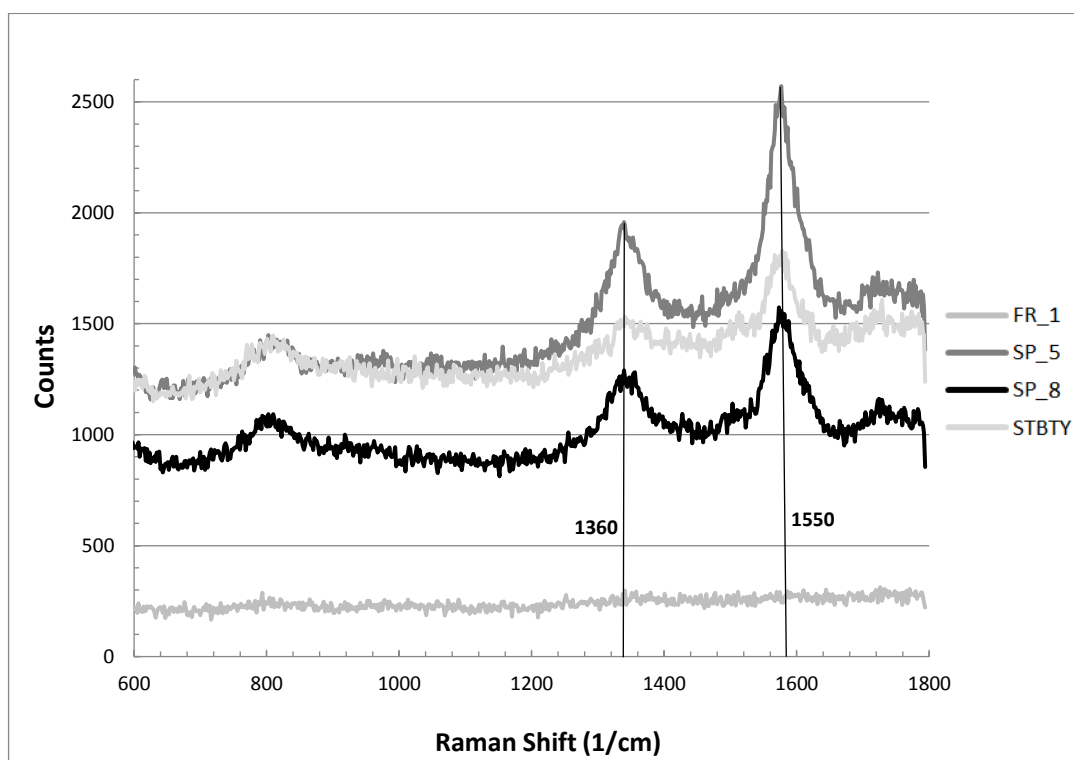


Figure 4.43. Raman Spectra of FR_1 (Calcination at 750 °C for 6 hours with 2 °C/min ramping rate in air), SP_5: (Calcination at 550 °C for 6 hours without any ramping rate in air), SP_8 (Calcination at 750 °C for 2 hours with 2 °C/min ramping rate in air,) and STBLTY (Calcination at 750 °C for 6 hours with 2 °C/min ramping rate in air)

Further analysis for coke deposition and its properties was conducted via XPS in order to understand this phenomenon better. *For this study, freshly reduced and spent catalyst samples of experiment 1, 5, 8 and 16 denoted with FR_1 (10% Ni/SBA-15 calcined at 750 °C for 6 hours with 2 °C/min ramping rate and reduced at 750 °C for 2 hours in H₂ flow), FR_5 (10% Ni/SBA-15 calcined at 550 °C for 6 hours without any ramping rate and reduced at 750 °C for 2 hours in H₂ flow), FR_8 (10% Ni/SBA-15 calcined at 750 °C for 2 hours with 2 °C/min ramping rate and reduced at 750 °C for 2 hours in H₂ flow), FR_16 (15% Ni/SBA-15 calcined at 750 °C for 6 hours with 2 °C/min ramping rate and reduced at 750 °C for 2 hours in H₂ flow), SP_1 (reaction at 750 °C for 6 hours), SP_5 (reaction at 750 °C for 6 hours), SP_8 (reaction at 750 °C for 6 hours) and SP_16 (reaction at 750 °C for 6 hours) respectively, were used.* The comparative analysis of the XPS profiles of the freshly reduced samples (Figure 4.44), reveals that all have the same peak at 284.5 with the similar intensity trend; whereas two of the catalyst samples (FR_1 and FR_16) had another peak at 288.4 eV. When these peaks were examined, it was found that the peak at 284.5 eV is known as the graphite carbon peak which is the main form of carbon deposition in its crystalline form with larger nanoparticles (Fang *et al.*, 2012). The increase in the sharpness of the 284.5 eV peak in the spent catalyst samples proved that there was a carbon deposition in these samples.

