

STUDY OF OXIDATIVE COUPLING OF METHANE OVER $\text{Mn}/\text{Na}_2\text{WO}_4$
CATALYST IN VARIOUS FORMS

by

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ABSTRACT

STUDY OF OXIDATIVE COUPLING OF METHANE OVER Mn/Na₂WO₄ CATALYST IN VARIOUS FORMS

In this thesis, the oxidative coupling of methane reaction over Mn-Na₂WO₄/SiO₂ catalyst was investigated. The support silica was prepared with sol-gel, sol-gel under DC voltage and wash-coating methods, and then 2wt.% Mn and 5wt.% Na₂WO₄ were impregnated on silica support. The OCM performance of the catalyst was tested using quartz microreactor. Inside diameter of the quartz reactor was chosen as 10 mm and after the catalyst bed, the diameter was reduced to 2 mm to prevent by-product formation. The outlet of the reactor was analyzed using gas chromatography and CH₄ conversion, C₂ selectivity and yield were calculated. Catalysts, which was prepared with sol-gel method, have shown the best performance with 16.6% yield. Also, to observe the stability of the catalyst performance, an experiment was done for 10 hours and it was found that the C₂ selectivity and yield did not change significantly during that time. During the sol-gel preparation, DC voltage was applied to the catalyst. However, the electricity affected neither the structure nor the performance of the catalyst. Performance of catalysts, which were prepared with this method was close to the performance of the blank reactor. In the same way, the catalysts, which were synthesized with wash-coating method, showed quite low performance.

ÖZET

METANIN OKSİJEN VARLIĞINDA Mn/Na_2WO_4 KATALİZÖRÜNÜN FARKLI FORMLARI ÜZERİNDE YÜKSEK HİDROKARBONLU MOLEKÜLLERE DÖNÜŞÜMÜ

Bu çalışmada metanın oksijen varlığında etan ve etilene dönüşüm reaksiyonu (OCM) $Mn-Na_2WO_4/SiO_2$ üzerinde incelenmiştir. Sol-gel hazırlama, elektrik akımı vererek sol-gel hazırlama metodu ve kaplama yöntemleri ile hazırlanan silika üzerine ağırlıkça %2 Mn ve %4 Na_2WO_4 metalleri ıslak emdirme yöntemi ile eklenmiştir. Hazırlanan katalizörün OCM performansı kuvars mikro reaktör kullanılarak incelenmiştir. Kullanılan kuvars reaktörün çapı 10 mm olarak seçilmiş ve katalizör yatağından sonra çap 2 mm'ye düşürülerek ürünlerin istenmeyen yan ürünlere dönüşmesinin önüne geçilmeye çalışılmıştır. Reaktör çıkışındaki akımın içeriği gaz kromatografi cihazı yardımıyla analiz edilerek CH_4 dönüşümü, C_2 seçiciliği ve verimliliği hesaplanmıştır. Sol-gel hazırlama yöntemi ile hazırlanan katalizör en yüksek performansı göstererek %16,6 verim değerine ulaşmıştır. Ayrıca aynı yöntemle hazırlanan katalizörün kararlılığı, gerçekleştirilen 10 saatlik reaksiyon ile ölçülmüş, katalizör veriminin ve C_2 seçiciliğinin neredeyse sabit kaldığı görülmüştür. Sol-gel hazırlama yöntemi ile katalizörün sentezlenmesi sırasında uygulanan elektrik akımı katalizörün yapısında önemli değişikliğe sebep olmadığı gibi OCM performansını da arttıramamıştır. Bu yöntemle sentezlenen katalizör kullanılarak yapılan deneylerde elde edilen sonuçlar katalizör kullanılmadan yapılan testlere yakınlık göstermektedir. Aynı şekilde alüminyum oksit bazlı seramik köpük üzerine kaplama yapılarak hazırlanan katalizörlerin de verimi oldukça düşük kalmıştır.

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LIST OF ACRONYMS/ABBREVIATIONS

CTMABr	Cetyltrimethylammonium Bromide
GC	Gas Chromatography
MFC	Mass Flow Controller
OCM	Oxidative Coupling of Methane
TCD	Thermal Conductivity Detector
TEOS	Tetraethylorthosilicate
TMOS	Tetramethylorthosilicate

1. INTRODUCTION

As the major component of natural gas, the methane can be considered as an ideal fuel in many aspects. The known natural gas reserves are much larger than those of crude petroleum; however, the greater parts of these reserves are found in remote areas, which are in long distances from industrial areas, and the transportation with pipelines is not always a suitable way. Because of that, the methane in these remote areas is generally burned and vented. This cause not only to the waste of methane but also to the environmental pollution by greenhouse gases (Lunsford, 2000; Arndt *et al.*, 2012). This unutilized methane can be used to transform methane into chemicals and fuels in direct and indirect processes (Alvarez-Galvan *et al.*, 2011). Theoretically, the direct methods are more economical than indirect methods because the syngas production step, which has an extra cost, have been skipped in direct processes. However, it is hard to reach high product yields with these processes. Because of that, direct methods could not be commercially implemented yet (Lunsford, 2000).

Oxidative coupling of methane (OCM), which is one of the direct processes for the natural gas utilization, is an auspicious technology for higher hydrocarbon production. The objective of this process is the production of C₂ products, which are mainly ethane (C₂H₆) and ethylene (C₂H₄). These products, especially ethylene, are among the fundamental chemicals for the industry (Simon *et al.*, 2011).

Methane is a highly stable molecule because of the C-H bonds, hence OCM needs high temperatures (Yildiz *et al.*, 2016). However, at high temperatures, not only the methane but also the ethylene is favorably converted to CO₂. Because of that, for a single pass reaction, the C₂ yield is usually limited to about 25% (Alvarez-Galvan *et al.*, 2011; Simon *et al.*, 2011; Tang *et al.*, 2011; Serres *et al.*, 2015; Yildiz *et al.*, 2016). To increase this yield, many variations of catalysts have been studied for OCM reaction (Serres *et al.*, 2015). Among all alternative catalysts, it was found that lanthanum and strontium oxides-based catalysts have a high activity while their C₂ selectivity is average. The reason for that is the selectivity of this catalyst is poor due to the active sites, which are suitable for the

direct oxidation of methane into CO_x (Olivier *et al.*, 2008). On the other hand, manganese, tungsten and sodium doped on silica catalysts show high selectivity for C_2 products, however their activities found to be lower than lanthanum-based catalysts (Olivier *et al.*, 2008; Arndt *et al.*, 2012).

Literature survey for oxidative coupling of methane reaction is given in Section 2. Methane utilization methods are explained first and then the mechanism of OCM is detailed. Different catalyst types, which are used through the OCM, are explained with the focus on the $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ catalyst. Finally, at the end of Section 2, the preparation methods for the catalyst are explained in detail. Section 3 is about the experimental work performed; the preparation of the catalysts and the catalytic reaction system is explained in detail in this section. The performance results of the study are given and discussed in Chapter 4 while Chapter 5 contains the major conclusions and the recommendations for the future studies.

2. LITERATURE SURVEY

Fossil fuels have the largest share of world's energy demand; however, they are also the main source of CO₂ emission, which is believed to cause climate changes. Hence, the search for renewable and cleaner energy sources has been continuously increased in recent years. Additionally, the development of new production methods for chemicals also became an important task; in this context, the methane utilization is one of the topics, which draws significant interest in last few decades.

2.1. Methane Utilization

Methane is the fundamental constituent of natural gas, because of that, the natural gas has been used as a feedstock to produce energy and chemicals. There are substantial amounts of natural gas reserves around the world (Alvarez-Galvan *et al.*, 2011); the natural gas and methane will seem to be important energy source into the 21st century.

Methane is very stable molecule because of its C-H bonds. Because of its symmetric structure and strong C-H bonds, it needs high activation energy to react. Methane has not only high ionization potential but also low proton affinity. Additionally, it has not any functional groups. Due to all of these, it needs high temperatures and oxidation agents to break C-H bonds, (Holmen, 2009).

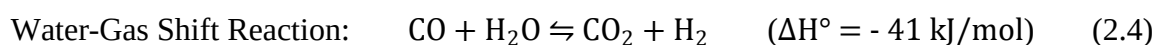
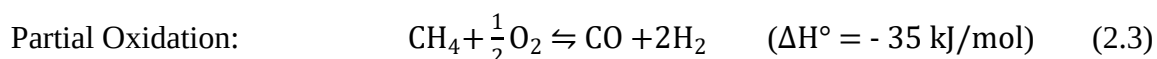
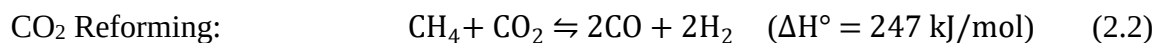
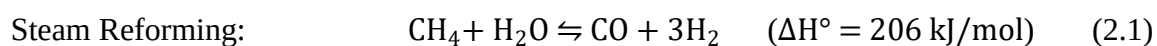
Availability in many areas, its convenience to purification and having the largest combustion heat make the methane an ideal fuel. Thereby, the methane and natural gas have been using in the electrical power generation, home and industrial heating extensively. Apart from the primary source of energy, methane is an also significant material for chemical industry. It can be used for a raw material to syngas, methanol, liquid fuels, ethylene, formaldehyde and olefins (Lunsford, 2000; Holmen, 2009).

There are two types of processes for utilization of methane, indirect and direct methods. Currently, the indirect methods for methane utilization are more favored

commercially; a large amount of natural gas convert to the syngas and then other chemicals are produced (Lunsford, 2000). However, there are also significant amount of efforts to develop direct methods because they are potentially more economical.

2.2.1. Indirect Methods for Methane Utilization

Carbon monoxide and hydrogen mixture, which is termed as synthesis gas, is the important mid-product for the indirect methane utilization methods. Hydrogen can be used as a fuel or a raw material for industry such ammonia synthesis. The syngas, as the mixture, is also used in different ways. The ratio of carbon monoxide and hydrogen in the synthesis gas is varied from method to method, and each of these methods has advantages and disadvantages. the main reactions in these methods are given as follows, (Lunsford, 2000; Alvarez-Galvan *et al.*, 2011; Arndt *et al.*, 2012).



Reforming of methane reactions are endothermic, so they need substantial heat input; a catalyst is also necessary for these processes. In partial oxidation method, the hydrogen is produced from hydrocarbons, and the reaction is barely exothermic. Finally, the water gas shift is a supplementary reaction for other three processes; it takes place after reforming to convert some of remaining CO into CO₂ and produce additional hydrogen (Lunsford, 2000).

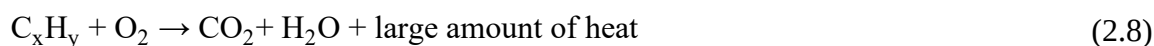
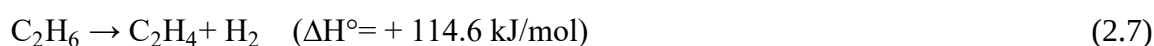
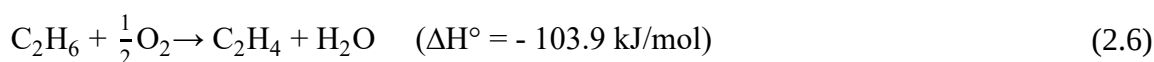
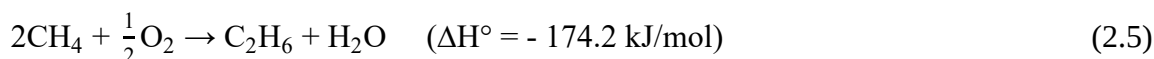
2.2.2. Direct Methods for Methane Utilization

Methane is a very stable molecule with its symmetrical strong C-H bonds. Because of that, in most methane conversion processes, catalysis has a crucial role. Recently, direct methane utilization processes became important and many researches started to be

conducted on this topic. However, not only the kinetics but also the thermodynamics are still the problem for direct utilization of methane (Holmen, 2009). Although skipping the costly synthesis gas step is an important advantage, the single-pass direct process can not have a significant economic advantage due to the low product yields (Lunsford, 2000). Some of the processes, which are used for the direct methane conversion, are partial oxidation of methane to methanol and formaldehyde, oxidative coupling of methane to C₂ hydrocarbons and conversion to aromatics without an oxidant.

2.3. Oxidative Coupling of Methane

The oxidative coupling of methane (OCM) is carried over a solid catalyst, and as the result of the reaction between CH₄ and O₂, C₂H₆ and C₂H₄ are obtained as the primary products. OCM process consists of some desired and undesired reactions, which are given as follows (Alvarez-Galvan *et al.*, 2011).



These selective and non-selective reactions occur simultaneously at the high temperatures. The yield of the C₂ products are limited to about 25% and C₂ selectivity is about 80%. OCM takes place at around 600-800°C, and as a result, the CO_x formation is observed as the by-product of the combustion reactions. Although there are many researches about the OCM process, a suitable catalyst has not been found yet. Because of the extreme operational conditions and limitations of catalysts, OCM has not been commercialized yet (Lunsford, 2000; Holmen, 2009).

2.3.1. Reaction Mechanism

Since OCM has very complex reaction mechanism, it has not been understood completely for a long time. The reaction is reversible microscopically, and the overall reaction includes homogenous and heterogeneous reactions. The reaction network of OCM can be investigated in three steps; they are adsorption, catalytic surface reactions and gas phase reactions respectively (Lee *et al.*, 2012). Reaction network includes 17 reaction steps and these are given in Figure 2.1 (Thybaut *et al.*, 2011).

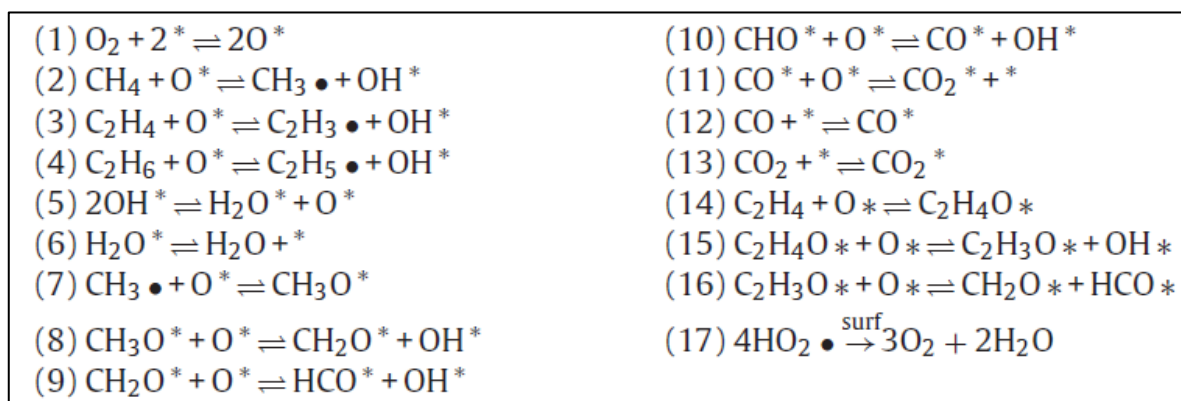


Figure 2.1. Catalytic reaction steps of oxidative coupling of methane (Thybaut *et al.*, 2011).

The first two reactions are oxygen dissociation and hydrogen abstraction of methane. Through the gas phase reactions, the methyl radical is formed and produced higher hydrocarbons by interacting with another methyl radical. In other words, methyl radicals coupled and produce ethane and ethylene with dehydrogenation (Mahmoodi and Ehsani, 2011). The slower step of the reaction mechanism is the methyl radical formation reaction; consequently, this step has an important role in OCM reaction (Salehoun *et al.*, 2008). The by-product CO_2 produced by four different pathways. Reactions 7 to 13 show the first mechanism. According to these reactions, the CO_2 produced from methoxy species through the abstraction of hydrogen. Through the third and fourth reactions, the radicals, which can be oxidized to CO_2 , are formed from C_2 species by hydrogen abstraction. The third way of CO_2 formation is CO oxidation, which is given in reactions 11 to 13. Lastly, ethylene oxidation is caused to CO_2 formation heterogeneously. Increasing the temperature

brings about the decrease in CH_3O_2 concentration. Therefore, the OCM reaction needs very high temperatures to happen (Takanabe and Iglesia, 2009; Thybaut *et al.*, 2011).

2.3.2. Limitations of Oxidative Coupling of Methane

OCM has drawn considerable interest since the products ethane and ethylene are very useful for chemical industry. However, there are some limitations, which do not allow for the commercialization of OCM reaction. These limitations are:

- (i) Low values for C_2 selectivity and yield
- (ii) Uncertainty for scale-up
- (iii) Cost of by-product separation

Although reaching the high conversion is possible, the products have higher reactivity than methane causing to the low selectivity for C_2 products (Holmen, 2009). OCM is an exothermic reaction and heat resulting from the reaction leads to by-product formation. Through the carbon oxides formation, the heat of reaction increases, as well as the selectivity, decreases. Hence, heat control and management become another critical problem for OCM (Galadima and Muraza, 2016).

It is necessary to achieve a yield over 35% in order to be an economically feasible system for OCM. To increase the total yield and C_2 selectivity, the researchers investigate the reaction by analyzing reaction parameters such as kinetics, reactor selection and operation (Beck *et al.*, 2014). Temperature, methane to oxygen ratio and GHSV are also the reaction parameters, which affect the catalytic performance of OCM significantly due to the complicated reaction network and including catalytic gas phase reactions (Karimi *et al.*, 2007).

2.4. Catalysts for Oxidative Coupling of Methane

Oxidative coupling of methane reaction was first reported by Keller and Bhasin (1982). After that, many researchers have studied the OCM reaction. However, due to the

complexity of the OCM, developing an influent catalyst to make this reaction commercially is challenging. Different variations of catalysts were developed to achieve the necessary selectivity and yield values.

