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Faculté de Génie
Département de Génie Chimique

REFORMAGE DE L’ETHANOL AU DIOXYDE DE CARBONE

Mémoire de maîtrise en sciences appliquées
Spécialité : génie chimique

Sepideh JANKHAH

Sherbrooke (Québec), Canada

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SOMMAIRE

La réaction catalytique de l'éthanol avec du CO₂, définie comme le reformage à sec de l'éthanol, est un moyen pour produire du gaz de synthèse (Syngas), un mélange d'H₂ et de CO, et séquestrer simultanément un gaz à effet de serre comme le CO₂ sous forme de nano-filaments de carbone. Cette réaction est favorisée à des températures élevées sur des surfaces catalytiques. L'importante consommation énergétique de cette réaction et la désactivation du catalyseur sont les raisons principales de l'absence d'applications industrielles pour ce type de réaction. Un des défis est, donc, de trouver une formulation catalytique active qui peut séquestrer le CO₂ sous forme de nano-filaments de carbone, un produit avec une valeur ajoutée, sans perdre son activité. La commercialisation des nano-filaments de carbone pourra compenser la totalité ou, du moins, une partie de la consommation énergétique due à l'endothermicité des réactions ainsi que la mise sur le marché de la séquestration du CO₂ pourront aider à l'essor de la technologie proposée.

Ce projet de maîtrise étudie les propriétés catalytiques de l'acier carbone pour la réaction de reformage à sec de l'éthanol. L'objectif spécifique est de mesurer les performances et de comprendre les mécanismes d'action de ce type de catalyseur lors du reformage de l'éthanol au CO₂. L'effet des conditions de prétraitement du catalyseur sur son efficacité ainsi que sur les propriétés des nano-filaments de carbone est étudié. Les essais sont effectués à l'aide d'un réacteur de laboratoire à lit fixe isotherme. Les surfaces catalytiques et le carbone déposé sont analysés par MEB (Microscopie Électronique à Balayage), MET (Microscopie Électronique en Transmission) et DRX (Diffraction des Rayons X) tandis que des analyses CG (Chromatographie de Gaz) permettent d'évaluer l'étendue de la réaction et faire les bilans de matière et d'énergie. Les résultats montrent que :

> l'acier catalyse tant le craquage que le reformage à sec de l'éthanol;
> un prétraitement oxydatif est nécessaire pour activer les propriétés catalytiques;
> un dépôt de carbone sous forme de nano-filaments est obtenu sans perte de l'activité catalytique;
> ces nano-filaments conservent l'activité catalytique via la présence de carbures insérés dans leur structure tubulaire.
ABSTRACT

The catalytic reaction of ethanol with CO₂, defined as the dry reforming of ethanol, is a method to produce synthesis gas (Syngas), a mixture of H₂ and CO, and simultaneously to sequester the greenhouse effect gas CO₂ in the form of carbon nano-filaments. This reaction is favoured at high temperatures on catalytic surfaces. High energy consumption of this reaction and the deactivation of catalyst are the principal reasons of the absence of industrial applications for this type of reaction. One of the challenges is, therefore, to find an active catalytic formulation which can sequester CO₂ in the form of carbon nano-filaments, a valuable product, without losing its activity. The marketing of the carbon nano-filaments should be able to compensate for the cost of the energy consumption, due to the endothermicity of the reactions. This master project studies the catalytic properties of the carbon steel for the reaction of dry reforming of ethanol. The specific objective is to investigate the performance of carbon steel as the catalyst and to understand the mechanisms of the reforming of ethanol with CO₂ over this catalyst. The effect of the conditions of pretreatment of catalyst on its activity as well as on the properties of the carbon nano-filaments is studied. The tests are carried out using an isothermal fixed bed laboratory reactor. Catalytic surfaces and carbon deposited are analyzed by SEM (Scanning Electron Microscopy), TEM (Transmission Electron Microscopy), and XRD (X ray diffraction) while analyses by GC make it possible to evaluate the extent of the reaction and to make the mass and energy balances.

The results obtained are as follows:

- Carbon steel catalyzes both reactions of ethanol dry reforming and ethanol cracking
- An oxidative pre-treatment is necessary to activate the catalytic properties of carbon steel
- Carbon deposit under the form of carbon nano-filaments was obtained without reducing the catalytic activity of carbon steel
- These nano-filaments preserve the catalytic activity because of the presence of carbides inserted in their tubular structure.
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CHAPTER 1

INTRODUCTION

1.1 Abstract

Hydrogen production is the first step toward the goal of the transition to a hydrogen economy. The goal is to reduce dependence on non-renewable resources and reduce the emission of environmentally harmful gases. Once in its pure form (H₂), hydrogen may be used in fuel cells and hydrogen combustion engines to cleanly release its energy. Several proven technologies such as steam reforming, autothermal reforming, partial oxidation, coal gasification and water gas shift can be used to extract hydrogen from fuels such as gasoline, diesel, LPG, methane, ethanol and methanol [PRIGENT, 1997]. Presently methane steam reforming is the main commercial route for H₂ production. Nevertheless, several research groups have also studied alcohol reforming (more specifically methanol [AUPRETRE, et al., 2004; DE WILD, 2000] and ethanol due to their availability and their low cost comparing to other molecules of this organic family).

Alcohol reforming is of a great interest since both ethanol and methanol can be produced renewably from several biomass sources, such as energy plants, waste materials from agro-industries or forestry residuals, or organic materials of municipal solid waste. Thus, alcohol reforming can be a particularly attractive energy and hydrogen source for countries that lack fossil fuel resources, but have developed agricultural industry.

Furthermore, alcohol reforming proceeds at temperatures in the range of 300-600°C, which is significantly lower than temperatures required for CH₄ or gasoline reforming, about 700°C [GARCIA, et al., 2000; HAGA, et al.; 1997, HAGA, et al.; 1998]. Unlike other hydrocarbons, alcohols are also free of sulfur, which is considered as a catalyst poison in the reforming of hydrocarbons [CAVALLARO, et al., 1996]. Ethanol has been preferred to methanol since its industrial production is a well-known and well established process, and it is safe to handle, transport and store [CAVALLARO, et al., 1996]. It is also significantly less toxic than methanol [KLOUZ, et al., 2002], and provides less risk to the public health. The application of ethanol for the production and use of H₂ energy is
CO₂ free [FATSIKOSTAS, et al., 2002], it is a renewable and CO₂-neutral energy source that can be obtained from fermentation of biomass [MIELENZ, 2001].

In addition, Maggie et al. [MAGGIO, et al., 1998] proved theoretically that the use of the ethanol as the feedstock in fuel cells is preferred to methanol and methane since ethanol has a higher power density for any inlet flow rate, and higher electromotive force at each current density. They also showed that ethanol can be considered as a good fuel for solid oxide fuel cells.

Besides, ethanol is believed to be a clean carbon source in the production of carbon nano-tubes that does not produce amorphous carbon upon its dissociation and decomposition [ZHENG, et al., 2004]. Maruyama et al. [MARUYAMA, et al., 2002] reported the synthesis of very clean single-wall carbon nano-tubes using ethanol as the carbon source. They attributed the production and growth of clean single wall CNTs to OH⁻ radicals of ethanol, which are believed to be responsible for etching away the amorphous graphitic deposits formed during the reforming reactions of ethanol. All these considerations render ethanol economically and environmentally an attractive energy source for the production of hydrogen.

However, as it was mentioned, the first step in the process of producing hydrogen fuel is the production of pure hydrogen. The energy required for this reaction is either stored within the fuel used as the feed to the system or comes from an external energy supply. Fuels like methane, coal, and biomass will produce carbon monoxide or carbon dioxide as by-products of the hydrogen production since they are all carbon-based fuels. Carbon dioxide is a greenhouse effect gas and due to its effect on the global warming its sequestration is a significant concern for many of the hydrogen production technologies. Therefore, the reforming of ethanol with CO₂ as the oxidant (Ethanol Dry Reforming) would be an interesting approach to convert the greenhouse effect gas (CO₂) in to inert carbon via reforming reactions, and hence remove it from the carbon biosphere cycle. However, it is just recently that few research groups have been studying the dry reforming of ethanol. Tsiakaras et al. [TSIAKARAS, et al., 2001] studied the thermodynamics of ethanol dry reforming, but they did not compare their results to any experimental work. De Oliveira-Vigier et al. [DE OLIVEIRA-VIGIER, et al., 2005] and Abatzoglou et al. [ABATZOGLOU, et al., 2006a] showed that iron alloy is a promising catalyst for ethanol dry reforming.
1.2 Problematic

The catalytic reaction of ethanol with CO$_2$ which produces hydrogen and CO is defined as the ethanol dry reforming (CO$_2$ reforming). This reaction is endothermic and takes place at high temperatures (higher than 500°C) on catalytic surfaces. Using catalysts for reforming reactions allows us to carry out this reaction at higher reaction rates and consequently to decrease the operating requirements, e.g. high rates of heat losses, materials resistant at high temperatures, as well as the rapid corrosion of material. However, the deactivation of the catalyst by carbon production during the reaction is the main reason for the absence of a commercial catalyst for ethanol dry reforming. Therefore, an issue of major importance is to develop a highly active and durable catalyst which is highly selective toward hydrogen production.

Recently, De Oliveira-Vigier et al. [DE OLIVEIRA-VIGIER, et al., 2005] and Abatzoglou et al. [ABATZOGLOU, et al., 2006a] revealed that a low carbon iron alloy (stainless steel) is a highly active and stable catalyst for ethanol dry reforming. This is due to the 2-dimensional structure of the catalyst which permits mechanical removal of the carbon deposits without decreasing the activity of the catalyst. This catalyst is also capable of sequestration of CO$_2$ under the form of carbon nano-filaments. The latter can be a potential valuable by-product. Nevertheless, the mechanisms of this catalytic reaction of this catalyst are still not fully known. Therefore, the main objective of this project would be to carry out a comprehensive study of the catalytic reforming of ethanol with CO$_2$. The performance, activity and stability, of a low carbon iron alloy (Carbon Steel, 0.1%) as the catalyst of ethanol dry reforming were studied under different operating conditions.

The choice of carbon steel as the catalyst was primarily based on the results of De Oliveira-Vigier's [DE OLIVEIRA-VIGIER, et al., 2005] and Abatzoglou et al. [ ABATZOGLOU, et al., 2006a] experiments and also on the literature review findings that, as illustrated in the following reactions, the carbon deposited through ethanol reforming is, at least partially, produced from the Boudouard reaction. Therefore the catalyst should be active for the Boudouard reaction, but meanwhile it should be able to initiate the formation of CO, therefore
iron and iron alloys are good candidates [FATSIKOSTAS, et al., 2002, TSIAKARAS, et al.,
2001]:

\[ 2\text{CO} \leftrightarrow \text{CO}_2 + \text{C} \quad \text{(Boudouard)} \]

\[ \text{CH}_4 \leftrightarrow \text{C} + 2 \text{H}_2 \]

\[ \text{CO} + \text{H}_2 \leftrightarrow \text{H}_2\text{O} + \text{C} \quad \text{(WGS)} \]

In addition, Auprêtre et al. [AUPRETRE, et al., 2002] reported the use of Fe/γ-Al₂O₃ for
ethanol steam reforming and showed that Fe/γ-Al₂O₃ has a lower activity for ethanol steam
reforming compared to Rh/γ-Al₂O₃ and Ni/γ-Al₂O₃. Chen et al. [CHEN, et al., 2003] have
also reported that stainless steel can efficiently form carbon filaments of 10μm average
diameter at high temperatures from hydrocarbons pyrolysis. Furthermore, iron alloys are
interesting catalysts as their costs are low and can be easily regenerated (activated) by
removing the carbon deposit mechanically, if carbon is deposited on its surface as nano-
filaments or nano-tubes of carbon [DE OLIVEIRA-VIGIER, et al., 2005].

This work studies the catalytic reforming of ethanol with CO₂ through the following global
reaction:

\[ \text{CH}_2\text{CH}_2\text{OH} + \text{CO}_2 \leftrightarrow 2\text{H}_2 + 2\text{CO} + \text{C} + \text{H}_2\text{O} \]

In addition to the catalytic properties of carbon steel, physical and chemical properties of the
carbon nano-filaments deposited through the reforming reaction are also measured in order to
estimate the value of the carbon deposit by-product.

### 1.3 Objectives of the project

The objective of this project was to carry out a comprehensive study of catalytic reforming of
ethanol with CO₂ (ethanol dry reforming) in presence of steel as catalyst. Carbon steel (0.1%
w/w C) was proposed as a promising active and stable catalyst for ethanol dry reforming and
CO₂ sequestration under the form of carbon nano-filaments. The aim was to maximize the
ethanol and CO₂ conversions and the hydrogen selectivity; along with following the properties
of the produced carbon nano-filaments in all experiments. The performance of the carbon steel
catalyst was studied for different variables such as different pre-treatment conditions of the
catalyst, ethanol/CO₂ ratio, reaction temperatures, and catalyst weight.
The catalyst was characterized by Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) analyses in each stage of the reaction in order to obtain comprehensive understandings of the catalyst's transformation along the reaction and also the mechanism of the reaction. The properties of the nano-filaments of carbon deposited were studied by SEM, XRD, BET surface area, Transmission electron microscopy (TEM) and X-Ray Photoelectron Spectroscopy (XPS) analyses.
CHAPTER 2

REFORMING OF ETHANOL WITH CO₂

As mentioned earlier, only few references exist on reforming of ethanol with CO₂. Therefore, since thermodynamics, catalytic mechanisms, and reaction configuration of the catalytic reaction are similar for steam and dry reforming of ethanol, this project started with a comprehensive literature review of steam reforming of ethanol.

2.1 Chemical reactions

The thermodynamic equilibrium gas mixture obtained from the reaction of ethanol with oxidants may contain carbon monoxide, carbon dioxide, hydrogen, steam and methane. Therefore, “the full transformation of the initial ethanol–oxidant system into the equilibrium mixture can be expressed as follows

\[ \text{Ethanol} + \text{Ox} \rightarrow n_{\text{CO}} \text{CO} + n_{\text{CO₂}} \text{CO₂} + n_{\text{H₂}} \text{H₂} + n_{\text{H₂O}} \text{H₂O} + n_{\text{CH₄}} \text{CH₄} \]

Ox represents anyone of possible oxidants or their mixture” [TSIARAKAS, et al., 2001].

The mostly used oxidants for ethanol oxidation by now are steam, carbon dioxide and oxygen summarized as :

“A: ethanol + r₁H₂O
B: ethanol + r₂CO₂
C: ethanol + r₃O₂” [TSIARAKAS, et al., 2001]

Ethanol dry reforming is a complex reaction where many reactions are taking place. The main reaction mechanisms involve dehydration or dehydrogenation reactions. Dehydrogenation reactions produce intermediate products such as acetaldehyde which will be transformed to methane. Methane will react with CO₂ and produce H₂ and CO. Dehydration reactions produce intermediate products such as ethylene, which can be transformed into carbon by dehydrogenation; the latter is either producing catalyst poisoning through the deposition of amorphous or graphitic carbon on the catalyst or dissolves in the metal (here Fe) to produce
carbides which are considered as the initiators of the carbon nano-filaments [ERMAKOVA, et al., 2001/7/25].

The chemical reactions taking place during the catalytic reforming are various: dehydrogenation, dehydratation, and isomerisation. However the two most important reactions are the breaking of the C-C bonds and the dehydrogenation, which produce carbon and hydrogen. These reactions are endothermic and, consequently, they are favored at high temperatures.

The reactions taking place during the reforming of ethanol with CO₂ [BENITO, et al., 2005], can be summarized as follows:

\[ \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2 \]
\[ \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \]
\[ \text{CH}_3\text{CHO} \leftrightarrow \text{CO} + \text{CH}_4 \]
\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \]
\[ \text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \]
\[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \]
\[ 2\text{CO} \leftrightarrow \text{CO}_2 + \text{C} \]
\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \]
\[ 2\text{CH}_3\text{CH}_2\text{OH} \leftrightarrow \text{CH}_3\text{COCH}_3 + \text{CO} + 3\text{H}_2 \]
\[ \text{C}_2\text{H}_4 \leftrightarrow 2\text{C} + 2\text{H}_2 \]
\[ \text{CH}_4 \leftrightarrow \text{C} + 2\text{H}_2 \]

### 2.2 Thermodynamic analysis

Yields of H₂, CO, CO₂, CH₄ and carbon, Gibbs free energy(ΔG), and Enthalpy (ΔH) for the global equilibrium reaction of \( \text{CH}_3\text{CH}_2\text{OH} + \text{CO}_2 \leftrightarrow 2\text{H}_2 + 2\text{CO} + \text{C} + \text{H}_2\text{O} \) were calculated in a temperature range between 250°C and 850°C by FactSage software. These calculations were repeated for different ratios of Oxidant (CO₂)/Ethanol. The results are graphically summarized in this section and a brief analysis is presented. The theoretical calculations at equilibrium are also compared to this project’s experimental results in section 2.2.3.

7
2.2.1 The effect of Temperature

Yields of H$_2$, CO, CO$_2$, CH$_4$ and carbon were calculated for the global reaction at equilibrium in a temperature range of 250-850°C and for the CO$_2$/Ethanol ratios of: 0, 1/3, 1/2, 1, 2, and 3. Based on the results of the equilibrium calculations graphed in Figure 2.1, H$_2$ yield will increase at high temperatures.

![Figure 2.1 The effect of temperature and CO$_2$/ethanol ratio on hydrogen yield at equilibrium](image)

Carbon's yield at equilibrium is presented in Figure 2.2. It is seen that for oxidant/ethanol mole ratios of 1, 2/1 and 3/1, carbon formation is thermodynamically impossible for temperatures higher than 900, 750 and 700°C respectively. Our results are in a complete agreement with Tsiakaras's observations; Tsiakaras studied the SOFC being fed with the thermodynamic equilibrium products of ethanol reforming with CO$_2$. Equilibrium calculations were performed in the temperature range between 800 and 1200 K (528-927°C) [TSIAKARAS, et al., 2001]. They determined regions where carbon formation is thermodynamically impossible, assuming different oxidant/ethanol ratios. They showed (Figure 2.3) that the oxidant/ethanol mole ratio, at which carbon formation in the equilibrium mixture is thermodynamically impossible, is greater than 4 for the temperatures below 500°C.
As it is seen in Figure 2.4, methane selectivity at equilibrium conditions is decreased by increasing the temperature. This fact was observed by Sun et al. [SUN, et al., 2004] in practice; they showed that the reason for the lower selectivity of methane at higher temperatures is that the rates of steam and CO$_2$ reforming of methane become significant at higher temperatures. Higher rates of methane dry reforming will result in a decrease in the CO$_2$ yield for temperatures higher than 650°C; this is in agreement with CO$_2$ yields calculated at equilibrium for this temperature range as shown in Figure 2.5. According to our
calculations, the highest CO$_2$ yield is expected at 550°C. This can be explained by the fact that
the Boudouard reaction toward the production of carbon and CO$_2$ is favored at the temperature
range of 500-550°C.

