

Oxidative dehydrogenation of ethylbenzene as a test reaction for carbon-based catalyst

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Omar Alberto Mayorga Vielma

Fakultät für Chemie
der Universität Duisburg-Essen

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Gutachter: Prof. Dr. Robert Schlögl
Prof. Dr. Malte Behrens
Vorsitzender: Prof. Dr. Gebhard Haberhauer

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Motivation

In the continuous searching of new alternatives for processes with high environmental impact on the production of chemicals, the industrial process of styrene can be considered among the technologies that need to be optimized or even replaced to diminish the required high energy demand.

Many progresses on the development of improved methods at industrial scale have been accomplished. However, all those processes are based on the catalytic dehydrogenation of ethylbenzene which is a highly endothermic reaction that requires high temperatures to take place.

On the other hand, the oxidative dehydrogenation of ethylbenzene (ODH) as an exothermic reaction could be considered a good alternative to create a sustainable energy technology. Carbon-based materials have been one of the most popular catalysts for this reaction showing in general good performance and high stability. Our motivation was to use this reaction as an application of multiwalled carbon nanotubes (MWCNT) with vanadium deposited by means of atomic layer deposition (ALD). We focused mainly on how their morphology plays a role in the catalytic activity, analyzed the active sites and the contribution of the vanadium species on the catalytic performance. Therefore, we wanted to obtain deeper knowledge of this reaction and the role of the catalysts by identifying the active sites, and thus, contributing with new ideas that could help on the development of carbon-based materials as effective catalysts at industrial scale.

Summary

The development of green sustainable energy technologies has been one of the biggest challenges in the chemical industry nowadays. Many processes must be enhanced in order to avoid high waste of energy and natural resources. Undoubtedly, the industrial production of styrene is a method that due to its high endothermicity and harsh conditions, consumes large amounts of energy. The waste of water is significant in this technology, since it is used as steam to meet the requirements of reaching high temperatures in order to perform the reaction. Many other drawbacks such as low equilibrium conversion and high production costs increase the necessity of developing new alternatives for this process.

Among many new technologies applied in order to develop new systems that allow decreasing the waste of energy and misuse of water in a large degree, the progress on the ODH of ethylbenzene studies has been playing an important role in this matter. The addition of oxygen to the catalytic dehydrogenation turns this reaction in exothermic, which means that it can be carried out at lower temperatures and milder conditions. The use of steam is omitted and it can reach higher conversions since it is a non-equilibrium reaction.

However, so far the big challenges in the ODH research have been to find a proper catalyst that gives good results regarding activity and stability in order to be able of being used at industrial scale. The evaluation of carbon-based catalysts for this reaction is not a new topic in this field. Normally, these materials are active due to the availability of oxygen functional groups on their surface. Nevertheless, the main drawback is the tendency of total oxidation of the catalyst, mainly due to their structure and the interaction with the oxygen present in the reaction stream. Therefore, to get the right morphology is a critical step for this catalytic system.

Nanocarbons are considered among the most promising catalysts due to its unique structure that unlike amorphous carbon materials has the property of keeping high stability towards total oxidation.

In this work, catalytic measurements of different carbon-based catalysts were performed. These catalysts were MWCNTs functionalized by means of acid treatment and afterwards vanadium was deposited with different concentrations on the carbon surface using the ALD method. Vanadium is a well-known metal with good catalytic properties for many reactions including the ethylbenzene ODH. Previous studies point out that vanadium could be active for this reaction only when it is well dispersed on the catalyst surface. A uniform and effective deposition was possible by using the ALD device developed in our group.

The first step in this work was to design and built-up a reactor setup able to perform the catalytic test. Afterwards, the evaluation of all MWCNTs took place and it was mainly focused on the study of the activity and stability of the carbon structures itself and to determine whether the vanadium species on the surface have an influence on the catalytic properties of the nanotubes.

The kinetic results suggested that all the materials were active and stable at the chosen reaction conditions even at long time on stream, confirming the already known good properties of these materials. Regarding the influence of vanadium there was an improvement on the activity with low loadings and a negative influence with higher loadings. The contribution of vanadium active sites only takes place when there are single sites that form the active V^{5+} species which are able to react with the ethylbenzene and form styrene. Nevertheless, higher vanadium loadings lead to agglomerations and deactivation of the catalyst.

Further characterizations of the tested materials in the ODH reaction were carried out in order to get more information regarding modifications on the structure and content of the active groups before and after the reaction.

Thermogravimetry combined with mass spectrometry (TG-MS), temperature program oxidation (TPO) and transmission electron microscopy images (TEM) provided valuable information regarding the modification that the nanocarbon structures undergo during the reaction. It was found that there is always the presence of an active coke layer on the surface that is formed during the reaction and remains stable after long time on stream. The most active catalysts showed on the TEM images a thicker layer of this amorphous carbon which was almost negligible for the less active samples. Further analysis confirmed that most of the active groups were presumably located on this coke layer. Therefore, the formation of active amorphous carbon was the critical step where vanadium at low concentrations might play a role of enhancing building up of this layer.

Zusammenfassung

Die Entwicklung umweltfreundlicher nachhaltiger Energietechnologien ist heute eine der größten Herausforderungen in der chemischen Industrie. Viele Prozesse müssen verbessert werden, um einen hohen Verbrauch von Energie und natürlichen Ressourcen zu vermeiden. Zweifellos ist die industrielle Herstellung von Styrol ein Verfahren, das aufgrund seiner hohen Endothermität und der rauen Bedingungen große Mengen an Energie verbraucht. Die verwendete Menge an Wasser ist bei dieser Technologie erheblich, da es als Dampf eingesetzt wird, um die Anforderungen an das Erreichen hoher Temperaturen für die Durchführung der Reaktion zu erfüllen. Viele weitere Nachteile wie der geringe Gleichgewichtsumsatz und die hohen Produktionskosten erhöhen die Notwendigkeit, neue Alternativen für diesen Prozess zu entwickeln.

Unter vielen neuen Technologien zur Entwicklung neuer Systeme, mit denen der Verbrauch von Energie und Wasser in hohem Maße verringert werden können, spielen die Fortschritte bei der ODH von Ethylbenzol in diesem Bereich eine wichtige Rolle. Durch die Zugabe von Sauerstoff zur katalytischen Dehydrierung wird diese Reaktion exotherm, was bedeutet, dass sie bei niedrigeren Temperaturen und milderen Bedingungen durchgeführt werden kann. Die Verwendung von Dampf entfällt und sie kann höhere Konversionen erreichen, da es sich um eine Nicht-Gleichgewichtsreaktion handelt.

Bisher waren die großen Herausforderungen in der ODH-Forschung jedoch, einen geeigneten Katalysator zu finden, der gute Ergebnisse in Bezug auf Aktivität und Stabilität liefert, um im industriellen Maßstab eingesetzt werden zu können. Die Bewertung von Katalysatoren auf Kohlenstoffbasis für diese Reaktion ist in diesem Bereich kein neues Thema. Normalerweise sind diese Materialien aufgrund der

Verfügbarkeit von Sauerstoff-funktionalisierten Gruppen auf ihrer Oberfläche aktiv. Der Hauptnachteil ist jedoch die Tendenz zur Totaloxidation des Katalysators, hauptsächlich aufgrund ihrer Struktur und der Wechselwirkung mit dem im Reaktionsstrom vorhandenen Sauerstoff. Daher ist die richtige Morphologie ein kritischer Schritt für dieses katalytische System. Nanokohlenstoffe gelten aufgrund ihrer einzigartigen Struktur, die im Gegensatz zu amorphen Kohlenstoffmaterialien die Eigenschaft hat, eine hohe Stabilität gegenüber der Totaloxidation zu gewährleisten, als einer der vielversprechendsten Katalysatoren.

In dieser Arbeit, wurden katalytische Messungen an verschiedenen Katalysatoren auf Kohlenstoffbasis durchgeführt. Diese Katalysatoren waren MWCNTs, die durch Säurebehandlung funktionalisiert wurden, und anschließend wurde Vanadium mit unterschiedlichen Konzentrationen auf der Kohlenstoffoberfläche mit der ALD-Methode abgeschieden. Vanadium ist ein bekanntes Metall mit guten katalytischen Eigenschaften für viele Reaktionen, einschließlich des Ethylbenzols ODH. Frühere Studien zeigen, dass Vanadium für diese Reaktion nur dann aktiv ist, wenn es auf der Katalysatoroberfläche gut verteilt ist. Eine gleichmäßige und effektive Abscheidung war durch den Einsatz des in unserer Gruppe entwickelten ALD-Ansatzes möglich.

Der erste Schritt in dieser Arbeit bestand darin, einen Reaktordesign zu entwerfen und aufzubauen, das die katalytische Prüfung erfolgreich machen kann. Anschließend fand die Auswertung aller MWCNTs statt und konzentrierte sich hauptsächlich auf die Untersuchung der Aktivität und Stabilität der Kohlenstoffstrukturen selbst und der Bestimmung, ob die Vanadiumarten an der Oberfläche einen Einfluss auf die katalytischen Eigenschaften der Nanoröhren haben.

Die kinetischen Ergebnisse deuten darauf hin, dass alle Materialien unter den gewählten Reaktionsbedingungen auch bei langer Betriebszeit aktiv und stabil waren, was die bereits bekannten guten Eigenschaften dieser Materialien bestätigt. In Bezug auf den Einfluss von Vanadium gab es eine Verbesserung der Aktivität bei niedrigen Belastungen und einen negativen Einfluss bei höheren Belastungen. Ein Beitrag des Vanadiums erfolgt nur, wenn es einzelne Stellen gibt, die die aktiven V^{5+} -Spezies bilden, die mit dem Ethylbenzol reagieren und Styrol bilden können. Dennoch führt eine höhere Vanadiumbelastung zu Agglomerationen und Deaktivierung des Katalysators.

Weitere Charakterisierungen der getesteten Materialien in der ODH-Reaktion wurden durchgeführt, um mehr Informationen über Veränderungen an der Struktur und dem Inhalt der aktiven Gruppen vor und nach der Reaktion zu erhalten.

Die Thermogravimetrie in Kombination mit Massenspektrometrie (TG-MS), Temperaturprogramm-Oxidation (TPO) und Transmissionselektronenmikroskopie (TEM) lieferte wertvolle Informationen über die Modifikation, die die Nanokohlenstoffstrukturen während der Reaktion erfahren. Es wurde festgestellt, dass immer eine aktive Koksschicht auf der Oberfläche vorhanden ist, die während der Reaktion gebildet wird und nach langer Zeit im Betrieb stabil bleibt. Die aktivsten Katalysatoren zeigten auf den TEM-Bildern eine dickere Schicht dieses amorphen Kohlenstoffs, die für die weniger aktiven Proben fast vernachlässigbar war. Weitere Analysen bestätigten, dass sich die meisten aktiven Gruppen vermutlich auf dieser Koksschicht befanden. Daher war die Bildung von aktivem amorphem Kohlenstoff ein kritischer Schritt, bei dem Vanadium in niedrigen Konzentrationen eine Rolle beim Aufbau dieser Schicht spielen könnte.