Choudhary *et al.* (1999) have been investigated catalytic activity of both alkaline earth metals such as Mg, Ca, Sr and Ba and rare earth metals like La, Ce, Nd, Sm, etc. According to their studies, acid/base distribution of catalyst and surface properties depending on metal selection affected the activity of the catalyst. It was found that adding an alkaline earth promoter to both alkaline earth and rare earth metals had a positive effect on catalyst performance (Choudhary and Mulla, 1997; Rane, Mulla and Choudhary, 1998). Due to having strong basic sites, activity and selectivity of unsupported catalysts like Nd_2O_3 , Eu_2O_3 and La_2O_3 were better. Besides that, La_2O_3 with the Sr-promote had the best performance (Rane, Chaudhari and Choudhary, 2008). Promoting the catalyst with Ce and Nd brings increase on the activity of the catalyst and C_2 selectivity (Tiemersma *et al.*, 2012).

Comparison of Sr-promoted and un-promoted La_2O_3 catalysts were investigated by Choudhary *et al.* (1997). According to their study, the CH_4 conversion was 30.1% and C_2 selectivity was 65.6% at 800°C with the ratio of CH_4/O_2 as 4 and Sr/La ratios of 0.3. Increasing the Sr/La ratio increased the alkaline sites of the catalyst support and the performance of the catalyst. Therefore, based on the basicity of surface, size of the surface area and the cost, the catalyst support may have a significant role on the performance of catalyst (Choudhary and Mulla, 1997). On the other hand, Tiemersma *et al.* (2012) studied on the La support and they were found that through the industrial scale applications lower pressure drop was occurred.

Elkins *et al.* (2013) studied the effect of changing properties of the Al_2O_3 support on the performance. They found that acidic sites of support decrease the C_2 selectivity; hence more active catalyst could be developed by blocking acidic sites. The nano- CeO_2/ZnO catalysts were studied by He *et al.* (2004); who used a novel precipitation technique; they found that changing average size of nanoparticles did not change methane conversion proportionally. Besides that, methane conversion increased with the increase of

nanoparticles' fractal dimensions. When it compared with the performance of the catalyst synthesized by the conventional impregnation method, they achieved the higher conversion by using the CeO₂/ZnO nanocatalysts (He, Yang and Cheng, 2004).

Perrichon and Durupty (1988) studied the MgO, SiO₂, Al₂O₃ and Cr₂O₃ supports promoted with Li, Na and K metals. They found that, in calcination step, which was occurred at higher than 500°C, alkaline metals were missed. Alkaline metals with SiO₂, Al₂O₃ and Cr₂O₃ supports showed more stable performance than MgO support. Although it has high activity, Li/MgO catalyst had not a stable performance for OCM reaction due to the Li lost, and many researchers investigated to increase the stability of Li/MgO catalyst. Although many variations for preparation was tested, none of them improved the stability of catalyst (Tang *et al.*, 2011). Li-doped catalyst was performed through the reaction time of 40 hours with different amounts of Li (0, 0.5, 1, 2, 4 and 8 wt.%) but the stability of the catalyst could not be retained. During the reaction, Li metals on the support surface have evaporated and it brings about the catalyst deactivation. Thus, Li/MgO catalyst found inconvenient for industrial applications because of the limiting life time and instability (Tiemersma *et al.*, 2012).

Through the kinetic studies in the literature, lanthanides are found to be suitable for increasing activity and selectivity of the catalyst. La₂O₃ promoted CaO catalyst was investigated by Ching, Mohamed and Bhatia (2002) in a fixed bed reactor with different operation modes such as isothermal, adiabatic and non-adiabatic. According to their catalytic tests, non-isothermal conditions provided higher C₂ yield than the other operation modes.

Since the selectivity could be increased by using BaX₂, Au, Liu and Ng (1998) worked on BaO/Nd₂O₃ catalyst. When Nd₂O₃ used without doping, the selectivity was 33.3%, and BaX₂ addition to Nd₂O₃ support increased selectivity value to 50.7%. Also, C₂ yield was doubled at the 750°C. In another work, BaCO₃ promoted with 0, 2.5, 5, 10, and 15 wt.% on La₂O₃ was synthesized with urea combustion method by Kou *et al.* (1998). It was found that BaCO₃ provided an increase on catalytic performance of La₂O₃. Increasing

BaCO₃ from 0 to 15 wt.% led to increasing on conversion and selectivity from 32.8% and 40.0% to 35.2% and 48.6% respectively at 550°C (Au, Liu and Ng, 1998).

Oshima *et al.* (2013) investigated the effect of electric field and they used CO₂ as an oxidative agent. Through their studies over the La-ZrO₂ catalyst, it was found that catalyst activity was low at 1173 K. Besides that, electric field provided reaching increased activity at 423 K. The maximum yield they achieved was 5.4%.

Niobium promoted Li/MgO catalyst was reported by Swaan *et al.*, (1993). It was clarified that activity of 16 wt.% Nb-Li/MgO catalyst was ten times higher than the activity of Li/MgO at the 873 K. However, there was a limitation because of the melting point of the lithium phase. The activity of the catalyst was started to decrease at the higher temperatures than 993 K.

Inert oxides were also investigated as a support by many researchers. TiO₂ support was studied with the Li, Na, Mn and W metals addition by Gong *et al.* (1995). Although Li addition on Mn/TiO₂, La/TiO₂ and La-Mn/TiO₂ caused to decrease on the catalyst activity, it provided significant increase in C₂ selectivity for W/TiO₂, Mn-W/TiO₂, La-W/ TiO₂ and La-Mn-W/TiO₂ catalysts. During the reaction at 1043 K with the CH₄/O₂ ratio of 1.4, the methane conversion was obtained as 41.6% over the Li-La-Mn-W/TiO₂ catalyst; the selectivity and yield were 61.7% and 25.6% respectively for the same catalyst.

Although many variations of catalysts have been studied, the higher yields than 25-30% could not be obtained for OCM process. The best catalytic activity was achieved using Mn, Na and W metals together (Li, 2003). Details of this trimetallic system are given in Section 2.5.

2.5. Mn-Na₂WO₄/SiO₂ Catalyst for Oxidative Coupling of Methane

Through the studies on OCM reaction, Mn-Na₂WO₄/SiO₂ which was reported by Li *et al.* first (Fang *et al.*, 1992; Li *et al.*, 1992), is found to be one of the most auspicious catalysts because of its stability and activity. Each metal and silica has a diversified role on

the process and stability of catalyst is enhanced by mutual interactions between metals and silica support (Godini *et al.*, 2014). Although Mn-Na₂WO₄/SiO₂ is thought to be the best catalyst for OCM reaction, the reason for this is not clarified completely because of the complicated structure of the catalyst (Kim *et al.*, 2017).

2.5.1. Silica as a Catalyst Support for OCM Reaction

Palermo *et al.* (1998) examined the silica as the support of Mn-Na₂WO₄ catalyst. According to their studies, a form of the silica was changed with the impregnation. Although the amorphous silica is active but unselective, α -cristobalite, which obtained by the change of amorphous silica, is active and very selective. Due to the low surface area which caused by this transition, the undesired reactions on the surface is prevented and selectivity is increased (Elkins and Hagelin-Weaver, 2015).

To investigate the silica transformation to α -cristobalite, the studies were conducted by Palermo *et al.* (1998). That transformation decreases the temperature and it influences the conversion and selectivity greatly. They tested not only the Mn-Na₂WO₄/SiO₂ catalyst but also the catalyst samples including only Mn, W and Na metals. While the transition is affected by Na, the use of Mn or W metals did not have an impact on the silica transition. Thus, Na has not only the structural but also the chemical promoter role. Even though the W metal only is ineffective on transition, it accelerates the crystalline formation at 750°C.

Differences between the SiO₂ and MgO supports were studied by Elkins and Hagelin-Weaver (2015); with their characterizations results of XRD and XPS, they found that including α -cristobalite with Na₂WO₄ and Mn₂O₃ increased the active catalyst for OCM reaction. With the catalyst containing MgO, the formation of Na_xWO_y compounds occurred on the surface while there were not any α -cristobalites and Mn₂O₃ compounds. Since Na₂WO₄ was stabilized with SiO₂, and oxygen transfer between the surface and gaseous phases was provided by Mn₂O₃ presence, the catalyst with silica support showed high activity. However, the activity of MgO supported catalyst decreases during the long time reaction (Pak, Qiu and Lunsford, 1998).

2.5.2. The Role of the Sodium over the OCM Reaction

Sodium is the fundamental dynamic part; it assumes double roles of which one is to increase the CH₄ conversion and C₂H₄ selectivity while decreasing the CO production. Another role of the Na in the reaction is to keep the total oxidation of methane with separating the Mn particles in Na₂O, NaO₂ and Na₂CO₃ surface stage to get high selectivity. In addition, the Na⁺ ions promote to raise basicity of surface and change over non-selective manganese oxide into a more specific frame as announced by Ji *et al.* (2003).

In their other work, Ji *et al.* (2002) study the sodium, tungsten and manganese content of catalyst to see the synergetic effects; the highest yield of C₂ was acquired at 1.6 wt.% Na content. The response happened to be the best with substance of 0.4-2.3 wt.% Na, 0.5-3 wt.% Mn and 2.2-8.9 wt.% W. Na affected the close surface organization of W and Mn at the surface; the selectivity toward C₂H₆ and CO increased marginally with the further increment in the Na while the change of CH₄ and selectivity towards C₂H₄ and CO diminished. When the Na increased over 2.3 %, it causes the increase of Na on the surface, which makes that the surface fixation of W and Mn decreased enormously. This demonstrates the relocation of W and Mn was conveyed out with the assistance of Na⁺ particles.

2.5.3. The Role of the Manganese over the OCM Reaction

The relationship of the electrical conductivity, performance of catalyst and more basic highlights for Na₂WO₄/SiO₂ promoted with V, Cr, Mn, Fe, Co and Zn was researched (Malekzadeh *et al.*, 2001, 2007). The possibility of this work depends on the discoveries of Voskresenskaya, Roguleva and Anshits (1995), who detected that there are immediate connections between the properties of mass and surface and the achievement in the OCM. The conductivity was deal under oxygen and OCM conditions. An unmistakable relationship between the reactant execution and the conductivity under the OCM conditions was observed. Mn had the most astounding electrical conductivity and displayed the best synergist application. In Figure 2.2, the revealed C₂ yield is plotted to the (left) conductivity, (right) the normal logarithm of the conductivity. Be that as it may,

according to plot between yield and conductivity, there is not any relationship. However, for metals only with conductivity between 1000 and 4000 σ^e/σ^d , it can be concluded that yield and the conductivity have an exponential dependency.

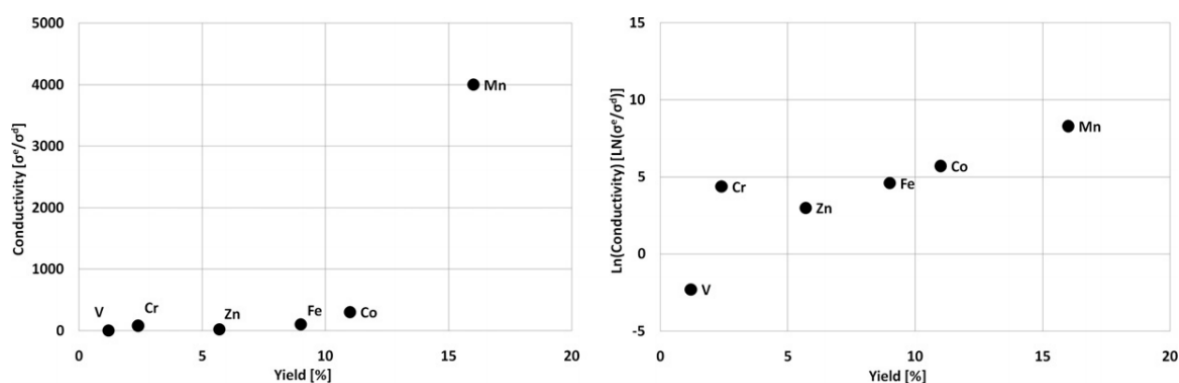


Figure 2.2. Dependency between C_2 yield and – left) conductivity, right) the natural logarithm of the conductivity (Arndt *et al.*, 2012).

Koirala *et al.* (2014) investigated the role of the Mn on OCM catalyst. They reached to 5% conversion and 1% yield when they did not load Mn. However, when they promoted the catalyst with 1.9 wt.% Mn, they achieved 18.5% yield. They also found that despite its positive effect on catalyst activity, using more than 1.9 wt.% Mn decreased both conversion and yield. Besides it was found that formation of CO_x products was effected Mn loading. When 3 wt.% Mn was added to the catalyst CO/CO_2 ratio was decreased and it could be concluded that Mn loading makes CO_2 formation is more favorable (Koirala *et al.*, 2014).

2.5.4. The Role of the Tungstate over the OCM Reaction

Effect of W loading was researched by Ji *et al.* (2002) and they found that W influences the C_2H_4 selectivity and CH_4 conversion directly. When W was not loaded into catalyst, combustion reaction was more favorable, and CO_2 was produced greatly. Although promoting catalyst with 0.4-1.6% W has a positive effect on both conversion and selectivity, after the value of 8.9%, W loading decreases the performance of catalyst.

Ji *et al* (2003) also investigated the effect of the geometry and for their research they used WO_4 tetrahedra and WO_6 octahedra. They claimed that WO_6 octahedra has a complex geometry and because of that WO_4 tetrahedra is more suitable with CH_4 . They found that C_2 selectivity of the WO_4 tetrahedra is six times greater than the WO_6 octahedra.

Mahmoodi, Ehsani and Goreishi (2010) was investigated $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ catalyst and they also replaced W with other metal oxides such as Mo, Nb, V and Cr. They stated that V and Cr was showed very low selectivity for OCM and Mo was better than these metals. However, they found that W showed the best activity among the other metals.

2.6. Catalyst Preparation Methods

2.6.1. Incipient to Wetness Impregnation Method

The incipient to wetness impregnation is a common method for preparing catalysts. In order to fill pores of the support homogeneously, the precursor solutions are dropped to the support surface slowly under the vacuum. An active and highly selective catalyst can be obtained with dispersion of active metals on the support surface homogeneously.

$\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ catalyst was prepared with various methods such as incipient to wetness, slurry mixing and wet impregnation to investigate the effect of the preparation methods on catalyst activity by many researchers. It was stated that, owing to the well-dispersion of the active components, the best catalytic performance was obtained with incipient to wetness impregnation method (Li *et al.*, 2006). Besides, the stability of catalyst was better when it compared with the other two methods for 500 h run (Wang *et al.*, 2006). Moreover, incipient to wetness impregnation method is an effective solution for avoiding loss of active materials (Lee *et al.*, 2012).

Chemical degeneracy could occur through the impregnation. For preventing that, the active components must be impregnated on the support in a certain order. For this reason, precursor solution of Mn was impregnated first on the silica support. The slurry

obtained from the Mn impregnation is dried at 130°C and then the second metal, Na₂WO₄ is added (Malekzadeh *et al.*, 2002; Li *et al.*, 2006; Godini *et al.*, 2014).

2.6.2. Sol-Gel Preparation Method

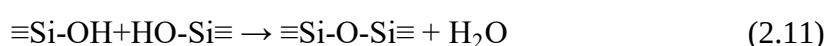
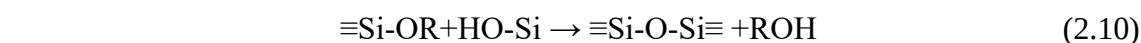
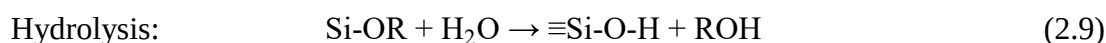
An alternative method for Mn-Na₂WO₄/SiO₂ catalyst preparation is the sol-gel method. As it is understood by the name, the process is a transition a gel from the sol. While a sol is a liquid with including small particles, rigid non-fluid mass is a gel. Through the sol-gel process, developing colloidal particles are ensured by hydrolysis and converting them into a gel form by condensation reactions. Since alkoxides can be hydrolyzed in water, they are generally used for sol-gel formation (Allothman, 2012).

Production of silica gels were performed using alkoxy silanes like tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS). However, the cost and the danger of the TMOS leads to the preferation of TEOS for silica aerogel formation (Venkateswara Rao and Bhagat, 2004).

According to Gawel, Gawel and Øye (2010), sol-gel process is carried out as follows.

- (i) Sol formation by hydrolysis of precursors
- (ii) Gelation by hydrolyzed precursors' polycondensation
- (iii) Aging
- (iv) Drying
- (v) Calcination

A series of reactions are occurred during the silica aerogel formation and these are shown in Equations (2.9), (2.10) and (2.11).



Reactions showed in Equation (2.10) and (2.11) are reversible, and due to that gel form could be destructed. According to the researches, there are two ways of solving this problem. The first solution is varying the acidity in the process to optimize hydrolysis by removing the alcohol. Using drying control chemical additives (DCCA) is the second solution and it also increases the pore sizes. Thereby, it provides to growth three-dimensional network uniformly (Khimich, 2004).

When siloxane solution used for washing, stiffness and the strength of the silica aerogels are increased during the aging step. It caused by an addition of new monomers to the network by the siloxane solution and it leads to low permeability for silica gel (Siouffi, 2003).

After all these steps, types of porous silica gels, which are macrospores and mesopores, can be obtained with phase separation and a following solvent exchange process by sol-gel reactions (Alothman, 2012).

2.6.3. Monolithic Catalyst Preparation

A monolithic catalyst was generally prepared by depositing active species onto a wash-coated stone. The wash-coat is basically a secondary support that can offer for higher adherence and homogenous distribution of the active sites. High surface area oxides like γ - Al_2O_3 , SiO_2 , ZrO_2 are generally used as a secondary support layer. Metallic and ceramic monoliths can be coated with different methods for achieving good adherence. Typical strategies used for depositing γ - Al_2O_3 onto ceramic structures area unit mixture coating, sol-gel and suspension coating. However, these coating methods have to be modified for metallic structures (Farrauto, Gulati and Ronald, 2001; Govender and Friedrich, 2017).

For monolithic catalysts not only coating the secondary support but also coating the active layer is important. Character of the active species uses to determine the coating method of the active layer. Generally, metal oxides are used as support layer. Wet impregnation method can be use for coating however, homogeneous distribution could not be achieved by this method (Govender and Friedrich, 2017).