![Figure 2.4 The effect of temperature and CO$_2$/ethanol ratio on methane yield at equilibrium](image1)

![Figure 2.5 The effect of temperature and CO$_2$/ethanol ratio on CO$_2$ yield at equilibrium](image2)

As it is shown in Figure 2.6, CO yield increases significantly at temperatures higher than
600°C. This is due to the exothermic nature of the WGS reaction: WGS is thermodynamically
favored at low temperatures, therefore for the higher temperatures the contribution of the
reaction of WGS is less and the result would be a reduction in the CO yield.
2.2.2 Effect of Oxidant (CO$_2$)/Ethanol Ratio

The ratio of Delta Gibbs free energy/mole of ethanol was calculated for the global reaction at equilibrium in a temperature range of 250-850°C and for the CO$_2$/Ethanol ratios of: 0, 1/3, 1/2, 1, 2, and 3 (Figure 2.7). It is observed at temperatures less than 250°C $\Delta G$ is very small and therefore the reforming reaction is thermodynamically impossible. The increase of $\Delta G$ with temperature illustrates that equilibrium will be attained faster at higher temperatures. It is also seen that $\Delta G$ is increased at higher ratio of CO$_2$/ethanol, therefore it is expected that equilibrium will be favored at higher ratios of CO$_2$/ethanol.
Figure 2.7 Effect of temperature and CO₂/ethanol ratio on ΔG of the reaction at equilibrium

The ratio of ΔH of the reaction / mole of ethanol was calculated for the same temperature range and CO₂/ethanol ratios (Figure 2.8). Based on the thermodynamic calculations it is expected to have higher energy requirements at higher temperature. This is explained by the endothermic nature of the global reaction: at higher temperatures the equilibrium is more favored toward the products and consequently more energy is required to attain the equilibrium.
2.2.3 Equilibrium calculations for experimental parameters of this project

2.2.3.1 Ratio

Yields of H₂, CO₂, CO, C, CH₄, and H₂O were calculated at equilibrium at 550°C and for CO₂/ethanol ratios of 1 and 1/3. (Figure 2.9 and 2.10). Based on the thermodynamic calculations at equilibrium it is expected to have almost the same yield for H₂ (Figure 2.9) but higher yields of CO₂ and CH₄ (Figure 2.10 b) for the CO₂/ethanol ratio of 1/3. Therefore it will be more preferable to choose a ratio of 1 for CO₂/ethanol in order to minimize the formation of CO₂ and CH₄, yet at the ratio of 1, a lower yield of carbon is expected. In Section 5.2.2 the experimental results will be compared with the equilibrium calculations.
2.2.3.2 Temperature

In Figure 2.11 yields of H₂, CO₂, CO, C, CH₄, and H₂O calculated at equilibrium are shown. The ratio of CO₂/ethanol of 1 was chosen based on the results of Section 2.2.3.1. It is observed that for temperatures above 550°C the volumes of H₂ and CO increase, while the volume of methane decreases. According to this graph it is also observed that at 550°C we have the highest volume of CO₂ at equilibrium. Up to 550°C the quantity of the carbon deposit decreases slightly with increasing temperature, however above 550°C it decreases much faster and at about 850 °C carbon deposition is thermodynamically impossible. The effect of temperature was investigated and the experimental results will be compared in Section 5.6 with the theoretical equilibrium calculations.
2.2.3.3 Reforming/cracking

Yields of H₂, CO₂, CO, C, CH₄, and H₂O at equilibrium were calculated for ethanol reforming (CO₂/ethanol ratio of 1 and at 550°C) and ethanol cracking at 550°C (Figure 2.12, 2.13). Equilibrium calculations shows higher yields of H₂, CH₄ and C for ethanol cracking compared to ethanol reforming, which is in a complete agreement with the experimental results obtained in this project (Section 5.4).

Figure 2.12 Gas product yields mole/mole H₂ at equilibrium for cracking and reforming of ethanol
Figure 2.13 Gas product yields \( \text{mole/mole C} \) at equilibrium for cracking and reforming of ethanol

2.2.4 Two stage reactor

Equilibrium calculations illustrated in Section 2.2.3.2 for a CO\(_2\)/ethanol ratio of 1 proves that the yield of H\(_2\) and CO increase at higher temperatures however the yield of carbon decreases significantly for temperatures higher than 600°C. As mentioned in Section 1.3 one of the objectives of this project is the production of carbon in the form of carbon nano-filaments as a valuable product of ethanol dry reforming. Therefore temperatures higher than 500°C will not be favorable, since the yield of carbon decrease significantly at these temperatures. However, at low temperatures, the yield of hydrogen and CO are low as well as the conversion of CO\(_2\). Consequently, a simulation was performed on a two stage reactor design. The ethanol dry reforming with a CO\(_2\)/ethanol ratio of 1 will take place in a first reactor using carbon steel as the catalyst and at low temperatures around 550°C. The produced gas mixture will contain high volumes of CH\(_4\), CO\(_2\), CO and also a small volume of H\(_2\)O. This mixture will be introduced to a second reactor containing a catalyst appropriate for methane dry reforming and the reaction will take place at temperatures higher than 550°C. The thermodynamic calculations were performed using the concentration of the gas mixtures produced from dry reforming of ethanol for three temperatures of 500, 550, and 600°C at equilibrium as the feed for the second reactor. For each of these three gas mixtures the thermodynamic calculations at
equilibrium was performed between 500-900°C. The results are presented in Figure 2.14. It can be seen that the maximum yield of H₂ is obtained at 650°C in the second reactor and the gas mixture obtained at 600°C in the first reactor.

Figure 2.14 H₂ yield at equilibrium for the two stage reactor

However, as it is shown in Figure 2.15 a and b, the yield of CO₂ is also high at this temperature, but it decreases at higher temperatures.

Figure 2.15 CO₂ yield at equilibrium for the two stage reactor

ΔG of the reaction is calculated and shown in Figure 2.16. It is seen that ΔG for the gas mixture obtained from ethanol dry reforming at 600°C is positive for temperatures lower than 600°C, proving that for these conditions the reaction in the second reactor is thermodynamically impossible. The gas mixture produced from ethanol dry reforming at
550°C has the largest G for all the temperatures studied, therefore it is expected that this mixture reach equilibrium faster than the other two mixtures.

Figure 2.16 ΔG at equilibrium for the two stage reactor
CHAPTER 3

LITERATURE REVIEW

3.1 Literature on steam and dry reforming relative to this work

Steam reforming of ethanol has been studied by several research groups so far. It was shown that hydrogen can be obtained by steam reforming of ethanol at atmospheric pressure and at temperatures above 280°C [GARCIA, et al., 1991]. Vasudeva et al. performed thermodynamic studies and showed that under the considered operating conditions ethanol was converted completely [VASUDEVA, et al., 1996]. They reported the presence of traces of acetaldehyde and ethylene at equilibrium mixture.

Ethanol steam reforming at temperature range of 600°C to 700°C, pressure 1 atmosphere was investigated by Freni et al. [FRENI, et al., 1996]. They observed that the amount of hydrogen produced by the ethanol reforming was increased as temperature was increased. It was also shown that hydrogen, carbon monoxide, methane, acetaldehyde, ethylene and carbon were the thermodynamically favoured products.

Liguras et al. [LIGURAS, et al., 2003] compared the catalytic performance of supported noble metals for the steam reforming of ethanol in the temperature range of 600-850°C at an R&D level. They revealed that Rh is significantly more active and selective toward hydrogen production compared to Ru, Pt, and Pd. They also showed that, at these operating conditions and for a low-loaded catalyst the activity of Pd, Pt and Ru for ethanol steam reforming are comparable to the activity of γ-Al₂O₃, however, all these metals show a higher CO₂ selectivity than γ-Al₂O₃. Nevertheless, the high price of the Rh, represent a considerable handicap for the commercialization of this process. Considering that Rh is a rare metal and expensive, higher metal loads of Ru has been selected as an alternative for the reaction of ethanol reforming because of its lower prices [LIGURAS, et al., 2003].

Aboudheir et al. [ABOUDHEIR, et al., 2006] studied the steam reforming of crude ethanol using Ni/Al₂O₃ as the catalyst. They showed that Al₂O₃-supported Ni catalyst initiates the
formation of ethylene, which will be transformed into CO, CO₂ and H₂ through the reforming reactions at temperatures higher than 550°C. This catalyst also produces significant quantities of methane at higher temperatures.

Co is also considered as a catalyst for steam reforming of ethanol; however it is deactivated due to coke formation, its sintering and its surface oxidation [CAVALLARO, et al., 2001]. Rostrup-Nielsen et al. [ROSTRUP-NIELSEN, et al., 1977] proved that the Co based catalyst, is strongly influenced by the substrates effect, i.e. Al₂O₃ support causes the ethanol dehydration to ethylene. Ethylene is transformed to carbon deposits and this results a fast deactivation of the catalyst. They also showed that a more selective and stable Co-based catalyst can be obtained by using basic supports like MgO.

Deactivation of the catalyst by carbon deposits through the reforming reactions was observed in all the studies. Many attempts have been made to decrease the amount of carbon deposit and to develop more stable catalysts (with longer life times). An approach to decrease carbon deposit formation on the catalyst is the addition of other metals. This would be due to change of the surface reactions through the presence of other metals, yet, it is unknown whether the reduction of carbon formation is due to the change occurred in the crystallite size distribution, or it is due to the formation of alloys that hinder the dissolution and diffusion of carbon in the metal [TRIMM, 1997].

Bartholomew et al. [BARTHOLOMEW, et al., 1980] proved that cobalt-promoted Ni/Al₂O₃ is significantly more resistant (longer life time) to deactivation caused by carbon formation than nickel. It has been reported in several researched that the presence of magnesium considerably changes Ni/Al₂O₃ catalytic properties [RUCKENSTEIN, et al., 1997, WANG, et al., 1998a]. In the case of Ni-Cu, Cu favors the WGS reaction; however the formation of the carbon deposits still deactivated this catalyst [FIERRO, et al., 2002]. Garcia et al. [GARCIA, et al., 2000] compared the activity of two catalysts, Ni/MgO-Al₂O₃ and Ni/MgO-La₂O₃-Al₂O₃ doped with cobalt or chromium to the commercial steam reforming catalysts. They observed that cobalt-promoted nickel and chromium-promoted nickel supported on MgO-La₂O₃-Al₂O₃ catalysts showed the highest activity and performance.
De Oliveira-Vigier et al. [DE OLIVEIRA-VIGIER, et al., 2005] showed that although the carbon formation causes serious problems deactivating the catalyst, it can also be used to sequester carbon dioxide if the carbon deposits can be removed from the surface of the catalyst without harming its reactivity. They used a low carbon iron alloy (stainless steel), a catalyst with a surface such that the carbon formed can be removed easily while the activity of the catalyst is still maintained. They also proved that the carbon deposits in the form of carbon nano-filaments. The latter is potentially a valuable by-product; if its value is high enough, its economic utilization could help in compensating the higher energetic costs of the process. The choice of Stainless Steels (SS316) as the catalyst is based on the literature findings that Fe alloys are active catalysts for CO disproportionation through the Boudouard reaction [CHEN, et al., 2003] and ethanol steam reforming [AUPRETRE, et al., 2002].

3.2 The effect of support

The type of support used in the reforming reactions has a major role in the amount of carbon deposits formed on the surface of the catalyst. The quantity of carbon deposits during ethanol reforming can be decreased by neutralizing the acid sites of Al₂O₃ support; i.e. by adding potassium or by using basic supports such as La₂O₃ or MgO [RUCKENSTEIN, et al., 1997]. Nevertheless, Cavallero et al. [CAVALLARO, et al., 2001] showed that the activity of Rh catalysts for the formation of carbon is independent of the type of the support (Al₂O₃ or MgO). Co, a less than Rh active catalyst, is more selective and more stable when supported on MgO than on Al₂O₃ [LLORCA, et al., 2003]. Ni/La₂O₃ shows high activity and a very good stability for the dry reforming of methane as well as for the steam reforming of ethanol. “High stability of La₂O₃ is due to the oxidation of the carbon deposited on the Ni particles by lanthanum oxi-carbonate which is present on the Ni particles during the reaction”[AUPRETRE, et al., 2001]:

\[ \text{La}_2\text{O}_3 + \text{CO}_2 \leftrightarrow \text{La}_2\text{O}_2\text{CO}_3 \]

\[ \text{La}_2\text{O}_2\text{CO}_3 + \text{C} \rightarrow \text{La}_2\text{O}_3 + 2\text{CO} \]

Ethylene is not detected in the case of Ni/La₂O₃ catalysts, since Ni/La₂O₃ does not possess acid functions capable of ethanol dehydration to ethylene at significant extent; nevertheless,
the dehydrogenation of ethanol is still possible. The latter produces intermediate species such as acetaldehyde which subsequently decomposes to CO and CH₄.

The selectivity of the supported catalysts containing Ni and Co for H₂ follows the order: La₂O₃>YSZ>Al₂O₃>MgO [LLORCA, et al., 2002]. For dry reforming of methane, Al₂O₃, La₂O₃ and MgO are used as catalytic supports [HAGA, et al., 1997].

3.3 The effect of the alkaline metals

The results of the experiments as reported by Frusteri et al.[FRUSTERI, et al, 2004] show that the addition of alkaline metals to catalysts during the reactions of the reforming of ethanol with CO₂ and the steam reforming of methane can affect the stability of catalyst.

The effect of potassium on the reactions of ethanol reforming using Ni as the catalyst is described as follows:

1. It increases the diameter of the Ni particles
2. It gives narrower distribution of the Ni particles diameters
3. It increases the TOF (Turnover frequency) of ethanol on catalyst of Ni/MgO by transferring the electron of alkaline oxide to Ni, which enhance the force of bond C-Ni and weakens the C-O bonds. The result is then the easy dissociation of CO.
4. It stabilizes Ni catalyst by preventing the sintering of metal during reforming
5. Decreases specific surface and the coefficient of adsorption
6. It increases the conversion of the X_{EtOH} ethanol

It was shown that alkaline metals could introduce an electronic enrichment of the active catalytic phase, by increasing the surface concentration of OH⁻, which induces a decrease in the rate of Boudouard reaction as well as the decomposition of hydrocarbons; which are well known as the main cause of coke formation in reforming reactions [FRUSTERI, et al., 2004].

The effect of potassium on the reactions of methane reforming using Ni as the catalyst is described as follows [SNOECK, et al., 2002]:

\[
\begin{align*}
\text{CH}_4 & \leftrightarrow C + 2H_2 & \text{(a)} \\
\text{CO} + 3H_2 & \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} & \text{(b)} \\
\text{CO} + \text{H}_2 & \leftrightarrow C + \text{H}_2\text{O} & \text{(c)} \\
2\text{CO} & \leftrightarrow C + \text{CO}_2 & \text{(d)} 
\end{align*}
\]
1. K decreases the quantity of carbon deposited
2. K does not have an influence on the reactions (a) and (d)
3. K can affect the reaction (c)
4. K increases the quantity of O present on the surface of catalyst. This behavior can be explained by supposing that the sites present for the adsorption of water and the reactions of gasification by water are increased which decreases the carbon formation. Indeed the reduction in carbon deposited is not due to the reduction of carbon filaments occurrence since the speed of the reactions (a) and (d) does not change by the addition of K. The principal cause is the displacement of reaction (c) towards the gasification of the carbon deposited [SNOECK, et al., 2002].

3.4 The precursor choice

The effect of precursor's type on the stability and the activity of transition metals catalysts of steam reforming of ethanol has been studied as well. It was proved that the choice of nitrate, chlorate or carbonate precursors depends on the nature of the catalyst and the support. Liorca et al. [LLORCA, et al., 2003] studied the steam reforming of ethanol on Co/ZnO catalyst. They proved that under the applied conditions, the use of Co₂ (CO)₈ as the precursor leads to a catalyst which is very stable and selective for the formation of a gas richer in H₂ and poorer in CO at low temperatures (about 627K) than that in the case of nitrate precursors.

It has been shown in the literature [WANG, et al., 1998b] that the Ni/Al₂O₃ nitrate-derived catalyst has a higher stability (or low deactivation rate) for ethanol steam reforming than Ni catalysts derived from chlorite solutions. It was observed that carbon deposits mainly under the form of graphitic carbon with a close contact with the metal particles in the nitrate derived catalysts [WANG, et al., 1998b] and therefore it will be removed more easily by the following gasification reactions. In the case of Ni/Al₂O₃, at atmospheric pressure, chlorine-free precursors would be preferred [AUPRETRE, et al., 2002, AUPRETRE, et al., 2005]. This is due to the presence of Cl⁻ which gives acidic properties to the support and consequently favors the dehydration of ethanol into ethylene, which will be followed by carbon formation [AUPRETRE, et al., 2004].
3.5 The stability of the catalyst

If the reactants do not contain halogens or sulfur, the deactivation of the catalyst would be due to either the deposition of carbon or the sintering of the catalyst particles. The extent of sintering of the metal particles depends on porosity and the specific surface of the catalyst. In the case of carbon deposition, the stability of the catalyst is influenced by the type of carbon deposited; formation of amorphous carbon deactivates the catalyst more rapidly, since graphitic carbon is more active than the amorphous carbon and will be gasified rapidly during the reforming reaction [WANG, et al., 1998b]. The localization of the deposit (i.e. if at the surface of the metal particles, it can easily react with CO₂) as well as the quantity of carbon deposited also influence the stability of the catalyst. Moreover, metal load and the calcinations temperature can affect the reducibility of metal oxides [LI, et al., 2000]. However, as widely reported with regard to the hydrogen production by methane reforming, the deactivation mainly occurs through the formation of amorphous carbon encapsulating the active catalytic particles [LI, et al., 2000, LI, et al., 1997, SNOECK, et al., 1997].

3.6 Catalytic mechanism

It was recently proposed that the steam reforming of ethanol takes place according to the following mechanism: “(I) dehydrogenation of ethanol to acetaldehyde; (II) decomposition of the acetaldehyde which produces the CH₄ and CO; (III) steam reforming (SR) of CH₄ and the reaction of water gas shift (WGS)” [CAVALLARO, et al., 2003a].