1. Introduction

1.1 Industrial styrene production

Styrene (ST) is a very important monomer well known for its application in the polymeric industry. It is considered as main raw material for the production of many goods that are widely used in the daily life like disposable cups, trays, packaging, household devices and construction materials.^[1]

Almost half of the styrene production is destined for polystyrene, a key material in the manufacture of plastics. There are many other applications from styrene like styrene-butadiene rubber (SBR), acrylonitrile-butadiene-styrene resins (ABS), styrene-butadiene latex (SBL) and expanded polystyrene (EPS). The demand of styrene and the number of its applications is still growing. In 2010 the total production was 26.4 million metric tons, making it the 4th largest production in the world with respect to a monomer.^[1,2]

Currently, styrene is mainly produced by catalytic dehydrogenation that uses ethylbenzene (EB) as raw material. Since all styrene is produced from ethylbenzene, a styrene production process is always built in combination with an ethylbenzene production process. Ethylbenzene is produced by the alkylation of benzene with ethane. This is a very efficient process with an extremely high selectivity (98-99%).^[3,4]

Around 85-90% of the commercial styrene is produced by direct steam dehydrogenation of ethylbenzene (Figure 1). Conventional production of styrene by steam dehydrogenation of ethylbenzene has several disadvantages. The process is highly energy demanding due to the use of superheated steam. Furthermore, the

reaction is thermodynamically limited at 50-60% and requires a reactant recycle. In addition, EB and ST are difficult to separate due to their similar boiling point of 136°C and 145°C respectively.^[3]

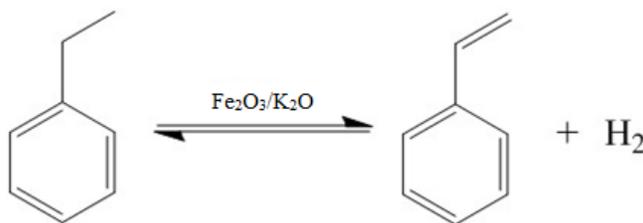


Figure 1: Dehydrogenation of ethylbenzene.

This reaction requires high temperatures (between 600 and 700°C) due to its high endothermicity ($\Delta H^0 = 118$ kJ/mol), slow kinetics and reaction equilibrium. In order to obtain these high temperatures an excess of overheated steam (steam to EB ratio 10:1) is used. Furthermore, the steam plays a role for three more reasons:

- Shifting the equilibrium of the reaction to higher ethylbenzene conversions by decreasing of partial pressures of the reactants.
- Decreasing the amount of coke formation by limiting accumulation through the gasification of the carbonaceous deposits.
- Keeping the catalyst in appropriate oxidation state by avoiding over-reduction. Here, the valence state of iron is controlled by means of diminishing the partial pressures of the products. ^[5,6]

To avoid styrene polymerization the reactor outlet stream needs to be cooled down rapidly. Water and unconverted ethylbenzene are both recycled and the main products are separated in further process steps.

The direct ethylbenzene dehydrogenation is catalyzed by potassium promoted iron oxide ^[5]. The catalyst also contains several other promoters like magnesium, chromium and aluminium to increase activity and enhance its stability ^[5,6]. The deactivation of the catalyst due to the formation of carbonaceous deposits, loss of the potassium promoters by the migration of potassium hydroxide to the cool region at the exit of the reactor and physical degradation resulting in a catalysts lifetime of around 2 years ^[6]. Different methods have been developed to enlarge the catalyst lifetime like increasing the potassium amount among the promoters (from 5 to 10%) or by using other alkali metals like rubidium and cesium. However, the lower prices of potassium lead to a more feasible employment of this metal. The role of potassium as a promoter has been a main topic of many studies and it has been suggested that the active phase for this reaction is KFeO_2 formed from the precursors and the pure Fe_2O_3 .^[7]

Since the current industrial process suffers from many drawbacks like the high energy demand and use of massive amount of steam, there is still a large room for improvement regarding the process efficiency. Modifications on the catalyst to improve selectivity and lifetime have been performed with some promising results. Although, many optimizations have been made on the industrial scale no further improvements for the direct dehydrogenation are expected.^[8]

1.2 Current styrene production technologies

Since the initial commercial production of styrene in the 1930s there have been many technologies for styrene production available around the world. Companies such as Badger, Lummus, LyondellBasell, Shell, DOW and BASF are considered as the main licensors of styrene production processes.^[8,9]

1.2.1 Badger-Total Styrene process

The Badger-Total process is one of the most important technologies for the styrene production. This process is used for around 9 million tons of the total styrene production and 47 licensed plants around the world. The catalyst is iron-based promoted with mainly potassium. First, the fresh ethylbenzene is mixed with recycled ethylbenzene recovered from the distillation units. Then the ethylbenzene stream is first vaporized and superheated and afterwards mixed with additional superheated steam to reach the reaction temperature. Next, the ethylbenzene is delivered to the catalytic reactor, where styrene and some other byproducts like benzene and toluene are produced. The distillation section consists of three main steps. First, the byproducts are separated from the ethylbenzene/styrene mixture, in the second step the ethylbenzene is separated from the styrene and recycled to the reactor feed and finally the styrene is purified in the last step (see Figure 2).^[10,11]

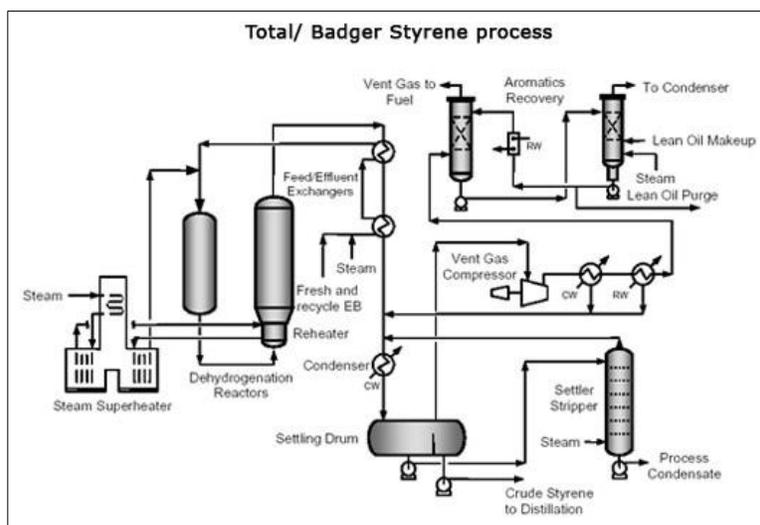


Figure 2: Schematic flow-scheme of the industrial Total/Badger process.^[12]

1.2.2 Lummus/UOP Process

The Lummus/UOP process developed by the two companies UOP and Lummus was first commercialized in 1990.^[13] It is comparable to the Badger/Total process. However, some differences in the reaction pathway and separation exist. In the dehydrogenation step there is more than one reactor that works under a theoretically adiabatic condition. This process works also with coupled reaction pathways where first the hydrogen from the feed (or recycle) is oxidized and the heat produced by this exothermic reaction is then delivered to the second reactor, where the dehydrogenation step takes place.^[5]

There is also a more developed process called Lummus/UOP SMARTSM that is an improvement to the classic Lummus/UOP process. It consists of three reactors and the reactor placed in the middle performs a combination of hydrogen oxidation and dehydrogenation. The additional conversion of hydrogen shifts the equilibrium to higher styrene yields and also lowers need of superheated steam.^[9,10]

1.2.3 The SNOW process

The process developed by the companies Snamprogetti and Dow consists of an integrated plant for both, ethylbenzene and styrene production. Ethane and Benzene are the main raw materials for this process. Therefore, the use of ethylene in the normal ethylbenzene production is replaced by the cheaper ethane which is obtained from petrochemical plants. The ethane is dehydrogenated and then recycled in the separation part to the ethylbenzene process (Figure 3). The ethylbenzene is also dehydrogenated in the same section to produce the styrene.^[8,14]

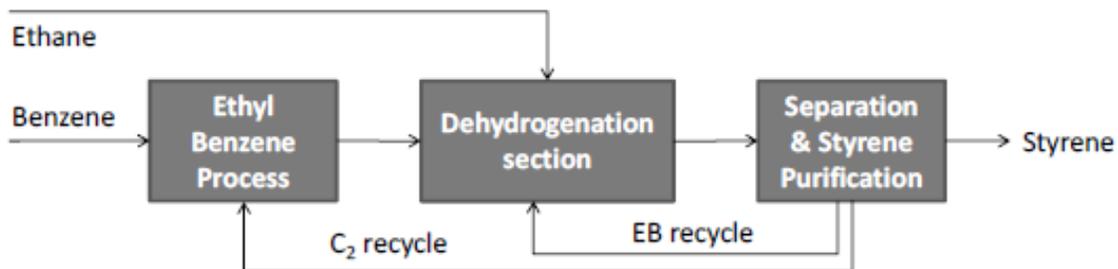


Figure 3: Snow process. ^[8]

The main difference to the former described processes is the use of a fluidized bed reactor where the inlet stream is mixed with fresh catalyst, then dehydrogenation takes place very rapidly and afterwards the catalyst is regenerated since a small amount of coke is formed during the catalytic process. Then, in this section the catalyst gets clean by the burning of the coke deposited on its surface. ^[14]

1.2.4 PO/SM Process

Around 15% of the styrene produced around the world is coming from the Propylene Oxide (PO)/Styrene Monomer (SM) process that was developed by Shell. The EB is first oxidized to ethylbenzene-hydroperoxide and then it reacts with propylene by means of a Ti/SiO₂ catalyst to propylene oxide. The styrene is obtained in the final step in a reaction with the byproduct of the previous reaction by using an Al₂O₃-based catalyst. This process gives styrene and propylene oxide as co-product and the PO is produced in a mass ratio of 2:1. Although this process is economically effective the two co-products need a complex separation and purification section and the main drawback is that it depends on the propylene oxide market requirements. There are already some technologies developed, where the PO can be produced without any byproduct. Hence, further improvements in this process regarding the styrene production are very unlikely. ^[8,15]

1.2.5 Oxidative dehydrogenation of ethylbenzene (ODH)

The oxidative dehydrogenation of ethylbenzene to styrene is one of the most attractive alternatives to the industrially applied processes. Big issues like waste of energy, catalyst deactivation and thermodynamic limitation can be avoided by means of this reaction. The reaction is showed in Figure 4. This reaction is free of thermodynamic constrains and can be performed at considerably lower operational temperatures of around 300-450°C. ODH is also an exothermic reaction ($\Delta H^0 = -124$ kJ/mol) and, thus, the energy efficiency of the system could be clearly improved by elimination or strongly decreasing the amount of superheated steam used in the current production process.^[5,16,17,18]

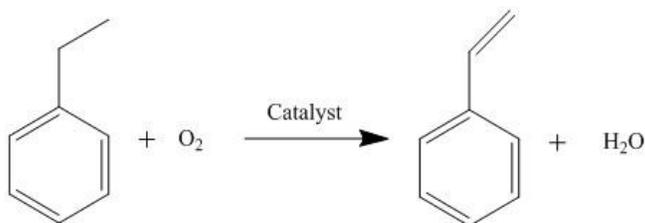


Figure 4: Oxidative dehydrogenation of ethylbenzene.