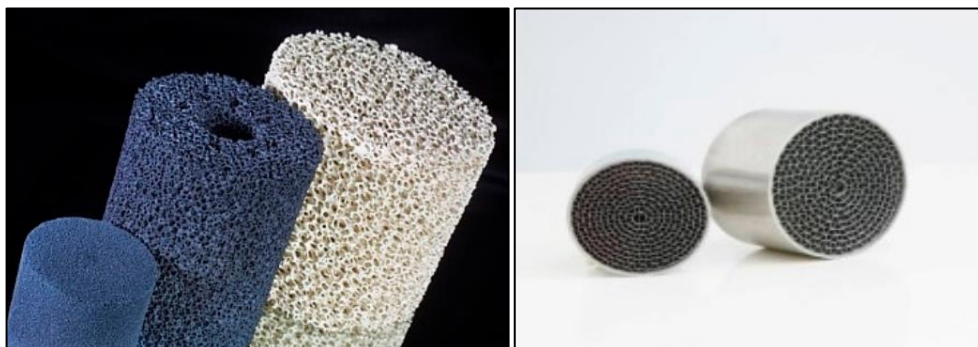


Figure 2.3. Samples of Monoliths – a) ceramic foams, b) metallic monoliths (Govender and Friedrich, 2017).

Monolithic catalysts have some benefits like having high surface area and small pressure drop. Also, diffusion transfer of monolithic catalyst is good. These catalysts provide simplicity to scale up (Moulijn *et al.*, 2001). Having lots of channels provides the high specific area and the high surface area leads to low residence to flow. Thus, pressure drop is low through the catalyst and it brings about the lower energy loss (Farrauto, Gulati and Ronald, 2001).

Preparation of ceramic associated metallic monoliths will be a demanding method and an art requiring special instrumentation. Thus, most researchers purchase these structures instead of preparing them from the beginning. However, the coating a secondary support and the active layer is still an unavoidable and difficult task to accomplish (Tomašić and Jović, 2006).

Generally, the monolithic catalysts are used in the areas like the natural gas engine, hydrogen generation for the fuel cell and automobile exhaust treatment. Monolithic catalyst provides high specific volume and sensible interphase mass transfer; on the opposite hand, it's a streamline flow regime that ends up in a high residence time distribution, which is undesired for high conversion (Özdemir, 2009).

2.6.4. Effect of Electricity on Catalyst Structure

The catalyst morphology and nanowire composition are significant parameters for catalyst performance like the composition of the feed gas, temperature of calcination and operation conditions during the reaction. Panciera *et al.* (2016) investigated the effect of electric field on the growing nanowire and they found that it was possible to change the growth shape, position or contact angle of the catalytic droplet. Controlling growth of nanowire provides to modify structures of nanowires for their applications.

According to Zhao, Xue and Jin (2016), nanowires can be used directly and they get attention because of this possibility and their shapes. They also argued that, due to the usage in many industries, they need to be synthesized innovatively with controlling their structures depending on their applications. They used electric field with 5 A during the nanowire synthesis by thermal oxidation. An electric field was supplied perpendicularly, and they found that the nanowire also grew perpendicularly.

Englander *et al.* (2005) were also studied on silicon nanowires growth under DC electric field. Electricity was supplied between a MEMS structure and it was found that structure of the nanowires affected by the electricity.

Porous alumina templates were used to control nanowire growth with electricity by many researchers (Lu *et al.*, 2004; Jin, Yao and Wang, 2005; Yamaguchi *et al.*, 2008; Mekawy, 2016). Anodic alumina template was used as a substrate to control nanowire grown. Synthesizing nanomaterials inside the hard templates was first reported by Martin (1996). The synthesized silica (SBA-15) was filled in the channels of porous alumina as is shown in Figure 2.3, to obtain ordered mesoporous. With the other words, AAM channels provided a form of silica nanowires. The gelation time of mesoporous silica was depending on the procedure used. After the gelation, aging the hybrid membrane occurred at 60°C for 12 hours. The procedure also affected the orientation of silica nanowires (Meoto and Coppens, 2014).

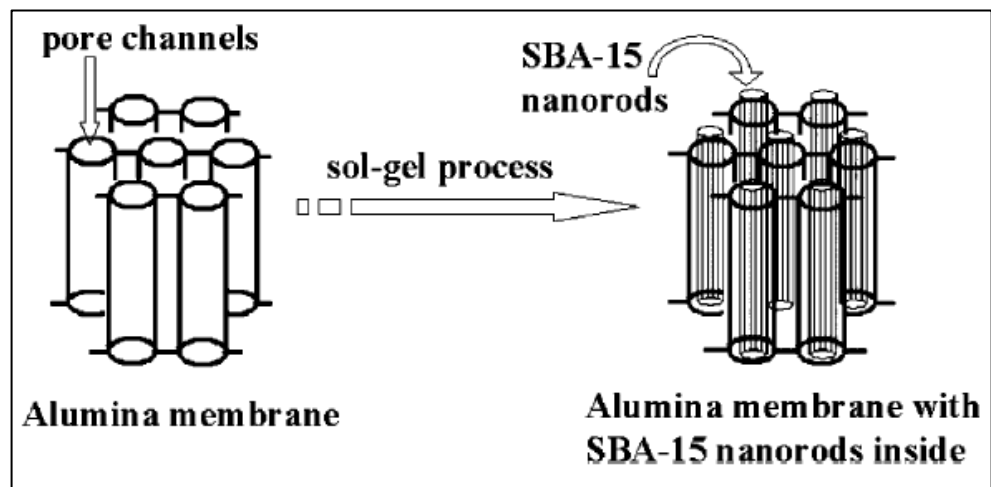


Figure 2.4. Alumina membrane – left) fresh, right) including SBA-15 nanorods (Lu *et al.*, 2004)

3. EXPERIMENTAL WORK

In this chapter, the preparation of Mn/Na₂WO₄/SiO₂ catalysts and catalytic reaction system are explained. The catalysts were prepared and tested with the system in the Catalysis and Reaction Engineering Laboratory of Chemical Engineering Department, Boğaziçi University.

3.1. Materials

3.1.1. Chemicals

All chemicals that were used in this study during the preparation of Mn/Na₂WO₄/SiO₂ catalysts are shown in Table 3.1.

Table 3.1. Materials used during the experiments

Chemicals	Formula	Purity	Source	Specification	Molecular Weight (g/mol)
Acetic acid	CH ₃ COOH	≥99%	Merck	Aqueous solution	60.1
Ammonia solution	NH ₃	≥99%	Aksın	25%	17
Colloidal silica	SiO ₂	≥99%	Sigma-Aldrich	40 wt.% aqueous suspension	60.1
Ethanol	C ₂ H ₅ OH				
Hydrochloric acid	HCl				36.5

Table 3.1. Materials used during the experiments (cont.)

Chemicals	Formula	Purity	Source	Specification	Molecular Weight (g/mol)
N-Cetyl-N, N, N-trimethylammonium bromide (C ₁₆ TAB)	C ₁₆ H ₃₃ N(CH ₃) ₃ Br	≥99%	Merck	Fine powder	364.5
Nitric acid	HNO ₃	≥98%	Sigma-Aldrich	Aqueous solution	63.0
Polyethylene glycol 20,000	HO(C ₂ H ₄ O) _n H	≥98%	Merck	Aqueous solution	20000
Quartz Wool	SiO ₂	≥99%	Leco	Fibrous	60.1
Manganese(II) Nitrate Tetrahydrate	Mn(NO ₃)*4H ₂ O	≥99%	Merck	Fine powder	251.0
Triethanolamine (TEOA)	C ₆ H ₁₅ NO ₃				149.2
Triethylamine (TEA)	C ₆ H ₁₅ N				101.2
Sodium tungstate di-hydrate	Na ₂ WO ₄ .2H ₂ O	≥99%	Sigma-Aldrich	Fine powder	329.9
Tetraethyl orthosilicate (TEOS)	C ₈ H ₂₀ O ₄ Si	≥98%	Merck	Aqueous solution	208.3

3.1.2. Gases

All gases that were used in catalytic reaction system are shown in Table 3.2.

Table 3.2. Gases used during the experiments

Gas	Formula	Specification	Type	Application
Helium	He	99.998%	Inert	GC Carrier Gas
Methane	CH ₄	99.995%	Reactant	GC Calibration
Nitrogen	N ₂	99.998%	Standard	Gas Volume Change indicator
Oxygen	O ₂	99.999%	Reactant	GC Calibration

3.2. Catalyst Preparation Techniques

Various catalyst preparation methods were used during this study; in all, the preparation of catalyst support was changed while the metals and their loadings remained same.

3.2.1. Sol Gel Method

3.2.1.1. Particulate Catalyst Preparation. For the preparation of SiO₂ support, 26 ml deionized water and 2 ml ethanol were mixed at room temperature. After that, 4 ml 25% CTABr solution and 1.8 ml acid or base source were added to the solution and stirred for 30 minutes by magnetic stirrer. When HCl and nitric acid were used as acid source, triethanolamine or triethylamine were used as the base source. Finally, 3 ml TEOS was added under magnetic stirring and the mixture was kept at 60°C oven for 2 hours. Final opaque mixture was treated with ethanol and filtered. Preparation steps of silica support were shown in Figure 3.1.

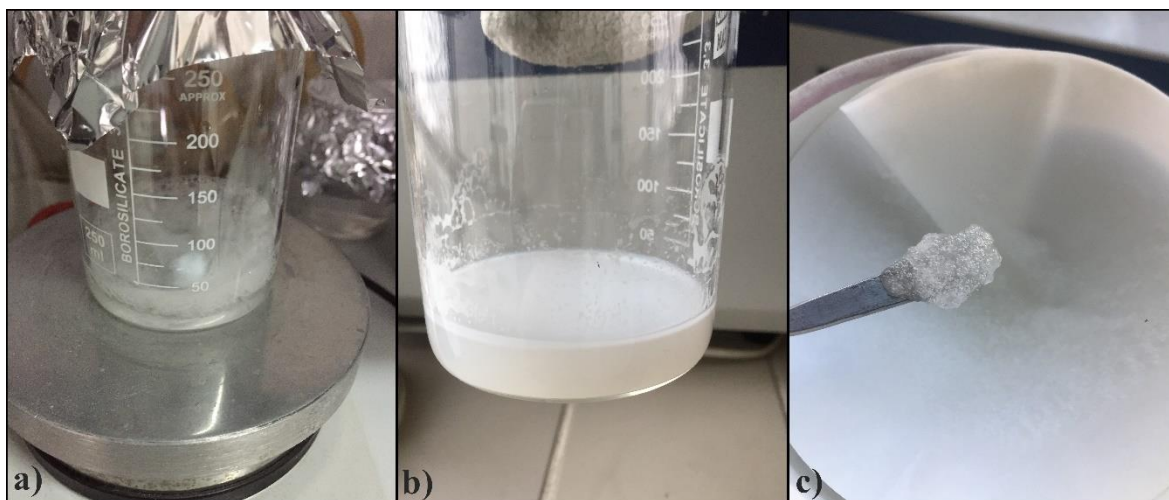


Figure 3.1. Preparation steps of silica support. a) synthesizing over magnetic stirring, b) after oven, c) during filtration

After filtration, the precipitate was dried at 60°C overnight. The mesoporous silica nanowires obtained were calcined at 550°C for 6 hours with a heating rate of 1°/min. In order to calcine silica nanowires, two different procedures were followed. The first one was the calcination in muffle furnace. The second procedure was calcination in a reactor under the flow of N₂ and O₂ gases.

After the calcination step, Mn/Na₂WO₄/SiO₂ particulate catalyst was produced by incipient to wetness impregnation method. The aqueous solutions of Mn(NO₃)₂ tetrahydrate and Na₂WO₄ dihydrate were impregnated on the silica nanowire respectively. Impregnation system, shown in Figure 3.2 schematically, consist of an ultrasonic mixer (Retsch UR1), a vacuum pump, a Buchner flask and a digital peristaltic pump (MasterFlex).

In order to achieve impregnation, a determined amount of mesoporous silica was weighed and kept under a vacuum in ultrasonic mixer for 30 minutes. In the meantime, necessary amount of Mn(NO₃)₂ tetrahydrate was dissolved in deionized water. 5 ml deionized water were used for 1 g mesoporous silica. Mn(NO₃)₂ tetrahydrate aqueous solution was fed to the silica nanowires by using a silicone tubing system. Flow rate of the feed solution was 0.5 ml/min and it was adjusted by using a computerized-drive peristaltic

pump. After impregnation of all solution, the silica nanowires kept under vacuum with ultrasonically mixing to obtain uniform distribution. After 1 hour and 30 minutes, the flask, which contained impregnated silica, was separated from the vacuum system and dried at 130°C for 5 hours. The dried material was cooled in the desiccator. Then it was ultrasonically mixed under vacuum for 30 minutes. The required amount of Na_2WO_4 dihydrate was dissolved in deionized water on the basis 1 g silica gel/ 5.2 ml solution. Aqueous solution was fed to the Mn impregnated silica material with using the same procedure explained above. Then the impregnated silica was dried overnight in the 130°C oven and calcined 800 °C for 8 hours. After the calcination, the $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ particulate catalyst was obtained.

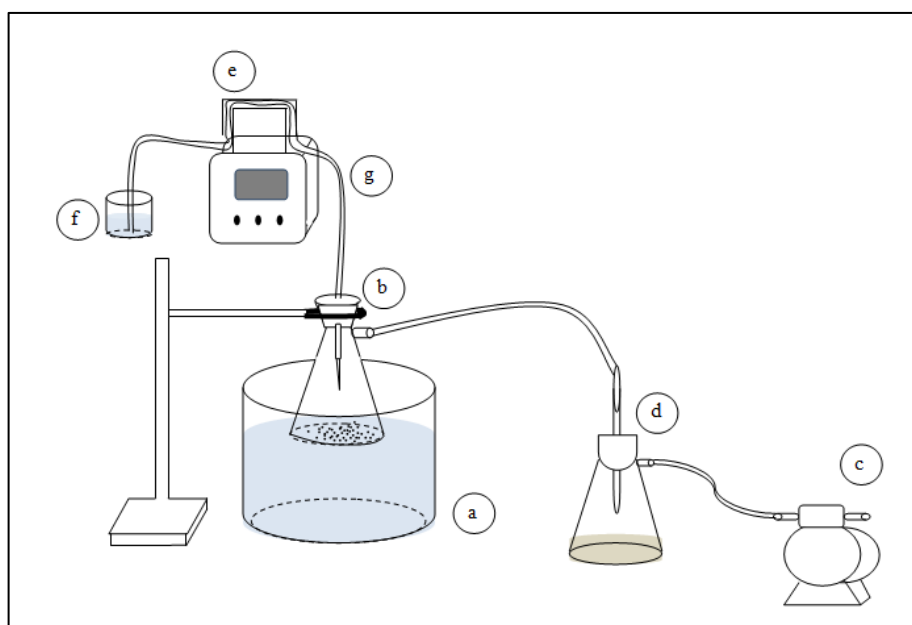


Figure 3.2. Schematic diagram of the impregnation system, a) ultrasonic mixer, b) Buchner flask, c) vacuum pump, d) trap, e) peristaltic pump, f) reactant storage, g) silicone tubing

In some runs, $\text{Mn}(\text{NO}_3)_2$ tetrahydrate was added to the solution during gelation process. The procedure was the same with the previous one until the TEOS addition; after that, $\text{Mn}(\text{NO}_3)_2$ tetrahydrate was added as a final component and solution stirred 20 more minutes. Then mixture was heated at 60°C for 2 hours. Finally, obtained slurry was filtered with ethanol as it shown in Figure 3.3. First calcination, which was carried out at 500°C in previous catalyst, was not required in this process; hence, the precipitate was dried

overnight at 60°C, and then the aqueous solution of Na₂WO₄ dihydrate was impregnated. After that, the silica particles were dried at 130°C for 5 hours and calcined at 800°C for 8h with 10°C/min ramping.



Figure 3.3. Preparation steps of Mn-SiO₂ support. a) slurry after oven
b) during filtration, c) after filtration

3.2.3.2. Monolithic Catalyst Preparation. Synthesis of monolithic SiO₂ resembles synthesis of particulate SiO₂. The only difference is that, for monolithic silica preparation, the precipitate was filled in the molds after filtration. As it shown in Figure 3.4, the syringes, which internally covered with aluminum foil or filter paper, were used as molds.

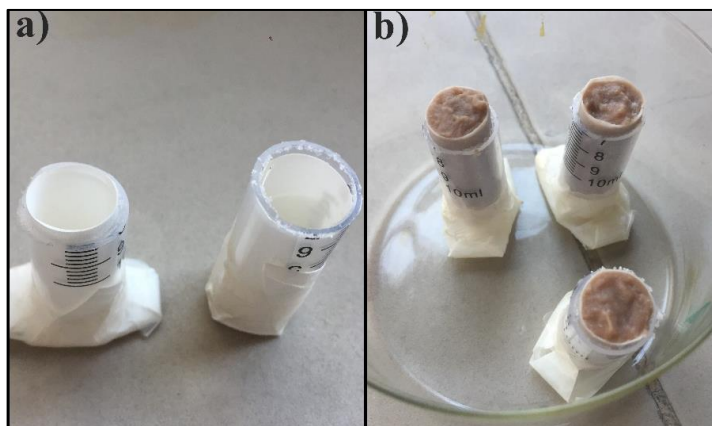


Figure 3.4. Syringes which used as molds. a) empty syringes, b) loaded syringes

Syringes were chosen as 2 cm inside diameter and 2 cm length. The molds were kept in desiccator in order to release their wetness. After silica monoliths were completely dried, they were removed from the syringes. Then, they were ready to impregnation. Required amount of Na_2WO_4 dihydrate was dissolved in deionized water and aqueous solution was impregnated entire body of each monolith with the help of a syringe. After impregnation, all monoliths were heated to 130°C with $1^\circ\text{C}/\text{min}$ ramping rate and they kept 6 hours at that temperature. Then the monoliths were calcined at 800°C (Figure 3.5).