In this work, the catalytic mechanism of the growth of the carbon nano-filaments was proposed as follows:

- Formation of particles of magnetite through the oxidation step with air
- Reduction of magnetite with hydrogen produced by the dehydration of ethanol
- Transformation of magnetite to cementite (Fe₃C) and Hagg-carbide (Fe₅C₂)
- Reforming of ethanol with CO₂ on the iron carbide particles
- Formation of nano-filaments on the cementite particles

This mechanism is proposed and confirmed through the catalyst characterizations and analyses performed during our ethanol reforming experiments. Nevertheless, this is in good agreement with the mechanisms proposed in the literature for Boudouard reaction and
catalytic reactions of hydrocarbons over iron based catalysts. Few authors have claimed that the active catalyst could be an iron carbide such as Fe₃C [RUSTON, et al., 1969], FeC [OBERLIN, et al., 1976] or Fe₇C₃ [BOEHM, 1973]. Sacco et al. [SACCO, et al., 1984] studied the growth of carbon nano-filaments from a H₂, CH₄, H₂O CO₂ and CO gas mixture using α-Fe as the catalyst. They revealed that cementite (Fe₃C) is a better catalyst for the growth of carbon nano-filaments than α-Fe and that the growth rate of carbon nano-filaments was increased by the formation of the cementite. Oberlin et al. [OBERLIN, et al., 1976] reported the pyrolysis of a mixture of benzene and hydrogen at about 1100°C on an iron based catalyst. They observed that growth of primary carbon fibers was initiated by the presence of very small iron oxide particles that were reduced to pure iron by the presence of hydrogen in the gas mixture, followed by the formation of FeC. Emmenegger et al. [EMMENEGGER, et al., 2003] reported the results of the pyrolysis of acetylene over iron catalysts. They revealed that the iron oxide layer (Fe₂O₃) formed from the initial Fe catalyst, transforms to other forms of iron oxide (magnetite,Fe₃O₄, and wuestite, FeO) by the hydrogen released from the pyrolysis of the acetylene. Iron oxide is finally transformed to iron carbide (Fe₃C), and the growth of carbon nano-filaments starts over the Fe₃C. Chung et al. [CHUNG, et al., 2005] proposed a similar catalytic mechanism for growth of carbon nano-tubes under a CO-H₂ gas mixture over iron oxide catalyst. They revealed that Fe is transformed to Fe₃C and the growth of carbon nano-tubes is initiated on the iron carbide particles. However, the initiation of the growth of the carbon filaments is not entirely understood. A generally admitted mechanism includes (I) the decomposition of hydrocarbons on the surface of the metal particle; (II) the dissolution of the isolated atoms of carbon in the metal and (III) the diffusion of carbon through the faces favorable for the growth of the filaments [BENGAARD, et al., 2002].

Ermakova et al. [ERMAKOVA, et al., 2001] also suggested a mechanism for the formation and growth of carbon nano-filaments over iron particles. According to this model cementite is formed on the surface of the catalyst by decomposition of the reactive gases. Cementite is partially disintegrated to graphitic carbon which covers the catalyst surface. The resulted carbon gradient is the driving force for the further diffusion of carbon into the nearby carbide particle and to start the formation of carbon nano-filaments. Figure 3.1 shows the mechanism
of nucleation of carbon nano-filaments suggested by Ermakova et al. They suggested that graphite layers are deposited in parallel to the catalyst particle surface at the beginning however after a certain time the particle becomes fluid and the orientation of the graphite layers change and the result will be the formation of a hollow structure (Figure 3.1 d–f).

![Diagram](image)

**Figure 3.1 Carbon nano-filaments growth mechanism (Ermakova et al., 2001)**

There are two general modes of growth of the carbon nano-filaments (illustrated in Figure 3.2). If the rate of nucleation is low compared to the rate of diffusion of carbon into the interface of metal and filaments, full carbon nano-filaments are formed (a). Otherwise, when the rate of nucleation is faster than the rate of diffusion of carbon, probably at higher temperatures, hollow filaments are formed (b)[SNOECK, et al., 1997].

![Diagram](image)

**Figure 3.2 Carbon nano-filaments growth models (S noeck, et al. 1997)**
3.7 Reaction configuration

Several types of reactors exist and the form of the catalyst is adapted to that of the reactor. The PFR (Plug Flow Reactor), the CSTR ( Completely Stirred Tank Reactor) and the batch are the three reactor types used. The PFR is a pipe equipped with a catalyst retained by a support. The flow of the reagents is continuous and the concentration of the substances varies along the length. The catalyst can take any form: powder, pellet or a monolith.

The CSTR and the batch are fully homogenized vessels where the concentration of the substances is supposed to be the same everywhere. The fluidized bed is also used which in certain cases (granular/bubbling bed) behave and can be simulated as a CSTR. The flow is continuous in the CSTR while in the batch reactor is discontinuous (transient state).

In the majority of the studies, differential reactors (PFR) have been used. For the catalytic reactions of ethanol with CO₂ or steam as well as the dry reforming or the steam reforming of methane, the experiments were carried out under atmospheric pressure in a quartz fixed bed micro-reactor [CAVALLARO, et al., 2003a, CAVALLARO, et al., 2003b, FIERRO, et al., 2002, IDRISS, et al., 2000, LIGURAS, et al., 2003, MARIÑO, et al., 2003, PEÑA, et al., 1996, SNOECK, et al., 1997, WANG, et al., 1998].
CHAPTER 4

METHODOLOGY

4.1 Catalyst preparation

Our preliminary experiments showed that if stainless steel and carbon steel were preheated to 800°C and kept at this temperature, at least for one hour, carbon nano-filaments with a higher quality and higher conversion of CO₂ was obtained. The phase diagrams for Fe-C alloy containing less than 0.5% of C show that these alloys form a eutectic mixture, made up of structures of α-ferrite and of γ-austenite at temperatures higher than 750°C (Figure 4.1). Up to now the only explanation for this effect is the change of the structure of this alloy during the heating which could make catalyst more active; a higher activity of surface because of a change of conformations is possible. Nevertheless, other studies are necessary to understand the phenomenon and thus to control and optimize the process of reforming [ABATZOGLOU, et al., 2006, DE OLIVEIRA-VIGIER, et al., 2005].

Figure 4.1 Iron-carbon phase diagram (Materials Science and Metallurgy, 4th ed., Pollack, Prentice-Hall, 1988)
A similar phenomenon was observed by Ermakova et al. [ERMAKOVA, et al., 2001]. They proved that the mechanism of carbon nano-filaments from methane dry reforming in the presence of iron based is different from Ni and Co based catalysts: the activity of iron based catalyst increases abruptly at temperatures higher than 680°C while Ni and Co catalyst are active catalysts for the formation of carbon nano-filaments from methane decomposition at lower temperatures (450°C). Ermakova et al.[ ERMAKOVA, et al., 2001 ] reported that in a temperature range of 450–650°C cementite was formed from methane decomposition however cementite did not show any activity for the formation of carbon nano-filaments. At 700°C cementite was decomposed to α-Fe and carbon formation started.

Based on these results, in this master project the catalysts were preheated and kept at 800°C in pure Argon or N₂ atmosphere for one hour.

### 4.2 Operational conditions and reactor configuration

#### 4.2.1 System descriptions

The system is composed of a vertically positioned tubular quartz bench-scale fixed-bed reactor (BSFBR) with a length of 122 cm and an external diameter of 4.6 cm. The reactor is placed in a 3.3kW electric oven; 44 cm of the reactor is exposed to the heating elements of the oven leaving about 30 cm on each side (top and bottom) of the reactor exposed at room conditions. The catalyst chosen for this project is an AISI 1010 carbon steel in sheet. Besides Fe, The carbon steel catalyst contains a maximum of 0.13% C, 0.3-0.6% Mn, maximum of 0.04% P and maximum of 0.05% S. The thickness of the sheet is 0.13 mm (+/- 10%) and the UPC number is 13320 (16AS). All content percentages are w/w. The catalyst comes as strips of carbon steel 1.8 cm wide, 58 cm long. The catalyst is fixed on the quartz tube which contains a thermocouple placed at the center of the reactor. The reagents are EtOH and CO₂. 98%vol liquid ethanol was pumped at a liquid flow rate of 0.2 to 12 ml/min and vaporized by the heating jackets around the metallic conduit, containing ethanol, just before its entrance to the reactor.
CO₂ is provided by a gas bottle/container with a capacity of 10 m³. It is added to the ethanol vapor on the head of the reactor. Other gases (Ar, Air, or N₂) are also provided in the bottles of 10m³. All gases are supplied by Praxair and their purity are 99.99% for CO₂, 99.99% for Ar.

The humidity of the produced gas, water or other liquids products, as well as the unconverted ethanol is captured in an ice-bath condenser followed by a molecular sieve. The flow of the produced gas is measured by a volumetric flow meter with a precision of 10ml. The schematic of the system is described in the following diagram (Figure 4.2)

![Figure 4.2 Experimental set-up](image)

**4.2.2 Data acquisition**

Using a multipoint thermocouple (K-type), ten points of temperature were taken in the bed at every 6.35 cm. Temperatures were registered by an acquisition system, and provide us with the temperature profile along the reactor. The temperature of ethanol vapor and CO₂ at the entry of the reactor was also measured and registered by the same acquisition system. The flow of output gases was measured by a volumetric flowmeter. The flow of ethanol was controlled by the pump. A pressure probe measured the gas pressure at the head of the reactor.
Considering that the liquid trapped in the condenser was mainly composed of water and ethanol, we calculated the quantity of each having the volume and the weight of this liquid. The difference in mass of the molecular sieve before and after the test gave us the additional quantity of the vapor captured in the molecular sieve; this was added to the calculated mass of the water captured in the condenser. The composition of the produced gases was determined by Gas Chromatography analysis (GC Model CP3800 from Varian Inc., Hayesepe Q CP81073, Hayesepe Q 81069, and Hayesepe T CP81072 columns and Molsieve 13X CP81071 and Molsieve 5A CP81025, with column temperatures maintained at 50°C).

4.3 Characterization of the catalyst and the carbon deposit

Characterization of the catalyst was carried out before and after the reaction, as well after each intermediate stage of the pre-treatment of the catalyst. The analyses of the surface were carried out by high resolution Scanning Electron Microscopy (SEM) (Hitachi S-4700). Elementary analysis (Mapping) done by the high resolution electron microscopy on the surface of the catalyst, provided us with the information about the local concentration of Fe, C, O or other elements on the surface.

XRD analyses were obtained by a Panalytical X’pert PrO diffractometer using CuKα radiation at room temperature with instrumental settings at 45 kV and 40 mA. Analyses by X-ray Diffraction (XRD) were used to follow the transformation of the crystalline phases of the catalyst during the tests, if any. The surface and the cross section of the Shim strips were analyzed by Optical Microscope as well. This analysis provided us with images of the catalyst illustrating its different phases.

Carbon deposit was also analyzed by SEM, XRD and TEM. SEM analyses provided us with the information about the structure of the carbon deposits (graphitic, amorphous or filamentous). Information about size distribution of the diameters of the carbon nano-filaments (CNF) was also obtained by the SEM. Elementary analysis was done on the CNF in order to determine the elements present in the carbon deposit. XRD analyses on the CNF
identified the crystalline phases present in the carbon deposits. The analysis of Transmission Electron Microscopy (TEM) was to obtain information about the structure of the CNF. The quantity of the metal encapsulated in the carbon nano-filaments was measured by Absorption Atomic Varian SpectrAA-50/55 Spectrometer (AA).
CHAPTER 5

CATALYTIC PROPERTIES OF CARBON STEEL

In this chapter the catalytic properties of carbon steel are studied in details. We will start by explaining the preliminary experiments that led us to develop an experimental operating protocol. This is followed by the results of the studies done in order to improve this experimental protocol and at last the experiments done to find the favorable reaction conditions.

5.1 Preliminary experiments

According to the literature review of the reforming reactions, it was concluded that the most probable reaction for the sequestration of carbon is the Boudouard reaction:

\[ 2\text{CO} \leftrightarrow \text{CO}_2 + \text{C} \]

This is a catalytic reaction, favored at high temperatures (about 500°C). The active catalysts for this reaction are iron and its alloys. However, in the literature there are only few references available so as to prove the activity of these types of catalysts for the dry reforming of ethanol [ABATZOGLOU, et al., 2006, DE OLIVEIRA-VIGIER, et al., 2005]. The recent experiments proved that stainless steel (SS316) can be an appropriate catalyst for ethanol dry reforming [DE OLIVEIRA-VIGIER, et al., 2005]. Therefore, based on this information, and the literature reviews (Section 3.1) carbon steel 0.1% (AISI 1010) was chosen to be studied as the catalyst of dry reforming of ethanol in this master project. The choice of carbon steel was based on the fact that carbon steel contains only iron and carbon, iron being the reactive agent for the carbon sequestration.

As it was illustrated in section 4.1, it was found experimentally that the steel needs to be heated up to 800°C and to be kept at this temperature for about an hour in order to show high catalytic activities. Therefore, the first experiments were designed as follows:

1. Heat the carbon steel up to 800°C under industrial N\(_2\) (containing less than 1% oxygen) and keep it for an hour at this temperature.
2. The catalyst was cooled down to the room temperature still under N₂.
3. Samples for SEM, XRD and optic microscope analyses were taken by bringing out the catalyst from the reactor at room temperature.
4. The catalyst was then placed back in the reactor, heated up to 550°C under an N₂ atmosphere.
5. At this temperature ethanol and CO₂ gases with volumetric flows of 0.81 ml/min and 145 ml/min were inserted into the reactor.
6. The reaction was continued for an hour.
7. Once the reaction was finished, ethanol and CO₂ were replaced by N₂ and the reactor was left to cool down to the room temperature.

Carbon deposit was observed on the catalyst strips and a conversion of about 76% was measured for ethanol (Table 5.1, Test A).

<table>
<thead>
<tr>
<th>Test</th>
<th>Test A</th>
<th>Test B</th>
<th>Test C</th>
<th>Test D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid EtOH (ml/min)</td>
<td>0.81</td>
<td>0.77</td>
<td>0.85</td>
<td>0.8</td>
</tr>
<tr>
<td>CO₂</td>
<td>145</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Weight of catalyst(g)</td>
<td>15</td>
<td>21</td>
<td>21</td>
<td>11</td>
</tr>
<tr>
<td>Duration (min)</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>mole EtOH/moleCO₂</td>
<td>2.4</td>
<td>2.2</td>
<td>2.4</td>
<td>2.2</td>
</tr>
<tr>
<td>Activating gas</td>
<td>N₂</td>
<td>Ar</td>
<td>Ar</td>
<td>Ar</td>
</tr>
<tr>
<td>Carbon (g)</td>
<td>3.9</td>
<td>10.8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Exit gas (ml/min)</td>
<td>240</td>
<td>594</td>
<td>200</td>
<td>220</td>
</tr>
<tr>
<td>Exit EtOH (ml)</td>
<td>12</td>
<td>8</td>
<td>31</td>
<td>24</td>
</tr>
<tr>
<td>Contact with oxygen</td>
<td>Industrial N₂ 550°C,</td>
<td>Ambient air 25°C,</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>EtOH conversion (%)</td>
<td>76</td>
<td>83</td>
<td>35</td>
<td>50</td>
</tr>
</tbody>
</table>

The surface of the sample of the catalyst taken at room temperature after the thermal treatment at 800°C was analyzed by high resolution electron microscopy. Figure 5.1 shows the SEM
analyses of the surface of the carbon steel after treatment with N$_2$ at 800°C. Elemental analysis was also done on this sample (Figure 5.2) and it was found that carbon, iron and oxygen are the present elements on the catalyst. Based on these observations it is concluded that the crystalline structures seen in Figure 5.1 are composed of iron oxide probably formed at room temperature while in contact with air.

Figure 5.1 SEM analyses of carbon steel surface after treatment with N$_2$ at 800°C

![SEM analyses of carbon steel surface after treatment with N$_2$ at 800°C](image)

Figure 5.2 Elemental analysis of carbon steel surface after treatment with N$_2$ at 800°C

![Elemental analysis of carbon steel surface after treatment with N$_2$ at 800°C](image)

Figure 5.3 shows the SEM analysis of the carbon deposit. It was found that the carbon deposit was in the form of carbon nano-filaments with diameters ranging between 5nm to 200nm.
Figure 5.3 a,b SEM analyses of carbon deposit formed during Test A

The same procedure was repeated replacing industrial N$_2$ with pure Ar (Table 5.1, Test B). In this experiment also the catalyst was cooled down to the room temperature after the thermal treatment with pure argon. A sample of carbon steel was taken at room temperature; therefore the catalyst was in contact with air at room temperature before the reforming reaction. At the end of the reaction we had an ethanol conversion of 83%. The carbon deposited during this experiment was analyzed by SEM. Figure 5.4 shows that the carbon deposit is in the form of carbon nano-filaments.
On the other hand, in an experiment we repeated the same procedure, using Ar zero as the inert gas, but eliminating the 3\textsuperscript{rd} step: taking samples of carbon steel at room temperature (Table 5.1, Test C). Consequently, the carbon steel was always in an inert atmosphere and was never exposed to air. Surprisingly at the end of an hour of reaction, no carbon was deposited on the surface of the catalyst and the conversion of ethanol was only about 35%.

This result made us repeat the former reaction two times. In the first repeated experiment no carbon deposit was found (Table 5.1, Test D), confirming that a partial oxidation is necessary to activate the catalyst. However, in the second one another phenomenon was experienced. The flow rate of ethanol at the beginning of the reforming reaction was negligible. Consequently, for a few minutes the catalyst was in contact with an oxidizing gas, CO\textsubscript{2} at 550\textdegree C before entering ethanol with the usual flow. It was interesting to see that the carbon was deposited on the surface of the catalyst this time. These results were important since they proved the hypothesis that a partial oxidation is necessary to activate the catalyst.
5.1.1 First experiment with medical air at 550°C with a ratio of 1/3 for CO₂/EtOH

The preliminary experiments, described in Section 5.1 have proved that an oxidation step is necessary in order to activate the carbon steel as the catalyst for reforming. Therefore an experiment was designed to test the effect of oxygen on the reactivity of carbon steel.

The stages of the reaction are as follows:

1- Heating the catalyst to 800°C in an atmosphere of pure Ar and keeping at this temperature for one hour
2- Turning off the heater and let the catalyst to cool down to the ambient temperature in an Ar atmosphere.
3- Heating the catalyst to 500°C and leave it for one hour still in a pure Ar atmosphere.
4- Stopping Ar flow and insert medical Air with the flow rate of 73ml/min for 20 minutes.
5- Stop Air flow and insert CO₂ for 5 minutes as to purge out the remaining of air or Ar.
6- Start the reaction with EtOH with a gas flow rate of 137.7 ml/min and CO₂ with the flow of 42ml/min for 4:15 hours.
7- After the reaction is done the heater is turned off and let to cool down under the flow of Ar.