This reaction has been widely studied and a big variety of catalysts have been tested. Supported metals and active carbons can be considered as promising catalytic systems for the ODH reaction.

1.2.5.1 Metal based catalysts in ODH

Many transition metals have been studied for the oxidative dehydrogenation of ethylbenzene. Different kinds of catalysts like monometallic and bimetallic oxides, as well as several supports and promoters have been considered. Normally transition mixed metal oxides showed a better performance than monometallic materials. Different systems like TiO₂-ZrO₂, MnO₂-ZrO₂, V₂O₅-CeO₂, SnO₂-ZrO₂, FeO_x-Al₂O₃, TiO_x-Al₂O₃ and CeO₂-ZrO₂ showed an increase in the

strength of the acidic-basic sites and, therefore, improve the activity in comparison with monometallic catalysts. The activity of the metal based catalysts in ODH can be explained in two different ways: The redox properties of the transition metals and the actual catalytic surface defined by the coke deposition formed.^[5,19]

Actually, most of the studies agreed that when a metal oxide catalyst is used, there is normally an induction period where a significant increase in activity is taking place. This period can be related to the deposition of carbonaceous material on the surface during the reaction that could be considered as the real active phase for this reaction. Many authors confirmed that the active functional groups for the dehydrogenation reaction are present in the carbon species formed on the surface and the metal oxides acts as a support for this “active coke” formation. A proposed mechanism of this coke formation is illustrated in Figure 5.^[5,19]

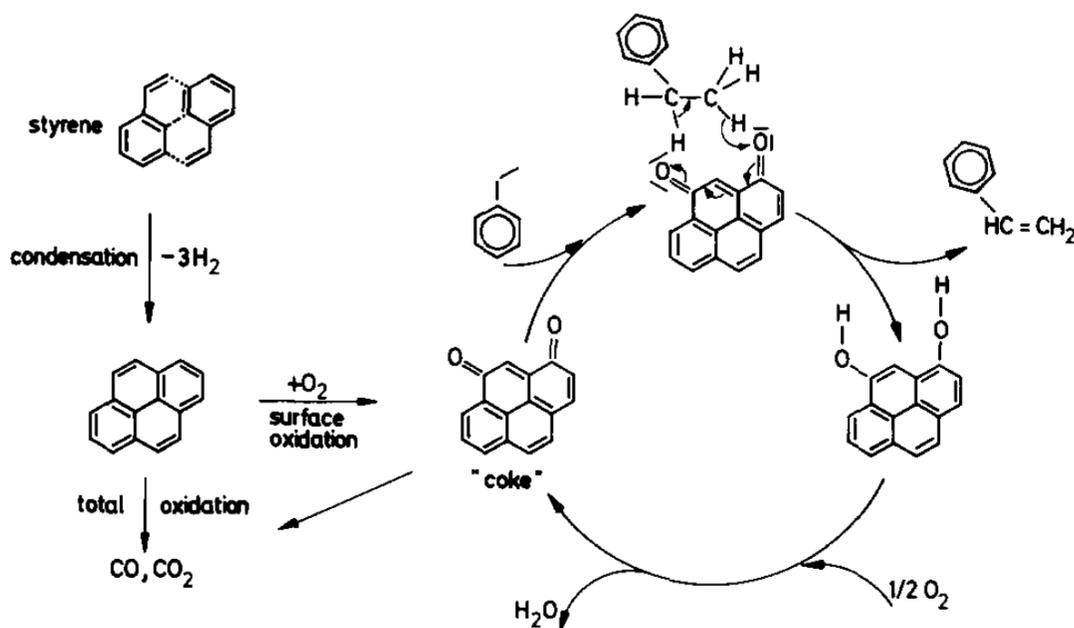


Figure 5: Proposed mechanism for the coke formation and ODH reaction on metal based catalysts (Reprinted with permission Copyright © 1983 Elsevier).^[20]

In this mechanism the first step is the condensation of styrene in polycyclic aromatic rings that deposit on the surface of the metal base catalyst. Afterwards the oxidation step takes place either totally oxidizing the aromatics rings to form CO and CO₂ or forming the active “coke”. This active coke consists of polyquinone structures that are formed at the edge of its graphitic structure. Here, the ethylbenzene molecule can be oxidized and forms the styrene. It has been proven by many studies that in the absence of molecular oxygen the coke is practically inactive.^[21-24] Therefore, the reoxidation of reduced active species after the styrene formation plays a crucial role to close the cycle and form again the polyquinone structures.

The metal support plays a role in the formation of the coke. In general, metal species with low or moderate acidic sites enhance the formation of the catalytic active coke. High acidities could also be unfavorable due to possible enhancement of cracking reaction and, thus, formation of other side products.^[20]

A clear observation of previous catalytic measurements is that the apparent active sites are located on the coke layer.^[17] Quinone/hydroquinone groups are commonly assigned as active functional groups. Some studies showed a strong relation between the catalytic activity and the concentration of carbonyl groups located on the carbon deposition. Therefore, the use of structured carbon materials as catalyst for the ethylbenzene ODH has become very attractive. The possible reduction or elimination of the activation period besides the higher availability and lower prices has made the use of these materials greatly promising for a possible industrial application.^[17,25]

1.2.5.2 Carbon materials in ODH

One of the biggest advantages of using carbon for ODH is the possibility to have a wide variety of structures that can be easily modified. It is well known how to control the surface acidity/basicity and the electron density by functionalization and, therefore, changing the chemical properties of carbon materials. The morphology of carbon allows the addition of foreign atoms localized either in the termination of the graphene sheets or on the basal planes of the graphene surface. Oxygen and nitrogen are frequently used as foreign atoms and they can form stable functional groups with high chemical reactivity (Figure 6).^[17,26-28]

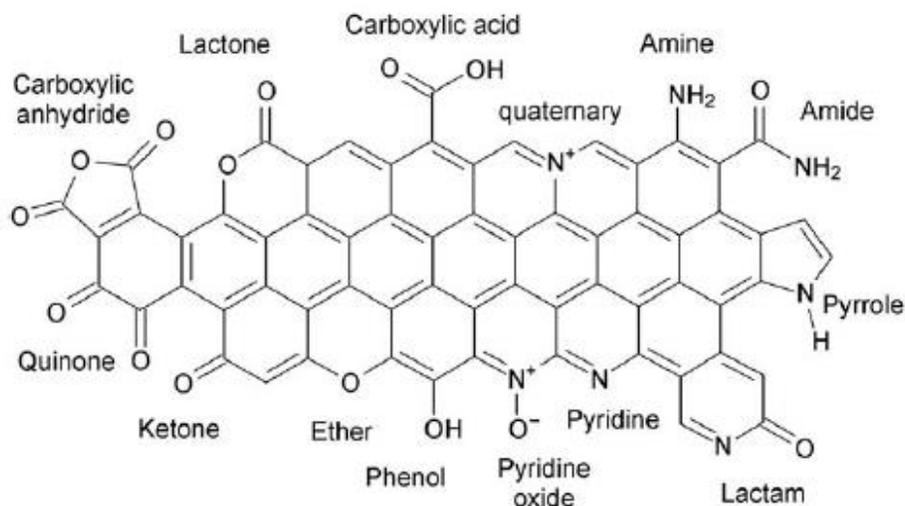


Figure 6: Functional groups at the surface of carbon materials. (Reprinted with permission Copyright © 2010 John Wiley & Sons)^[17]

It has been proven theoretically and experimentally that there is a large energy barrier for chemical adsorption of alkane or oxygen molecules on a perfect graphene surface. On the other hand, the energy for chemical adsorption of oxygen on defects or edge sites is considerably low (around 7 kcal/mol) indicating that these sites may be responsible for oxygen activation. The oxygen functionalities on

defect sites, especially the ones with higher electronegativity (ketone or lactone groups), are possible active sites for hydrocarbon activation.^[17,18]

As mentioned previously, specifically for the oxidative dehydrogenation of ethylbenzene there are several agreements that the active sites are the oxygen-containing functional groups with strong basicity like diketonic or quinoidic groups. There are many studies that showed a good correlation between oxygen content and catalytic activity.^[18,19] However, further analyses also showed that not all the oxygen functional groups favor the formation of styrene but also some of them somehow enhance secondary reactions that form undesired products like benzene, toluene and CO₂.^[29,30]

Regarding the morphology, materials with amorphous structures and micropores like activated carbon or carbon foams normally show high activation in the beginning of the reaction. However, these kinds of materials with low range of order usually generate a rapid destruction of the disordered unit cells by the attack of oxygen molecules at high temperatures. Furthermore, a high and continuous deactivation is unavoidable due to the deposition of carbon inside the micropores present in those materials even at low temperatures.^[31]

Another kind of material like mesoporous carbon showed also a high activity and better stability towards total oxidation than amorphous carbon. However, when micropores are used, an eventual deactivation could appear since the styrene produced in the reaction as a monomer can be easily polymerized inside the pore and, thus, causing undesired deposition of disordered carbon. Other studies also showed that although carbon nanofibers with really small micropores deactivate rapidly by the blockage with deposited coke, fibers with wider micropores are

much more active and stable. Therefore, the pore size also plays an important role in the performance of the materials.^[18,19,28,32]

It has been also possible to produce carbon materials free of micro-mesopores with really high crystallinity. These materials, called nanocarbons, showed higher stability and much better activities than amorphous carbon. A big variety of nanostructured carbon has been proven in catalytic measurements of ODH reaction being more efficient with higher activities in comparison with all the previous materials studied, either metal oxides or activated carbon. Their good performance is due to their cleaner surface with absence of amorphous carbon (see Figure 7) that decreases greatly the combustion of the carbon materials. Besides their stable structure, nanocarbon catalysts have significant advantages like high acid/base resistance and the possibility of activate oxygen molecules by the unpaired electrons on their surface that allow containing different surface functional groups. More recent studies showed a good performance of nanocarbon catalysis under industrially relevant conditions and suggested that these structures could be very promising for industrial application.^[17,18,29,33]