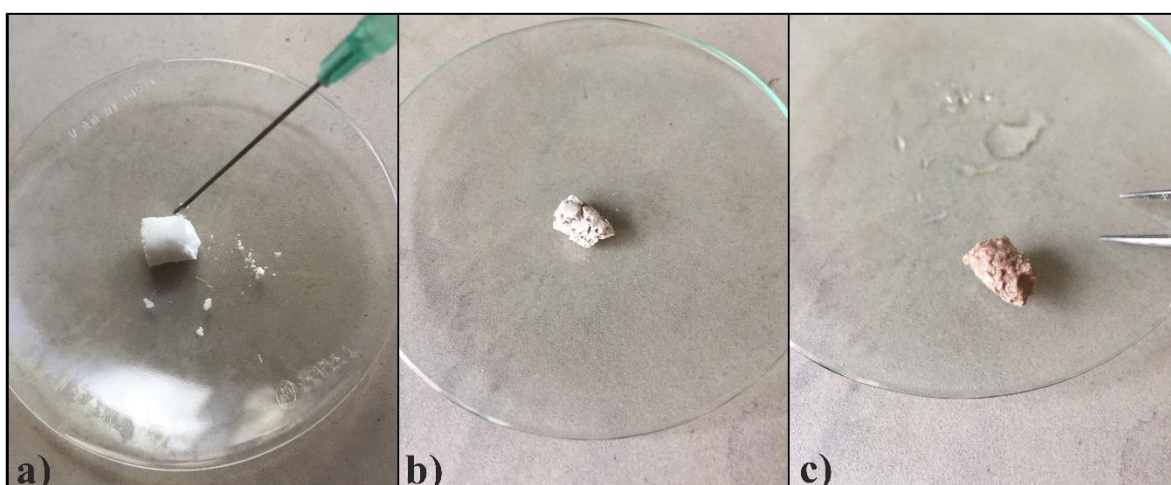


Figure 3.5. Monolithic silica. a) during impregnation, b) dried impregnated catalyst before calcination, c) after calcination

3.2.2. Sol Gel Method Under DC Voltage

Firstly, the catalysts were synthesized as mentioned by Uzunoglu (2017). Experiments were conducted at 0°C . In order to kept temperature at that point, a programmable water bath was used. The water bath temperature was set to 0°C before the experiment, and after it reached 0°C , the 23.15 ml distilled water and 1.6 ml 69% nitric acid solution were mixed at 0°C for 15 minutes. Then, 2 g PEG 20000 was added to the solution and stirred for 1 hour. After that, the last component, 20.2 ml TEOS, was added to mixture and stirred another 1 hour. Finally, when a gel form occurred, solution was infused into molds.

Top and bottoms of mold are coated with conductive plates in order to introduce electricity. Copper plates, Pt-coated copper plates, ITO coated glass plates and Pt-coated plastics were used as conductive plate.



Figure 3.6. Different systems for sol-gel preparation under electric field. a) system with using copper plates, b) with Pt-coated copper plates, c) ITO coated glass plates, d) synthesized catalyst with using ITO coated glass plates

Molds were kept at 40°C oven for 5 days. At the meantime, the electricity was supplied to the molds at different three durations by using an electric supply (1) one minute for every hour to first sample during gelation, (2) during entire gelation time to second sample and (3) first six hours of gelation for the third sample. For all samples electricity was supplied with 30 volt and 1 ampere. Also, there was a reference set to which electricity was not supplied for comparison.

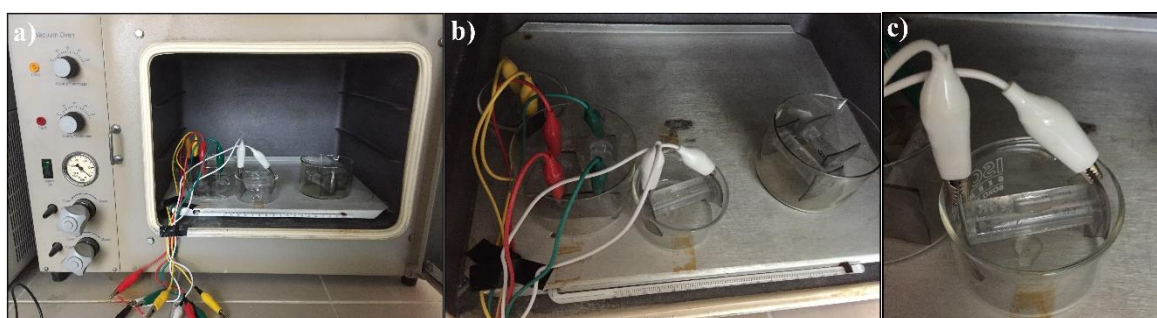


Figure 3.7. System with using Pt-coated plastics

After 5 days, monolithic catalysts were removed from molds and treated with deionized water. Washed monoliths were treated with 0.01 M ammonia solution at 40°C

for another 20 hours and dried in 40°C oven for 2 days. Then, they were calcined at 550°C for 6 hours. After calcination, the monoliths were impregnated with metal precursors. Each monolith was weighted and required amounts of metal precursors were determined. Firstly, determined amount of $\text{Mn}(\text{NO}_3)_2$ tetrahydrate was dissolved in deionized water as the bases of 1 g silica/1.1 ml water. Prepared solution was impregnated on the monoliths by using a syringe. Entire monoliths were wetted with solution. After $\text{Mn}(\text{NO}_3)_2$ tetrahydrate impregnation monoliths were dried at 130°C for 5 hours, they were kept in desiccator until they cooled to room temperature. After that, required amount of Na_2WO_4 dihydrate solution was prepared and Na_2WO_4 impregnation was done as it was explained in the previous samples. After impregnation, the monoliths were kept 130°C overnight. Finally, they were calcined at 800°C oven for 8 hours with 10°C/min heating ramp.

3.2.3. Wash-Coating Method

For this method, the commercial ceramic foam filter made of aluminum oxide was used. Ceramic foam was cut with optimum dimensions and were washed distilled water, ethanol and acetone in order. After cleaned all impurities, the monoliths were dried in the oven for 1 hour. The commercial ceramic foam and the monoliths obtained from this were shown in Figure 3.8 (a).



Figure 3.8. Wash coating preparation system. a) commercial ceramic foam, b-c) wash coating under ultrasonic mixing, d) obtained coated monoliths

Dried monoliths were weighted and immersed into coating solution under ultrasonic mixing. In order to coat monolithic supports, three different solutions were used

and details are shown in Table 3.3. Monoliths were kept in the solution 40 minutes. To avoid clogging the pores, after every 5 minutes, the air was injected to the monoliths in order to remove excess solution inside the pores. After that, monoliths were dried by using microwave at 180 W for 40 minutes. This process is showed in Figure 3.9 schematically. Dried monoliths were weighted again, and the process was repeated until the required amount of coated silica (0.3 g) was reached.

Table 3.3. Details of Coating Procedures

Coating Procedure	Calcination	Impregnation	T _{calcination} (°C)
Colloidal Silica (40%) Solution	40 minutes in microwave (180 Watt)	Mn and Na ₂ WO ₄ impregnation	800
Wash coated during SiO ₂ nanoparticle synthesis	40 minutes in microwave (180 Watt)	Mn and Na ₂ WO ₄ impregnation	800
Wash coated with filtrated Mn-SiO ₂ nanoparticles	40 minutes in microwave (180 Watt)	Na ₂ WO ₄ impregnation	800

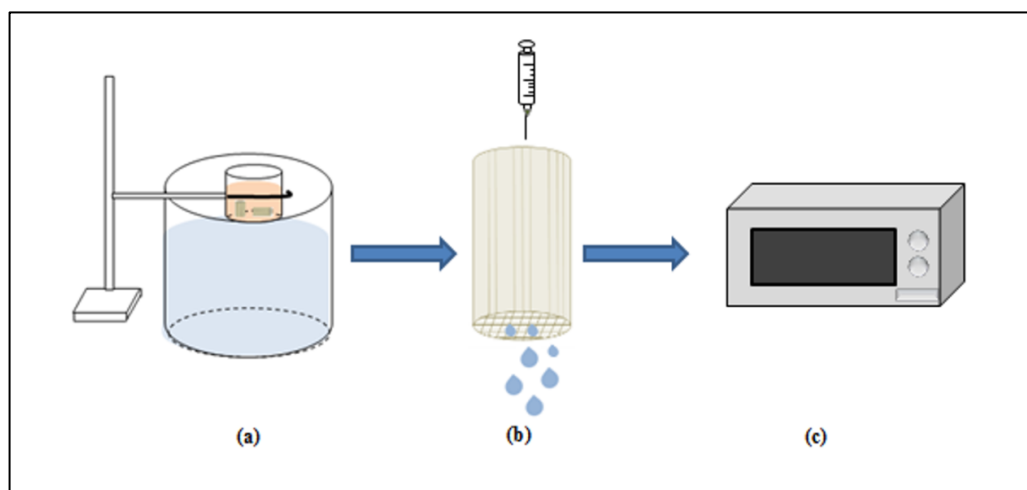


Figure 3.9. Schematic demonstration of monolith coating system. a) wash coating under ultrasonic mixing, b) removing excess solution, c) dried monoliths in microwave

The coated silicas monoliths were impregnated; $\text{Mn}(\text{NO}_3)_2$ tetrahydrate solution was injected on the coated monoliths with using syringe. Excess solution was removed by injecting air and impregnated on the monoliths again. After impregnation of $\text{Mn}(\text{NO}_3)_2$ tetrahydrate, monoliths dried at 130°C oven for 5 hours and cooled at desiccator. After that, Na_2WO_4 dihydrate impregnation was done with the same method. Then, impregnated monoliths were dried overnight at 130°C . Finally, they were calcined at 800°C for 8 hours with $10^\circ\text{C}/\text{min}$ heating ramp rate.

3.3. Experimental System

In this thesis, the catalytic reaction system in the Catalysis and Reaction Engineering Laboratory of Chemical Engineering Department of Boğaziçi University was used. The system is shown in Figure 3.10 schematically. 1/4", 1/8" and 1/16" OD stainless steel and copper tubing and valves were used to design and construct of the system. Reaction gases were connected to the system and their set points were adjusted with mass flow controllers. For feed analysis, required amount of high purity gases were mixed and sent to GC with the by-pass line and for catalytic test gases sent to the reactor; this was regulated with a two-way valve. A K-type thermocouple attached to Shimaden FP21 programmable controller was used to control the temperature inside the furnace and reactor. After reactor, there were two series of condensers in order to trap any liquid products before they reached to GC system. Also, for calibration, a bubble flow meter was used in the system.

4% nitrogen was used as inert for all experiments to calculate the concentration of product gases. Analysis in the GC took 21 minutes for analysis and 29 minutes for cooling requiring a total 50 minutes for each injection. First, reactor furnace heated to requested temperature and feed gases mixed for 20 minutes at that temperature to provide homogeneous mixture. After that data was taken.

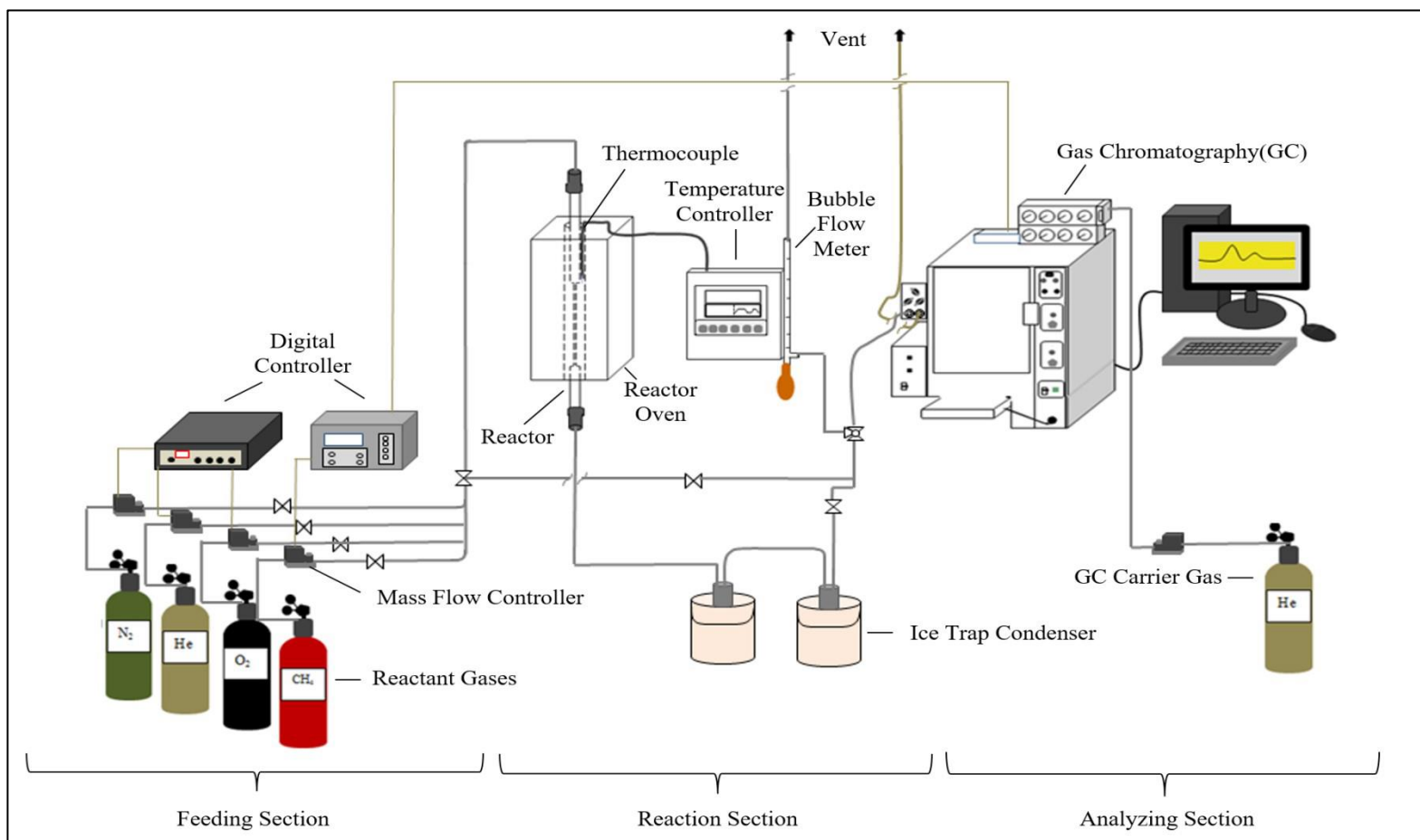


Figure 3.10. Schematic demonstration of experimental system

3.3.1. Mass Flow Controller

Digital controllers were used to adjust the flow rates of reaction gases. There were two different types in the system. Oxygen and nitrogen passed through Omega Model 7878 digital controllers which are regulated to the specific set point. Brooks 5850E digital mass flow controllers were connected to the helium which used for GC and methane gases. A bubble flow meter was used for calibration of the MFCs manually. For calibration, each gas was feed to the system with determined flow rate. Approximately 10 minutes was needed to stabilize gas flow. After that, time of bubble motion between two specific points was measured. The real flow rate calculated with using measured time for determined set value. Procedure was repeated for other set points and a calibration curve was obtained for each gas. Flow rates were chosen between a narrow range for oxygen and nitrogen (2-40 ml/min for oxygen and 2-10 ml/min for nitrogen) as higher values could not be used for experiments. On the other hand, for methane range was defined wider (10-90ml/min) because this gas was used with high flow rates.

3.3.2. Gas Chromatography

Shimadzu GC 14A type gas chromatograph was used to analyze the reaction gases. Thermal Conductivity Detector (TCD) was used with GC and the specifications of the gas chromatography are given in Table 3.4.

Table 3.4. The specifications of the Gas Chromatography

GC	Shimadzu GC 14A
Carrier gas	Helium
Carrier gas flow rate	30 ml/min
Column final temperature	220 °C
Column final time	15 min
Column injection temperature	220 °C
Column initial temperature	40 °C
Column initial time	5 min

Table 3.5. The specifications of the Gas Chromatography (cont.)

GC	Shimadzu GC 14A
Column temperature increment rate	20 °C.min ⁻¹
Column length & ID	6 m, 2mm ID, 1/8 inch OD
Column type	CBXN-1000 60/80
Detector temperature	230 °C
Detector type	TCD
Sample loop	2 mL
Sampling rate	100 ms

The helium was used as the carrier gas, and volume changes throughout the reaction was calculated by using nitrogen as an internal standard. Unfortunately, peaks of nitrogen and oxygen were overlapped and it lead to significant errors in selectivity and yield calculations in some experiments. In order to prevent overlapping, a heating program, which was developed by Nadjafi for GC oven, was used (Nadjafi, 2015). According to this program, the temperature of the column was kept at 40°C for 5 minutes and increased with 20°C/min ramping rate until reach 220°C which was the final temperature. This heating program ensured to separate nitrogen and oxygen peaks as shown in Figure 3.11.