The produced gas was analyzed by the GC and the results of these analyses are summarized in Figure 5.5. The percentage of hydrogen increases very fast; it reaches 67.98% after only 15 minutes. The conversion of ethanol and CO₂ were 93% and 30% respectively. The results of this experiment are summarized in Table 5.2.
5.1.2 Preliminary reactions results

The preliminary experiments proved that in order to activate carbon steel, not only it has to be pre-treated at 800°C, but also it needs to be exposed to an oxidizing gas, either industrial N₂ containing less than 1% oxygen, CO₂ or ambient air; without the oxidation step no carbon deposit is formed and the conversion of ethanol is very small. This is in agreement with Ermakova’s [ERMAKOVA, et al. 2001] observations. They proved that iron cannot catalyze the decomposition of hydrocarbons to carbon filaments. To initiate this process, iron must be dispersed. They showed the addition of carbon monoxide to methane or the oxidation of bulky iron followed by reduction can be used for this purpose Therefore, the effect of concentration of oxygen in the oxidizing gas the duration and the temperature of the oxidation remains to be determined.
<table>
<thead>
<tr>
<th>Test</th>
<th>5.1.1</th>
<th>5.2.1</th>
<th>5.2.2</th>
<th>5.2.3</th>
<th>5.3.1</th>
<th>5.3.2</th>
<th>5.3.3</th>
<th>5.3.4</th>
<th>5.4.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtOH(ml/min)</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.35</td>
<td>0.37</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td>EtOH(mlSTP/min)</td>
<td>138</td>
<td>137</td>
<td>138</td>
<td>138</td>
<td>147</td>
<td>154</td>
<td>146</td>
<td>146</td>
<td>146</td>
</tr>
<tr>
<td>CO2(mlSTP/min)</td>
<td>42</td>
<td>42</td>
<td>140</td>
<td>140</td>
<td>140</td>
<td>140</td>
<td>140</td>
<td>140</td>
<td>0</td>
</tr>
<tr>
<td>weight of catalyst(g)</td>
<td>12.8</td>
<td>12.8</td>
<td>10.9</td>
<td>24.3</td>
<td>20.8</td>
<td>10.3</td>
<td>10.3</td>
<td>10.1</td>
<td>10.0</td>
</tr>
<tr>
<td>duration (min)</td>
<td>255</td>
<td>480</td>
<td>390</td>
<td>240</td>
<td>150</td>
<td>120</td>
<td>180</td>
<td>165</td>
<td>120</td>
</tr>
<tr>
<td>GHSV(ml/h/gram)</td>
<td>2335</td>
<td>2330</td>
<td>4217</td>
<td>1896</td>
<td>2282</td>
<td>4740</td>
<td>4593</td>
<td>4686</td>
<td>2420</td>
</tr>
<tr>
<td>Surface(㎡)</td>
<td>0.0209</td>
<td>0.0209</td>
<td>0.0209</td>
<td>0.0418</td>
<td>0.0410</td>
<td>0.0209</td>
<td>0.0201</td>
<td>0.0201</td>
<td>0.0201</td>
</tr>
<tr>
<td>GHSV(㎡/hM³)</td>
<td>1.43</td>
<td>1.42</td>
<td>2.20</td>
<td>1.10</td>
<td>1.16</td>
<td>2.34</td>
<td>2.36</td>
<td>2.36</td>
<td>1.21</td>
</tr>
<tr>
<td>EtOH/CO2(in)</td>
<td>3.3</td>
<td>3.3</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.1</td>
<td>1.0</td>
<td>1.0</td>
<td>N/A</td>
</tr>
<tr>
<td>CO2/EtOH converted</td>
<td>10.1</td>
<td>9.4</td>
<td>3.8</td>
<td>3.8</td>
<td>10.5</td>
<td>4.9</td>
<td>8.1</td>
<td>8.8</td>
<td>N/A</td>
</tr>
<tr>
<td>Activating gas</td>
<td>Ar/Air</td>
<td>Ar/O</td>
<td>Ar/Air</td>
<td>Ar/Air</td>
<td>No activation</td>
<td>Ar/Air</td>
<td>N2</td>
<td>Air(150)</td>
<td>Air</td>
</tr>
<tr>
<td>Carbon (g)</td>
<td>16.00</td>
<td>15.66</td>
<td>20.00</td>
<td>12.83</td>
<td>9.13</td>
<td>6.29</td>
<td>7.07</td>
<td>8.43</td>
<td>8.45</td>
</tr>
<tr>
<td>Rate of carbon production (g/min)</td>
<td>0.06</td>
<td>0.03</td>
<td>0.05</td>
<td>0.05</td>
<td>0.06</td>
<td>0.05</td>
<td>0.04</td>
<td>0.05</td>
<td>0.07</td>
</tr>
<tr>
<td>Mole C/Mole CO2</td>
<td>10.1</td>
<td>6.0</td>
<td>2.9</td>
<td>3.0</td>
<td>8.8</td>
<td>3.4</td>
<td>4.8</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>Exit Gas(mlSTP/min)</td>
<td>464</td>
<td>383</td>
<td>620</td>
<td>611</td>
<td>632</td>
<td>638</td>
<td>626</td>
<td>643</td>
<td>465</td>
</tr>
<tr>
<td>Exit EtOH (ml)</td>
<td>6</td>
<td>39</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Exit water (ml)</td>
<td>13.5</td>
<td>13.4</td>
<td>7.2</td>
<td>5.8</td>
<td>2.0</td>
<td>3.9</td>
<td>4.9</td>
<td>3.9</td>
<td>2.3</td>
</tr>
<tr>
<td>EtOH Conversion</td>
<td>0.93</td>
<td>0.75</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>0.92</td>
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<td>-0.04</td>
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<tr>
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<td>0.06</td>
<td>0.05</td>
<td>0.16</td>
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<td>0.08</td>
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<tr>
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<td>0.00</td>
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<td>-0.04</td>
<td>-0.10</td>
<td>-0.06</td>
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</table>
5.2 Reaction Parameters

5.2.1 The effect of the concentration of the reagents

The following experiment was designed in order to study the effect of concentration of the reagents in contact with the catalytic surface (GHSV). The GHSV in this project is defined as the ratio of the total volume of the gases at reaction temperature to the weight of the catalyst (ml/ min. g).

The steps of the reaction were as follows:

1- Heating the catalyst to 800°C in an atmosphere of pure Ar and keeping at this temperature for one hour.
2- Turning off the electric furnace and let the catalyst to cool down to the ambient temperature in an Ar atmosphere.
3- Heating the catalyst to 500°C and leave it for one hour still in a pure Ar atmosphere.
4- Turning the furnace off and let the catalyst to cool down to the ambient temperature under the current of Ar.
5- Repeat the 3rd and 4th steps.
6- Heating the catalyst to 500°C, with the pure Ar flow rate of 1818ml/min for an hour
7- Entering EtOH with a flow rate of 137.3 ml/min and CO₂ with a flow of 42ml/min for two hours.
8- Stop the Ar flow and continue the reaction with the same flow rate of EtOH and CO₂ for 8 hours.

The gas produced during this experiment was analyzed by the gas chromatograph. The results of these analyses are shown in Table 5.2 and on the following diagram (Figure 5.6 ).
As it is seen on the graph when Ar was stopped, the volumes of gases were reduced abruptly. However, it took few hours before they reached the maximum observed volumes of the gases produced at the end of the reaction. Because of the presence of high volumes of argon in the beginning of this reaction, the gas analysis by GC was not very precise and consequently the total error of the mass balance for this reaction is relatively high (50%). However, based on the results of this experiment (Figure 5.6) it is proved that without the oxidization step of the catalyst with air, the catalyst shows low activity for the ethanol reforming (at the beginning of the test). The activity of the catalyst increases gradually and the volumes of the produced gases increase, this can be because during this time from the begging of the reaction the catalyst has been oxidized in contact with CO and CO₂. The volumes of hydrogen and CO at the end of this reaction were comparable to the volumes of the gases obtained at the beginning of the experiment with oxidation step with air (Figure 5.5). The conversion of ethanol and CO₂ were 75% and 26% respectively, which are relatively lower than the conversion observed in Section 5.1.1.
5.2.2 Changing the Ratio of CO₂ /EtOH to 1/1

After finding that an oxidation at 550°C is very efficient for activating carbon steel as a reforming catalyst (Section 5.1.1) the following experiment was designed in order to study the effect of the ratio of the reactive gases, changing the ratio of CO₂ /EtOH from 1/3 to 1/1.

The steps of the reaction:

1. Heating the catalyst to 800°C in an atmosphere of pure Ar and keeping at this temperature for one hour.
2. Turning off the heater and let the catalyst to cool down to the ambient temperature. Still under the Ar atmosphere.
3. Heating the catalyst to 500°C and leave it for one hour in a pure Ar atmosphere.
4. Stopping Ar flow and insert medical Air with the flow rate of 250 ml/min for 20 minutes.
5. Cut Air flow and insert CO₂ for 5 minutes to purge out the air or Ar.
6. Start the reaction with EtOH with the gas flow rate of 137.7 ml/min and CO₂ with the flow of 140ml/min for 6:30 hours.
7. After the reaction is done the heater is turned off and let to cool down under the flow of Ar.

The results of the produced gas analyzed by GC are showed in the following graph (Figure 5.7).
Figure 5.7 Gas product compositions during the Test 5.2.2

Table 5.2 compares the results of section 5.1.1, 5.2.2, 5.2.1. It is seen that, in this experiment we had higher volumes of hydrogen and CO comparing to section 5.1.1, experiment with a CO₂/EtOH ratio of 1/3. In addition, a higher ratio of “moles of CO₂ converted / moles of ethanol converted” was observed (0.3 compared to 0.1); considering that the conversion of ethanol was higher in this test. The rate of carbon production in this experiment was slightly lower than the test in section 5.1.1. The conversion of ethanol and CO₂ were 100% and 26% respectively.

At the beginning of this experiment, carbon powder was falling down to the bottom of the reactor. This carbon was analyzed separately by SEM and agglomerated carbon and many filaments with different shapes were also found (Figure 5.8).
It was explained in Section 2.2.3.1 that based on the thermodynamic calculations at equilibrium it was expected to have almost the same yield for H₂ (Figure 2.9) but higher yields of CO₂ and CH₄ (Figure 2.10 b) for the CO₂/ethanol ratio of 1/3. However, as it is seen in Figure 5.9, the yield of H₂ obtained for CO₂/ethanol ratio of 1 in experiment was even higher than the H₂ yield for CO₂/ethanol ratio of 1/3 (Figure 5.10). Higher experimental yields of H₂ can be explained by the fact that the reaction has not had the time to reach the equilibrium.
Figure 5.10 Equilibrium and experimental yields (mole/mole CO₂) for CO₂/ethanol ratio of 1 and 1/3

5.2.3 Increasing the quantity of the catalyst

This experiment was designed in order to study the effect of the quantity of the catalyst on the conversions of gases and the carbon production rate. The operating conditions of this experiment were the same as in section 5.2.2, however the quantity of the catalyst was doubled. The produced gas was analyzed by the GC and the results of these analyses are summarized in the following graph (Figure 5.11).
Figure 5. 11 Gas product compositions during the Test 5.2.3

The results of this experiments showed that the composition of the produced gas was not changed significantly by increasing the quantity of the catalyst (Table 5.2). The rate of carbon production and the ratio of Mole of produced carbon to mole of CO₂ were slightly higher in this experiment as well as the volume of hydrogen. The conversion of ethanol and CO₂ were 100% and 26% respectively.

5.2.4 Conclusion

It was proved in section 5.2.2 that a higher volume of hydrogen and also a higher rate of CO₂ consumption were observed for a ratio of 1 for CO₂/Ethanol compared to that of 1/3. Therefore, the ratio of 1/1 was chosen for the proceeding experiments. It was also shown that increasing the quantity of the catalyst does not make any significant changes in the conversions of the reactive gases.
5.3 Developing the experimental protocol

As mentioned in the previous section (5.1.2), it was found experimentally that the carbon steel needs to go through an activating pre-treatment: pre-heating at 800°C followed by an oxidation step. In this section we study this pre-treatment procedure in more details. The challenge was to obtain experimental conditions which favor the ethanol dry reforming reaction and the production of nano-filaments of carbon. Consequently, the effect of cooling temperature, oxidation temperature and the concentration of oxygen on the activity of the catalyst for ethanol reforming reaction and on the quality of the carbon deposit were chosen to be studied.

5.3.1 Eliminating the step of thermal treatment at 800°C

This experiment was designed to study the effect of thermal treatment at 800°C on the activity of the catalyst and the quality of the carbon deposit. The results are summarized in Table 5.2. It was found that that carbon steel is an active catalyst without the thermal treatment step with Ar at 800°C, a low CO₂ conversion of 10% was observed and no small nano-filaments were deposited. However, ethanol was 100% converted and the rate of carbon production is 0.061g/min. The gas product composition is graphed in Figure 5.12.

![Gas product compositions during the Test 5.3.1](image)

Figure 5.12 Gas product compositions during the Test 5.3.1
5.3.2 Eliminating the step of cooling down to the ambient temperature

This experiment was designed to study the effect of the cooling temperature of the catalyst during its pre-treatment process. Until this point the catalyst was heated to 800 °C, cooled down to the room temperature, and heated again up to 550°C, the reaction temperature. On the contrary, in this experiment we eliminated the step of cooling down the catalyst to the room temperature (25°C).

The steps of the reaction are as follows:
1. Heating the catalyst to 800°C under pure Ar with the flow rate of 100ml/min, and keeping at 800°C for an hour under Ar
2. Let the reactor cool down to 550°C still under Ar
3. Oxidation at 550°C with air with the flow rate of 250 ml/min and for 15 min
4. At this temperature opening the CO₂ with the flow rate of 140 ml/min for 10 minutes
5. Opening the pump of ethanol with the flow of 0.37 ml/min (154.4ml/hr/min)
6. Continue the reaction with this flow for 2 hours

The results of the produced gas analysis (Figure 5.13) show that the concentration of methane was lower than for the previous experiences (section 5.2.2). This may be an indicator for having higher rates of ethanol reforming comparing to ethanol cracking. The concentration of H₂ and CO was about the same as in the previous experiences. The conversion of ethanol and CO₂ were 100 % and 23% respectively (Table 5.2).
The carbon deposits were analyzed by SEM, and it was found that the carbon deposit was in the form of nano filaments of carbon. Comparing to the same operating conditions of the reaction but with the step of cooling down the catalyst until the room temperature (section 5.2.2), the nano-filaments of carbon had smaller diameters. Therefore it was concluded that without cooling down the catalyst to 25°C, not only the concentrations of H₂ and CO were not changed but also a higher quality of nano-filaments of carbon was observed.

5.3.3 Activating with industrial nitrogen

In this experiment the catalyst was activated using industrial N₂ with an oxygen concentration of less than 1%. The cooling temperature of the catalyst was set at 550°C as it was proved previously that cooling to 25°C was not necessary.

The steps of the reaction were as follows:

1- Heating the catalyst to 800°C under industrial N₂ with the flow rate of 100 ml/min
2- Keeping at 800°C for an hour under N₂
3- Let the reactor cool down until 550°C still in an N₂ atmosphere
4- At this temperature opening the CO₂ with the flow rate of 140 ml/min for 10 minutes
5- Starting the pump of ethanol with the flow of 0.35 ml/min (146 ml atm/min)
6- Continue the reaction with this flow for 3 hours

At the beginning of the reaction the concentration of CO$_2$ was very high and almost not converted (Figure 5.14). But after 3 hours the percentages of the gases at the exit was almost the same as in the reactions with oxidation step but only after 15 minute. The conversion of ethanol and CO$_2$ were 92% and 12% respectively (Table 5.2). In this experiment the catalyst had no contact with air. These results show that even the small amount of oxygen present in industrial N$_2$ is capable of activating the catalyst for the reforming reaction of ethanol. However, as it can be seen in Table 5.2, the conversions of ethanol and CO$_2$ were smaller than the experiment of section 5.2.2.

![Graph of gas product compositions](image)

**Figure 5.14 Gas product compositions during the Test 5.3.3**

Carbon samples were taken from both sides of the catalyst's surface, and from the bulk of carbon deposit. Compared to the experiment of activating with Ar and oxidation with air at 550°C (section 5.2.2), the carbon nano-filaments had larger diameters (Figure 5.15).
5.3.4 Oxidation at 150°C

Until this point the oxidation of catalyst at 25°C and at 550°C was studied. It was proved that oxidation at 25°C was not efficient enough for activating the catalyst (Table 5.1, Test B); however 550°C was apparently an appropriate temperature for oxidation (Table 5.2, Test 5.2.2). So, another temperature in between, such as 150°C, was chosen for the oxidation step of the catalyst in order to see the effect of the oxidation temperature on the gas conversions and the quality of the carbon nano-filaments.

The steps of the reaction were as follows:

1. Heating the catalyst until 800°C under pure Ar with the flow rate of 100ml/min and keeping it at 800°C for an hour still under Ar
2. Let the reactor cool down to 150°C still under Ar
3. At this temperature we inserted air for 15 minute with the flow rate of 250ml/min
4. Close the Air and open the Ar with a flow rate of 100ml/min
5. Start heating the reactor until 550°C under the pure Ar
6. At this temperature opening the CO₂ with the flow rate of 140 ml/min for 10 minutes
7. Opening the pump of ethanol with the debit of 0.35 ml/min (146mlstp/min )
8. Continue the reaction with this flow for 165 min

As it is seen in Figure 5.16, at the beginning of the reaction the concentration of CO₂ was high and almost not converted. However, CO₂ concentration was decreased during the
reaction. Ethanol conversion was 100% and CO₂ conversion was about 11% (Table 2) which was lower than the experiments with oxidation at 550°C (5.2.2). The carbon deposited was also analyzed by SEM (Figure 5.17) and it was found that its quality was not as good as for the oxidation at 550°C: in this experiment the nano-filaments have larger diameters. Consequently, the 550°C was chosen to be an appropriate temperature of oxidation.