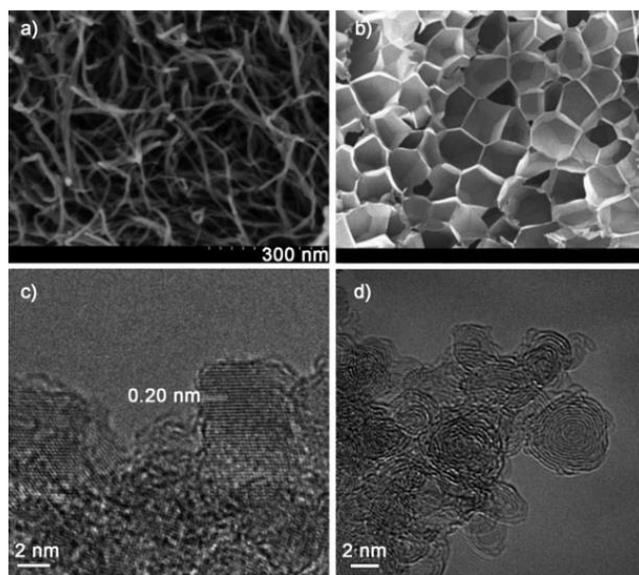


Figure 7: Micrographs of nanocarbons used as catalysts for ODH reactions: a) CNTs. b) Mesoporous carbon derived from popcorn. c) Nanodiamond. d) Onion-like carbon. (Reprinted with permission Copyright © 2010 John Wiley & Sons)^[17]

In the Figure 7, some of the studied nanocarbon materials are displayed. Carbon nanotubes (CNTs) have been widely studied being active and selective catalysts in the EB ODH reaction. Some measurements by using CNTs showed high stability without any deactivation even for 32 days.^[18] Another nanocarbon material that showed great performance is the onion-like carbon (OLC), which has higher surface area in comparison with CNTs.^[34] It also shows a very high activity in ODH reactions.

It is generally accepted that the ODH-reaction on carbon catalysts is mainly performed by active oxide species, but the detailed catalytic mechanism and its elementary steps are still not completely clarified. Most authors suggest a sequential elimination of the hydrogen atoms with a reactive intermediate after the adsorption of the saturated hydrocarbon.^[18]

The reoxidation via Langmuir-Hinshelwood is the widely assumed mechanism where the oxygen adsorbs at defect sites of the carbon material first and forms an active peroxide species.^[27] This species diffuses over the basal planes of sp^2 -carbon to the reduced oxide groups and oxidizes them. Figure 8 shows a general scheme of this process. It should be mentioned that the hydrogen abstraction and the O_2 activation are not necessarily sequential. The formation of the active oxygen species can happen independently.^[18]

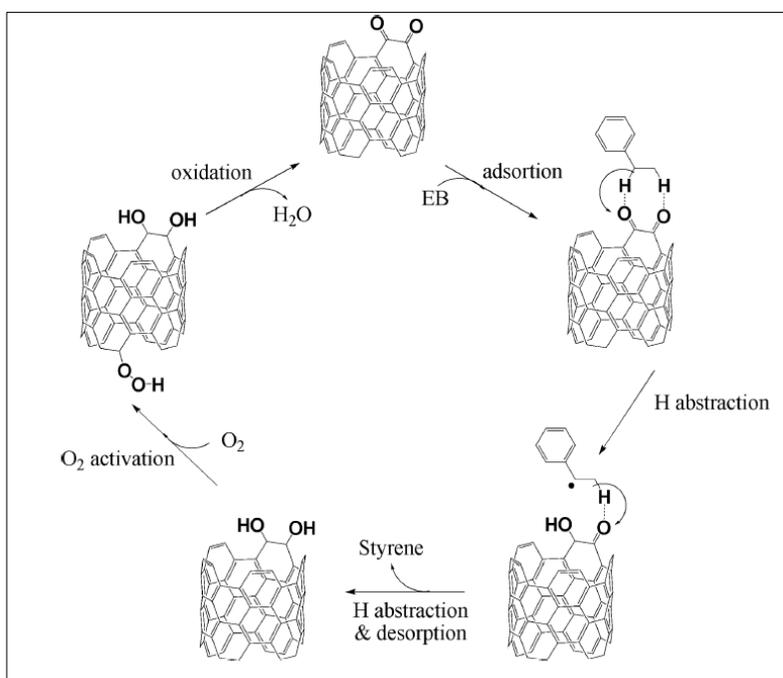


Figure 8: Schematic carbon catalyzed ODH of ethylbenzene with reoxidation by a Langmuir-Hinshelwood mechanism (Reprinted with permission Copyright © 2014, American Chemical Society).^[18]

However, this mechanism has not been completely confirmed yet. It is also possible that the mechanism depends on the carbon material used in the reaction. For example the diffusion of the active oxygen species in the Langmuir-

Hinshelwood mechanism seems to work only on carbon materials with a high amount of sp^2 carbon.^[17]

Several carbon materials and structures have been studied for their catalytic properties in the ODH reaction. Some examples for the catalytic performance of different carbon materials are shown in Table 1.

Table 1: Catalytic performance of various carbon catalysts for ODH of ethylbenzene to styrene (Reprinted with permission Copyright © 2014, American Chemical Society).^[18]

Catalysts	Optimum yield (%)
Carbon nanotubes	~ 70
Carbon nanofibers	~50
Mesoporous carbon	41
Nanodiamond	38
Onion like carbon	62
Active carbon	56
Carbon foam	23
Phenanthrenequinone	84

It can be seen in Table 1 that the highest styrene yields are reached with the already mentioned CNTs and OLCs carbon materials. This is mainly due to the content of high quantity of ordered sp^2 -carbon. Materials with a high amount of amorphous carbon like mesoporous carbon, active carbon and carbon foams show in general a lower styrene yield than ordered sp^2 -carbon materials. This good performance of the ordered sp^2 -carbon materials is explained by the electron conductivity of the aromatic graphene structures.^[17] This improves the ability of the oxide groups to be reduced and oxidized. Also the electron-density of the

oxygen-containing groups increases by the aromaticity, which improves the interactions between the oxide and the hydrogen atoms of the EB.^[27]

A central problem of the carbon-catalyzed ODH is that oxygen-containing groups are the active sites for the ODH reaction and also the starting points for the total oxidation of the catalyst. Therefore, a high number of oxygen-containing groups results in a high ODH activity, but it can also lead to a low lifetime due to total oxidation. Many amorphous carbon materials like activated carbon exhibit high initial activity for the ODH reaction, because they contain many oxygen functionalized groups, but they lose their activity very fast due to total oxidation. Ordered sp^2 -carbon materials have normally a lower amount of functional groups on the surface compared to amorphous carbon. The oxide groups for sp^2 -carbon materials are only found at the edges and defects of the graphite layers while the rest of the layers have no functional groups. Because of the higher total oxidation resistance of ordered sp^2 -carbon those materials loose less surface area and mass, so that the activity of ordered sp^2 -carbon material remains stable at a relatively high level for a longer time. It is possible to increase the number of functional groups in ordered sp^2 -carbon materials by oxidation with an oxygen-containing oxidizing agent, but this decreases the resistance against total oxidation. In general the design of a carbon catalyst for ODH reaction is always a compromise between activity and stability.^[18,27,35,36]

It has been reported that the activity of some carbon-based catalysts can increase during the reaction over longer reaction time periods. It is possible that the oxidation of the catalyst forms new functional groups on the surface and the total oxidation can also increase the surface area of the catalyst by increasing the pore sizes. This increases the number of the active sites for the ODH reaction and, thereby, the activity of the catalyst. The ODH reaction also shows some coke

formation as a side reaction. If the coke formation is faster than the total oxidation of the catalyst this would increase the mass of the carbon material and give new material for the formation of functional groups.^[37]

1.2.5.3 Vanadium-based catalysts for ODH

A big variety of vanadium-based catalysts have been tested for the dehydrogenation of ethylbenzene to styrene. It has been probed that the active phase is the tetrahedral vanadium and the V^{5+} species, that show a better activity when it is highly dispersed on the surface. Reduced species like V^{4+} and V^{3+} are much less active for the reaction.^[19] The abstraction of the hydrogen from the ethylbenzene occurs by the interaction with V-O bonds and then the nucleophilic attack of ethylbenzene to the V^{5+} takes place to finally form styrene. The dependence of activity with vanadium concentration is crucial.^[38] While really low vanadium concentrations have almost no impact on the catalytic performance, high concentrations also inhibits the dehydrogenation reaction. Although the presence of V^{5+} clearly improves the activity, high amounts of those species lead to less active catalysts due to reduction of active species and formation of bulk vanadium oxide crystallites. This reaction follows a redox cycle (see Figure 9). The active vanadium specie is reduced after dehydrogenation and then regains its initial oxidation state by means of oxygen or another oxidant like CO_2 .^[19,39]

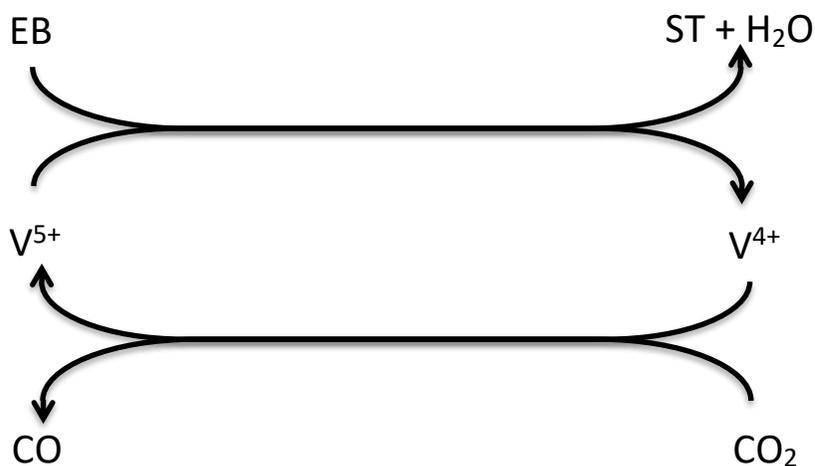


Figure 9: Proposed reaction mechanism of ethylbenzene ODH reaction on Vanadium based catalyst. (Adapted from ^[19])