On the other hand, the peak at 288.4 eV, which were seen in FR_1 and FR_16 samples, was generated by the formation of metal carbonates in the form of O-C=O bonding which are widely used in the perovskite based catalyst in order to prevent the activity loss over the chosen reaction route (Christie *et al.*, 1981). Since metal carbonates favor the CO production via CO gasification of carbon (one of the side reactions of the catalytic dry reforming of methane), the carbon deposition over the catalyst surface was inhibited strongly. This may be the reason why the catalysts used in experiment 1, *calcined at 750 °C for 6 hours with 2 °C/min ramping rate*, showed the best performance over CDRM. The same peak was also observed for experiment 16 case, in which the catalyst was prepared with the same calcination route.

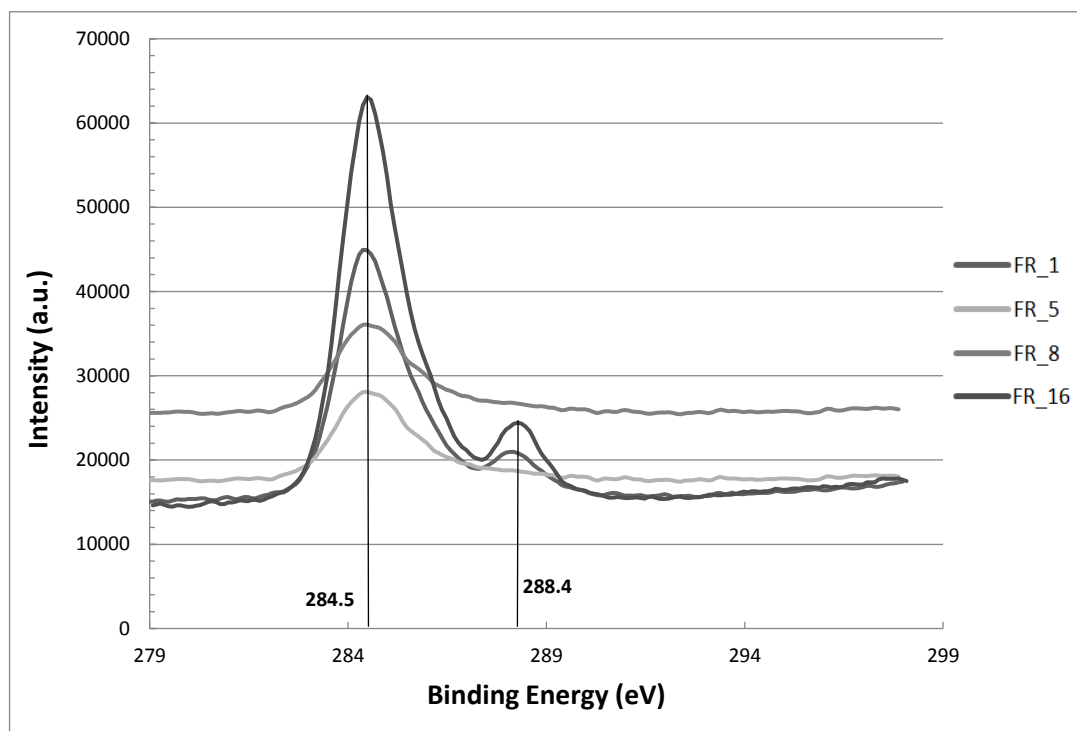


Figure 4.44. XPS Results of Freshly Reduced Samples (FR_1: 10% Ni/SBA-15 calcined at 750 °C for 6 hours with 2 °C/min ramping rate in air; FR_5: 10% Ni/SBA-15 calcined at 550 °C without any ramping for 6 hours in air; FR_8: 10% Ni/SBA-15 calcined at 750 °C for 2 hours with 2 °C/min ramping rate in air; FR_16: 15% Ni/SBA-15 calcined at 750 °C for 6 hours with 2 °C/min ramping rate in air)

When the XPS results of the spent samples were examined in Figure 4.45, the increase in the intensities of 284.5 eV peak compared to the corresponding peaks in the spectra of the catalysts' freshly reduced forms, proved that all samples had some carbon deposition over the catalyst surface regardless of its preparation procedure. It was also observed that the spent catalyst of experiment 5 showed a peak at 288.4 eV. As it was mentioned before, the results of Exp 5 showed that there was a decrease in the activity for the first 2 hours and an increase after that. This phenomenon might be explained with the formation of metal carbonates confirmed by the C1s XP spectrum of SP_5 sample.