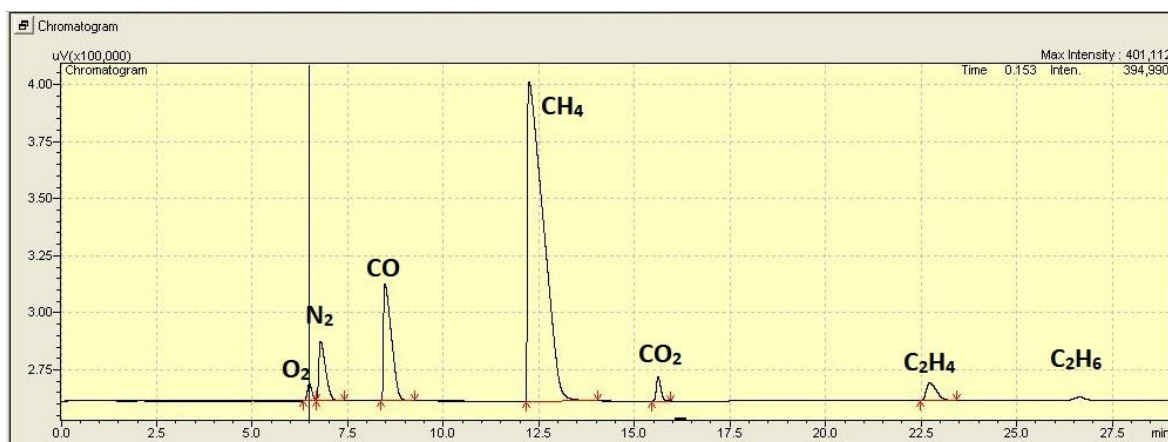


Figure 3.11. Peak times of product gases on GC program

3.3.3. Furnace and Temperature Controller

Tubular electric furnace with 30 mm diameter and 480 mm length was used in a 25-1000°C temperature range. A Shimaden FP-21 type programmable controller was connected to a K-type thermocouple (Chromel - 95% nickel, 2% manganese, 2% aluminum and 1% silicon, Alumel - 95% nickel, 2% manganese, 2% aluminum and 1% silicon), which was placed just between the furnace and quartz reactor connected to the furnace. Through the experiments, the thermocouple was imbedded to the furnace and aligned to the catalyst bed, outside of the reactor. Reactor was longer than the furnace so the parts, which was outside of furnace, was in touch with ambient air. This connection made difficult to heat reactor. Because of that, quartz wool which enveloped with aluminum foil was used to insulate the upper part (gas entrance) of reactor. On the other hand, the lower part (exit) was not insulated to prevent by-product formation.

3.3.4. Catalytic Reaction System

All experiments were performed with 300 mg 2 wt.% Mn 5 wt.% Na₂WO₄/SiO₂ catalyst and the total flow was chosen as 120 ml/min. Experiments were done in a downward flow tubular reactor. Quartz reactor was 810 mm length and 10 mm inside diameter. Quartz was chosen to resist high temperatures. Also, after the catalyst bed, inside diameter of reactor reduced of 2 mm. That reduction of diameter prevented desired products conversion to by-products by accelerating the exit of products gases from the reactor.; this configuration was proven to be beneficial in previous works (Uzunoglu, 2016). In addition, to avoid the undesirable gas phase reactions, the reactor was filled with different sizes of quartz chips.

Reactor preparation was done as follows. Firstly, the slim part of reactor was closed with quartz wool from the bottom. Then, the lower part of reactor filled with 1-2 mm quartz chips. After loading the chips, quartz wool was used again to cover the bottom of the chips. Then, 0.63-1 mm quartz chips were used to load slim part of reactor. Top of the slim part was closed with quartz wool again. Then, 300 mg catalyst was weighted and placed over the quartz wool. Another quartz wool was put on the catalyst bed to prevent

contamination. Finally, upper part of the reactor filled with 1-2 mm quartz chips again. These quartz chips were made of crushed quartz glasses. They were crushed, classified by their size and treated with hydrochloric acid and acetone. Before each catalytic run, quartz chips were cleaned with acetone and distilled water.

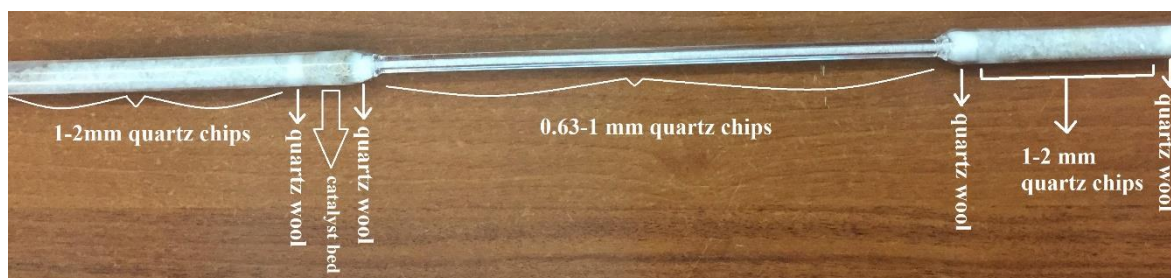


Figure 3.12. Schematic representation of the filled reactor

Each test was started with a feed analysis, which was used to check the accuracy of the feed gases and used for the calculations of conversion, selectivity and yield as calibration mixture. Nitrogen was also introduced to the feed with a constant 4% concentration. Feed gases were mixed for 15 minutes before the feed sample was taken for analysis. After the feed analysis, reactor was heated to desired temperature. Heating was done under 5 ml/min nitrogen flow and it took 40 minutes. When the temperature of reactor reached the set point, first methane and 5 minutes later oxygen was fed to the system. To obtain accurate results, the reactants were mixed 20 minutes before the first data was taken.

In this study, not only the different catalyst preparation techniques, but also the effect of temperature on catalytic performance was investigated. Temperature range was 600 - 800°C and there was 50°C interval between each temperature level. Total flow was always 120 ml/min for all experiments and different CH_4/O_2 ratios were tested.

For all experiments, calculations were done according to our previous works (Nadjafi, 2015). Flow rate, conversion, selectivity and yield were calculated as follows.

$$F_{\text{out}} = \frac{X_{\text{N}_2, \text{in}} \times F_{\text{in}}}{X_{\text{N}_2, \text{out}}} \quad (3.1)$$

$$\text{Conversion} = \frac{X_{\text{CH}_4, \text{in}} \times F_{\text{in}} - X_{\text{CH}_4, \text{out}} \times F_{\text{out}}}{X_{\text{CH}_4, \text{in}} \times F_{\text{in}}} \quad (3.2)$$

$$\text{Selectivity} = \frac{2 \times F_{\text{out}} (X_{\text{C}_2\text{H}_4} + X_{\text{C}_2\text{H}_6})}{X_{\text{CH}_4, \text{in}} \times F_{\text{in}} - X_{\text{CH}_4, \text{out}} \times F_{\text{out}}} \quad (3.3)$$

$$\text{Yield} = \text{Selectivity} \times \text{Conversion} \quad (3.4)$$

4. RESULTS AND DISCUSSION

Different forms of $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts with different synthesis methods were synthesized and the oxidative coupling of methane performance of each were investigated in a micro-structured packed bed reactor. In the following sections, catalytic activity results and SEM images of these methods are given.

4.1. Performance of Catalysts Prepared by Sol-Gel Method

4.1.1. Characterization of Sol-Gel Method

First, to examine the effect of calcination type, two $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts which were calcined with different methods were screened with SEM. Both catalysts were prepared with trimethylamine and one of them was calcined in the air inside the reactor while the other calcined in a muffle furnace. SEM images of catalysts are shown in Figure 4.1. According to SEM images, calcination type did not affect the structure of catalysts significantly. Because of that, next experiments were carried out with muffle furnace calcination.

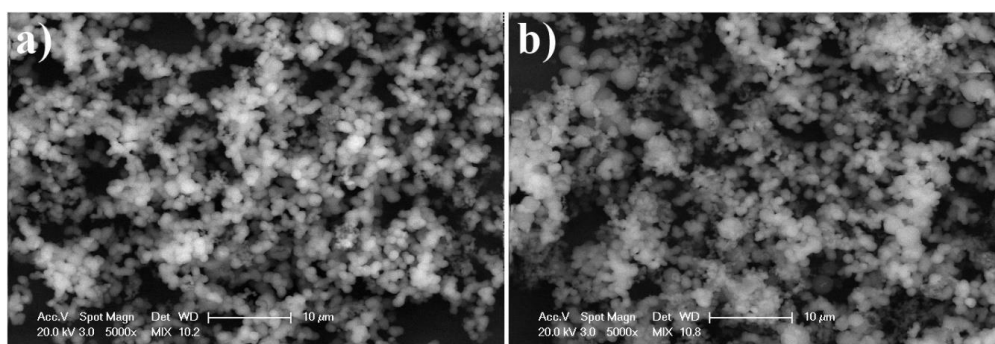


Figure 4.1. SEM images of $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ particulate catalyst – 5000x. a) calcined in air, b) calcined in muffle furnace

During the synthesis of particulate and monolithic $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts, different acid and base sources were used to determine the effects of acid or base type on

the structure of catalysts. As is shown in Figure 4.2, 4.3 4.4 & 4.5, using acid or base sources changed the structure of catalyst significantly. Although the use of acid or base affected the structure of the catalyst, the type of the acid or base did not make a significant difference.

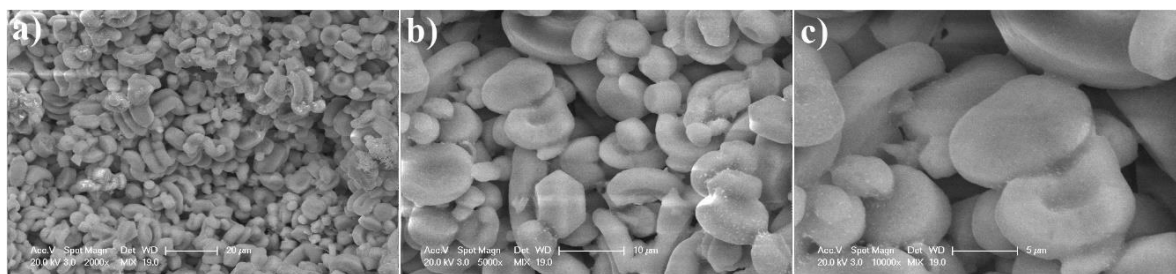


Figure 4.2. SEM images of $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ particulate catalyst which synthesized with using nitric acid. a) – 2000x, b) – 5000x, c) – 10000x

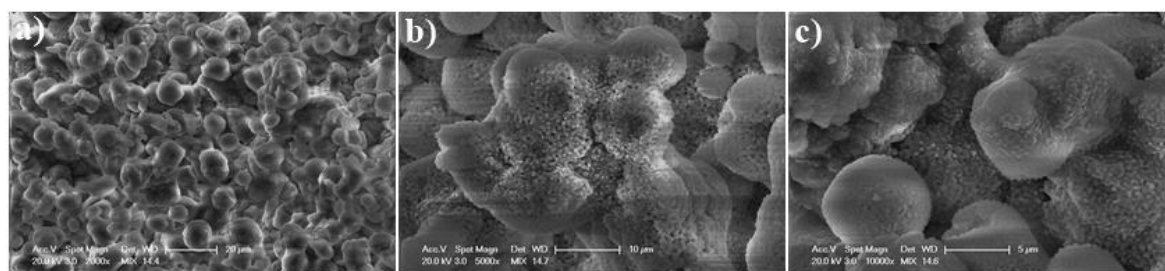


Figure 4.3. SEM images of $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ particulate catalyst which synthesized with using hydrochloric acid. a) – 2000x, b) – 5000x, c) – 10000x

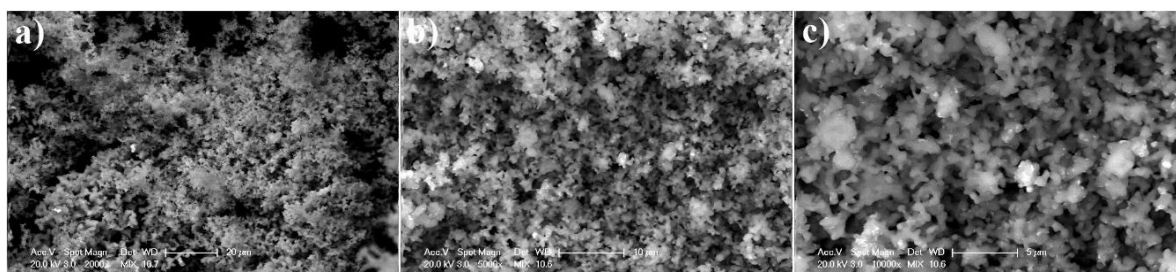


Figure 4.4. SEM images of $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ particulate catalyst which synthesized with using triethylamine. a) – 2000x, b) – 5000x, c) – 10000x

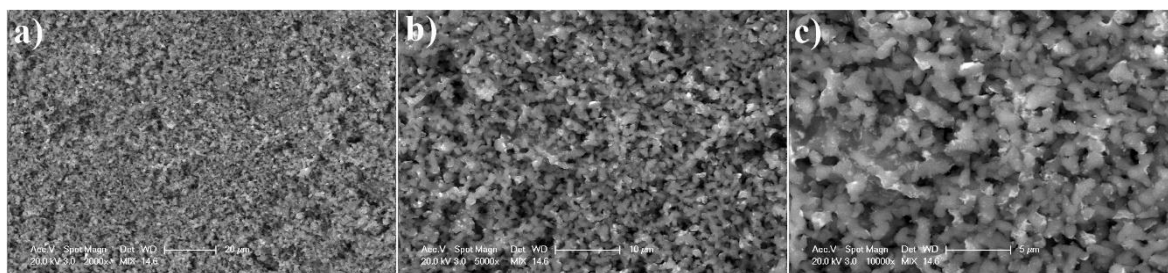


Figure 4.5. SEM images of Mn/Na₂WO₄/SiO₂ particulate catalyst which synthesized with using triethanolamine. a) – 2000x, b) – 5000x, c) – 10000x

4.1.2. Effect of the Temperature Variations

Monolithic Mn/Na₂WO₄/SiO₂ catalysts, which were synthesized using the sol-gel method, were tested to observe the effect of temperature on performance. The first experiment was performed with monolithic Mn/Na₂WO₄/SiO₂, catalyst which was prepared using hydrochloric acid.

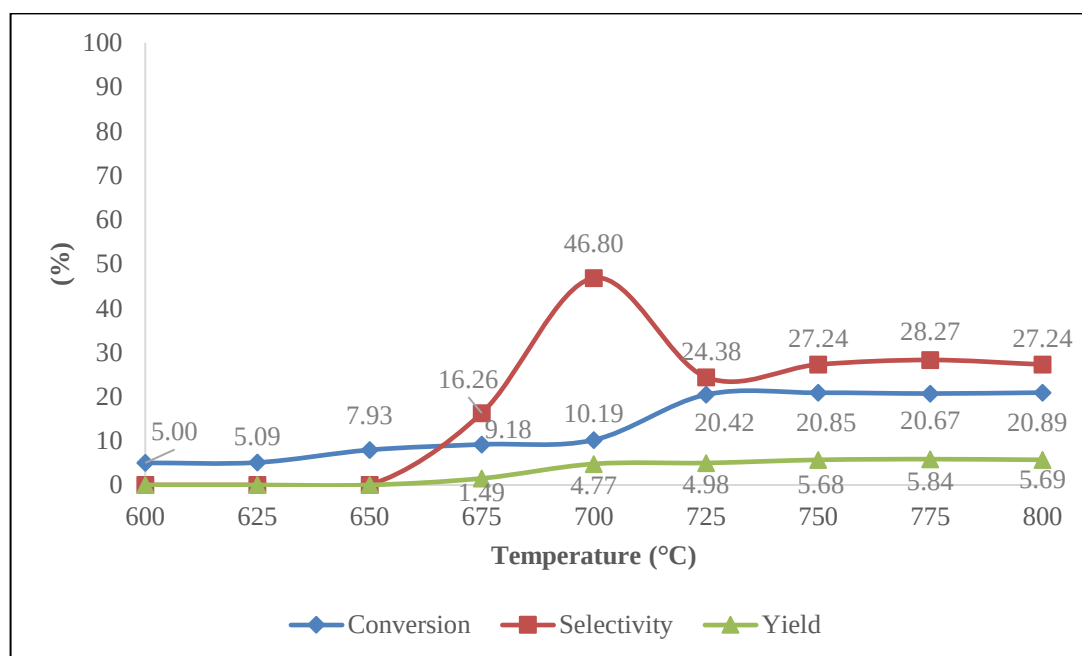


Figure 4.6. Influence of the temperature over the particulate catalyst which synthesized with hydrochloric acid when the CH₄/O₂=5.

The conversion was low at the beginning of the experiment at low temperatures (at 600-650°C); the selectivity and yield did not change either. This demonstrates that the low temperatures are not suitable for OCM reaction. Conversion started to increase at 650°C and fluctuated between 650 and 725°C. The yield was showed almost the same behavior with conversion, and it was reached the maximum point of about 5% when the catalyst bed at 725°C. Above this temperature, the yield was almost not changed. Differently from conversion and yield, selectivity rose sharply between 650°C and 700°C, before plunging back down to its original level at 750°C. It can be concluded for this catalyst that, the optimum temperature is the 725°C when the CH₄/O₂ ratio is 5.

Another acidic source, nitric acid was also used in the catalyst synthesis and its performance was similar to hydrochloric acid between the temperature of 600-800°C and the CH₄/O₂ ratio of 5 (Figure 4.7). It can be concluded that acidic sources has very low activity for OCM reaction.

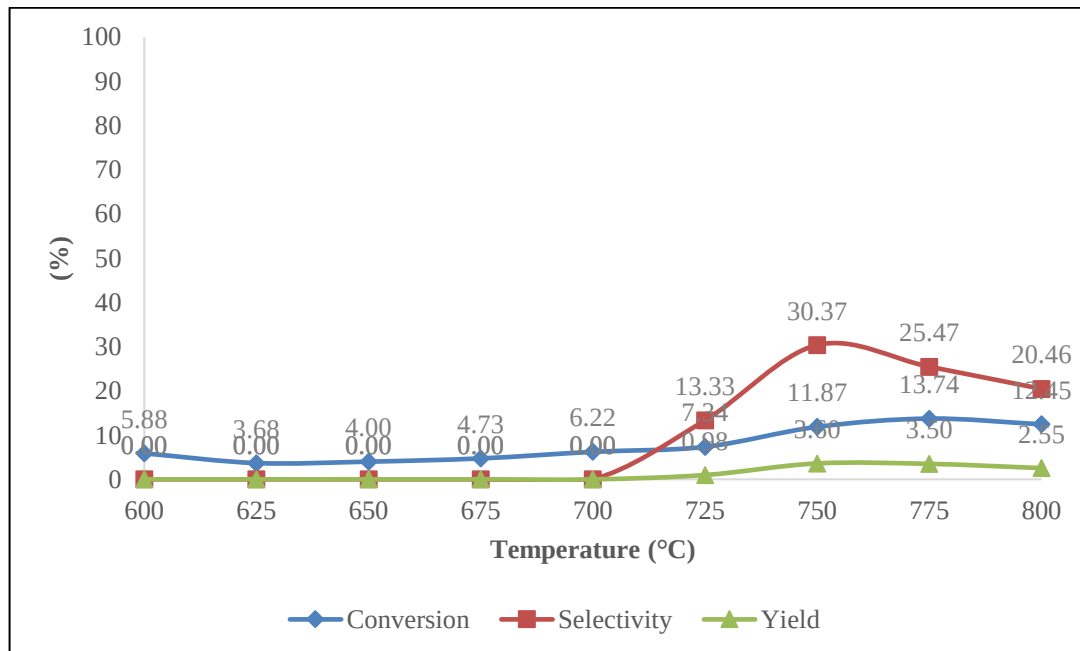


Figure 4.7. Influence of the temperature over the particulate catalyst which synthesized with nitric acid when CH₄/O₂=5.