Regarding the use of vanadium on different catalyst supports for the ODH reaction many studies have been performed in order to evaluate their activity. ^[19] Alumina, silica and activated carbon can be considered the most used vanadium supports for the ODH reaction. Normally, the good supports are the ones able to improve the dispersion of the vanadium species and enhance the adsorption of the reactants. Even some modifications on the supports either by forming bimetallic supports with Mg or by using promoters such as Li, K and Cr have been made in order to improve the catalytic activity by means of mainly increasing of surface area. Vanadium species that are highly dispersed on the surface normally show better activity. Among the high variety of supports the activated carbon-supported vanadium catalysts are considered among the most active, having also a higher styrene yield of around 54%, which can be probably explained by the large surface area. The deactivation of the catalyst is normally due to coke deposition leading to a pore blocking on the activated carbon and, thus, a strong decrease of the surface area. It is important to mention that there is still a lack of research regarding the interaction between the active vanadium and the carbon support and the performance of vanadium species on different carbon materials. ^[19,40-42]

1.3 Aim of this work

Considering the promising results on previous studies when nanocarbon materials and vanadium-based catalyst were used for the ethylbenzene ODH reaction, the core of the thesis was to evaluate the catalytic performance of catalysts that combine both materials (nanocarbon and vanadium). Those catalysts were multiwalled carbon nanotubes (MWCNT) with different vanadium concentration on their surface. The vanadium species were deposited by means of the atomic layer deposition method (ALD). The main goal was to investigate the influence of the vanadium concentration on the activity and determine the role of vanadium species during the reaction and their interaction with the carbon material. A big part of this project was to investigate the influence of the functional groups placed either on the carbon surface or directly in the vanadium species that are believed to be active in ODH. In order to get valuable information about what are the real active sites and the relationship between the catalyst structures and their activity, the use of complementary characterization methods besides the catalytic test played a key role in this study. Finally, it was important to determine the use of the ODH reaction as an effective application of carbon nanotubes treated by the ALD method.

2. Experimental Methods

A reactor setup was used in order to perform the catalytic tests. The development of this setup took place at the beginning of this work and a detailed description of the device can be found next. Furthermore, all the samples were characterized before and after the activity measurements. The explanations of all the methods applied to the materials also take part of this chapter.

2.1 ODH set-up

The kinetic experiments for ODH were performed in a flow set-up, which was designed and constructed as a first part of this work. A flow-scheme of the set-up is shown in Figure 10. A gas mixture of oxygen and nitrogen gets in contact with ethylbenzene that is placed in the saturator. Then, this stream goes to the reactor and, finally, is delivered to the analytic area, where a gas chromatograph is connected on-line to the reactor outlet.

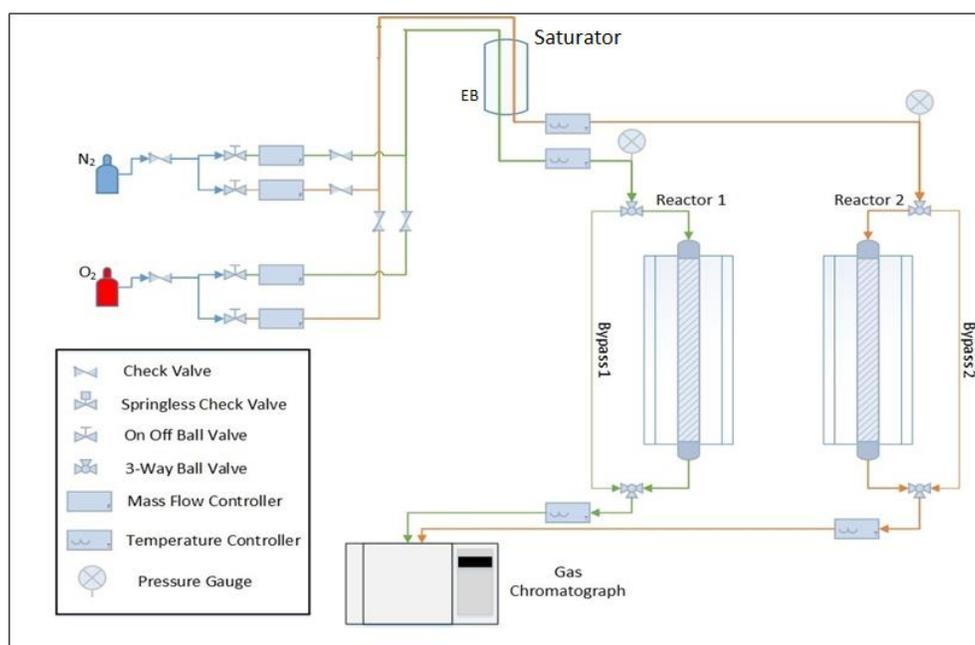


Figure 10: Flow-scheme of the ODH set-up.

The feed gas is mixed in the desired composition with respect to ethylbenzene and oxygen as reactants and nitrogen as an inert carrier gas. Nitrogen and oxygen are directly introduced by pressurized gas cylinders and their flow rates are controlled by mass flow controllers (Bronkhorst). The ethylbenzene (Sigma Aldrich, 99.8 %) is added to the gas flow mixture (oxygen and nitrogen) by means of a tempered glass saturator. The ethylbenzene amount in the gas phase could be varied by adjusting the saturator temperature and, as a consequence changing the vapor pressure of ethylbenzene. This vapor pressure is calculated through the Antoine equation as follows:

$$\text{Log}_{10} p = A - \frac{B}{C + T} \quad (1)$$

Where p is the calculated vapor pressure, T is the temperature in the saturator which is regulated by means of a thermostat (model Julabo 200F) and A , B and C are component-specific constants (ethylbenzene in this case).

All pipelines of the system downstream of the saturator are heated to 170-180 °C to prevent condensation of the EB (boiling point: 136 °C) and the main product styrene (boiling point: 145 °C). The stream coming from the saturator can be directed either to the reactors or to the bypass connections directly to the analytics.

The catalyst is placed in a glass reactor that includes an inner pipe where a thermocouple is used to measure the temperature directly inside the catalyst bed. A schematic picture of the reactor is shown in Figure 11. The glass reactor is located inside an electrical heated oven (model HTM Reetz LK 1000-20-300-3-V with three heating zones).

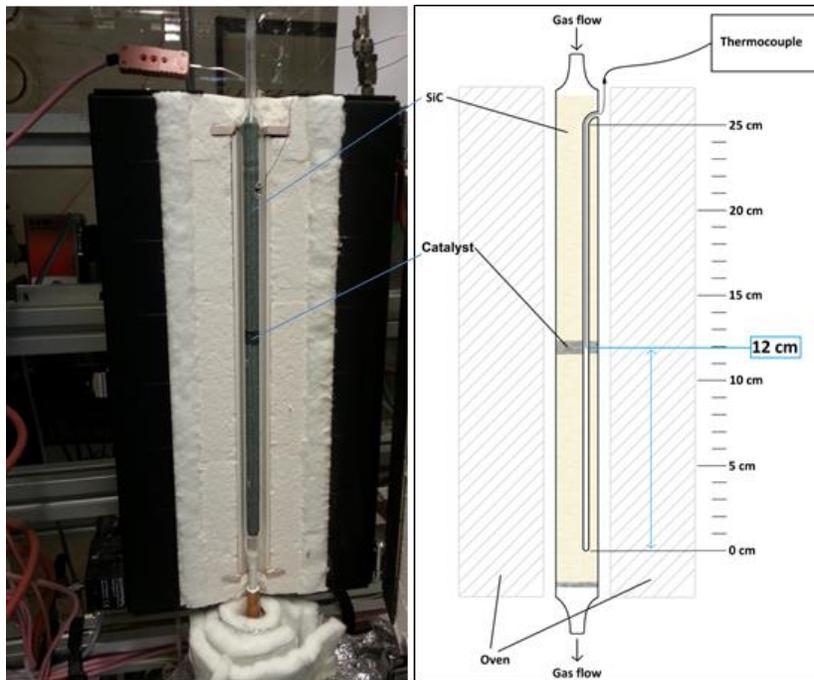


Figure 11: Photograph (left) and schematic picture (right) of the reactor of the ODH set-up.

The reactors were filled with silicon carbide (SiC) as shown in Figure 11. The SiC was used as inert material that improves the heat distribution inside the reactor, reduces dead volumes and ensures plug flow conditions.

Although the temperature of the oven is measured by a controlled system from the manufacturer, it was further calibrated by using an additional thermocouple. The isothermal zone of the oven was determined by placing the thermocouple inside the reactor at different heights from the bottom to the top. The catalyst bed was then placed inside the isothermal zone.

2.1.1 Gas chromatographic analysis

Analytical gas chromatography is a separation technique that allows obtaining information regarding the amount and molecular composition of a gas mixture. The different compounds of the mixture are separated inside a chromatographic

column. Then, the separated compounds that leave the column at different times (retention times) are identified and quantified by means of suitable detectors.

The chromatographic column can be described as a long and narrow tube that contains a stationary phase inside. In the standard procedure a stream of inert gas continuously pass through the column and the mixture that has to be separated is introduced at the beginning of the column and is carried by this gas. The sample to be analyzed should be either a gas or a volatile liquid.^[43,44]

The principle of this method is based on the interaction between the sample mixture and the stationary phase inside the column. Every component of the sample behaves independently from the other and the adsorption on the stationary phase is depending on the interaction with the component. Therefore, they are separated in the column and the speed of the elution depends on the strength of the adsorption. Also the temperature and pressure of the system play an important role in the analysis by modifying the retention times of each compound inside the column.

After the sample is separated and the single compounds leave the column there is a detector at the end for detection of the separate components in the mixture as they emerge from the column. The thermal conductivity detector (TCD) and the flame ionization detector (FID) are considered among the most common detectors in GC systems. Finally, the compounds detected can be quantified knowing the total flow and the exact concentration by using a calibration curve that is made before the measurements take place.^[45]

The gas chromatography is very useful quantification method where a complete separation of the compounds in a mixture is possible. Furthermore, chromatography allows a qualitative analysis of a sample and also quantitative if

the system is calibrated. This makes the gas chromatography a very effective technique for on-line analysis for gas phase reactions. Additionally, the FID and TCD detectors have a long-term stability that allow getting stable results during steady-state measurements.