![Graph showing gas product compositions during the Test 5.3.4](image)

**Figure 5.16** Gas product compositions during the Test 5.3.4

![SEM image showing carbon deposit formed during Test 5.3.4](image)

**Figure 5.17** SEM analyses of carbon deposit formed during Test 5.3.4
5.3.5 Conclusion

As mentioned in section 5.1.2 it was found that a thermal-oxidative pre-treatment is necessary to activate carbon steel as the catalyst of ethanol dry reforming. In section 5.2 reaction parameters were studied in details. It was proved in 5.2.1 that when the reactive gases (EtOH and CO₂) are dilute, the yields of the reforming reaction are small. Comparing the experimental results of 5.1.1, to 5.2.2 it is found that the ratio of 1/1 for CO₂/EtOH favors the production of hydrogen. Besides, the molar ratio of CO₂/Ethanol converted are higher than in the experiments with a ratio of CO₂/EtOH=1/3. Consequently, the ratio of 1/1 was chosen as the preferred operating ratio.

In section 5.2.3 it was proved that the quantity of the catalyst (10 g) was already enough for bringing the ethanol reforming reactions to the maximum yields of the reactions; consequently increasing the quantity of the catalyst did not affect the conversions or the volumes of the produced gases.

In section 5.3 final adjustments on the experimental protocol were studied. It was proved (5.3.1) that it is not necessary to cool down the catalyst to the room temperature after the heating treatment at 800°C and before its oxidization. It was also shown in 5.3.3 that even the very small amount of oxygen present in industrial N₂ is enough to oxidize the carbon steel and make it active as a dry reforming catalyst. Finally, it is proved in 5.3.4 that with the present operating conditions the best oxidization temperature is 550°C; with highest conversions of ethanol and best qualities of carbon nano-filaments.

5.4 Reforming against cracking

At this stage of the project it was necessary to know if it is possible to differentiate between catalytic reforming and catalytic cracking of ethanol, using carbon steel as the catalyst, at these operating conditions. Experiments in the absence of carbon steel were also designed so as to distinguish between thermal and catalytic reforming/cracking reactions.
5.4.1 Catalytic cracking of ethanol

This experiment was designed to study the ethanol cracking in the same operating conditions as in the experiments of reforming (section 5.2.2). Therefore CO₂ was replaced by pure Ar; this will let us maintain the same GHSV in the reactor as in section 5.2.2.

The steps of the reactions were as follows:

1- Heating the catalyst to 800°C under a flow rate of 100ml/min of pure Ar, keeping at 800°C for an hour under Ar
2- Let the reactor cool down to 550°C still under Ar
3- At this temperature air was inserted for 15 minute with a flow rate of 250ml/min
4- Close the Air and open the Ar with a flow rate of 100ml/min
5- Starting the pump of ethanol with a flow rate of 0.35 ml/min (146mlstp/min)
6- Continue the reaction for 120 min

The results of this experiment are summarized in Table 5.2. The gas analysis proved that ethanol was cracked easily at 550°C in the presence of carbon steel with a complete conversion. We observed higher volumes of hydrogen than in the reforming reaction (Section 5.2.2), but lower volumes of CO and CH₄ gases Figure 5.18. Carbon deposited on the catalyst and it was proved to be in the form of nano-filaments of carbon by SEM (Figure 5.19).

![Figure 5.18 Gas product compositions during the Test 5.4.1](image-url)
Based on the equilibrium calculations presented in section 2.2.3.3 higher yields of H₂, CH₄, and C for ethanol cracking at 550° was expected compared to ethanol reforming (CO₂/ethanol ratio of 1 and at 550°C). This was in complete agreement with the experimental results obtained in this project. However, the experimental yield of H₂ was higher than its yields at equilibrium (Figure 5.20) and the yield of C were lower than its yield calculated at equilibrium, for both ethanol reforming and ethanol cracking (Figure 5.21).

Figure 5. 20 Equilibrium(Y) and experimental (Y’) yields (mole/mole H₂) for ethanol cracking and reforming
5.4.2 Conclusion

At these operation conditions, 550°C and 1 atmosphere, catalytic cracking of ethanol is taking place. Consequently, in the experiments with both CO₂ and ethanol as the reactive gases and in the presence of carbon steel, both the cracking and reforming reactions may take place in the reactor. The indices which show which reaction one is more favored are the conversion of CO₂ and the volumes of methane or ethylene, if any. The higher the conversion of CO₂ and the lower the volume of methane or ethylene, the higher is the rate of ethanol catalytic reforming compared to ethanol cracking.

5.5 Distinction between thermal and catalytic reactions

In order to study the activity of the carbon steel for reforming reaction, it is important to study the possibility of thermal reforming of ethanol or thermal cracking at the same operating conditions. Therefore the following experiments in the absence of the catalyst were designed. In section 5.5.1, 5.5.2 thermal cracking of ethanol was studied. Therefore, only ethanol was inserted to the reactor at the reaction temperature 550°C.
In section 5.5.3 and 5.5.4 the thermal reforming of ethanol at the same conditions of ethanol catalytic reforming as described in section 5.2.2 is studied. The difference between the experiments in 5.5.1 and 5.5.3 with the experiments described in sections 5.5.2, 5.5.4 is the presence of an inert support of glass wool at the middle of the reactor. This choice was based on the hypothesis that the presence of an inert support may increase the probability of adsorption, dissociation and reaction of the reactive gases.

5.5.1 Thermal cracking of ethanol

This experiment was designed to study the possibility of thermal cracking of ethanol. The stages of the reaction are as follows:

1- Heating the reactor until 550°C under Ar
2- At 550°C inserting the EtOH with the flow rate of 0.2 ml/ min for two hours

No carbon deposit was formed at the end of this reaction. Compared to the catalytic cracking of EtOH (section 5.4.1) the yield of H₂ was negligible (Figure 5.22), demonstrating that thermal cracking of ethanol at these conditions was not favored. This was confirmed by low ethanol conversion, 34%, (Table 5.3) compared to 100% in the presence of the carbon steel (section 5.4.1).

![Figure 5.22 Gas product compositions during the reaction 5.5.1](image)

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### TABLE 5. 3 THERMAL AND CATALYTICAL REFORMING/CRACKING COMPARISON

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<th>Test</th>
<th>Catalytic reforming</th>
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<th>Thermal cracking</th>
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<td>N/A</td>
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<td>N/A</td>
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<tr>
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<td>N/A</td>
<td>N/A</td>
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<td>87.2</td>
<td>0.2</td>
<td>83.1</td>
<td>3.5</td>
</tr>
<tr>
<td>%CH4</td>
<td>2.9</td>
<td>3.8</td>
<td>3.0</td>
<td>18.7</td>
<td>3.8</td>
<td>33.9</td>
</tr>
<tr>
<td>%C2H4</td>
<td>2.7</td>
<td>0</td>
<td>0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>H2 (ml/min)</td>
<td>322</td>
<td>349</td>
<td>15</td>
<td>30</td>
<td>19</td>
<td>16</td>
</tr>
<tr>
<td>CO (ml/min)</td>
<td>180</td>
<td>80</td>
<td>4</td>
<td>6</td>
<td>5</td>
<td>12</td>
</tr>
<tr>
<td>CO2 (ml/min)</td>
<td>95.0</td>
<td>21.4</td>
<td>165.8</td>
<td>0.1</td>
<td>155.2</td>
<td>1.6</td>
</tr>
<tr>
<td>CH4 (ml/min)</td>
<td>18.1</td>
<td>17.8</td>
<td>5.7</td>
<td>8.4</td>
<td>7.1</td>
<td>15.6</td>
</tr>
<tr>
<td>Treaction</td>
<td>550</td>
<td>550</td>
<td>550</td>
<td>550</td>
<td>550</td>
<td>550</td>
</tr>
<tr>
<td>Error total C</td>
<td>-0.03</td>
<td>0.11</td>
<td>0.14</td>
<td>0.30</td>
<td>-0.07</td>
<td>0.16</td>
</tr>
<tr>
<td>Error total H</td>
<td>0.00</td>
<td>0.07</td>
<td>0.17</td>
<td>0.10</td>
<td>-0.12</td>
<td>0.14</td>
</tr>
<tr>
<td>Error total O</td>
<td>0.03</td>
<td>-0.01</td>
<td>-0.12</td>
<td>-0.13</td>
<td>-0.12</td>
<td>0.15</td>
</tr>
</tbody>
</table>

59
5.5.2 Thermal cracking of ethanol using glass wool support

The same experimental conditions as for the thermal cracking of ethanol were applied (section 5.5.1). However, in this experiment an inert support of glass wool was put in the middle of the reactor, supported on the central quartz tube containing the thermocouple. This experiment was designed based on the fact that the presence of a support might increase the probability of adsorption, dissociation and reaction of the reactive gases and consequently higher conversions of the reactive gases. The results of this experiment are shown in Figure 5.23. As it is seen in Table 5.3, this hypothesis was proved by a higher yield of H\textsubscript{2} and higher conversion of ethanol, 46\%, compared to an ethanol conversion of 34 % in the experiment without any support (section 5.5.1). However, as it is seen in Table 5.3 the volume of H\textsubscript{2} produced is still much lower than the volume of hydrogen in catalytic cracking of ethanol (5.4.1).

![Figure 5.23 Gas product compositions during the reaction 5.5.2](image-url)
5.5.3 Thermal reforming of ethanol

A test was designed in order to investigate the thermal reforming of ethanol with CO₂ in the absence of the catalyst. The same operating conditions as in section 5.2.2 were applied in this experiment.

The steps of the reaction:

1- Heating the reactor to 550°C with Ar flowing inside the reactor.
2- Stop Ar
3- At this temperature opening the CO₂ with the flow rate of 142 ml/min
4- Starting the pump of ethanol with the flow rate of 0.33 ml/min
5- Continue the reaction with these flow rates for one hour

The results of this experiment are shown in Table 5.3. The produced gas analysis Figure 5.24 showed an average concentration of 10% for hydrogen and 2.9% for CO, which is much lower than the concentration of the gas produced in the experiments of catalytic reforming (section 5.2.2). The volume of CO₂ at the exit of the reactor was slightly higher than its volume at the entrance. Ethanol conversion was zero.

At this stage it was decided to study the effect of GHSV on the yield of reaction. However, because of the pump operating limits, the volume of ethanol could not be decreased to below 0.3 ml/min, and therefore it was not possible to study the effect of GHSV for gas volumes inferior to their initial volumes. As a result it was decided to increase the flow rate of ethanol and CO₂ by a factor of two in order to see if the GHSV has an effect on the gas conversions. Therefore the flow rate of ethanol was increased to 0.66 ml/min and the flow rate of CO₂ to 280 ml/min. As it is observed on Figure 5.24, the volumes of CO and hydrogen decreased slightly. The conversion of ethanol was still zero. No carbon deposit was observed in this experiment. These results prove that thermal reforming of ethanol at these conditions is not possible.
5.5.4 Thermal reforming of ethanol using glass wool support

This experiment was the repetition of the thermal reforming of ethanol (section 5.5.3). However, in this experiment, glass wool was put inside the reactor in order to provide an inert support for the gas adsorption. This decision was based on the fact that the presence of a support for the reactive gases may increase the probability of their dissociation, their reaction and consequently higher conversions for the gases.

Comparing the produced gas analysis, Figure 5.25, with that of thermal reforming without any support shows similar results. However, as it is seen in Table 5.3, a higher conversion of ethanol was observed. Ethanol conversion and CO₂ conversion were 44% and -18% respectively.
5.5.5 Conclusion

The results of the above experiment are summarized in Table 5.3. Comparing the results of the experiments with no catalyst and no support with the experiments using glass wool as an inert support, validated our hypothesis about the probability of having higher gas conversions in the presence of an inert support such as glass wool.

As demonstrated in Table 5.3, the volume of produced hydrogen in the experiments of ethanol catalytic reforming is about 10 times the hydrogen volume in the experiment of ethanol thermal reforming. Besides, ethanol is completely converted with the presence of carbon steel; however, its conversion is only 43% in the absence of carbon steel. Carbon is not deposited without carbon steel. Therefore based on these results it is proved that at these operating conditions, temperature of 550°C and pressure of 1 atm, carbon steel is an active catalyst for ethanol dry reforming reaction and sequestration of CO₂ in the form of carbon nano-filaments. Thermal reforming of ethanol may take place but it does not play a major role in hydrogen production and obviously it does not produce carbon deposits.
Table 5.3 compares also ethanol thermal cracking reactions with ethanol catalytic reaction. It is observed that in the presence of carbon steel the volume of produced hydrogen is about 20 times higher than the hydrogen volume in the experiment without carbon steel. Ethanol is completely converted in experiment of catalytic cracking however it is converted only about 48% in the thermal cracking experiment. In addition no carbon is deposited in the experiments without catalyst. These results confirm that carbon steel is an active catalyst for ethanol cracking at temperature of 550°C and pressure of 1 atmosphere.

5.6 Reaction temperature

As illustrated in section 2.2.1 temperature of reaction has an influence on the rate of carbon production, as well as on ethanol and CO₂ conversion. The choice of 550°C for the dry reforming of ethanol was based on the previous experiments [DE OLIVEIRA-VIGIER, et al., 2005] and the literature references as well as on the thermodynamic calculations (section 2.2.3.2). The results of thermodynamic calculation with FactSage software (Section 2.2.3.2) showed that for temperatures above 550°C the volumes of hydrogen and CO increase, while the volume of methane decreases. Up to 550°C the quantity of the carbon deposit decreases slightly with increasing temperature, however after this temperature it decreases rapidly. Consequently, since one of the objects of this project is to find favorable conditions for the production of nano-filaments of carbon, as a valuable product of reforming reaction, temperatures higher than 650°C are not of interest in our studies. Temperatures lower than 500°C are not of interest due to low volumes of produced hydrogen. As a result only two temperatures were chosen to be studied furthermore; 500°C and 600°C.

5.6.1 600°C as the reforming temperature

In this experiment reaction temperature is set at 600°C. The procedure is described in the following:

1. Heating the catalyst until 800°C under pure Ar with the flow rate of 100ml/min and keeping it at 800°C for an hour still under Ar
2. Let the reactor cool down to 550°C under Ar
3. At this temperature we entered air for 15 minute with the flow rate of 250ml/min
4. Close the Air and open the Ar with a flow rate of 100ml/min
5. Start heating the reactor up to 600°C under the pure Ar
6. At this temperature, closing Ar and opening the CO₂ with the flow rate of 140 ml/min for 10 minutes
7. Starting the pump of ethanol with the flow rate of 0.35 ml/min
8. Continue the reaction with this flow for 120 min

At the beginning of this experiment high rate of carbon production was observed. The conversion of CO₂ was higher in the first 30 minutes of the reaction compared to the next 90 minutes of the experiment (Figure 5.26). Ethanol and CO₂ conversion was 99% and 21% respectively (Table 5.4). After 30 minutes from the reaction start, the volumes of the produced gases were constant. The carbon deposit was mostly deposited on the first top part of the catalyst; however there was a thin layer of carbon all over the surface of the catalyst.

![Figure 5.26 Gas product compositions during the reaction 5.6.1](image-url)
These observations can be explained as follows:
At the beginning of the reaction, the catalyst was very active for ethanol reforming. Therefore, the surface of the catalyst on its top section was enough to adsorb most of the reactive gases and reaction was taking place with a high rate at this section; as a result carbon deposit is mostly added in this top part. High conversion of CO$_2$ and high rate of carbon production during the first 30 minutes can be related to the high rate of reforming reaction on the surface of steel. However, after a short time from the beginning of the reaction, e.g. 30 minutes, a large amount of carbon is deposited on the catalyst. As it will be described in Chapter 8, this carbon is also an active catalyst for ethanol reforming. Therefore, CO$_2$ and ethanol will be mostly absorbed on the carbon deposit and reforming reaction will continue but with a lower rate; since the activity of carbon deposits is lower than the steel. The carbon deposit was analyzed by SEM and it was in the form of CNF.

5.6.2 500°C as the reforming temperature

In this experiment catalytic reforming of ethanol at 500°C is studied. The steps of the reaction are:

1. Heating the catalyst until 800°C under pure Ar with the flow rate of 100ml/min and keeping it at 800°C for an hour under Ar
2. Let the reactor cool down to 550°C still under Ar
3. At this temperature we entered air for 15 minute with the flow rate of 250ml/min
4. Close the Air and open the Ar with a flow rate of 100ml/min
5. Let the reactor cool down to 500°C under the pure Ar
6. At this temperature close Ar and entering CO$_2$ with the flow rate of 140 ml/min for 10 minutes
7. Opening the pump of ethanol with a flow rate of 0.35 ml/min
8. Continue the reaction with these flows for 120 min

In this reaction, ethanol and CO$_2$ conversion were 96.4% and -6 % respectively (Table 5.4). It is observed that not only CO$_2$ is not converted but also it is produced during this experiment. As it is seen in Figure 5.27, the volumes of the produced gases increased during this reaction. The carbon deposit was proved to be in the form of CNF by SEM analyses.
5.6.3 Comparison of experimental results with calculations at equilibrium

The calculated yields of H₂, CO₂, CO, C, CH₄, and H₂O at equilibrium were compared to the experimental results obtained in this project for CO₂/ethanol ratio of 1 and for three temperatures of 500, 550 and 600°C. (Figures 5.28, 5.29).

Figure 5.28 Effect of reforming temperature on equilibrium and experimental yields (mole/mole H₂)
Figure 5.29 Effect of reforming temperature on equilibrium and experimental yields (mole/mole C)

It is seen that the experimental results at 600°C are closer to the equilibrium calculations than at the other two temperatures. As it is seen in Figure 5.28, the experimental yields do not follow the equilibrium yields trend. The maximum experimental yields were observed at 500°C, meanwhile, the experimental H₂ yield is always higher than its yield at equilibrium.