Since the acidic sources were not effective with this method, the alkaline sources were also tested; triethylamine and triethanolamine were used for this purpose. For understanding the effect of temperature on catalytic performance, the experiments were carried out between 600-800°C temperature range; the CH₄/O₂ ratio was 5 as the previous experiment.

The performance of the catalyst, which was synthesized with triethylamine source, was shown in Figure 4.8. At the beginning of the experiment, the conversion was low and it started to increase after 625°C. Between the temperatures of 650-725°C, the conversion was fluctuated at about 20% and after 725°C, it decreased slightly to 15%. The yield showed a similar behavior with the conversion. At the low temperatures, the yield and selectivity were zero; there were no desired products. Selectivity was dramatically increased after 625°C indicating that ethane and ethylene production started at this point. Between the temperatures of 650-725°C, it also fluctuated between 70-80%; it reached the maximum point of 79.9% at 675°C. At 725°C, the selectivity was 70% and after that point, it was decreased swiftly to the final value of 34.7. After 625°C, there was an increase in the yield too. However, it was increased (to about 16%) until 675°C; and then declined. At the end of the experiment, the yield decreased to 5-6% between 750-800°C temperature range. To conclude, the optimum temperature is 675°C for OCM reaction on triethylamine included Mn/Na₂WO₄/SiO₂ catalyst.

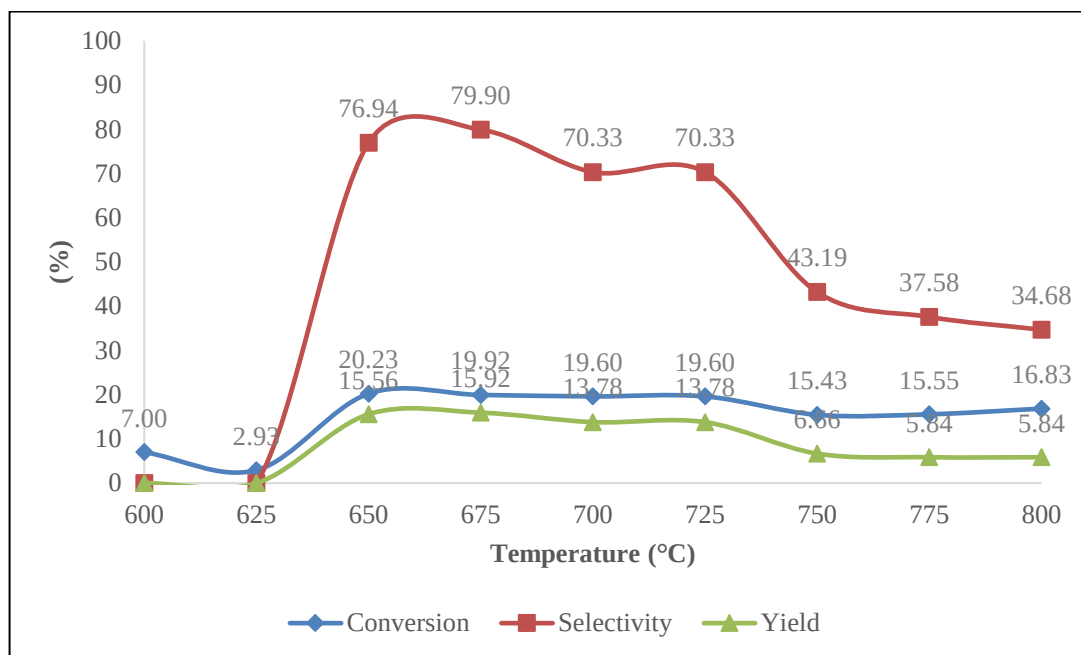


Figure 4.8. Influence of the temperature over the particulate catalyst which synthesized with triethylamine when $\text{CH}_4/\text{O}_2=5$.

Finally, the tests for temperature effects were performed for $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst produced with using triethanolamine; The experiments were conducted between 600-800°C and methane to oxygen ratio was 5. As different from the previous catalysts, the conversion and the production of desirable products were started at lower temperatures with the $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts prepared with triethanolamine. Also, the highest yield was obtained at 650°C which was lower than the previous catalyst. The catalytic performance of the triethanolamine included catalyst is given as Figure 4.9.

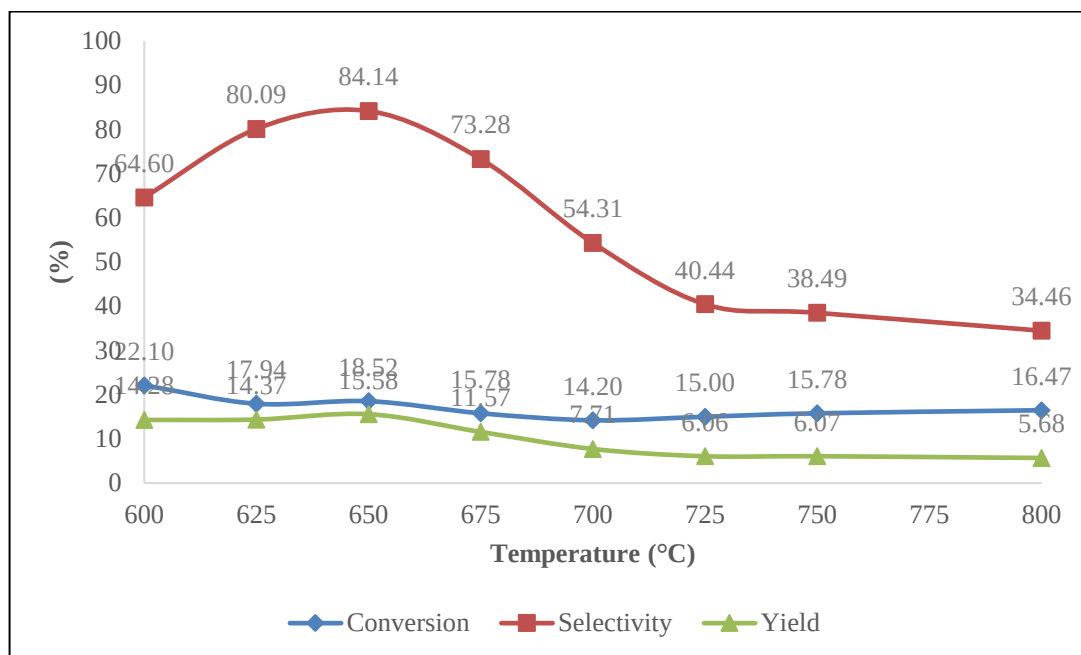


Figure 4.9. Influence of the temperature over the particulate catalyst which synthesized with triethanolamine when $\text{CH}_4/\text{O}_2=5$.

4.1.3. Effect of the Feed Gas Composition

Particulate $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts were tested for the effect of feed gas composition; The CH_4/O_2 ratio was adjusted as 2, 4.3, 5, 7 and 10, and for all values, the tests were performed at 600, 625 and 650°C. Figure 4.10 shows the performance at 650°C for different CH_4/O_2 ratios. Although the maximum conversion value was obtained when CH_4/O_2 was 2, selectivity and yield were low. It was caused from the by-product formation at 650°C. Performance of methane to oxygen ratio of 4.3 gave the best results for selectivity and yield at 650°C. The conversion was lower than the previous ratio of 2; however, the yield was reached to 16.5. When the CH_4/O_2 ratio was 5, results were also close to the 4.3. After that point, increasing the ratio was caused to decrease in selectivity and yield. According to that, the best ratios for 650°C are 4.3 and 5. Different feed compositions through 600 and 625°C are also given in Figure 4.11 and 4.12. Results of these temperatures also matched with 650°C. It can be concluded that the maximum selectivity and yield values could be obtained with this catalyst at the ratios 4.3 and 5.

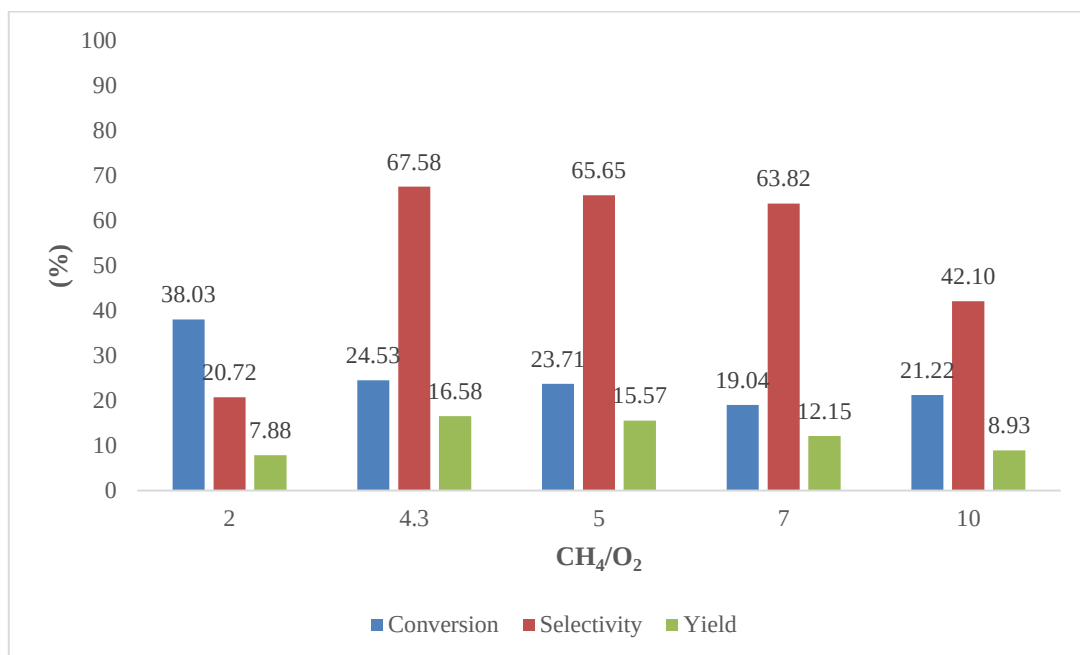


Figure 4.10. The effect of methane to oxygen ratio at 650 °C

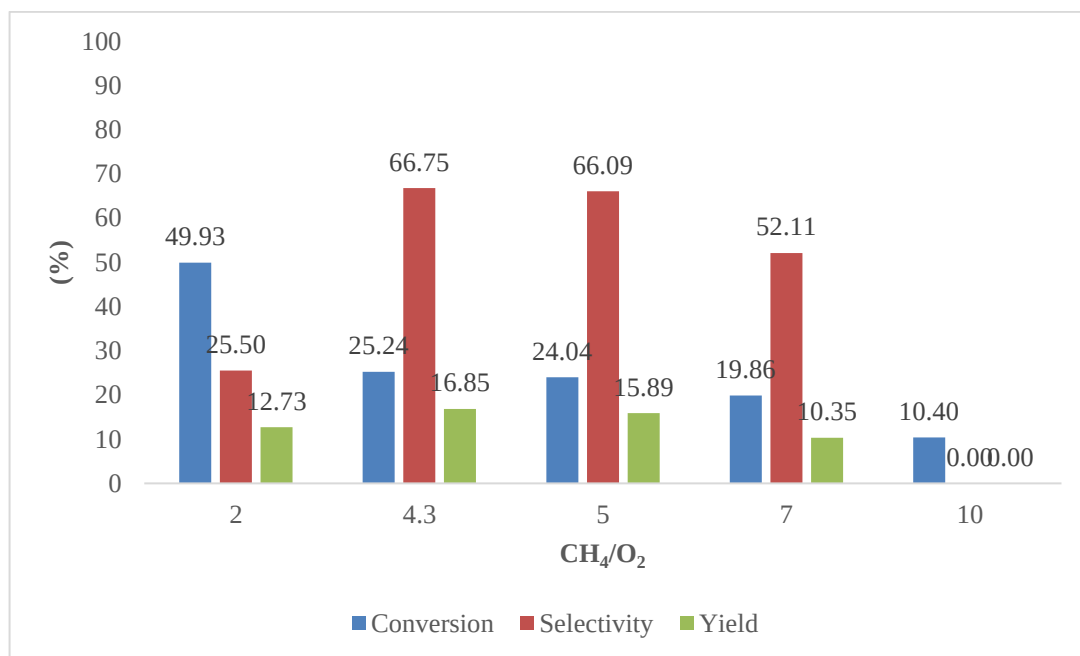


Figure 4.11. The effect of methane to oxygen ratio at 600 °C

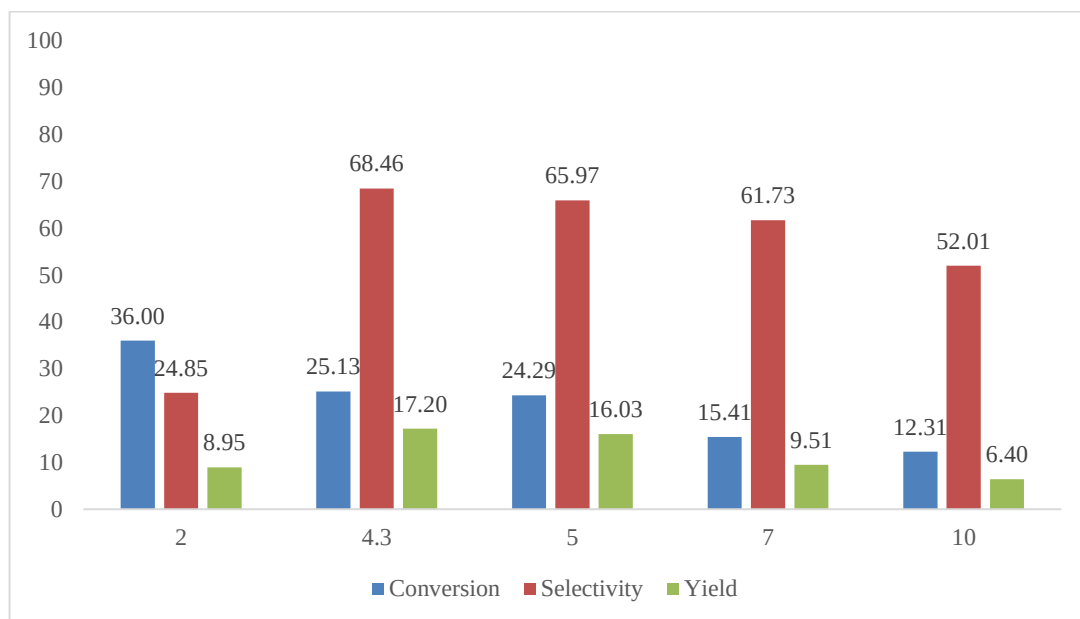


Figure 4.12. The effect of methane to oxygen ratio at 625 °C

4.1.4. Stability Test

Mn/Na₂WO₄/SiO₂ catalyst was tested to investigate catalyst stability with two different methods. For the first procedure, the OCM reaction was carried out for 600 minutes. During the reaction the temperature was set to the 650°C and CH₄/O₂ ratio was chosen as 5. Figure 4.13 shows the results of the stability test. According to Figure 4.13, it can be said that Mn/Na₂WO₄/SiO₂ catalyst has a stable activity for 600 minutes reaction.

Stability of catalyst depending on temperature was also tested. For this test, the reaction parameters were same as the previous test. The reaction started at 650°C and then the system heated to the 800°C gradually. When the reactor temperature reached to 800°C, the catalytic performance of the catalyst (conversion, selectivity and yield values) decreased. After that, catalyst bed was cooled to the 650°C step by step. When it reached to the initial temperature again, data was taken. Selectivity and yield data were almost same as the initial experiment. Details of the results are given as follows.

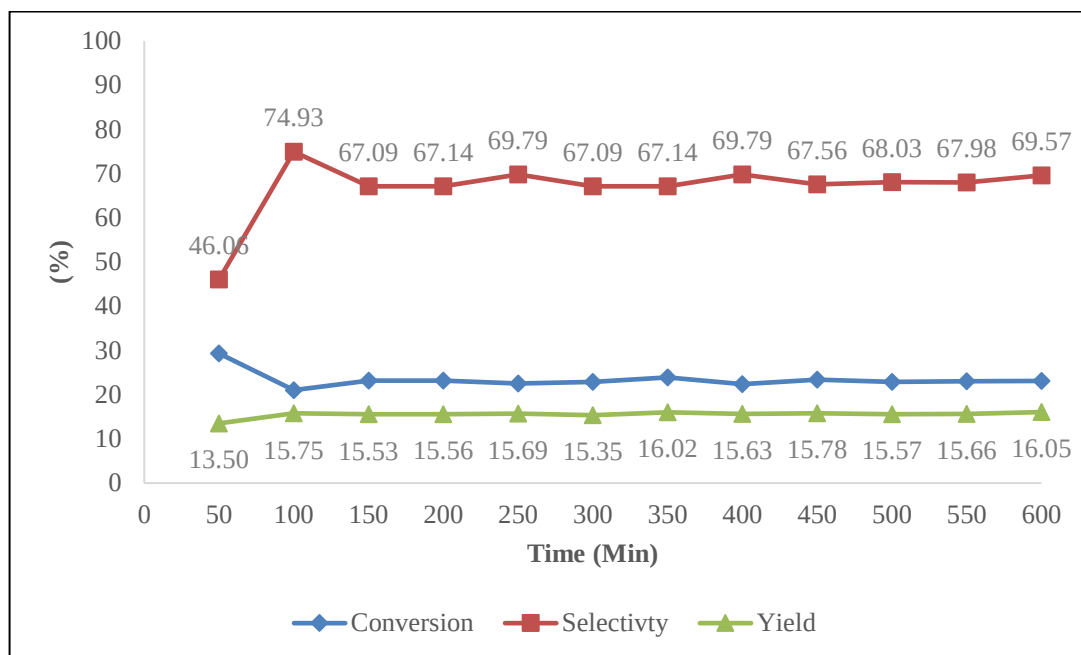


Figure 4.13. Results of the stability test at 650°C for 10 h with CH₄/O₂ ratio of 5.