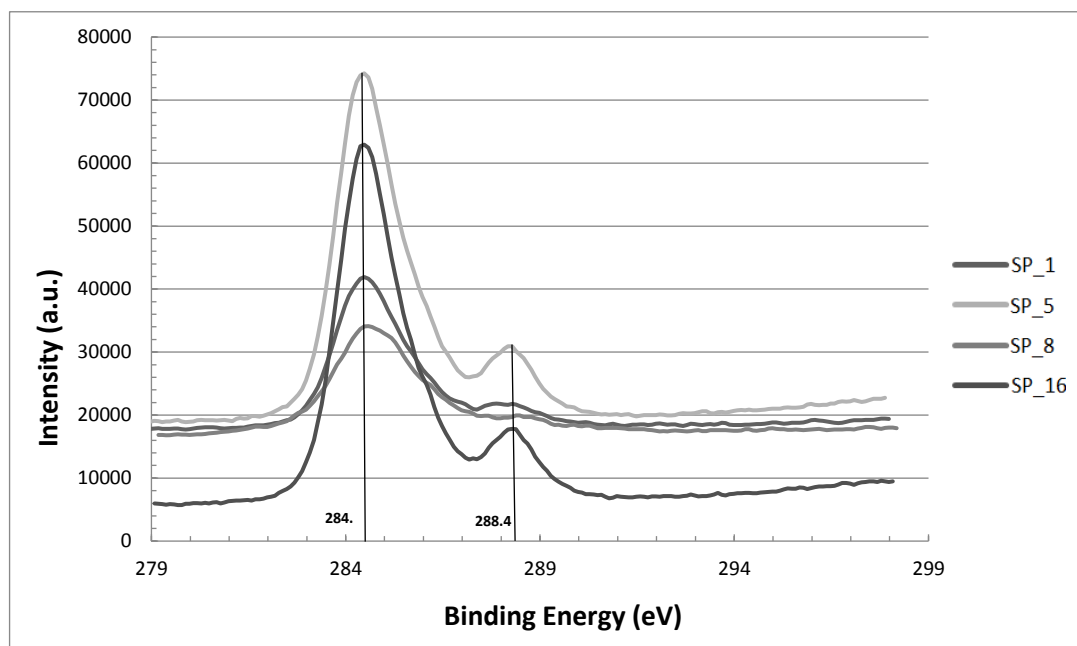


Figure 4.45. XPS Results of Spent Samples after Reaction at 750 °C for 6 hours (SP_1: 10% Ni/SBA-15 calcined at 750 °C for 6 hours with 2 °C/min ramping rate in air; SP_5: 10% Ni/SBA-15 calcined at 550 °C without any ramping for 6 hours in air; SP_8: 10% Ni/SBA-15 calcined at 750 °C for 2 hours with 2 °C/min ramping rate in air; SP_16: 15% Ni/SBA-15 calcined at 750 °C for 6 hours with 2 °C/min ramping rate in air)

As similar results were obtained for the catalyst used in stability test, its high performance and limited activity loss during 72 h TOS may stem from the formation of metal carbonates. It should be noted that decrease in Ni^0 was higher than that observed for experiment 1 (around 5.3 %), which is in accordance with its relatively higher activity loss in the stability test.

5. CONCLUSION

The primary results of the current experimental study are as follows;

The combined evaluation of the results of BET, XRD and SEM-EDX analyses confirm that an appropriate way for the production of mesoporous SBA-15 was constructed. Similar results with the literature were obtained.

Addition of co-solvent (TMB) and pore swelling agent (CTAB) had a direct impact on the physical and textural properties of the mesoporous SBA-15. Addition of both of them caused a decrease in the BET surface area and an increase in the average pore size of the mesoporous SBA-15. Additionally, CTAB addition led formation of hexagonally shaped SBA-15 chains and increased the uniformity and homogeneity.

Although most of the research was conducted with the TSI method, IWI method was found to be more effective yielding better catalytic performance.

Higher calcination and reduction temperatures for the temperature ranges tested found to have positive impact on the catalytic performance. Additionally, a ramping step in the calcination process led enough time for the stabilization of active metal over the catalyst surface; hence higher catalytic activity was observed.