Figure 5.29 compares the yield of carbon for CO₂/ethanol ratio of 1 and for three temperatures of 500, 550 and 600°C. It is seen that for 550° and 600°C, CO experimental yield is higher than its equilibrium yield; CO₂ and C experimental yields are less than their yields calculated at equilibrium. Comparing the calculated yields with the yields obtained experimentally proves that the reaction has not attained the equilibrium. Probably the Boudouard reaction is more favored toward CO production and the methane dry reforming is favored at higher temperatures. Consequently higher yields of CO and H₂ and lower yields of C and CO₂ are observed. However, at 500°C, the Boudouard reaction is probably more favored toward CO₂ production and consequently higher yields of CO₂ are observed at this temperature.
TABLE 5.4 EFFECT OF REACTION TEMPERATURE

<table>
<thead>
<tr>
<th>Treaction(°C)</th>
<th>500</th>
<th>550</th>
<th>600</th>
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<tr>
<td>Tactivation(°C)</td>
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<td>800</td>
<td>800</td>
</tr>
<tr>
<td>EtOH(ml/min)</td>
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<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td>EtOH(mlSTP/min)</td>
<td>147</td>
<td>145</td>
<td>146</td>
</tr>
<tr>
<td>CO₂(ml/min)</td>
<td>140</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td>Mole EtOH/min</td>
<td>0.006</td>
<td>0.006</td>
<td>0.006</td>
</tr>
<tr>
<td>Mole CO₂/min</td>
<td>0.006</td>
<td>0.006</td>
<td>0.006</td>
</tr>
<tr>
<td>Weight of catalyst(g)</td>
<td>21.4</td>
<td>20.6</td>
<td>20.6</td>
</tr>
<tr>
<td>Surface (m²)</td>
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<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Duration (min)</td>
<td>120</td>
<td>120</td>
<td>121</td>
</tr>
<tr>
<td>GHSV(ml/h/grad)</td>
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<td>2292</td>
<td>2300</td>
</tr>
<tr>
<td>GHSV(M³/h m⁻²)</td>
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<td>1.15</td>
<td>1.16</td>
</tr>
<tr>
<td>Mole EtOH/Mole CO₂(in)</td>
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<td>1.03</td>
<td>1.04</td>
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<tr>
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<td>5</td>
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<tr>
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<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>Mole C/Mole CO₂</td>
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<td>0.82</td>
<td>0.78</td>
</tr>
<tr>
<td>Mole C/Mole CO₂(Equilibrium)</td>
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<td>0.94</td>
<td>0.93</td>
</tr>
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<td>Exit Gas(ml/min)</td>
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<td>633</td>
<td>636</td>
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<tr>
<td>Exit liquid ETOH(ml)</td>
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<td>0.08</td>
<td>0.54</td>
</tr>
<tr>
<td>Exit liquid water</td>
<td>2.9</td>
<td>3.5</td>
<td>2.8</td>
</tr>
<tr>
<td>EtOH Conversion</td>
<td>96.40%</td>
<td>99.81%</td>
<td>98.86%</td>
</tr>
<tr>
<td>CO₂ Conversion</td>
<td>-6.36%</td>
<td>30.23%</td>
<td>21.06%</td>
</tr>
<tr>
<td>%H₂</td>
<td>49.2</td>
<td>52.34</td>
<td>48.34</td>
</tr>
<tr>
<td>%CO</td>
<td>21.6</td>
<td>29.29</td>
<td>31.11</td>
</tr>
<tr>
<td>%CO₂</td>
<td>27</td>
<td>15.43</td>
<td>17.37</td>
</tr>
<tr>
<td>%CH₄</td>
<td>2.18</td>
<td>2.94</td>
<td>3.18</td>
</tr>
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<td>H₂ (ml/min)</td>
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<td>331</td>
<td>308</td>
</tr>
<tr>
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<td>0.013</td>
<td>0.013</td>
</tr>
<tr>
<td>CO(ml/min)</td>
<td>1.19</td>
<td>185</td>
<td>198</td>
</tr>
<tr>
<td>mole/min</td>
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<td>0.007</td>
<td>0.008</td>
</tr>
<tr>
<td>CO₂(ml/min)</td>
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<td>98</td>
<td>110</td>
</tr>
<tr>
<td>mole/min</td>
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<td>0.003</td>
<td>0.004</td>
</tr>
<tr>
<td>CH₄(ml/min)</td>
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<td>19</td>
<td>20</td>
</tr>
<tr>
<td>mole/min</td>
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<td>0.00078</td>
<td>0.0008</td>
</tr>
<tr>
<td>mole C /min</td>
<td>0.0038</td>
<td>0.0047</td>
<td>0.0044</td>
</tr>
</tbody>
</table>

5.6.4 Conclusion

The results of reforming reactions at three temperatures of 500°C, 550°C and 600°C are summarized in the following table (Table 5.4). These results were compared to the theoretically thermodynamic calculations at equilibrium in section 5.6.3. It is observed that yields/volumes of Hydrogen and CO produced were always greater than the volume
calculated theoretically. The mass of carbon deposit was always less than the calculated weight. At 500°C the volume of CO₂ in the product gas mixture was higher than its initial volume as the reactant. This measured volume of CO₂ was higher than its volume at equilibrium. At 550°C the volume of CO₂ is less than what calculated at equilibrium. As it was expected by theoretical calculations (Figure 12), the highest rate of carbon production was observed at 550°C. The highest conversions of ethanol and more significantly CO₂ as well as the highest volume of hydrogen produced were attained at 550°C. However, comparing the volumes of the gases obtained experimentally at 500, 550, and 600°C with the equilibrium volumes calculated by FactSage shows that the results of the reforming at 600°C were the closest to the equilibrium. As described in Section 5.6.1, the catalyst may be more active at 600°C. This conclusion is based on the higher volumes of the hydrogen observed at the beginning of the reaction. However, after a short time the surface of the catalyst was covered with carbon deposit and ethanol and CO₂ mainly reacted with this active carbon and not the carbon steel itself afterward.

5.7 Reactivity of the catalyst

In this chapter the reactivity of the catalyst is presented. The results of our experiments proved that the carbon deposits on the surface of the carbon steel do not deactivate the catalyst, even after about seven hours of the reaction (Section 5.7.1). It was also found that the very minor loss of activity observed after a certain time of the reaction can be restored by removing the carbon deposit mechanically (Section 5.7.2). Sintering of the catalyst is not possible in these operating conditions of ethanol reforming. Consequently it was proved that carbon steel is a very stable catalyst for ethanol reforming reaction.

5.7.1 Deactivation of the catalyst

In a reforming experiment (section 5.2.2) we continued the reaction for a long period to find out if any loss of activity will be observed. The result of gas analyses is shown in Figure 5.30. As it is seen, the catalyst once activated, remained active even after about 400 minutes of reaction. The concentrations and the volumes of the produced gas (H₂, and CO) did not
change significantly during the time. The conversion of ethanol and CO$_2$ were 100% and 26 % respectively.

![Graph showing gas product compositions during the reaction](image)

**Figure 5.30 Gas product compositions during the reaction 5.7.1**

### 5.7.2 Reutilization of the catalyst

In an experiment (section 5.2.3) after two hours of the reaction, the flow rate of CO$_2$ increased and the flow rate of hydrogen decreased. So the oven was opened and it was seen through the quartz reactor that the carbon was mostly deposited on the 1/3 top part of the catalyst. The temperatures read on the thermocouple for this area was about 20°C lower than the highest temperature present at the lowest point of the catalyst, down in the reactor. Therefore, the top of the reactor was opened and the carbon was removed from the surface of the carbon steel and put back in to the reactor. As it is seen in Figure 5.31, the percentages of the produced H$_2$ and CO$_2$ reached that of the beginning of the reaction. But this time the slope of the reduced H$_2$ production over time was less than for the first stage of this experience when the reaction was started with the new catalyst.
One explanation may be that at the beginning of the reaction, ethanol and CO$_2$ were mostly adsorbed on the first 1/3 part of the catalyst: this surface of the catalyst was enough to catalyze most of the inserted ethanol and CO$_2$ into hydrogen and carbon. During the time, carbon was deposited on this catalytic surface and apparently caused the catalyst to lose its activity gradually. However, compared to the graph after removing the carbon deposit, it is obvious that this loss of activity was slightly faster before removing the carbon deposits than after. The reason why in the second stage of the reaction, the carbon deposit was found all over the catalyst and not only on the first part maybe that the first part of the catalyst has lost its activity to some extent in the first stage and therefore after removing the carbon deposit it could only adsorb a fraction of the inserted gas. This let the rest of ethanol and CO$_2$ to proceed through the reactor and consequently to react with the entire surface of the catalyst.
CHAPTER 6

ANALYSES OF CARBON STEEL

In this section the results of the analyses of carbon steel are presented. Two types of analysis were done; analysis of surface and analysis of phase. The analysis of surface was done using high resolution scanning electron microscopy (SEM) and optic microscope (section 6.1). Mapping and elemental analyses were also performed in order to find the composition of different regions of the catalyst. Phase analyses were performed using X-ray diffraction (XRD) (section 6.2).

6.1 Analyses of the surface

The surface of the catalyst, carbon steel, was analyzed by high resolution electronic microscope before any treatment, at different steps of pre-treatment and also after each reaction. As mentioned in the System Description (section 4.2.1), the catalyst is in the form of sheets of carbon steel. Therefore, in addition to the surface analyses of the carbon steel sheets, the sheets were also cut and the inner sectors were observed by SEM and Optic microscope. The latter help us study the phase changes inside the sheets after each treatment.

6.1.1 Carbon steel transformation after activation with Ar at 800°C

The surface of the catalyst before any treatment was analyzed by SEM. The results are shown in Figure 6.1.

![SEM analyses of carbon steel before any treatment](image)

Figure 6.1 a, b SEM analyses of carbon steel before any treatment
The catalyst was heated to 800°C and kept at this temperature for an hour, followed by its cooling down to the room temperature. The catalyst was kept in a desiccator under pure Ar in order to prevent any oxidation before the SEM analysis. The pictures of this sample taken by high resolution microscope are shown in Figure 6.2, a,b,c.

Figure 6.2 a, b,c SEM analyses of carbon steel activated at 800°C with pure Ar

Comparing the pictures of 1mm magnification before (Figure 6.1 a) and after the thermal treatment (Figure 6.2 a) shows a formation of black marks on the surface. Mapping analysis
was done on the surface after the thermal treatment in order to detect the composition of the black regions. It is seen clearly in Figure 6.3 that on these black regions higher concentrations in carbon, and lower in iron are detected. This was also proved by elemental analysis shown in Figure 6.4. It may be concluded that small quantities of the carbon, one of the elements of the carbon steel, was driven out of the alloy structure during its thermal treatment at 800°C.

Figure 6.3 a, b, c, d Mapping analyses of carbon steel activated at 800°C with pure Ar
Figure 6.4 Elemental analyses of carbon steel activated at 800°C with pure Ar

Pictures of the catalyst before and after the thermal treatment with a scale of 10 µm are presented in Figure 6.5 a, b. With a higher resolution, it is seen that the structure of the carbon steel sheets is changed during its treatment. The surface before any treatments (Figure 6.5 a) seemed to be homogenous but after its thermal treatment (Figure 6.5 b) some boundaries were formed.
This observation led us to cut the sheets of carbon steel and analyze the inner section by SEM in order to find out if this transformation was only limited to the surface or if it existed inside too. The pieces of carbon steel were put in a resin as shown in Figure 6.6. They were cut and polished before being analyzed by the microscope.

Figure 6.6 carbon steel sample prepared for SEM analyses of the inner sections of the steel

Figure 6.7 show the SEM analyses of inner sections of the catalyst before and after the thermal treatment. It was proved that this phase/structural changes have occurred not only on the surface but also in the inside of the carbon steel sheets.
Figure 6. 7 SEM analyses of the inner sections of the steel a,b)before any treatment, c,d)after thermal activation with pure Ar at 800°C

The analyses done by Optical microscopy showed the same phase changes inside the sheets of carbon steel, Figure 6.8 a, b.

Figure 6. 8 Optical microscopy analyses of the inner sections of the steel a)before any treatment, b)after thermal activation with pure Ar at 800°C
6.1.2 Carbon steel transformation during its oxidation with air at 550°C

The surface of the catalyst was analyzed by high resolution scanning electron microscopy (SEM) after its oxidization with air at 550°C. The results are shown in Figure 6.9. Comparing to Figure 6.2 a, it is seen that the surface is transformed once again. The black marks have disappeared and new layer is formed on the surface (Figure 6.9 c).

![Figure 6.9 SEM analyses of carbon steel after oxidation with air at 550°C](image)

The elemental analyses (Figure 6.10 a) shows the existence of higher concentrations of oxygen after the oxidation step compared to Figure 6.10 b before its oxidation.
Figure 6.10 Elemental analyses of carbon steel a) before treatment, b) after oxidation with air at 550°C

The sheet of carbon steel was cut and its inner section was also analyzed by SEM, Figure 6.11. It is observed that a thin layer is formed on the surface of the sheet.
Figure 6.11 Elemental analyses of the inner section of carbon steel after oxidation with air at 550°C

The mapping analysis was performed in order to determine the composition of this layer Figure 6.12. It was clearly proved that the thin layer formed on the surface of the carbon steel during the oxidation step is iron oxide. This layer was homogenous and continuous all over the surface.
Figure 6.12 Mapping analyses of the inner section of carbon steel after oxidation with air at 550°C

6.1.3 Carbon steel transformation during its oxidation with air at 150°C

The surface of carbon steel sheets was observed by high resolution scanning electron microscopy after its oxidation with air at 150°C (Figure 6.13). Compared to the SEM pictures of the activate catalyst, Figure 6.2, it is found that some grains with light boundaries are formed.
Figure 6.13 SEM analyses of carbon steel after oxidation with air at 150°C

The mapping analyses on these grains (Figure 6.14) prove the existence of higher concentrations of oxygen and lower concentration of iron on these light boundaries. Therefore it is concluded that the oxidation at 150°C was mostly limited to the boundaries of the grains formed during the thermal activation step (Figure 6.5 b).
6.1.4 Carbon steel transformation during its oxidation with air at 25°C

The carbon steel thermally treated with Ar at 800°C was cooled down to the room temperature still under pure Ar. subsequently; it was exposed to ambient air at room temperature for two days. The steel was then analyzed by SEM (Figure 6.15 a, b, c, d). The surface was not exactly the same as the surface after its thermal activation with Ar. The pictures of SEM using Secondary Electrons show some bright regions on the surface.
Figure 6.15 SEM analyses of carbon steel after oxidation with air at 25°C

The elemental analyses done on different spots of the surface proved that these brighter regions were composed of high concentrations of oxygen and carbon Figure 6.16; this was proved to be the iron oxide layer formed in contact with the ambient air at room temperature.
6.1.5 Carbon steel after reforming reaction

The surface of the carbon steel catalyst after the reforming reaction was also analyzed by SEM. Carbon deposits on the surface were removed as much as possible, mechanically by a glass lamella. The results of this analysis are shown in Figure 6.17.
Figure 6. 17 a,b,c,d SEM analyses of carbon steel after reforming at 550°C

The surface is covered by graphitic carbon. However, elemental analyses spectra taken from different spots showed that some regions with higher concentrations of iron were present.

Figure 6.18
Figure 6.18 Elemental analyses of carbon steel after reforming at 550°C

6.1.6 Carbon steel after reforming reaction, without thermal treatment at 800°C

The carbon steel after reforming reaction at 550°C was analyzed by SEM. The pre-treatment of this catalyst was oxidation with air at 550°C but no thermal treatment at 800°C was performed. As it is seen in Figure 6.19 without the thermal treatment at 800°C the phase change and the grains observed in Figure 6.11 were not formed.
6.2 X-ray Diffraction Analyses

The analyses by X-ray Diffraction (XRD) were done on the catalyst before any treatment, after each step of pre-treatment and after the reforming reactions. It can be seen that during the thermal treatment with Ar, no new crystalline phase is formed (Figure 6.20). In Figure 6.21 it is observed that with an oxidation at room temperature, only traces of iron oxide were found on the surface, and the peaks of iron are unchanged.
Figure 6. 20 XRD analyses of carbon steel after activation with pure Ar at 800°C

Figure 6. 21 XRD analyses of carbon steel after oxidation at 25°C
Figure 6.22, shows the XRD analysis after oxidation at 150°C. It is seen that the peaks of iron oxide are not detected, although the presence of iron oxide was proved by SEM and elemental analyses (Section 6.1.3). This observation was due to the thickness of the oxide layer which was very thin and therefore the system was not capable to detect it as a crystalline phase.

![Diagram showing XRD analysis](image)

**Figure 6.22 XRD analyses of carbon steel after oxidation at 150°C**

Figure 6.23, shows the result of the XRD analysis on the catalyst after its oxidation with air at 550°C. Compared to Figure 6.20, the catalyst after activation with Ar, it is clearly seen that a new crystalline phase has been formed. This new phase is iron oxide, as it was expected, and its type is magnetite (Fe$_3$O$_4$). The other interesting fact observed was that the height of the two peaks of iron in Figure 6.23 are lower than the height of iron peaks in Figure 6.21. The explanation are that the XRD analyze only a thin layer on the surface, therefore while a thick oxide layer was formed on the surface after the oxidation the XRD detects the iron in the oxide layer and not the iron in the carbon steel, consequently the height of the detected iron peaks are decreased.
In Figure 6.24 a, and b, XRD analyses of catalyst after reforming are shown. However, the duration of the reaction was different for these two experiments. By comparing these spectra to the spectrum after oxidation (Figure 6.23), it is seen that after reforming the magnetite phase has disappeared, but a new phase is formed. The new phase is iron carbide ($\text{Fe}_3\text{C}$). It is interesting to compare the XRD spectrum after 15 minutes of reforming (Figure 6.24 a) to the XRD spectrum from a 400 minutes reforming (Figure 6.24 b). The height of iron carbide peaks is noticeably higher after a longer reforming reaction. This explains that the thickness or the quantity of the cementite phase has increased during the reforming reaction. This observation was in agreement with Chung et al.’s findings [CHUNG, et al., 2005].
Figure 6.24 XRD analyses of carbon steel after oxidation at 550°C a) 15 min reforming, b) 400 min reforming
6.3 Catalyst’s analyses results

In section 6.1 and 6.2 the transformation of the catalyst during its thermal-oxidative pre-treatment was shown. It was found that catalyst goes under an entire phase transformation during its thermal treatment at 800°C. During the oxidation step, depending on the oxidation temperature, different forms of a new phase appear on the surface of the catalyst. The results of XRD analyses along with Mapping and Elemental Analyses proved that the new phase formed during the oxidation step is iron oxide (Fe$_2$O$_4$). It was also found by XRD analyses that iron carbide (Fe$_3$C) was formed during the ethanol dry reforming reaction on the surface of the catalyst.
CHAPTER 7

CARBON ANALYSES

The carbon deposited during the reforming reaction was analyzed by SEM, elemental analyses, XRD, BET specific surface and finally TEM. It is important to mention that in all the experiments, the carbon deposited was in the form of carbon nano-filament (CNF). The difference observed was about the diameter and the length of the nano-filaments, and also about their structures: tubular, spiral, or ribbons.