Table 4.1. The durability of the Mn/Na₂WO₄/SiO₂ catalyst when CH₄/O₂ ratio is 5.

Temperature (°C)	Specification	Conversion (%)	Selectivity (%)	Yield (%)
650	Temperature increment	22.97	69.49	15.96
800	Temperature increment	18.75	30.79	5.77
650	Temperature decline	22.49	69.79	15.69

4.2. Performance of Catalysts Prepared by Sol-Gel Method under DC Voltage

4.2.1. Characterization of Sol-Gel Method under DC Voltage

Electricity was supplied to catalysts with different durations as explained in Chapter 3. To observe the effect of electricity on the structure of catalyst, SEM images were taken. From Figure 4.14 and Figure 4.15, it can be said that electricity did not have

any effects on the pore structure of catalyst directly. However, particle size was affected by electricity.

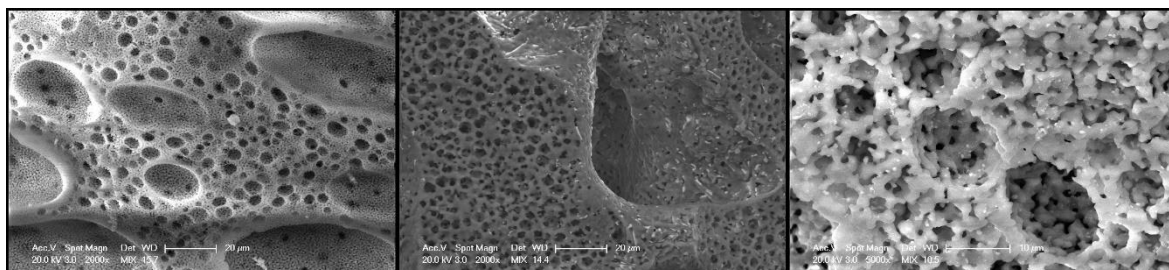


Figure 4.14. SEM images of Mn/Na₂WO₄/SiO₂ monolithic catalysts – 2000x. a) reference, no electricity, b) electricity supplied by the hour, c) electricity supplied continuously

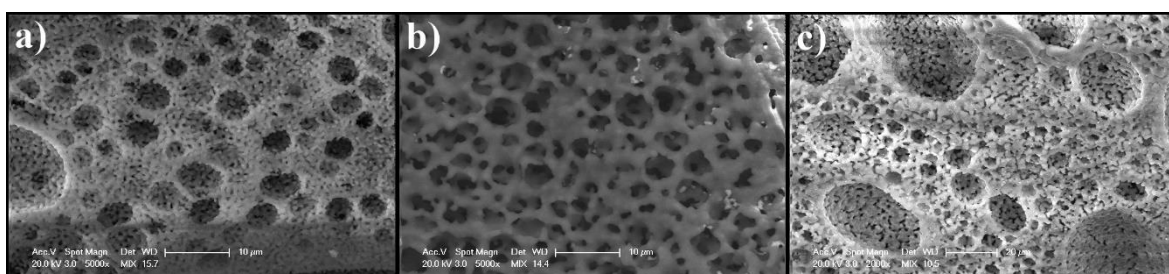


Figure 4.15. SEM images of Mn/Na₂WO₄/SiO₂ monolithic catalysts – 2000x. a) reference, no electricity, b) electricity supplied by the hour, c) electricity supplied continuously

4.2.2. Effect of the Temperature Variations

Mn/Na₂WO₄/SiO₂ catalyst, which was synthesized with electrical deposition method, was tested between 600-800°C; the CH₄/O₂ ratio was chosen as 5. Feed gases were mixed for 20 minutes at the required temperature before the data was taken. Then, the reactor was heated to the next level. The same procedure was applied for each temperature points.

First of all, the reference sample was tested, and the results are shown in Figure 4.16. At the low temperatures, the conversion was too low, selectivity and yield were zero because OCM reaction was not favorable at these low temperatures. The ethane and ethylene production started around 675°C. The conversion had a slight increase from the beginning of the experiment and it was reached the maximum point at 775°C. After that point, the conversion was decreased. Selectivity rose after 650°C and remained almost the same until the catalyst bed reached 775°C. When bed temperature was 800°C selectivity, as well as the conversion, was almost zero. The yield was generally low in this test and the best results were obtained at 775°C.

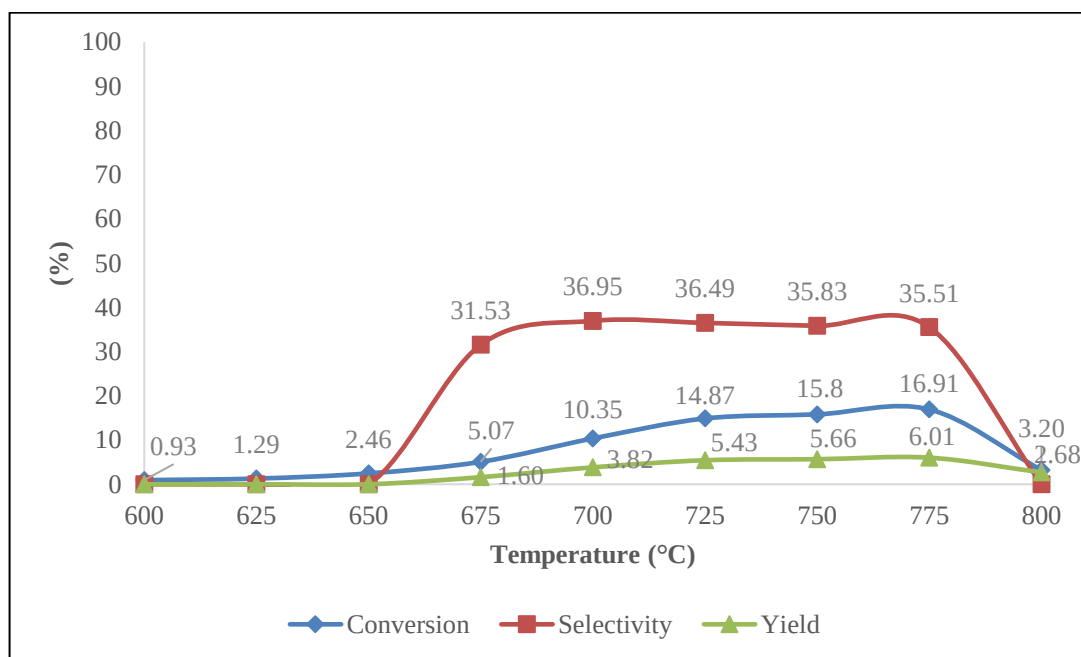


Figure 4.16. OCM Performance for Sol-Gel Method under DC Voltage – Reference Sample

The second sample was exposed to electricity one minute for every hour during its synthesis. Results of performance tests are shown in Figure 4.17. The behavior of this sample was similar with the reference but there was about 25-degree temperature shift. Conversion increased with the increase of temperature, and the desired products formation occurred above 650°C and selectivity sharply increase at that temperature. After the 675°C, selectivity started to decrease. Unlike to selectivity, yield was reached the

maximum value at 700°C and started to decrease above this temperature. Overall, the yield was nearly the same with the results of the reference sample.

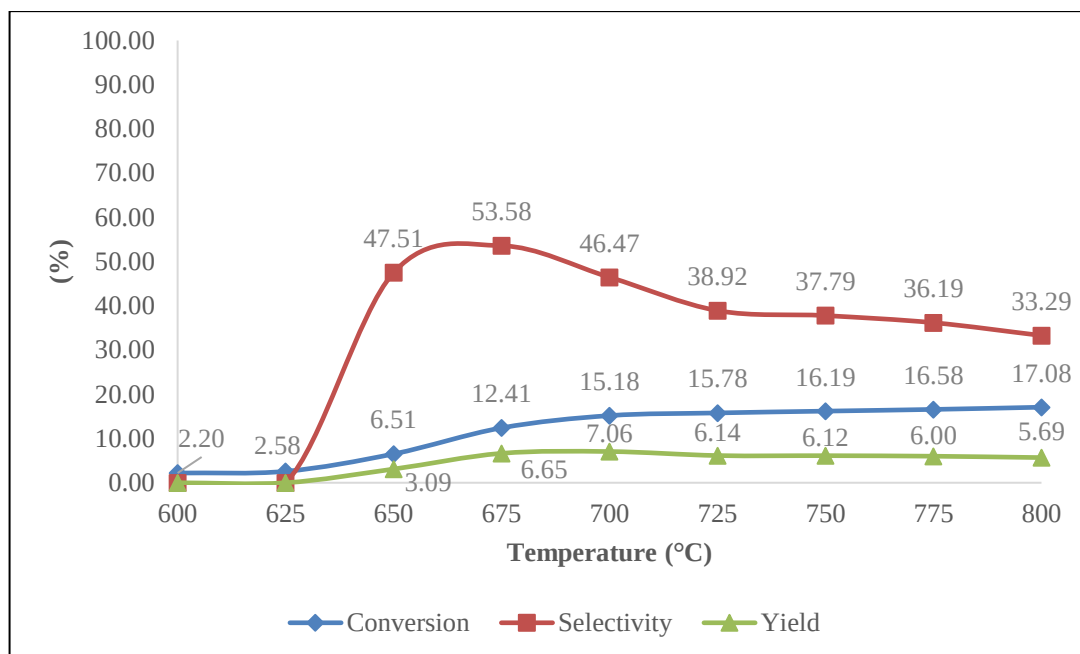


Figure 4.17. OCM Performance for Sol-Gel Method under DC Voltage – Electricity supplied by the hour

Finally, the catalytic performance test was carried for the third sample. This catalyst synthesized with supplying electricity continuously during its gelation. The results are shown in Figure 4.18. The behavior of this sample was also similar with the reference ones. During the experiment, conversion increased with the increase of temperature. However, at the low temperatures, selectivity and yield were zero; only the side reactions occurred. C₂ products production started at 675°C and selectivity increased rapidly at this temperature. After 700°C, the selectivity had a fall, and it was stabilized at the 725°C. This stabilization could be seen at yield too. Figure 4.18 indicates that the optimum temperature for OCM reaction on this catalyst is 700°C with about 5-6% yield.

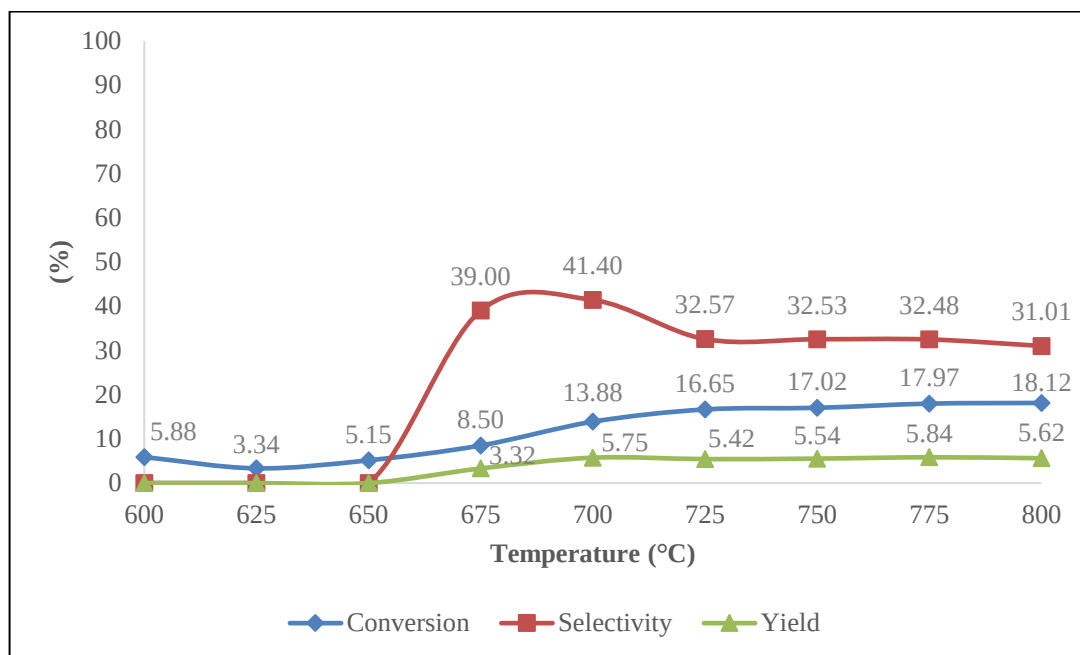


Figure 4.18. OCM Performance for Sol-Gel Method under DC Voltage – Electricity supplied continuously

Figure 4.19 summarized the effects of electricity by leads to observe the catalytic performance of these three samples clearly. Electricity seemed to increase the conversion, selectivity and yield slightly if the values at the single temperature of 675°C taken. However, the maximum yield in all electricity induced and reference samples are about 6-7% suggesting that electricity may slightly decrease the reaction temperature; on the other hand, these performances are almost the same as the blank test performed with the empty reactor (Section 4.5).

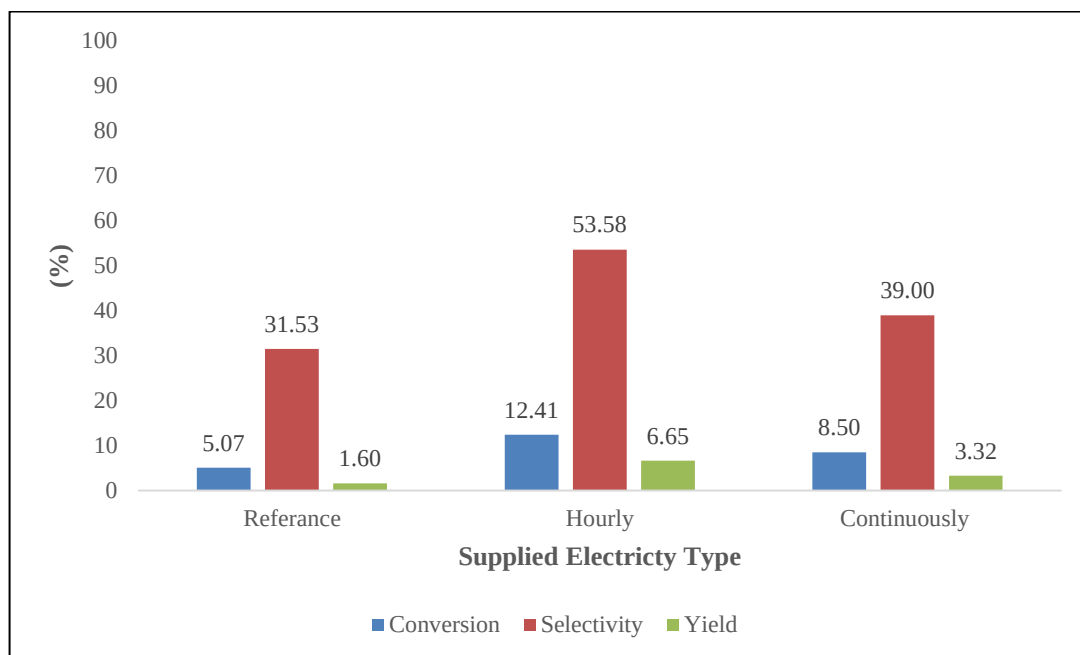


Figure 4.19. OCM Performance for Different Variations of Supplied Electricity – 675°C

4.3. Performance of Catalysts Prepared by Wash Coating Method

4.3.1. Effect of the Coating Method

Various methods were used to coat monolithic structures and these methods were listed in Table 4.1. Monoliths were weighted before and after the coating procedure to examine if the coating was successful or not. According to all procedures, only the colloidal silica solution holds on the aluminum oxide structure.

Table 4.2. Details of Coated Solutions

Coating Procedure	Result
Colloidal Silica (40%) Solution	Coated
Wash coated during SiO ₂ nanoparticle synthesis	Not coated
Wash coated with filtrated SiO ₂ nanoparticles	Not coated

SEM images of fresh alumina oxide foam filter and filter coated with colloidal silica were given in Figure 4.20.