In our setup the analysis of the reactor gas outlet is performed by an online GC system from Agilent Technologies (model 7890B). The gas chromatograph contains two columns for the separation of the most important reactants and products of the ODH of ethylbenzene. These reactants and products can be separated mainly in two groups. One group are the aromatic compounds like styrene, ethylbenzene, toluene and benzene and the second group are permanent gases like oxygen, nitrogen (carrier gas), carbon monoxide and carbon dioxide. The GC system consists of two columns, one Stabilwax® (30 m × 0.32 mmID, Restek) with a polar wax phase used for the separation of the aromatic compounds and a Molsieve 5A column (30 m × 0.53 mmID, Restek) for the separation of the permanent gases. The detection of the separated molecules is performed by flame ionization detector (FID) for the aromatics and a thermal conductivity detector (TCD) for the permanent gases. For the sampling of the reactor outlet stream a valve set on the GC was used. This valve set consisted of two valves. In one valve the sample loop and the column for the aromatics are connected and in the second valve the column for permanent gases and the two detectors are connected. By means of these two valve configuration it was possible to analyze the sample and separate the compounds properly. Figure 12 shows the different connections for the 6-port valve.

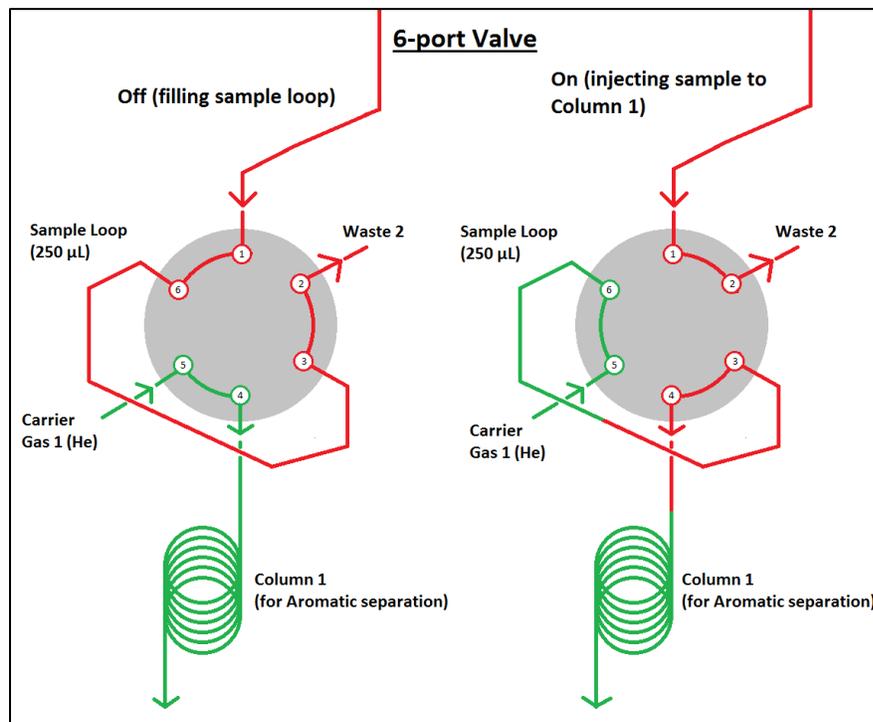


Figure 12: Configuration of the 6-port valve.

In the 6-port valve the sampling takes place by means of a sample loop of 250 µL. Furthermore, the Stabilwax® column (column 1) is also connected to this valve and is used for the aromatics separation. This valve can be switched in two positions (On/Off) by using a pneumatic system from VICI with pressurized air. In the Off position the sample loop is filled with the reactor outlet stream. Once the sample loop is filled the valve switches to the On position where the sample passes through column 1. At this part the sample gets separated, the permanent gases rapidly pass through the column 1 to column 2 (connected to the second valve) and the aromatics remain inside interacting with the stationary phase. Afterwards, the outlet of column 1 is flushed to the 10-port valve as shown in Figure 13.

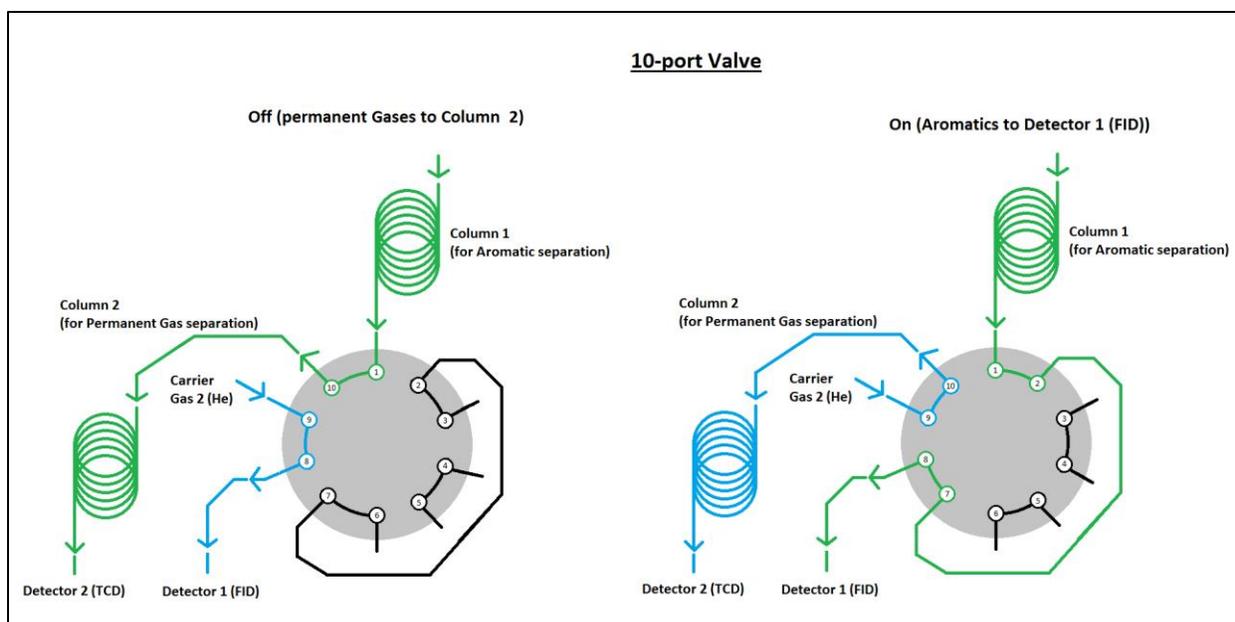


Figure 13: Configuration of the 10-port valve.

As soon as the permanent gases pass column 1 and reaches column 2 the 10-port valve switches its position from Off to On. In the On position the gases pass through the Molsieve column (column 2) and their separation is performed. Then, the separated gases are detected by the TCD and the aromatics compounds separated on column 1 are detected by the FID which is also connected to this valve.

With this configuration it is possible to analyze the main products coming from the reactor and at the same time to protect the Molsieve column for the permanent gases avoiding its contact with aromatic compounds that can block or damage the stationary phase of this column.

The received data from the gas chromatograph during the catalytic measurements was used to determine conversion, selectivity and yield for the different experiments. Equation 1 was used to calculate the conversion (X) of ethylbenzene with the molar flows of EB at the reactor outlet ($\dot{n}_{EB,out}$) and the molar flow of EB at

the reactor inlet ($\dot{n}_{EB,in}$). The molar flow of EB at the reactor inlet was determined by measuring the feed gas composition via the bypass connection of the reactors.

$$X = \frac{\dot{n}_{EB,in} - \dot{n}_{EB,out}}{\dot{n}_{EB,in}} \times 100 \% \quad (1)$$

As showed in equation 2 the selectivity to styrene S_{ST} was determined by dividing the molar flow of styrene (\dot{n}_{st}) by the molar flows of EB that reacts ($\dot{n}_{EB,in} - \dot{n}_{EB,out}$).

$$S_{st} = \frac{\dot{n}_{st}}{\dot{n}_{EB,in} - \dot{n}_{EB,out}} \times 100 \% \quad (2)$$

With the conversion of ethylbenzene and the selectivity to styrene it was possible to determine the styrene yield Y (equation 3).

$$Y = X * S_{st} \quad (3)$$

The carbon balance was calculated by dividing the sum of the carbon atoms content of all the compounds in the reactor outlet stream, normally styrene and unconverted ethylbenzene ($Carbon_{EB,out}$ and $Carbon_{ST,out}$) by the carbon atoms in the ethylbenzene that enter the reactor ($Carbon_{EB,in}$) as shown in equation 4.

$$Carbon_{bal} = \frac{Carbon_{EB,out} + Carbon_{ST,out}}{Carbon_{EB,in}} \quad (4)$$

This value gives information regarding the possible carbon deposition that might happen during the reaction and quality of the analytics.

The apparent activation energies E_a for the different catalysts were determined via an Arrhenius plot of the rate constant k and the temperature T in consideration of some simplifications and assumptions. Equation 5 shows the power law of the ODH reaction.

$$r = k \cdot p_{EB}^x \cdot p_{O_2}^y \quad \longleftrightarrow \quad k = \frac{r}{p_{EB}^x \cdot p_{O_2}^y} \quad (5)$$

It is possible to combine the power law with the Arrhenius equation (equation 5), which is shown in equation 6 and 7.

$$k = A \cdot e^{-\frac{Ea}{RT}} \quad \longleftrightarrow \quad \ln k = -\frac{Ea}{R} \cdot \frac{1}{T} + \ln A \quad (6)$$

$$\frac{r}{p_{EB}^x \cdot p_{O_2}^y} = A \cdot e^{-\frac{Ea}{RT}} \quad \longleftrightarrow \quad r = p_{EB}^x \cdot p_{O_2}^y \cdot A \cdot e^{-\frac{Ea}{RT}} \quad (7)$$

This combination of the power law and the Arrhenius equation can be converted to a linear equation (equation 8).

$$\ln r = -\frac{Ea}{R} \cdot \frac{1}{T} + \ln A + \ln p_{EB}^x + p_{O_2}^y \quad r \approx k \quad (8)$$

With the assumption that the partial pressures of the ethylbenzene p_{EB} and the oxygen p_{O_2} stay more or less constant in the measured temperature range it is possible to sum up the partial pressures and the pre-exponential factor A to a constant b in the linear equation. In this case the slope of the linear Arrhenius plot with the reaction rate r approximately is equal to the slope of the linear Arrhenius plot with the rate constant k . This allows a determination of the apparent activation energy by a plot of the natural logarithm (\ln) of reaction rate vs the inverse of temperature ($1/T$).