7.1 High Resolution Scanning electron microscopy (SEM)

7.1.1 Carbon steel; Pre-treated with Ar at 800°C, cooled down to the room temperature, Oxidized at 25°C, ethanol reforming at 550°C

As it is seen in Figure 7.1, the carbon deposit produced in this experiment was in the form of nano-filaments; a mixture of tubular and spirals, with diameters ranging between 50 to 300nm. Many nano-filaments with diameters about 50-100nm were found. However, some irregular structures were also found in between the nano-filaments (Figure 7.2).
Figure 7. 1 SEM analyses of carbon deposit, catalyst activated at 800°C, oxidized at 25°C

Figure 7. 2 Carbon structures, catalyst activated at 800°C, oxidized at 25°C
7.1.2 Carbon steel; Pre-treated with Ar at 800°C, cooled down to the room temperature, Oxidized at 150°C, ethanol reforming at 550°C

The carbon deposited was a combination of tubular and spiral nano-filaments, with diameters ranging between 100 to 300nm Figure 7.3. The filaments have larger diameters than the filaments in the section 7.1.1. Very few filaments with diameters around 10nm were found Figure 7.3. However, the filaments are not always tubular; they also have hexagonal or square shapes (Figure 7.4). Some filaments with damaged walls were also found (Figure 7.4).

Figure 7.3 SEM analyses of carbon deposit, catalyst activated at 800°C, oxidized at 150°C

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7.1.3 Carbon steel; Pre-treated with Ar at 800°C, cooled down to 550°C, oxidized at 550°C, ethanol reforming at 550°C

The carbon deposited was a mixture of tubular and spiral nano-filaments, with diameters ranging between 5 to 300nm (Figure 7.5). However, bundles of nano-filaments with diameters of around 5 nm were also found (Figure 7.6). In the samples analyzed the percentage of these very small nano-filaments was about 10%. This was the first time that bundles of several nano-filaments with a diameter of about 5 nm were found.
Figure 7.5 SEM analyses of carbon deposit, catalyst activated at 800°C, oxidized at 550°C.
**Figure 7.6** Small nano-filaments, catalyst activated at 800°C, oxidized at 550°C

### 7.1.4 Carbon steel; Pre-treated with industrial N₂ at 800°C, cooled down to 550°C, Oxidized at 550°C, ethanol reforming at 550°C

As it is seen in Figure 7.7, the samples of carbon deposit were a mixture of tubular and spiral nano-filaments, with diameters ranging between 100 to 300nm. Only very few nano-filaments
with diameters about 5nm to 10 nm were found (Figure 7.8). Catalyst particles were detected, by back scattered electrons, at the extremes or in the junctions of filaments (Figure 7.9).

Figure 7. 7 SEM analyses of carbon deposit, catalyst activated at 800°C with industrial N₂

Figure 7. 8 Minuscule carbon nano-filaments, catalyst activated at 800°C with industrial N₂
7.1.5 Carbon deposit configuration after a short time reforming reaction, ethanol reforming at 550°C

In an experiment of reforming, using the catalyst (Pre-treated with Ar at 800°C, cooled down to 550°C, Oxidized at 550°C), the reaction was stopped after 15 minutes. The carbon deposit produced during 15 minutes was analyzed; the results are presented in Figure 7.10. Compared to a 400 minutes reforming reaction with the same operating conditions (Figure 7.5), it was seen that the structure of the carbon deposit is completely different. The carbon deposit in this experiment was in the form of agglomerations of short filaments (less than 1μm long) and shapeless carbon structures; however, nano-filaments usually observed in long period reactions had lengths larger than 4 or 5 μm.
Figure 7.10 Carbon deposit after 15 minutes of ethanol dry reforming

7.1.6 Carbon steel; Pre-treated with pure argon at 800°C, cooled down to the 550°C, Oxidized at 550°C, ethanol reforming at 500°C

The carbon deposit analyzed by SEM was in the form of carbon nano-filaments (Figure 7.11). They are mostly in the form of spiral filaments or narrow ribbons with diameters around 100nm-300nm; however few nano-filaments with diameters of 20nm were found (Figure 7.12). Catalyst particles were showed to be encapsulated inside the filaments (Figure 7.13).
Figure 7.11 Carbon deposit from ethanol dry reforming at 500°C

Figure 7.12 Very few tiny carbon nano-filaments, ethanol dry reforming at 500°C
Figure 7.13 Catalyst particles in CNF, ethanol dry reforming at 500°C

7.1.7 Carbon steel; Pre-treated with pure argon at 800°C, cooled down to 550°C, Oxidized at 550°C, ethanol reforming at 600°C

The carbon deposit analyzed by SEM is in the form of carbon nano-filaments (Figure 7.14). The average diameter of the filaments was between 100-300 nm, only very few nano-filaments with diameters around 20 nm were found. Catalyst particles were found at the end of the filaments or at the junction of the filaments. However, there was a significance difference between the structure of the filaments produced by reforming at 600°C and reforming at 550°C. The filaments found by SEM were longer than the filaments produced by ethanol reforming at 550°C (Figures 7.5, 7.6). The percentage of the tubular shape filaments compared to of the percentage of the spiral shape filaments was also larger in this experiment compared to the ethanol reforming at 550°C.
7.1.8 Carbon steel; Pre-treated with pure argon at 800°C, cooled down to 550°C, Oxidized at 550°C, ethanol cracking at 550°C

The carbon deposited through the cracking reaction was analyzed by SEM. The carbon was still in the form of carbon nano filaments; however, as it is seen in Figure 7.15, the filaments were in the form of spirals and ribbons rather than tubes. They were not as long as the nano-filaments found in section 7.1.7. However, they were similar to what we had in Section 7.1.6. If we compare the gas analyses with the results of section 7.1.6, we will see that the experiment at 500°C was catalytic cracking of ethanol rather than the reforming of ethanol, since CO₂ was not converted in this test. Therefore, it may be concluded that in the reactions of catalytic cracking of ethanol the produced carbon nano-filaments did not have high qualities (long, tubular and small filaments) as in the case of ethanol dry reforming reactions.
7.1.9 Carbon steel; Oxidized at 550°C, ethanol reforming at 550°C

In this experiment carbon nano-filaments were formed on the surface of a catalyst that did not go through the thermal treatment at 800°C. However the oxidative treatment of the catalyst with air at 550°C was done. The carbon deposit analyses are shown in Figure 7.16. It was observed that the filaments were not as long as in experiments with thermal treatment at 800°C. In addition the carbon deposit contained higher concentrations of catalyst particles comparing to the experiments with the same operating condition but with the thermal pre-treatment.
7.1.10 Bulk and surface carbon deposits

In a few experiments, carbon samples were taken both from the bulk of the carbon deposit and also from the carbon deposited against the surface of the carbon steel catalyst. Interestingly it was noticed that their structures are generally different. The bulk carbon had more regular filaments and sometimes filaments with smaller diameters than the carbon deposited on the surface. However, the carbon deposits against the catalyst surface were more damaged and had shapeless structures. Figure 7.17 compares the carbon sample taken from the surface of the catalyst in the experience 5.3.1. to the carbon sample taken from the bulk of the carbon produced Figure 7.18.
Figure 7.17 Carbon samples of the carbon deposited on the surface of the catalyst

Figure 7.18 Carbon samples of the bulk of carbon deposited during from ethanol reforming at 550°C
7.2 Elemental analyses

Samples of carbon nano-filaments were analyzed by elemental analyses and also by SEM using back scattered electrons. These analyses present some bright spots inside the nano-filaments structures, and mostly at their tips Figure 7.19.

![Image](image_url)

Figure 7. 19 Catalyst particles encapsulated in CNF, ethanol reforming at 550°C

The observation of the brighter contrast of the carbon monofilament particles than the carbon filaments is explained by the fact that these particles were composed of elements heavier than carbon, probably iron. The elemental analyses done on the carbon nano filaments detected three elements in the carbon deposit, carbon, iron and oxygen Figure 7.20. Based on these analyses, we can conclude that these light spot are composed of iron, oxygen and certainly of carbon.
Figure 7. 20 Elemental analyses on carbon deposit from ethanol reforming at 550°C

7.3 XRD Analyses

Samples of carbon nano-filaments was analyzed by XRD Figure 7.21. It was observed that the peaks of graphitic carbon were present; however additional crystalline phases were detected by XRD. These crystalline phases were iron carbides: Cementite, Fe₃C and Hagge-Carbide, Fe₅C₂.
Figure 7. 21 a,b,c XRD analyses on carbon deposit from ethanol reforming at 550°C

By combining the results of elementary analyses, XRD and SEM pictures it is concluded that the bright particles encapsulated inside or at the extremes of the filaments are possibly iron carbide particles. However, the fact that we also found the presence of oxygen in the carbon deposits may imply that these particles were partially composed of iron oxide and also of iron carbide.

7.4 Transmission Electron Microscopy

The carbon nano-filaments were analyzed by Transmission Electron Microscopy (TEM). The results are shown in Figures 7.22. It was seen that the carbon nano-filaments were not single or multi-wall tubes; on the contrary they had multi layer filamentous structures.
7.5 Carbon analyses result

In section 7.1 SEM analyses of carbon deposit in different experiments were presented. By comparing these results, it is concluded that with carbon steel as the catalyst, the carbon deposit was always in the form of CNF. However, the best quality CNF was obtained in the experiment with a pre-treatment procedure consisting of a thermal treatment at 800°C with pure Ar, cooled down to 550°C and oxidized with air at 550°C followed by the reforming at 550°C. It was also shown that the carbon deposits against the catalyst surface did not have the same structures as the bulk carbon but they were damaged and shapeless. It was found that reforming at 600°C gave the longest CNF, while in the experiments with high rates of ethanol cracking the carbon nano-filaments are usually spiral, ribbon or damaged.

In section 7.2 and 7.3 the Elemental and XRD analyses of the CNF were illustrated. Based on these results it was concluded that the CNF were composed of several phases; graphitic carbon, iron carbide and probably iron oxide. The graphitic carbon is related to the CNF themselves, as they are composed of layers of graphitic carbon. The iron carbide and the iron oxide phases are related to the light particles encapsulated inside or at the ends of the nano-filaments. In Section 7.4 TEM analyses of the CNF are presented and it was shown that the carbon nano-filaments were multi layer filaments and not nano-tubes with single or multi-walls.
CHAPTER 8

CATALYTIC PROPERTIES OF CARBON NANO-FILAMENTS

8.1 Introduction

For the first 80 years of the last century, the occurrence of carbon nano-filaments (CNF) in certain chemical processes was considered as a nuisance. However, recently several researchers have explored the use of CNF in several applications, such as additives in polymers [KIM, et al., 2005, XU, et al., 2006], as gas storage medium [MENG, 2006] and as catalyst support material. In particular, Zhi-jun Sui et al. [ZHI-JUN SUI, et al., 2003] have studied their properties as an effective support for catalysts used in ethanol partial oxidation reactions. Other research groups have also used CNF products; as catalysts supports [BAKER, et al., 1999, BAKER, et al., 2001], or as an actual catalyst for the oxidative hydrogenation (ODH) of ethylbenzene, to produce styrene [LEDOUX, et al., 2003].

In the work reported by Zhi-jun Sui et al. [ZHI-JUN SUI, et al., 2003], in order to remove the metal-based inclusions, the used CNF was repeatedly washed in 2 mol/l HCl over a 7 day period, followed by thorough washing of the filtered CNF with large amounts of deionized water, until the filtrate was neutral with a pH close to 7, then dried at 120 °C overnight. Baker et al. [BAKER, et al., 1999], who also used the CNF as catalyst support, have previously removed the occluded metal-based particles through dissolution in 1M HCl and further thorough washing in deionised water, before overnight air drying treatment at 110°C. In the present work, the “as synthesized” CNF, without any special pre-treatment, have been tested for their catalytic activity in ethanol dry reforming ethanol cracking reactions.

Recent published work by Abatzoglou et al. [ABATZOGLOU, et al., 2006a, ABATZOGLOU, et al., 2006b] has shown that the catalytic dry reforming of ethanol can; a) produce a H₂-rich synthesis gas, and b) sequester gaseous CO₂ under the form of solid CNF, using iron alloy catalysts. It has also been shown that a two step, thermal-oxidative activation pre-treatment of the carbon steel is necessary.

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The present work examines the catalytic properties of CNF, produced through ethanol dry reforming and ethanol cracking reactions. For this purpose, the conversion of ethanol and CO₂, as well as the compositions and volumes of gases, produced in both the presence and the absence of CNF, are compared to those obtained in tests using carbon steel as the catalyst. The CNF produced were analyzed by SEM and TEM (Transmission Electron Microscope) to simultaneously explore their structures, size distribution and homogeneity. SEM analyses have confirmed the presence of iron-based particles encapsulated in the produced CNF. Elemental and X-Ray diffraction analyses of the CNF product have determined that the sub-particles, found inside their structures, are mainly composed of iron carbides. The latter part of this chapter reports the results of a series of experiments that have shown that the activity of the CNF is related to the presence of these iron carbide particles. The turnover frequency (TOF) values, defined as the rate of products generation, over the quantity of iron present in the catalyst, were calculated in order to compare the catalytic activity of the CNFs with that of the carbon steel. The iron content in the CNF was obtained by standard Atomic Absorption (AA) analyses.

Since the exact number of the active sites is not known, due to a lack of knowledge regarding the catalytic mechanism, the quantity of Fe was chosen as being representative of the active sites. The assumption is that all iron compounds, as used in all of the tests, have the same density of active sites (Number of active sites per unit mass of Fe). As mentioned by Boudart [BOUDART, 1995], TOF is a chemical reaction rate, dependant on the temperature, pressure and concentration values. The advantage of calculating the TOF is that although the value of TOF may be calculated only approximately, due to the approximations in counting the catalytically active sites, it is useful for assessing the potential of new catalytic materials, compared to the catalysts in current use.
8.2 Experimental procedure

The experimental work performed consisted of:

Step 1: Dry reforming of ethanol, using low carbon steel as the catalyst; this step produced the tested CNF;

Step 2: Ethanol Cracking and Dry reforming tests, using the produced in step 1 CNF as catalyst.

Dry reforming reactions of step 1 were conducted in the fixed-bed, isothermal reactor, at 550°C over a 2h period using the above described pretreated strips of carbon steel as catalyst. The molar ratio of the input Ethanol/CO₂ reactants was 1, and when catalysts were used, the overall GHSV (Gas Hourly Space Velocity) was of 2 300ml/h/g and 1.15 m³/ (h*m²), based on the geometrically calculated surface area of the catalyst (the strips of carbon steel are non porous and consequently the internal surface is negligible). In order to keep equivalent reaction conditions in the tests without catalysts, the chosen gas flow rates remained the same. The catalyst employed in step 1 consisted of a sheet of low carbon (0.1%) steel, having been thermally pre-treated at 800°C and then, partially oxidized at 550°C. Carbon nanostructures were formed on the carbon steel catalyst surface during the reforming reaction, being denoted as “first generation CNF”, and were shown to have diameters ranging between 5 and 200 nm (Figure 8.1). They are recovered by mechanical means and subsequently “analyzed”, using SEM, TEM, FEGSEM (Field Emission Gun Scanning Electron Microscope) and XRD methods.
The following experiments of step 2 were designed to study the catalytic properties of the CNF products:

1. Liquid ethanol, at a flow rate of 0.33 ml/min, Ar at a flow rate of 140 ml\textsubscript{STP}/min, (At Standard Temperature and Pressure) glass wool as the support.

2. Liquid ethanol at a flow rate of 0.33 ml/min, CO\textsubscript{2} at a flow rate of 140\textsubscript{STP}ml/min, glass wool as the support.

3. Liquid ethanol at a flow rate of 0.33 ml/min, Ar at a flow rate of 140ml\textsubscript{STP}/min, 4g CNF as the catalyst, glass wool as the support.

4. Liquid ethanol at a flow rate of 0.33 ml/min, CO\textsubscript{2} at a flow rate of 140ml\textsubscript{STP}/min, 4g CNF as the catalyst, glass wool as the support.

The CNF used as the catalyst was “fixed” at the reactor center, using an inert dispersion matrix of glass wool (3 g), supported on the tubular quartz cover of the central thermocouple. Tests, without CNF being present, were performed to set a “reference point” for the ethanol thermal cracking and thermal dry reforming reactions. Tests with EtOH and Ar (i.e., the absence of CO\textsubscript{2}) were planned in order to study the catalytic properties of the CNF, with respect to the ethanol cracking reaction. The temperature was set at 550\textdegree C for both the cracking and dry reforming tests, in order to maximize carbon formation (i.e., conditions thermodynamically favouring carbon formation). The molar ratio of the input EtOH/Ar was
set at 1. Ar was added in the case of thermal cracking in order to maintain the same overall GHSV, and consequently, to have the same ethanol concentration present in the gaseous reactants at the entrance of the reactor, as in the tests performed with CO₂. Tests with EtOH and CO₂ were planned to study the catalytic properties of the CNF in the dry reforming reaction. The operating parameters for the reaction of Ethanol and CO₂ are the same as for the Ethanol dry reforming case, using the carbon steel catalyst.

SEM analyses on the CNF product demonstrated the presence of particles encapsulated in their tubular structures (Figure 8.2) Elemental analyses of the CNF (Figure 8.3) showed that these particles were composed of iron, oxygen and carbon.

Figure 8.2 SEM of preliminary CNF

Figure 8.3 Elemental analysis CNF
In addition, the XRD analyses (See Figure 8.4) showed that these particles were mainly composed of Iron carbides. Following the initial reaction tests, an additional series of experiments was set-up in order to study the effect of the particles, encapsulated in the CNF, on the catalytic activity of the latter. Although it was found by the XRD analyses that “encapsulated” particles in the CNF are mainly composed of iron carbide(s), their exact role in the reforming reactions remains still unknown. Thus, the mass of Fe was chosen to be representative of the amount of catalytically active sites for the reforming reactions taking place. The actual amount of iron present in the CNF was obtained by AA analysis.

![Graph with peaks at different intensity levels](image)

**Figure 8.4 XRD analysis of the bulk of first-generation CNF**

For the purpose of studying the effect of encapsulated particles on the catalytic properties of CNF, some 25g of a “first generation” CNF was produced, via the reaction of ethanol dry reforming, using carbon steel as the catalyst. An additional series of experiments was designed as follows:

1- A 2h ethanol dry reforming experiment was performed, under operating conditions as described above, using 4g of “first generation” CNF as the catalyst. The GHSV in the experiment, using the “first generation” CNF as the catalyst, was 121 000ml/h/g, based on the quantity of Fe measured in the CNF, by AA analysis. The total weight of CNF recovered, at
the end of reaction, was 7.95 g. The carbon produced, named as the “second generation” CNF, was analysed by SEM, and was also under the form of CNF (Figure 8.5).

Figure 8.5 SEM analysis of second-generation CNF

2- This “second generation” CNF was thoroughly homogenized and 4g of the resulting material were used as the catalyst for another reforming experiment; at the end of the reforming experiment 7.7g of a third generation carbon product was obtained. The GHSV in this experiment was 348 000ml/h/g, based on the quantity of Fe present in the second generation CNF. This third generation material also proved to be in the form of CNF. (Figure 8.6)
3- The same procedure was repeated to produce a fourth generation CNF product, through the reforming reaction of ethanol, from the third generation CNF. The GHSV was 790 000ml/h/g, based on the quantity of Fe present in the third generation CNF.