Modifications on the reference catalyst samples showed that 7.5 and 15% Ni loaded samples had lower catalytic activity and stability than 10% Ni loaded SBA-15 samples. Despite the enhanced properties of TMB_SBA-15 and CTAB_SBA-15 samples, SBA-15 supported catalysts showed higher catalytic activity. However, experiments conducted with TMB_SBA-15 and CTAB_SBA-15 supported catalysts evinced higher thermal stability. Furthermore, lower drying temperatures had positive effect on the catalytic performance.

Raman analysis of the catalyst samples having relatively lower CDRM performance (Exp 5, 8 and 16) showed graphite-like carbon formations; whereas the analysis conducted on the best performing CDRM catalyst (Exp 1) showed very limited crystalline form of

carbon. Supportively, XPS analysis conducted on the same samples proved that all samples had some carbon deposition over the catalyst surface. However, the results of XPS analysis also showed the formation of metal carbonates (Exp 1 and 16) which prevents the coke deposition on the surface of the catalyst and catalytic deactivation via favoring CO gasification reaction. Therefore, it can be said that carbon deposition is strongly related with the preparation route of the catalyst and it can be inhibited and/or suppressed by choosing an appropriate preparation route for the reaction conditions used during the tests.

The results of the performance tests and characterizations showed that the most promising CDRM catalyst is 10% Ni/SBA-15, which was prepared by incipient wetness method, calcined at 750 °C for 6 hours with a 2 °C/min ramping rate in air.

6. REFERENCES

- Abbaspour, S., A.A. Nourbakhsh, R. J. Kalbasi and K. J. D. MacKenzie, “Investigating the properties of the nanocomposite (poly(4-vinyl pyridine)/Al-SBA-15): A precursor for β -SiAlON”, *Molecular Crystals and Liquid Crystals*, Vol. 555, pp. 104–111, 2012.
- Abdullah, B., N. A. Abd Ghani and D. V. N. Vo, “Recent advances in dry reforming of methane over Ni-based catalysts”, *Journal of Cleaner Production*, Vol. 162, pp. 170–185, 2017.
- Abdulrasheed, A., A. A. Jalil, Y. Gambo, M. Ibrahim, H. U. Hambali and M. Y. Shahul Hamid, “A review on catalyst development for dry reforming to syngas: Recent advances”, *Renewable and Sustainable Energy Reviews*, Vol. 108, pp. 175–193, 2019.
- Aramouni, N. A. K., J. G. Touma, B. A. Tarboush, J. Zeaiter and M. N. Ahmad, “Catalyst design for dry reforming of methane: Analysis review”, *Renewable and Sustainable Energy Reviews*, Vol. 82, pp. 2570–2585, 2017.
- Arora, S., and R. Prasad, “An overview on dry reforming of methane: Strategies to reduce carbonaceous deactivation of catalysts”, *RSC Advances*, Vol. 621, pp. 108668–108688, 2016.
- Aziz, M. A. A., H. D. Setiabudi, L. H. Teh, N. H. R. Annuar, and A. A. Jalil, “A review of heterogeneous catalysts for syngas production via dry reforming”, *Journal of the Taiwan Institute of Chemical Engineers*, Vol. 101, pp. 139–158, 2019.
- Beltrán, Y., C. Fernández, G. Pecchi and R. Jiménez, “Dry reforming of methane on grafted-supported Rh catalysts: effect of the metal-support interaction on the reaction rate”, *Reaction Kinetics, Mechanisms and Catalysis*, Vol. 120, pp. 459–475, 2017.