2.2 Characterization methods

Normally when carbon is used as a catalyst the electronic structure can give useful information to predict the reactivity of the catalyst. The structure of the carbon at nanoscale is not simple to characterize. However, depending on the preparation procedure of the carbon material there are different methods like X-ray diffraction (XRD), elemental analysis, thermogravimetric-mass spectrometry analysis (TG-MS), Raman spectroscopy, transmission electron microscopy (TEM), and infrared spectroscopy (IR) that could provide many information regarding structure, morphology and functional groups content and how all these features are modified during the reaction. The most important methods used in this study are explained in this chapter.^[46]

2.2.1 Combustion analysis

This method is used to determine the composition of carbon materials, and it is based on the combustion of their main components like hydrogen, nitrogen, sulfur and carbon at high temperatures by using oxygen. For the combustion analysis the sample is placed on a balance, where it is burned in pure oxygen at temperatures up to 1800 °C. This leads to the combustion products CO₂, H₂O, NO_x and SO₂ in gas phase that can be separated and quantified. The separation and quantification can be performed by any separation method like gas chromatography with a suitable detector. With a comparison of the mass loss of the sample and the determined amounts of C, H, N and S it is possible to indirectly determine the oxygen amount of the sample as the deviation. Normally, the oxygen content is calculated by the difference between 100 and the rest of the quantified components, as long as there are no considerably amounts of metal in the

materials. The metal content of the carbon materials can be determined by another complementary method.^[29]

2.2.2 N₂ physisorption

The measurement of gas-physisorption is nowadays an extensively used standard method for the determination of the surface area of solid materials. Physisorption is a form of adsorption where a molecule/atom, in this case nitrogen (N₂), is adsorbed on a surface with physical binding forces. In normal measurements the nitrogen gets in contact with a solid sample at 77 K (boiling point) and a specific number of gas molecules gets attracted to the sample by means of the van der Waals forces. The number of molecules physisorbed depends on the relative pressure of the N₂. This physisorption is reversible, since the physical binding forces are relatively weak. Therefore, desorption of the molecules/atoms is possible under relatively mild conditions.

A common method to determine the progression of physisorption is the measurement of adsorption/desorption isotherms. These isotherms can be constructed with the amount of adsorbed molecules measured against the partial pressure at a constant temperature.

One major method for the determination of the surface area of solids by physisorption isotherms is the BET equation, formulated by Brunauer, Emmett and Teller (BET). This equation describes a multilayer physisorption on a surface for low partial pressures. It is assumed that only the first layer on the surface has a different heat of adsorption (E_0). All layers beyond the first layer are identical in their heat of adsorption (E_L) and their adsorption/desorption rates are constant. With this assumption the following equations can be formulated.

$$\frac{n_{ads}}{n_m} = \frac{c \cdot \frac{p}{p_0}}{\left(1 - \frac{p}{p_0}\right) \left(1 + (c-1) \frac{p}{p_0}\right)} \quad (9)$$

$$c = \exp\left(\frac{E_0 - E_L}{RT}\right) \quad (10)$$

The equation 8 can be then arranged to a linear equation:

$$\frac{\frac{p}{p_0}}{n_{ads} \left(1 - \frac{p}{p_0}\right)} = \frac{1}{n_m c} + \frac{c-1}{n_m c} \cdot \frac{p}{p_0} \quad (11)$$

This allows a linear plot of the number of adsorbed molecules/atoms (n_{ads}) and the relative pressure (p/p_0) to determine the number of adsorbed molecules/atoms for a monolayer (n_m) out of the slope. With the number of adsorbed molecules for a monolayer and the area occupied by a molecule it is possible to calculate the surface area of a material.^[47]

2.2.3 Transmission Electron Microscopy (TEM)

TEM is an essential method to determine the structure of the catalyst that provides important information like size and shape of the carbon material and how the structure and surface changes by comparing images before and after reaction. Electron microscopy is an optical microscopy method to take a close-up of the surface of a material. Instead of light the microscope uses an electron beam as the source of illumination. The short wavelength of the electrons allows a much higher resolution than with light and it is even possible to reach an atomic resolution. In case of carbon materials this tool has become very important for well-defined carbon structures that are homogeneous at nanoscale. It is possible to analyze the defect states of the carbon material. In case of this work the TEM images gave

valuable information regarding the initial state of the catalysts structure and how it was modified after the reaction was performed.^[48]

2.2.4 Thermogravimetric mass spectrometry (TG-MS)

TG-MS is a common method for the investigation of functional groups in carbon materials. Oxygen-functional groups that are relevant for the ODH reaction can decompose in CO and CO₂ during the thermal treatment under inert atmosphere. This method also studies the influence of a temperature change on the mass of the material. For a thermogravimetric measurement the sample is usually placed on a highly sensitive microbalance, which measures the mass changes during a temperature increase.

For a better investigation the TG is commonly coupled with further quantification methods. A widely used method is the mass spectrometer (MS). A mass spectrometer can identify molecules and atoms in the gas phase by measuring their mass to charge-ratio (m/z) that can be defined as the mass of the ion in the atomic phase divided by the number of charges of the ions. This is experimentally measured by the mass of gas-phase ions that is produced from the molecules of the analyte. Those ions can be separated according to their m/z value and this method can be used for the detection of any element that can be ionized.^[49]

In the TG-MS analysis under inert atmosphere different functional groups decompose at characteristic temperatures generating gaseous decomposition products, which can be analyzed by means of mass spectrometry. Figure 14 shows the characteristic temperature ranges and the formed molecules for several different functional groups that can appear on the surface of carbon materials.^[50]

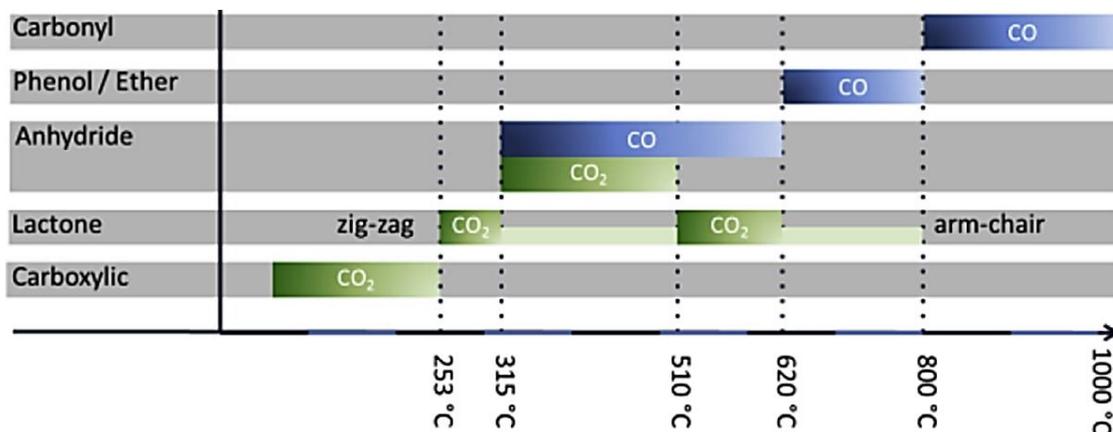


Figure 14: Oxygen-containing functional groups on the surface of a carbon material and their decomposition by TPD.^[50]

The oxygen-functional groups are then identified by their decomposition at different temperatures generating either CO or CO₂ quantified by mass spectrometry.

The instrument used was a STA 449 F3 Jupiter® QMS4 setup from Netzsch, the heating rate was 20 K/min. Six isotherms were used to determine the six different oxygen functional groups that have been identified in the carbon materials. The temperatures of each isotherm were the same as used in the previous study. All the measurements were performed in pure Argon by using a total flow rate of 70 ml/min.

2.2.5 Temperature-Programmed Oxidation (TPO)

TPO is a very useful technique where the catalyst is put through a temperature program in the presence of an oxidizing gas mixture. In case of carbon materials this technique allows to determine the different kind of carbonaceous species present on the sample. In many cases the analysis of samples by this method gives very valuable information regarding the presence of amorphous carbon deposited on the catalyst surface when reactions involve organic compounds like in the

ethylbenzene ODH reaction. This is also a good way to evaluate the stability of carbon materials under oxidative conditions where the presence of defects can be detected based on differences in CO and CO₂ evolution, knowing that a higher graphitization degree increase the resistance of the carbon to burning and, thus, the combustion of the sample shifts to much higher temperatures.^[16,51]

All the TPO experiments were performed at the same conditions, with 5% of oxygen under Argon atmosphere. The samples where heated up to 1000 K with a heating rate of 5 K/min. The instrument used was the same as used for the TG-MS analysis, but it was possible to re-adapt the instrument to perform TPO experiments

3. Results & discussion

In order to have a complete and reliable catalytic evaluation of the materials, the reaction conditions were carefully selected considering the setup limitations and the properties of the carbon catalysts. Afterwards, reproducibility and stability measurements were performed in order to check the reliability of the system. Finally, the catalytic measurements were performed with all the catalysts available with different vanadium concentrations as well as their further characterization.

3.1 Determination of suitable experimental conditions and test procedure

The correct experimental conditions are key facts for a sufficient kinetic evaluation of a catalyst and, thus, obtaining reliable results. Therefore, the selection of suitable conditions was based on the comparison of experimental conditions applied in previous studies where carbon-based materials were tested in the ODH reaction. It was intended to keep low conversions to obtain reliable kinetics results and to avoid undesired deposition of styrene due to polymerization (as mentioned in previous chapters) which can result in either pressure increases or even complete blocking in the pipe. Therefore, the reaction temperatures during the catalyst test were usually lower than in the previous studies in order to avoid higher ethylbenzene conversions and high styrene concentrations in the outlet stream of the reactor.

One of the most critical conditions that plays crucial role in the reaction is the reactant composition in the feed. The ethylbenzene and oxygen concentrations

elected to perform the experiments were based on the experiments that are shown in Table 3.

Table 3: Reaction conditions and tested catalyst in previous studies.

MATERIAL	REFERENCE	CONDITIONS
CNT/CNF	Rinaldi et al ^[52]	400 °C; 50mg of catalyst 2.1% O ₂ ; O ₂ /EB=1 Tot. flow= 15 mL/min
	J.J Delgado et al ^[16]	400 °C - 550 °C; 60 mg of catalyst 2.7% EB; O ₂ /EB=5 Space Velocity= 5000 ml/g/h
	J.J Delgado et al ^[53]	400°C; 60 mg of catalyst 2.6% EB; O ₂ /EB=2.6 Space Velocity= 5000 ml/g/h
	Zhang.J et al ^[27]	450 °C; 5mg of Catalyst 2.8%EB; O ₂ /EB=0.5 Flow rate=12.5 mL/min
	Zhang J. et al ^[54]	50 mg of catalyst 2.1%O ₂ ; O ₂ /EB=1
ONION LIKE CARBON	Keller N. et al ^[34]	517°C; 40 mg of Catalyst 2% EB; O ₂ /EB=1
	D. Su et al ^[55]	515°C; 40mg of Catalyst 2.1% EB; O ₂ /EB= 1 Total flow= 10 mL/min
SOOT, GRAPHITE AND NANOFILAMENT	Mestl G. et al ^[56]	547°C; 20mg 2% EB; EB/O ₂ =1
MESOPOROUS CARBON	D. Su et al ^[57]	350-400 °C; 60 mg 2.6% EB; O ₂ /EB=5

Looking at Table 3 there is a common trend of using low ethylbenzene concentrations, usually between 2-3% and also in most cases the oxygen to ethylbenzene ratio was 1:1. It has been demonstrated that in order to avoid total

oxidation it is better to keep low oxygen to ethylbenzene ratios. Furthermore, some previous studies established that higher oxygen contents barely improve the styrene formation rate.^[58]

All these conditions used in the past gave us an idea about the right way to proceed with the catalytic measurements. However, more aspects were taking into account in order to get the proper conditions for our experiments.