The experiment operating conditions, the produced gas composition and the mass of carbon nano-filaments produced, are shown in Table 8.1. By mixing and dividing the homogenized CNF into 2 equal mass samples at each step, we intrinsically made the hypothesis that the quantities of particles encapsulated in the CNF are also equally divided by 2. The precise quantities of Fe found in the “different generations” of the CNF product, as obtained by AA analyses, are shown in Table 8.1. It can be seen that this hypothesis cannot be rejected statistically. All tests were performed in the previously described, bench-scale isothermal, fixed-bed quartz reactor. The composition of the gas produced was analysed by means of the “on-line” gas chromatograph.
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<th>3rd generation CNF catalyst</th>
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<td>90.63%</td>
<td>96.76%</td>
<td>43.56%</td>
<td>46.07%</td>
</tr>
<tr>
<td>Conversion (CO₂)</td>
<td>32.13%</td>
<td>14.22%</td>
<td>-0.53%</td>
<td>-1.07%</td>
<td>-1.842%</td>
<td>-18.42%</td>
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</tr>
<tr>
<td>Exit liquid ETOH (ml)</td>
<td>0.08</td>
<td>0.34</td>
<td>3.17</td>
<td>3.99</td>
<td>1.32</td>
<td>18.17</td>
<td>16.94</td>
</tr>
<tr>
<td>Exit liquid water (ml)</td>
<td>3.52</td>
<td>2.49</td>
<td>3.05</td>
<td>4.37</td>
<td>2.73</td>
<td>2.48</td>
<td>3.58</td>
</tr>
<tr>
<td>H₂ (ml/min)</td>
<td>323</td>
<td>278</td>
<td>260</td>
<td>189</td>
<td>395</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>CO (ml/min)</td>
<td>181</td>
<td>155</td>
<td>138</td>
<td>108</td>
<td>73</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>CO₂ (ml/min)</td>
<td>95</td>
<td>120</td>
<td>141</td>
<td>142</td>
<td>16</td>
<td>166</td>
<td>0.1</td>
</tr>
<tr>
<td>CH₄ (ml/min)</td>
<td>18</td>
<td>21</td>
<td>19</td>
<td>20</td>
<td>21</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>TOF(H₂) (1/sec)</td>
<td>0.00002</td>
<td>0.00099</td>
<td>0.00267</td>
<td>0.00424</td>
<td>0.00143</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TOF(CO) (1/sec)</td>
<td>0.00017</td>
<td>0.00777</td>
<td>0.01884</td>
<td>0.03390</td>
<td>0.00369</td>
<td>N/A</td>
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</tr>
<tr>
<td>TOF(CO₂) (1/sec)</td>
<td>0.00014</td>
<td>0.00944</td>
<td>0.03184</td>
<td>0.06994</td>
<td>0.00124</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TOF(CH₄) (1/sec)</td>
<td>0.00001</td>
<td>0.00060</td>
<td>0.00153</td>
<td>0.00361</td>
<td>0.00061</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Treaction</td>
<td>550</td>
<td>550</td>
<td>550</td>
<td>550</td>
<td>550</td>
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<td>550</td>
</tr>
<tr>
<td>Total error C</td>
<td>-0.03</td>
<td>-0.09</td>
<td>-0.04</td>
<td>0.04</td>
<td>0.15</td>
<td>0.14</td>
<td>0.30</td>
</tr>
<tr>
<td>Total error H</td>
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<td>-0.06</td>
<td>0.00</td>
<td>0.12</td>
<td>-0.13</td>
<td>0.17</td>
<td>0.10</td>
</tr>
<tr>
<td>Total error O</td>
<td>0.03</td>
<td>-0.02</td>
<td>-0.11</td>
<td>-0.06</td>
<td>0.02</td>
<td>-0.12</td>
<td>-0.13</td>
</tr>
</tbody>
</table>
8.3 Results

8.3.1 CNF as the catalyst of ethanol dry reforming and ethanol cracking

The results of the series of ethanol dry reforming and ethanol cracking experiments described above are summarized in Tables 8.2 and 8.1.

The results of the reforming experiences, using carbon steel and CNF as the catalyst, can be compared by reference to Table 8.1. The first generation of CNF product shows 100% conversion of the input ethanol. The volume of H₂ and CO gases produced are also comparable to the volumes of H₂ and CO produced by the "dry reforming" of ethanol with carbon steel. It can be seen that the quantity of Fe present in the 1st generation CNF, used as the catalyst for the production of the 2nd generation CNF, is 1/53 times the quantity of iron present in the carbon steel used as the catalyst. However, its TOF is 46 times the TOF of the 1st generation CNF experiment. This observation indicates that the 1st generation CNF is slightly less active than the carbon steel catalyst, but this difference could be due to the systematic experimental error.

**TABLE 8.2 RESULTS OF THE DRY REFORMING WITH DIFFERENT GENERATIONS OF CNF**

<table>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂ (ml/min)</td>
<td>CO₂ (ml/min)</td>
<td>CH₄ (ml/min)</td>
<td>CO (ml/min)</td>
<td>EtOH</td>
<td>CO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st</td>
<td>323</td>
<td>95</td>
<td>18</td>
<td>181</td>
<td>99.8</td>
<td>32.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>2nd</td>
<td>278</td>
<td>120</td>
<td>21</td>
<td>155</td>
<td>99.1</td>
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<td>3rd</td>
<td>260</td>
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<td>19</td>
<td>138</td>
<td>92.0</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4th</td>
<td>189</td>
<td>142</td>
<td>20</td>
<td>108</td>
<td>90.6</td>
<td>-1.0</td>
<td></td>
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</tr>
</tbody>
</table>

The results of the experiments performed in the absence and the presence of CNF, can also be compared in Table 8.1. In the ethanol dry reforming experiments, using first generation CNF
as the catalyst, the ethanol conversion was 99%, while without the CNF catalyst, ethanol conversion was reduced to only 43%. A 100% increase in the CNF mass was also observed in the presence of the CNF, while no carbon was deposited on the surfaces of the glass wool used in the experiment performed without CNF. The volume of the \( \text{H}_2 \) produced through the dry reforming of ethanol in the presence of CNF, was about 20 times the volume of \( \text{H}_2 \) obtained under the same operating conditions, but without the CNF.

In the case of the experiment with EtOH/Ar, the volume of \( \text{H}_2 \), produced through the cracking of ethanol in presence of CNF, was some 10 times the volume of hydrogen obtained under the same operating conditions without CNF. Ethanol conversion in presence of the first generation CNF was 97%, while the conversion was only 46% for the experiment of EtOH/Ar, without CNF. A 180% increase in the CNF mass was observed in the presence of CNF, while no carbon was deposited on the surface of the glass wool in the experiment without CNF.

The greater volumes of the \( \text{H}_2 \) and CO gases produced, as well as the higher conversion levels of ethanol, along with the deposition of carbon nano-filaments, observed in the experiments performed with CNF, proves, once again, that the CNF, formed through the dry reforming reaction of ethanol over the carbon steel catalyst, is an active catalyst for both the ethanol cracking and the dry reforming reactions.

The first generation, carbon nano-filaments were analysed before being used as catalysts. The BET (N\(_2\)) surface area values of the nano-filaments range from 125 to 155 m\(^2\)/g, depending on the particular structural conformation adopted. TEM analysis (Figure 7.22) demonstrates that these tubular carbon filaments have multilayer structures. The average diameter for the primary produced CNF was between 100-200nm, while a few nano-filaments were also found in the diameter range of 5-50nm (See Figure 8.1).

In the SEM analyses of the first generation CNF, the existence of agglomerations of carbon that contain higher concentrations of catalyst particles than the carbon filaments (Figure 8.7 a) were observed. This can be explained by the fact that the first generation CNF also includes the layer of carbon, deposited directly on the surface of the carbon steel catalyst; this layer was removed by mechanical means and was added to the bulk of the CNF. The carbon that was in contact with the metal surface contains the highest amounts of catalyst particles. The XRD analyses (Figure 8.4, 8.8), as reported later in this section, validates this hypothesis.
8.3.2 Catalytic properties of CNF: Active Iron Carbide particles

The carbon deposits produced in subsequent reforming experiments, as described in the experimental procedure section, were analyzed by SEM. It was shown that they are also in the
form of CNF, however, it was also observed that the subsequent CNF materials have narrower size distributions than the first generation CNF (Figure 8.7 b). The other difference lies in the quantity of encapsulated catalyst particles found in the CNF. SEM analyses show that the quantity of the catalyst particles, detected by SEM analysis, decreases over successive reforming experiments (Figure 8.7 b). As is seen in Table 8.1, this observation was confirmed by the quantity of Fe, obtained by means of AA analyses of successive generations of CNF. As expected due to the addition of the new CNF, it was found that the %w/w of Fe is reduced through each successive generation of the CNF.

XRD analyses were carried out on the CNF from different generations. Graphite and two types of iron carbides are shown to be the crystalline phases present in the CNF (Figure 8.4). For the first generation, produced via the ethanol dry reforming process on the carbon steel catalyst, a sample of the thin layer of carbon, deposited directly on the surface of the steel, was analyzed separately from the bulk of the carbon. As can be seen in Figure 8.8, the carbon sample taken from the thin carbon layer, deposited directly on the carbon steel surface, contains higher concentrations of iron carbides, compared to samples taken from the bulk carbon nano-filaments (Figure 8.4). This observation is in agreement with our microscopic observations of catalyst particles present in the thin layer of the first generation CNF, deposited directly on the surface of the carbon steel catalyst.
Figure 8.8 XRD analysis of the thin layer of CNF deposited on the catalyst surface

The XRD analyses show significant differences between the spectrum of the first generation CNF, and the spectrum of successive CNF generations (Figure 8.9 a, b). This difference is related to the heights and widths of the peaks associated with iron carbide and graphite. In the first generation CNF, the iron carbide peaks are very well defined. As we go forward through our successive experiments, these peaks become broader; perhaps an indication of the formation of new crystalline phases or products having smaller iron carbide particles [LI, et al., 2004]. It is also important to note that the height of the peak related to the presence of graphite (2θ = 26.3°), increases with the number of the CNF generation. It is observed in Figure 8.9 a, that the greatest concentration of iron carbide is that of the sample taken from the first generation CNF. However, it is also seen that no significant difference is observed between successive generations, beyond the second generation.
Figure 8. 9 a Comparison of XRD analyses of successive CNF generations
8.4 Discussion

SEM analysis of the primary CNF shows several catalyst particles encapsulated within the nano-filaments (Figure 8.7). Elemental analysis of these particles (Figure 8.6) shows that they are composed of Fe and carbon. XRD analysis of the CNF (Figure 8.9) detects two types of iron carbide in the produced CNF, in addition to the graphite phase. Based on the results of the above analyses, it is confirmed that the encapsulated particles, as found in the CNF by SEM analyses, are composed of iron carbide. It is therefore concluded that iron carbide particles, formed during the dry reforming of ethanol on the surface of the carbon steel, were then separated from the metal surface and encapsulated in the CNF.

The results of the series of reforming reactions, as summarized in Table 8.2, prove that the first generation CNF have the greatest catalytic activity in ethanol dry reforming reaction. As we progress over the series of successive experiments, using the CNF derived from the first generation to the fourth generation tests, the conversion of both ethanol and CO₂ decrease. This decrease is accompanied by decreasing volumes of produced H₂. This phenomenon can
be explained by relating the catalytic properties of the CNF for promoting the ethanol dry reforming reaction, as well as for the catalytic cracking of the EtOH, to iron carbide particles encapsulated within the CNF. The particular catalytic activity of the iron carbides has been reported in the literature by Sacco et al.[ SACCO, et al., 1984] , Ruston et al. [RUSTON, et al., 1969], Boehm [BOEHM, 1973], Li et al. [LI, et al., 2004] and also by Emmenegger et al. [EMMENEGGER, et al., 2003].

As it has been described above, the particles identified by the SEM analyses are composed of iron carbide. By subdividing the homogenized CNF product produced during each process step, each succeeding generation of the CNF product contains lesser amounts of iron carbide than its predecessor. Therefore, based on the amounts of iron present, determined by AA analyses, the third generation CNF has only 0.16 of the iron quantity present in the first generation CNF. Consequently, the values of GHSV, generated in the tests producing the second and fourth generation CNFs, would be 121 000 ml/min/g and 790 000 ml/min/g respectively, based on the quantity of Fe involved (Table 8.1). By comparing the ethanol and CO₂ conversions, as well as the volume of hydrogen produced for these two experiments, it can be seen that the catalytic “activity” of third generation CNF is lower than that of first generation CNF. However, the change in the TOFs values is nearly proportional to the quantities of iron present in the successive CNF generations; the very small deviations observed may be due to experimental errors and are not considered to be statistically significant. These results validate the iron carbide “hypothesis”, i.e. their being the active catalysts involved in ethanol reforming. As seen in Table 8.2, following the third generation of CNF, the CO₂ conversion had fallen to zero, thus the series of “experiences” were stopped at the CNF fourth generation. However, it is also seen that, even when the conversion of CO₂ is reduced to zero, ethanol is still “converted” at the 90% level and the high hydrogen volumes are still produced. This is an indication that ethanol cracking is also catalyzed by the CNF.

Ermakova et al. [ERMAKOVA, et al., 2001]. Ermakova et al. [ERMAKOVA, et al., 2001] reported and proved the so-called carbide Fe₃C cycle, suggested by Buyanov, for the mechanism of the growth of carbon filaments over iron based catalysts. On the basis of this model, as reported by Ermakova et al. [ERMAKOVA, et al., 2001] and De Jong et al. [DE JONG, et al., 2000] the hydrocarbon gas dissociates fully to separate carbon and hydrogen atoms, on the metal surface. The H₂ molecules then desorbs, while the “solid” carbon dissolves in the bulk metal and forms metal carbides. The metal carbides then decompose to separate metal particles and molecular graphite. Individual metal particles are “squeezed out” because of the increasing internal pressure due to graphite layer formation at the internal surfaces of the graphite “envelope” and the “liquid like” behaviour of the metal phase under these conditions. As soon as the free metal phase is “forced out” the “fresh” particle surface is exposed to the hydrocarbon and the growth continues.

The same mechanism can now also be reasonably proposed to explain the catalytic properties of the CNF. The “preliminary” CNF material encapsulates several iron carbide particles, most often at their “extended” tips. The reactants, ethanol and CO₂ in this case, are adsorbed, then decomposed and being involved in reactions on these particles’ surfaces. Through the carbon phase deposited during this reaction, the growth of the CNF is able to continue at the rear surfaces of these iron carbide particles, or newly formed CNF may nucleate as well. However, the details of this nucleation mechanism are, as yet, unknown and additional work is required to elucidate the mechanism.

8.5 Conclusions

The results of this study confirm that the CNF, as produced by the dry reforming of ethanol, using low carbon steel as a catalyst, are active in the reactions of ethanol dry reforming and ethanol cracking, under the reaction conditions studied in this work. They are also able to sequester the CO₂ gas in the form of CNF. The reactivity of the so produced CNF, has proved to be related to iron carbide particles, encapsulated in their structures, and it is shown that the reactivity depends on the concentration of iron carbides present; i.e., the higher the concentration of iron carbides, the more active are the CNF particles. The mass of the CNF,
used as the catalyst, was increased by 100% and 180% through the ethanol reforming and ethanol cracking reaction tests, respectively. Carbon deposits, generated during these reactions, were shown to be made of CNF particles, of a lower average diameter than the primary CNF. These deposits contain considerable amounts of CNF particles, with diameters falling within the range of 5-50 nm.
CONCLUSION

Catalytic reforming of ethanol with CO₂ as a technique to produce hydrogen gas and to sequester the green house effect gas CO₂ in the form of carbon deposit was investigated. Carbon steel was proposed as a potential catalyst for ethanol reforming with CO₂ and the sequestration of CO₂ in the form of carbon nano-filaments. It was proved that a thermal-oxidative pre-treatment is necessary to activate catalytic properties of carbon steel for ethanol dry reforming. However for the oxidation step it was proved that even the very small amount of oxygen present in industrial N₂ or an oxidative gas such as CO or CO₂ is enough to oxidize the carbon steel and make it active as a dry reforming catalyst.

The effect of different operational conditions on the activity of carbon steel and the quality of the carbon nano-filaments was studied. Based on these experimental results an experimental protocol was developed through which the highest yield of hydrogen and highest quality of carbon nano-filaments were obtained.

It was proved that carbon steel is a stable catalyst for ethanol dry reforming and the carbon deposit formation on the surface does not deactivate the catalyst. Moreover the two dimensional structure of carbon steel made it possible to regenerate the slightly decrease of its activity during time by removing the carbon deposit mechanically from its surface without harming its activity.

At these operation conditions, it was proved that thermal reforming and thermal cracking of ethanol catalytic is not favored and no carbon deposit is formed in the absence of carbon steel. However, catalytic cracking of ethanol may take place. Consequently, in the experiments with both CO₂ and ethanol as the reactive gases and in the presence of carbon steel, both the cracking and reforming reactions may take place simultaneously. The higher the conversion of CO₂ and the lower the volume of methane or ethylene, the higher is the rate of ethanol catalytic reforming compared to ethanol cracking.
The experimental results were compared to the thermodynamic calculations at equilibrium. It was observed that yields/volumes of Hydrogen and CO produced were always greater than the volume calculated theoretically. The mass of carbon deposit was always less than the calculated weight.

The results of this study confirm that the CNF, produced by the dry reforming of ethanol over carbon steel, are active in the reactions of ethanol dry reforming and ethanol cracking, under the reaction conditions studied in this work. They are also able to sequester the CO$_2$ gas in the form of CNF. The reactivity of the so produced CNF, has proved to be related to iron carbide particles, encapsulated in their structures, and it is shown that the reactivity depends on the concentration of iron carbides present; i.e., the higher the concentration of iron carbides, the more active are the CNF particles. Carbon deposits, generated during these reactions, were shown to be made of CNF of a lower average diameter than the primary CNF.

A mechanism was proposed for the growth of carbon nano filaments from the formation of an intermediate iron carbide phase. However further investigations required in order to understand the exact mechanism of the formation of carbon nano-filaments.
The picture of a carbon nano-filament in the form of heart, taken by high resolution scanning electron microscopy (SEM) during analyzing the carbon deposited on the surface of carbon steel during ethanol dry reforming at 550°C.
REFERENCES


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