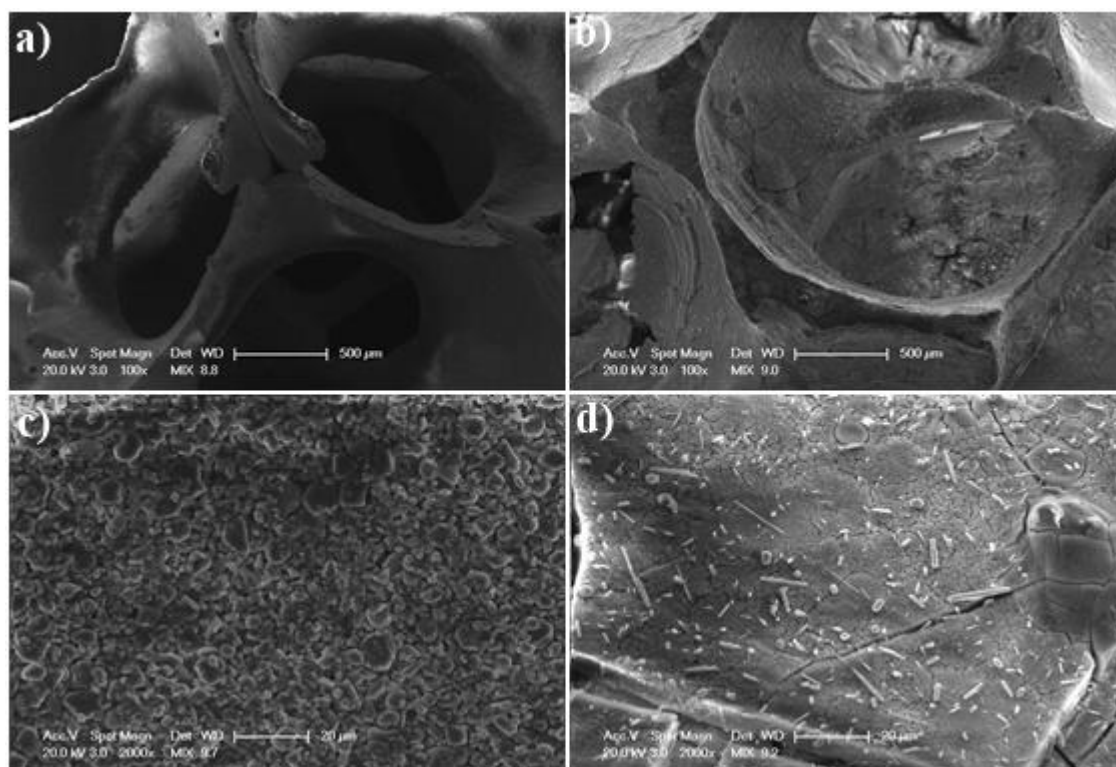


Figure 4.20. SEM images of monolithic ceramic filter. a) fresh alumina oxide foam filter – 100x, b) filter coated with colloidal silica – 100x, c) fresh alumina oxide foam filter – 5000x, d) filter coated with colloidal silica – 5000x.

4.3.2. Effect of the Temperature on Monolithic Alumina Foam Wash Coated by Colloidal Silica

OCM performance of monolithic structure coated by colloidal silica sample is given in Figure 4.21. At low temperatures, the conversion was almost zero, thereby selectivity and yield were not significant. Conversion increased with an increase of temperature directly. At 650°C, the selectivity increased substantially. It caused by the formation of desirable products at that temperature. The selectivity peaked at 675°C and then it started to decrease. Although selectivity decreased above 675°C temperature, the yield was slightly increased till the temperature reached to 750°C. The maximum point of

yield was observed at 750°C. According to all of these, 750°C is the optimum temperature for OCM reaction on monolithic structured ceramic foam. Also, because of its lower C₂ yield and selectivity, it was concluded that this ceramic foam is not a good catalyst for this reaction (the performance is almost the same as the blank test presented in Section 4.5).

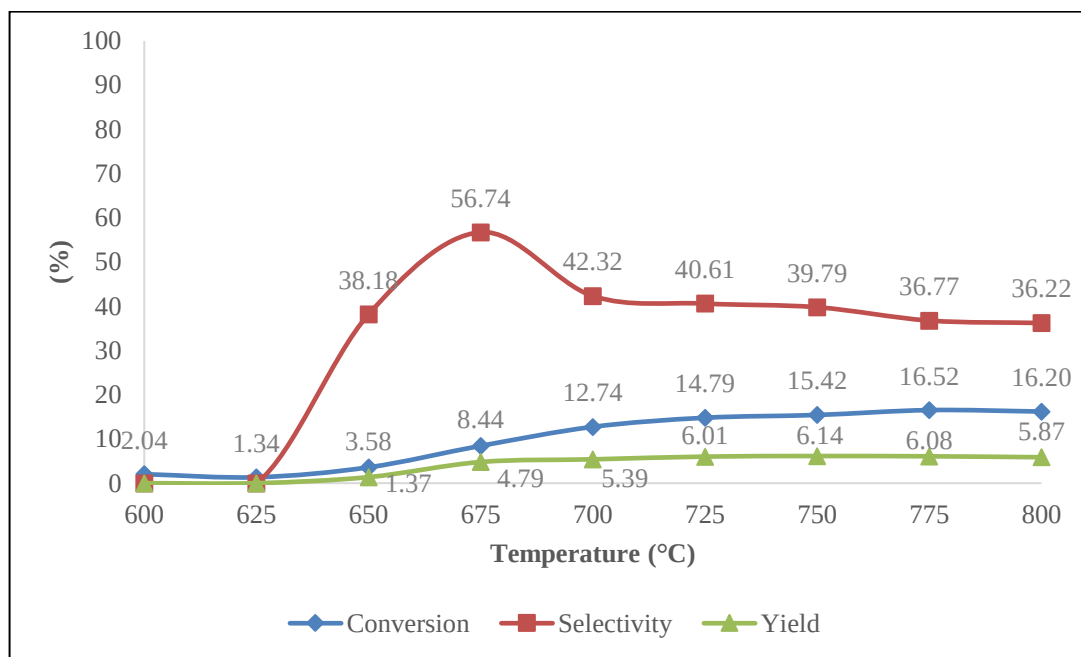


Figure 4.21. Influence of the temperature over the monolithic foam filter catalyst when CH₄/O₂=5.

4.3.3. Effect of Temperature on Granule Alumina Foam Wash Coated by Colloidal Silica

Besides the monolithic structured foam, the granulated ceramic foam was also coated with colloidal silica and tested for catalytic activity to observe the effect of catalyst particle size and pore volume. The experiment was carried out between 600-800°C and gas composition was adjusted as the previous experiments. Results of the performance test are given in Figure 4.22. There was almost no reaction at the temperatures under the 700°C. Selectivity and C₂ yield were zero and conversion were approximately zero at these low temperatures. As different from all other experiments, selectivity was increased with the

temperature above 700°C continuously and reached the maximum value at 800°C. The yield also behaved like selectivity however its maximum value was also low.

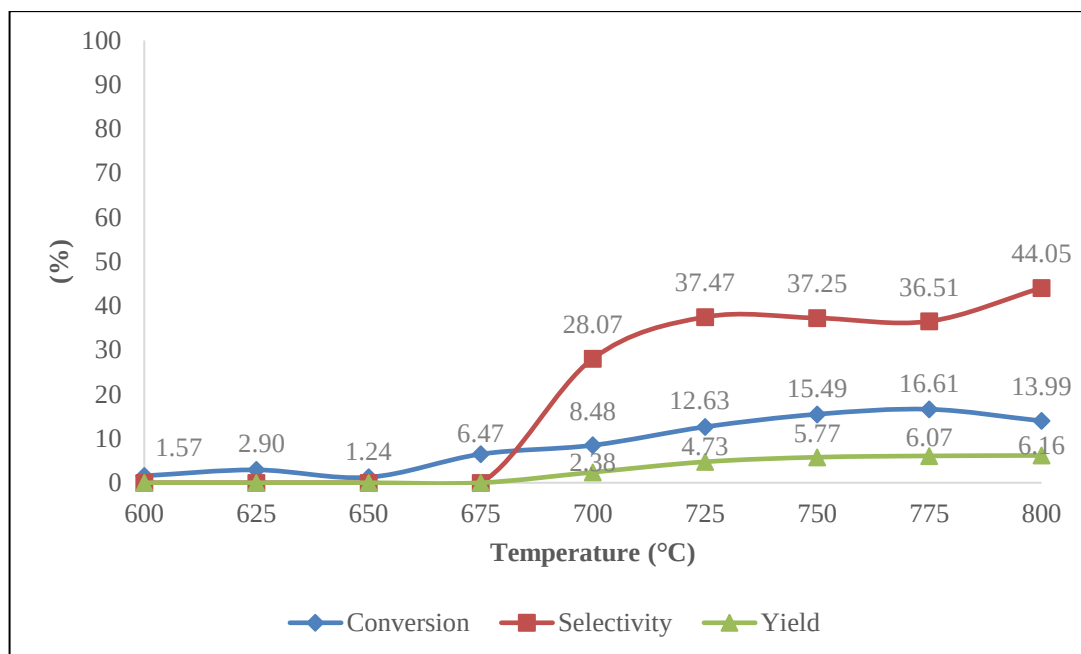


Figure 4.22. Influence of the temperature over the particulate foam filter catalyst when $\text{CH}_4/\text{O}_2=5$.

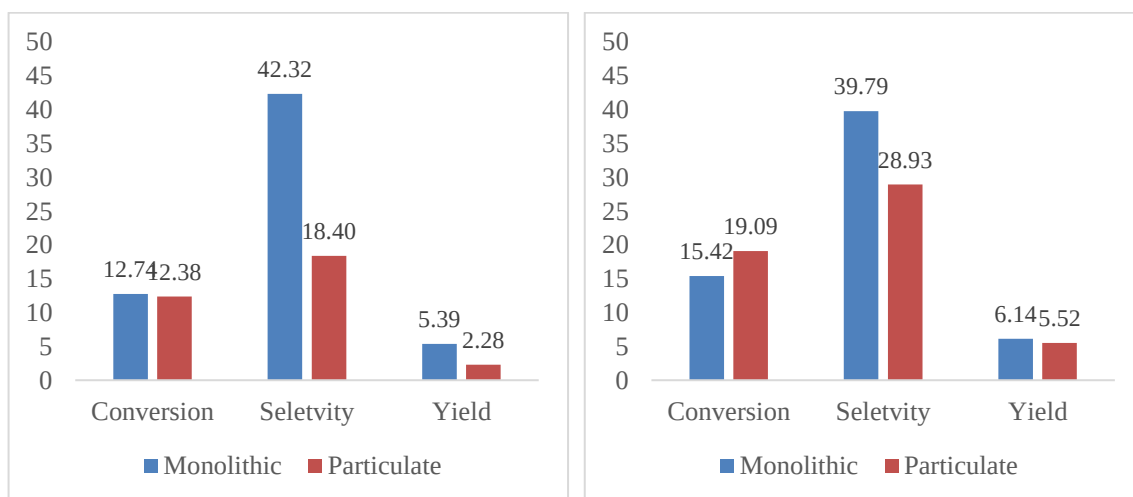


Figure 4.23. Comparison of the monolithic and particulate foam filter catalyst when $\text{CH}_4/\text{O}_2=5$, a) at 700°C, b) at 750°C

Comparison of the conversion, selectivity and yield of both foam filter catalysts is shown in Figure 4.23; none of them seems to be suitable for this reaction, and the performance is almost the same as the blank test performed with the empty reactor (Section 4.4).

4.4. Blank Test without Using Catalyst

To determine the effect of the catalyst on the performance of OCM reaction the blank test was also performed. For this experiment, the catalyst was replaced with quartz chips and by this way, the true performance of the oxidative coupling of methane reaction was also examined. These two tests indicate that the results obtained with the electricity induced sol-gel samples and samples prepared using alumina foams are not really due to the catalytic material but due to the reactions in the gas phase or reactor surface.

Figure 4.24 shows the catalytic performance of the OCM reaction between 600-800°C.

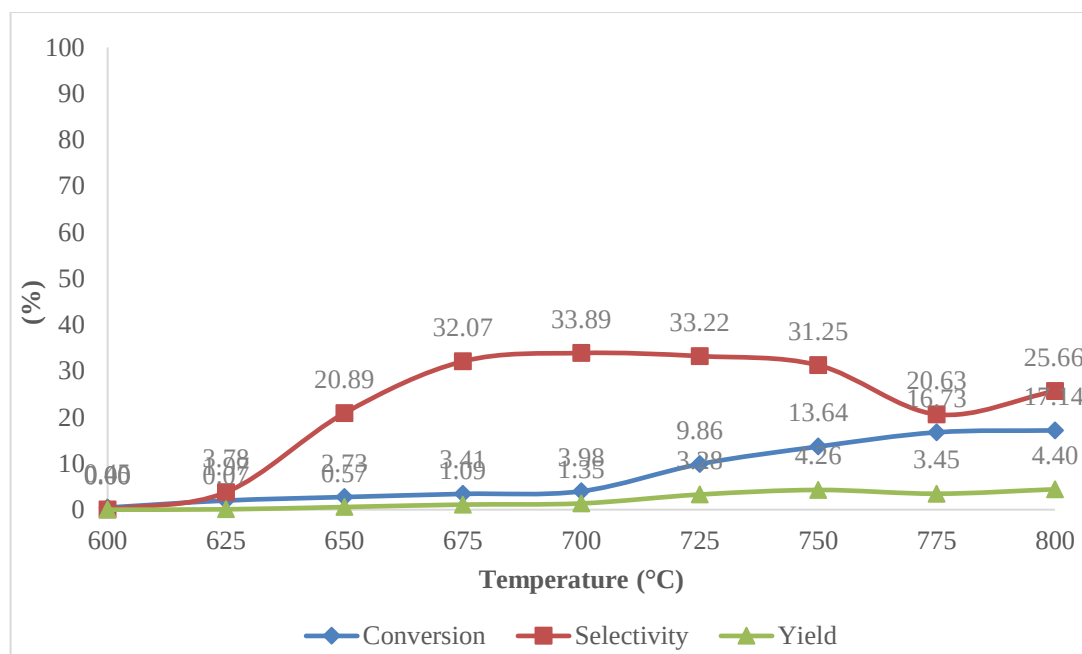


Figure 4.24. Catalytic Performance of the OCM reaction with quartz chips when $\text{CH}_4/\text{O}_2=5$.

Also, to observe the effect of quartz chips, the blank test was repeated without using quartz chips. For this experiment blank reactor was used and the results are given in Figure 4.25. According to Figure 4.24 and 4.25, it can be said that using quartz chips increase the C_2 selectivity when it does not affect the CH_4 conversion significantly.

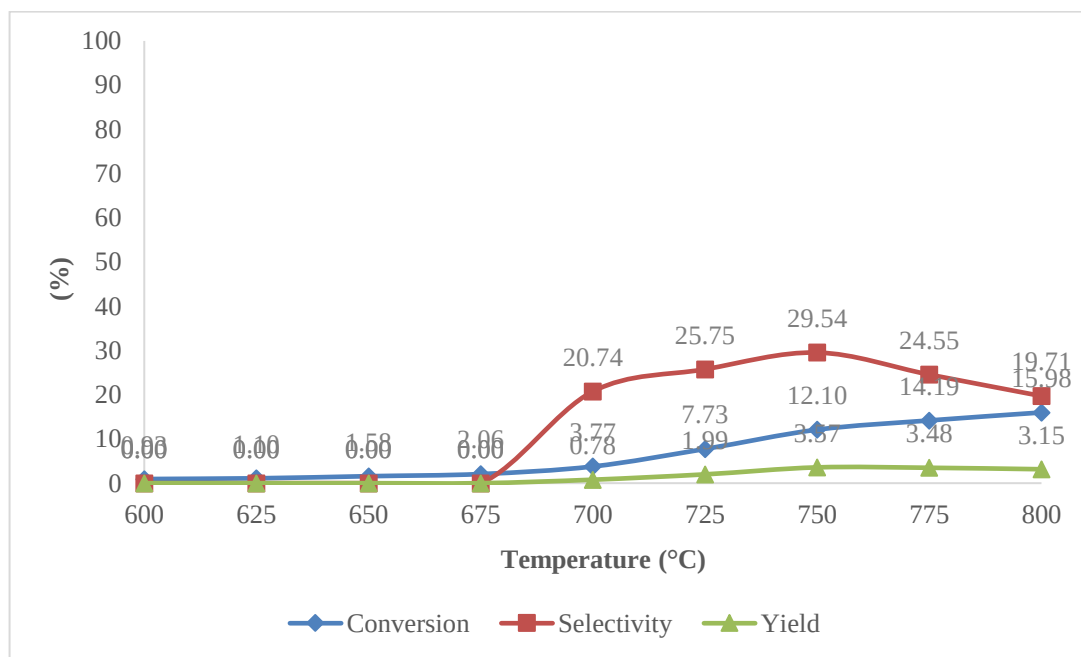


Figure 4.25. Catalytic Performance of the OCM Reaction without quartz chips when $CH_4/O_2=5$.

5. CONCLUSION

5.1. Conclusion

Major purpose of this thesis is to synthesize and develop alternative catalysts for oxidative coupling of methane reaction. Various preparation methods were tested for improving the performance of 2wt.% Mn and 5wt.% Na₂WO₄ catalyst, and the main conclusions can be listed as follows:

- The highest catalytic activity was obtained when the sol-gel method was used with alkaline precursors.
- When the CH₄/O₂ ratio was 5, the highest yields of triethylamine and triethanolamine containing catalysts were almost the same. However, the maximum yield (15.9%) of the triethylamine containing catalyst was obtained at 675°C while the yield of the Mn/Na₂WO₄/SiO₂ catalysts prepared with triethanolamine was reached to the maximum (15.6%) at 650°C.
- The highest yield (16.6%) was obtained with using the triethanolamine containing catalyst. For this catalyst, the highest conversion, selectivity and yield was obtained at 650°C when the CH₄/O₂ ratio was 4.3.
- Monosil (whole structural rod catalyst) could not be synthesized with these preparation methods. The monosils obtained were not stable; they were crushed after calcination step.
- Supplying DC voltage during the synthesis did not improve the catalytic performance. Also, it did not change the structure of catalyst significantly; it only affected the particle size of the catalyst.
- Wash-coating of the ceramic foam filters showed poor performance for this reaction. The results of this catalyst were very close with the blank test results.
- Experiment with the blank test showed that using quartz chips has a positive effect on OCM performance, especially on the selectivity. Quartz chips prevented products conversion to by-products.

5.2. Recommendations

According to the results of this study, the following points can be considered for future works:

- For sol-gel preparation method under DC voltage, the anodic alumina membranes can be used as a template to obtain nanorod structures.
- Other materials like copolymers (P123, F127) can be added during the preparation for obtaining a more stable monosils.
- Silica foams can be used as a support material.
- The thermocouple was placed outside of the reactor and it might be caused a deviation in the actual temperature. Another thermocouple can be used in the catalyst bed to observe regulated temperature accurately.
- Gas-phase reactions are not desired for this process, so they can be prevented by minimizing the reactor length.

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