- Biesinger, M. C., L. W. M. Lau, A. R. Gerson, and R. S. C. Smart, “The role of the Auger parameter in XPS studies of nickel metal, halides and oxides”, *Physical Chemistry Chemical Physics*, Vol. 14, pp. 2434–2442, 2012.
- Bracciale, M. P., B. de Caprariis, P. De Filippis, A. D. Hernandez, and M. Scarsella, “New synthetic route for the production of mayenite support to enhance Ni resistance to coke deposition in the reforming of tar model compounds”, *Applied Catalysis A: General*, Vol. 579, pp. 48–59, 2019.
- Chaudhary, V., and S. Sharma, “An overview of ordered mesoporous material SBA-15: synthesis, functionalization and application in oxidation reactions”, *Journal of Porous Materials*, Vol. 24, pp. 741–749, 2017.
- Chen, S. Y., Y. T. Chen, J. J. Lee, and S. Cheng, “Tuning pore diameter of platelet SBA-15 materials with short mesochannels for enzyme adsorption”, *Journal of Materials Chemistry*, Vol 21, pp. 5693–5703, 2011.
- Christie, A., I. Sutherland, and J. Walls, “An XPS study of ion-induced dissociation on metal carbonate surfaces”, *Vacuum*, Vol. 31, pp. 513–517, 1981.
- Cimino, S., L. Lisi and G. Mancino, “Effect of phosphorous addition to Rh-supported catalysts for the dry reforming of methane”, *International Journal of Hydrogen Energy*, Vol. 42, pp. 23587–23598, 2017.
- Das, S., M. Shah, R. K. Gupta and A. Bordoloi, “Enhanced dry methane reforming over Ru decorated mesoporous silica and its kinetic study”, *Journal of CO₂ Utilization*, Vol. 29, pp. 240–253, 2019.
- Drobná, H., M. Kout, A. Sołtysek, V. M. González-Delacruz, A. Caballero and L. Čapek, “Analysis of Ni species formed on zeolites, mesoporous silica and alumina supports and their catalytic behavior in the dry reforming of methane”, *Reaction Kinetics, Mechanisms and Catalysis*, Vol. 121, pp. 255–274, 2017.

- Erdogan, B., H. Arbag, and N. Yasyerli, “SBA-15 supported mesoporous Ni and Co catalysts with high coke resistance for dry reforming of methane”, *International Journal of Hydrogen Energy*, Vol. 43, pp. 1396–1405, 2018.
- Fang, W., C. Pirez, M. Capron, S. Paul, T. Raja, P. L. Dhepe, F. Dumeignil and L. Jalowiecki-Duhamel, “Ce-Ni mixed oxide as efficient catalyst for H₂ production and nanofibrous carbon material from ethanol in the presence of water”, *RSC Advances*, Vol. 25, pp. 9626–9634, 2012.
- Gaillard, M., M. Virginie and A. Y. Khodakov, “New molybdenum-based catalysts for dry reforming of methane in presence of sulfur: A promising way for biogas valorization”, *Catalysis Today*, Vol. 289, pp. 143–150, 2017.
- Gao, X., Z. Tan, K. Hidajat and S. Kawi, “Highly reactive Ni-Co/SiO₂ bimetallic catalyst via complexation with oleylamine/oleic acid organic pair for dry reforming of methane”, *Catalysis Today*, Vol. 281, pp. 250–258, 2017.
- García, R., G. Soto, N. Escalona, C. Sepúlveda, M. J. Orellana, N. Morales, L. R. Radovic, R. Buitrago-Sierra, F. Rodriguez-Reinoso, and A. Sepúlveda-Escribano, “Methane dry reforming over Ni supported on pine sawdust activated carbon: Effects of support surface properties and metal loading”, *Quimica Nova*, Vol. 38, pp. 506–509, 2015.
- Ghods, B., F. Meshkani, and M. Rezaei, “Effects of alkaline earth promoters on the catalytic performance of the nickel catalysts supported on high surface area mesoporous magnesium silicate in dry reforming reaction”, *International Journal of Hydrogen Energy*, Vol. 23, pp. 22913–22921, 2016.
- Gomez-Bolivar, J., I. P. Mikheenko, R. L. Orozco, S. Sharma, D. Banerjee, M. Walker, R. A. Hand, M. L. Merroun and L. E. Macaskie, “Synthesis of Pd/Ru bimetallic nanoparticles by *Escherichia coli* and potential as a catalyst for upgrading 5-hydroxymethyl furfural into liquid fuel precursors”, *Frontiers in Microbiology*, Vol. 10, pp. 1–17, 2019.

- González-Elípe, A. R., J. P. Holgado, R. Alvarez, and G. Munuera, “Use of factor analysis and XPS to study defective nickel oxide”, *Journal of Physical Chemistry*, Vol. 96, pp. 3080–3086, 1992.
- Goula, M. A., N. Charisiou, G. Siakavelas, L. Tzounis, I. Tsiaoussis, P. Panagiotopoulou, G. Goula and I. V. Yentekakis, “Syngas production via the biogas dry reforming reaction over Ni supported on zirconia modified with CeO₂ or La₂O₃ catalysts”. *International Journal of Hydrogen Energy*, Vol. 42, pp. 13724–13740, 2017.
- Gurav, H. R., S. Dama, V. Samuel and S. Chilukuri, “Influence of preparation method on activity and stability of Ni catalysts supported on Gd doped ceria in dry reforming of methane”, *Journal of CO₂ Utilization*, Vol. 20, pp. 357–367, 2017.
- Han, J. W., J. S. Park, M. S. Choi and H. Lee, “Uncoupling the size and support effects of Ni catalysts for dry reforming of methane”, *Applied Catalysis B: Environmental*, Vol. 23, pp. 625–632, 2017.
- Hassan Amin, M., “A Mini-Review on CO₂ Reforming of Methane”, *Progress in Petrochemical Science*, Vol. 2, pp. 1–5, 2018.
- Jabbour, K., N. El Hassan, S. Casale, J. Estephane and H. El Zakhem, “Promotional effect of Ru on the activity and stability of Co/SBA-15 catalysts in dry reforming of methane”, *International Journal of Hydrogen Energy*, Vol. 39, pp. 7780–7787, 2014.
- Jang, W. J., J. O. Shim, H. M. Kim, S. Y. Yoo and H. S. Rod, “A review on dry reforming of methane in aspect of catalytic properties”, *Catalysis Today*, Vol. 324, pp. 15–26, 2019.
- Kamieniak, J., E. Bernalte, A. M. Doyle, P. J. Kelly and C. E. Banks, “Can Ultrasound or pH Influence Pd Distribution on the Surface of HAP to Improve Its Catalytic Properties in the Dry Reforming of Methane?”, *Catalysis Letters*, Vol. 147, pp. 2200–2208, 2017.

- Kaydouh, M. N., N. El Hassan, A. Davidson, S. Casale, H. El Zakhem and P. Massiani, “Highly active and stable Ni/SBA-15 catalysts prepared by a “two solvents” method for dry reforming of methane”, *Microporous and Mesoporous Materials*, Vol. 220, pp. 99–109, 2016.
- Khani, Y., Z. Shariatnia and F. Bahadoran, “High catalytic activity and stability of ZnLaAlO₄ supported Ni, Pt and Ru nanocatalysts applied in the dry, steam and combined dry-steam reforming of methane”, *Chemical Engineering Journal*, Vol. 299, pp. 353–366, 2016.
- Kikhtyanin, O., V. Pospelova, J. Aubrecht, M. Lhotka and D. Kubička, “Effect of atmosphere calcination and temperature on the hydrogenolysis activity and selectivity of copper-zinc catalysts”, *Catalysts*, Vol. 8, pp. 14-23, 2018
- Lavoie, J. M., “Review on dry reforming of methane, a potentially more environmentally-friendly approach to the increasing natural gas exploitation”, *Frontiers in Chemistry*, Vol. 2, pp. 17-28, 2014.
- Li, D., R. Li, M. Lu, X. Lin, Y. Zhan and L. Jiang, “Carbon dioxide reforming of methane over Ru catalysts supported on MgAl oxides: A highly dispersed and stable Ru/Mg(Al)O catalyst”, *Applied Catalysis B: Environmental*, Vol. 2, pp. 66–77, 2017.
- Li, L., L. Zhou, S. Ould-Chikh, D. Anjum, M. B. Kanoun, J. Scaranto, M. Hedhili, S. Khalid, P. V. Laveille, L. D’Souza, A. Clo, and J. M. Basset, “Controlled surface segregation leads to efficient coke-resistant nickel/platinum bimetallic catalysts for the dry reforming of methane”, *ChemCatChem*, Vol. 5, pp. 819–829, 2015
- Lin, L., M. Lai, H. Li, F. Tian, Y. Chen, J. Sun, and J. M. Lin, “Investigation of carbon deposition induced by pyrolytic decomposition of ethylene”, *RSC Advances*, Vol. 7, pp. 29639–29644, 2017.
- Lin, X., R. Li, M. Lu, C. Chen, D. Li, Y. Zhan and L. Jiang, “Carbon dioxide reforming of methane over Ni catalysts prepared from Ni-Mg-Al layered double hydroxides: Influence of Ni loadings”, *Fuel*, Vol. 162, pp. 271–280, 2015.

- Liu, H., and J. M. “Zhang, Investigation on structure, electronic and magnetic properties of Cr doped $(\text{ZnO})_{12}$ clusters: First-principles calculations”, *Physica E: Low-Dimensional Systems and Nanostructures*, Vol. 99, pp. 51–57, 2018.
- Mourhly, A., M. Kacimi, M. Halim and S. Arsalane, “New low cost mesoporous silica (MSN) as a promising support of Ni-catalysts for high-hydrogen generation via dry reforming of methane (DRM)”, *International Journal of Hydrogen Energy*, Vol. 45, pp. 11449–11459, 2020.
- Movasati, A., S. M. Alavi and G. Mazloom, “ CO_2 reforming of methane over $\text{Ni}/\text{ZnAl}_2\text{O}_4$ catalysts: Influence of Ce addition on activity and stability”. *International Journal of Hydrogen Energy*, Vol. 42, pp. 16436–16448, 2020.
- Oliveira, A. C., D. C. Carvalho, H. S. A. De Souza, J. M. Filho, A. C. Oliveira, A. Campos, E. R. C. Milet, F. F. De Sousa and E. Padron-Hernandez, “A study on the modification of mesoporous mixed oxides supports for dry reforming of methane by Pt or Ru”, *Applied Catalysis A: General*, Vol. 473, pp. 132–145, 2014.
- Pakhare, D., C. Shaw, D. Haynes, D. Shekhawat and J. Spivey, “Effect of reaction temperature on activity of Pt- and Ru-substituted lanthanum zirconate pyrochlores ($\text{La}_2\text{Zr}_2\text{O}_7$) for dry (CO_2) reforming of methane (DRM)”. *Journal of CO_2 Utilization*, Vol. 1, pp. 37–42, 2014.
- Park, J. H., S. Yeo and T. S. Chang, “Effect of supports on the performance of Co-based catalysts in methane dry reforming”, *Journal of CO_2 Utilization*, Vol. 26, pp. 465–475, 2018.
- Renuka, N. K., A. K. Praveen and K. Anas, “Influence of CTAB molar ratio in tuning the texture of rice husk silica into MCM 41 and SBA-16”, *Materials Letters*, Vol. 109, pp. 70–73, 2013.
- Shariatinia, Z., Y. Khani and F. Bahadoran, “Synthesis of a novel 3 %Ru/ $\text{CeZr}_{0.5}\text{GdO}_4$ nanocatalyst and its application in the dry and steam reforming of methane”. *International Journal of Environmental Science*, Vol. 13, pp. 423–434, 2016.

- Silva, D. L. C., L. R. P. Kassab, A. D. dos Santos, and M. F. Pillis, "Evaluation of Carbon thin Films Using Raman Spectroscopy". *Materials Research*, Vol. 21, pp. 1–6, 2018.
- Singh, S. A., and G. Madras, "Sonochemical synthesis of Pt, Ru doped TiO₂ for methane reforming", *Applied Catalysis A: General*, Vol. 518, pp. 102–114, 2016.
- Singh, S., T. D. Nguyen, T. J. Siang, P. T. T. Phuong, N. H. Huy Phuc, Q. D. Truong, S. S. Lam and D. Vo, "Boron-doped Ni/SBA-15 catalysts with enhanced coke resistance and catalytic performance for dry reforming of methane", *Journal of the Energy Institute*, Vol. 93, pp. 31–42, 2020.
- Singha, R. K., A. Yadav, A. Shukla, M. Kumar and R. Bal, "Low temperature dry reforming of methane over Pd-CeO₂ nanocatalyst", *Catalysis Communications*, Vol. 92, pp. 19–22, 2017.
- Sokolov, S., J. Radnik, M. Schneider and U. Rodemerck, "Low-temperature CO₂ reforming of methane over Ni supported on ZnAl mixed metal oxides", *International Journal of Hydrogen Energy*, Vol. 42, pp. 9831–9839, 2017.
- Taherian, Z., M. Yousefpour, M. Tajally and B. Khoshandam, "Catalytic performance of Samaria-promoted Ni and Co/SBA-15 catalysts for dry reforming of methane", *International Journal of Hydrogen Energy*, Vol. 42, pp. 24811–24822, 2017.
- Taherian, Z., M. Yousefpour, M. Tajally and B. Khoshandam, "Promotional effect of samarium on the activity and stability of Ni-SBA-15 catalysts in dry reforming of methane", *Microporous and Mesoporous Materials*, Vol. 251., pp. 9–18, 2017.
- Titus, J., T. Roussière, G. Wasserschaff, S. Schunk, A. Milanov, E. Schwab, G. Wagner, O. Oeckler and R. Gläser, "Dry reforming of methane with carbon dioxide over NiO-MgO-ZrO₂", *Catalysis Today*, Vol. 270, pp. 68–75, 2016.
- Usman, M., W. M. A. Wan Daud and H. F. Abbas, "Dry reforming of methane: Influence of process parameters - A review", *Renewable and Sustainable Energy Reviews*, Vol. 45, pp. 710–744, 2015.

- Wang, F., L. Xu, W. Shi, J. Zhang, K. Wu, Y. Zhao, H. Li, H. X. Li, G. Q. Xu and W. Chen, “Thermally stable Ir/Ce_{0.9}La_{0.1}O₂ catalyst for high temperature methane dry reforming reaction”. *Nano Research*, Vol. 10, pp. 364–380, 2017.
- Wu, H., G. Pantaleo, V. La Parola, A. M. Venezia, X. Collard, C. Aprile and L. F. Liotta, “Bi and trimetallic Ni catalysts over Al₂O₃ and Al₂O₃-MO_x (M=Ce or Mg) oxides for methane dry reforming: Au and Pt additive effects”, *Applied Catalysis B: Environmental*, Vol. 156, pp. 350–361, 2014.
- Xu, J., Q. Xiao, J. Zhang, Y. Sun and Y. Zhu, “NiO-MgO nanoparticles confined inside SiO₂ frameworks to achieve highly catalytic performance for CO₂ reforming of methane”, *Molecular Catalysis*, Vol. 432, pp. 31–36, 2017.
- Yao, L., J. Shi, W. Shen and C. Hu, “Low-temperature CO₂ reforming of methane on Zr-promoted Ni/SiO₂ catalyst”, *Fuel Processing Technology*, Vol. 144, pp. 1–7, 2016.
- Yasmin, T. and K. Müller, “Synthesis and characterization of surface modified SBA-15 silica materials and their application in chromatography”, *Journal of Chromatography A*, Vol. 1218, pp. 6464–6475, 2011.
- Yentekakis, I. V., G. Goula, P. Panagiotopoulou, A. Katsoni, E. Diamadopoulos, D. Mantzavinos and A. Delimitis, “Dry reforming of methane: Catalytic performance and stability of Ir catalysts supported on γ -Al₂O₃, Zr_{0.92}Y_{0.08}O_{2- δ} (YSZ) or Ce_{0.9}Gd_{0.1}O_{2- δ} (GDC) supports”, *Topics in Catalysis*, Vol. 58, pp. 228–241, 2015.
- Yu, M., Y. A. Zhu, Y. Lu, G. Tong, K. Zhu and X. Zhou, “The promoting role of Ag in Ni-CeO₂ catalyzed CH₄-CO₂ dry reforming reaction”, *Applied Catalysis B: Environmental*, Vol. 165, pp. 43–56, 2015.
- Zeng, Y., S. Zhang, Y. Wang, G. Liu and Q. Zhong, “The effects of calcination atmosphere on the catalytic performance of Ce-doped TiO₂ catalysts for selective catalytic reduction of NO with NH₃”, *RSC Advances*, Vol. 7, pp. 23348–23354, 2017.

- Zhang, L., X. Wang, C. Chen, X. Zou, W. Ding and X. Lu, “Dry reforming of methane to syngas over lanthanum-modified mesoporous nickel aluminate/ γ -alumina nanocomposites by one-pot synthesis”, *International Journal of Hydrogen Energy*, Vol. 42, pp. 11333–11345, 2017.
- Zhang, R. J., G. F. Xia, M. F. Li, Y. Wu, H. Nie and D. Li, “Effect of support on catalytic performance of Ni-based catalyst in methane dry reforming”, *Ranliao Huaxue Xuebao/Journal of Fuel Chemistry and Technology*, Vol. 43, pp. 1359–1365, 2015.
- Zhao, D., J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, “Triblock Copolymer Syntheses of Mesoporous *Science*”, Vol. 279, pp. 48–52, 1998.
- Zhao, D., Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, “Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures”, *Journal of the American Chemical Society*, Vol. 120, 6024–6036, 1998.
- Zhao, Q., Y. Wang, L. Li, W. Zeng, G. Li and C. Hu, “Steam reforming of CH₄ at low temperature on Ni/ZrO₂ catalyst: Effect of H₂O/CH₄ ratio on carbon deposition”, *International Journal of Hydrogen Energy*, Vol. 45, pp. 14281–14292, 2020.
- Zhou, B., N. Qi, B. Wang and Z. Q. Chen, “Effect of swelling agent on the pore structure of SBA-15 studied by positron annihilation”, *Applied Surface Science*, Vol. 475, pp. 961–968, 2019.
- Zubenko, D., S. Singh and B.A. Rosen, “Exsolution of Re-alloy catalysts with enhanced stability for methane dry reforming”, *Applied Catalysis B: Environmental*, Vol. 209, pp. 711–719, 2017.