Regarding the reaction temperature, we used much lower temperatures than the previous studies showed in Table 3. One of the main reasons was the stability of the tested materials. The interaction and stability of the vanadium species on the MWCNT were properly evaluated before, and they showed that in oxygen atmosphere the vanadium single sites agglomerates to bigger V particles at around 310 °C.^[59] Those single sites are believed to be active for the ODH reaction, and the main part of our study was to analyze their influence on the catalytic activity. Therefore, the reaction temperature applied in our experiments was kept always below 310 °C. Furthermore, as mentioned before, it was not desirable to achieve high conversion of ethylbenzene due to the risk of blocking the pipes due styrene polymer deposition. Therefore, it was decided not to perform experiments at temperatures higher than 300 °C. The ethylbenzene concentration used in the reaction was also low (2%) and the ethylbenzene to oxygen ratio used was 1:1. Since a relatively high catalyst mass (100mg) was used in comparison with the former studies, mainly due to the dimensions of the reactor and setup, a total rate of 40 Nml/min was used in our experiments in order to keep roughly the same range of residence time.

These conditions were applied as standard for most of the experiments and thus, the same procedure to perform the catalytic measurements was applied. Having the

same conditions for all the experiments is necessary in order to have more reliable results by getting the right comparison of catalytic behavior from the different materials that were tested.

A normal catalytic measurement is operated with 100 mg catalyst (particle size: 200-300 μm), which is diluted with SiC (SIKA ABR I Saint Gobain with an average particle size 154 μm). The applied feed gas flow and composition is given in Table 4.

Table 4: Composition of the feed gas flow.

Compound	Volume gas flow [Nml/min]	Gas phase concentration [%]
Nitrogen	38.4	96.0
Oxygen	0.8	2.0
Ethylbenzene	0.8	2.0
Total flow	40.0	-

On the standard catalytic measurement the reaction is performed in a temperature range between 270-300 °C with temperature steps at 270, 290 and 300 °C. Every temperature step was kept for approximately 6h to ensure steady-state condition.

3.1.2 Applied catalysts

As mentioned in previous chapters, our aim was to test carbon based catalysts for the oxidative dehydrogenation of ethylbenzene. Specifically, the materials tested were all based on multiwalled carbon nanotubes (MWCNT). As it was explained in the introduction chapter, nanotubes are well known materials for the oxidative dehydrogenation of ethylbenzene that normally showed good performance with high activity and stability. In order to achieve high amounts of active functional

groups, the carbon nanotubes were functionalized by means of acid treatment using nitrosulfuric acid (NSA) (Vol% ratio: 1:1; nitric acid 65%: sulfuric acid 98%). The use of NSA acid seems to be the more efficient pretreatment method for MWCNTs that give a high stability of the oxygen functional groups.^[50,60]

However, the kinetic analysis of functionalized MWCNT is not a new topic for the ODH reactions. Therefore, new ideas have been developed that might improve the already good properties of those materials. In case of this work, the catalysts evaluated were MWCNT with deposited vanadium species at different concentrations.

In order to get a stable and uniform distribution of vanadium on the catalyst surface, the atomic layer deposition method (ALD) was applied on the functionalized catalysts; a better explanation of the addition of Vanadium by this method is presented below.

3.1.2.1 Atomic Layer Deposition on MWCNT

The atomic layer deposition is a technique that offers big advantages in comparison to other methods like chemical vapor deposition CVD (see Figure 15). Unlike CVD where the movements of the molecules follow only the direction of the flow, the ALD process allows having a well-controlled deposition. This is mainly due to the self-limiting behavior of the used metal-organic precursor. The ALD approach is defined in two independent half cycles: pulse injection of a metal precursor to transport it to the active surface (substrate) where the reaction occurs, and the second half cycle where the organic ligands of the metal-organic precursor get exchanged due to the non-metal precursor (oxygen sources like H₂O, H₂O₂, NO₂, O₃, etc.) pulse and the resulting formation of new anchor sites. A purging step

between every half cycle to get rid of precursor residuals and reaction products is essential to control the thickness of the deposited species.^[61]

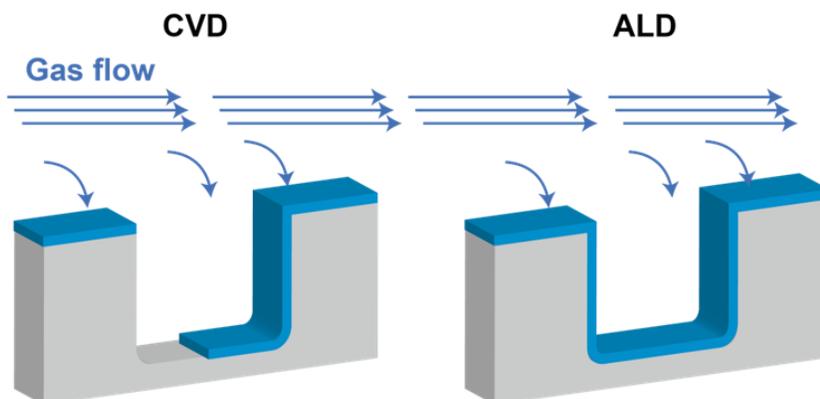


Figure 15: Comparison between coating of textured substrates via CVD and ALD.^[61]

The MWCNT tested in this work were modified by acid pre-treatment and thus create the functional groups that are active for the ODH reaction. A big advantage is that part of the functional groups formed during the acid pretreatment are active for the ALD process as well. The metal precursors can be anchored to the active functional groups and form stable chemical bonds with the catalyst surface. An ALD commercial setup (Savannah S200, Ultratech) was used to deposit vanadium oxide on the functionalized MWCNT. Vanadium (V) triisopropoxide was used as precursor in order to form the active vanadium species for the ODH reaction. A more detailed explanation of the ALD process applied to the samples used in this project is explained elsewhere.^[59]

The vanadium precursor reacts only with specific functional groups on the catalysts (carboxylic, anhydride and phenol groups) as shown in Figure 16. Afterwards, the active vanadium species are bonded to the surface.

One big advantage of the vanadium precursor reactivity with the functional groups is that it does not react with the carbonyl group. The carbonyl group is formed during the acid treatment and is already active for the ethylbenzene ODH reaction. Then, the pristine activity of the MWCNT by this functional group should not be affected by the ALD process. This gives the use of these catalysts a more promising application for this reaction, since the active groups from vanadium and one of the active carbon groups for ODH (carbonyl) are present in the nanotubes after the pre-treatment is completed.

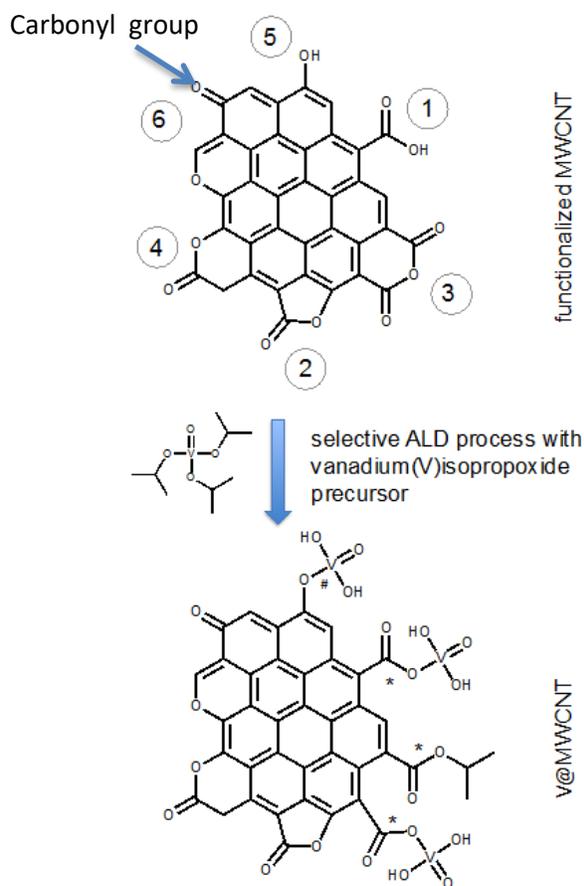


Figure 16: Selective reactivity of the vanadium (V) precursor in the ALD process with specific functional groups.^[50]

Different ALD parameters like dosing times of the precursor were adjusted to get stable chemical bonds between the vanadium and the MWCNT surface.

The MWCNT obtained were divided in six batches. Each batch was used for the ALD process where the number of cycles of the precursor was varied for each sample and thus, dosing diverse amounts of vanadium species on the nanotube surface. Finally, six different catalysts (see Table 4) were available for kinetic analysis by using the reactor ODH setup already explained in chapter 2.

Table 4: Catalyst tested in this study.

Catalyst	Vanadium concentration (mmol/g _{cat})
MWCNT-1	0.0
MWCNT-2	0.1
MWCNT-3	0.4
MWCNT-4	0.8
MWCNT-5	1.0
MWCNT-6	1.3

In order to have a complete screening of the catalytic behavior, the concentration of vanadium was gradually increased as seen in Table 4.

It is important to mention that functionalized MWCNT only by the acid pre-treatment (MWCNT-1) without vanadium deposition was part of the catalytic test. This catalyst was used as base material and thus giving an idea regarding the real influence of Vanadium on the activity of the catalyst in the reaction.

For each catalyst the experimental procedure was applied as mentioned in chapter 2. The main outcome of the catalyst test is explained in this chapter.

3.2 Catalyst deactivation and measurements reproducibility

In order to optimize the experimental procedure and thus to get reliable kinetic results for a correct evaluation of the carbon-based catalysts, many aspects were taken into account regarding obtained the results. One of them was the initial deactivation of the catalyst tested. During the initial measurements there was a constant behavior that appeared for all the materials tested in these experiments. This trend was present at the beginning of every measurement for all the catalyst (see chapter 5.1 in the appendix) where a deactivation based on the decreasing of the styrene rate with time on stream could be observed. In figure 17 the deactivation for the MWCNT-3 sample is shown.

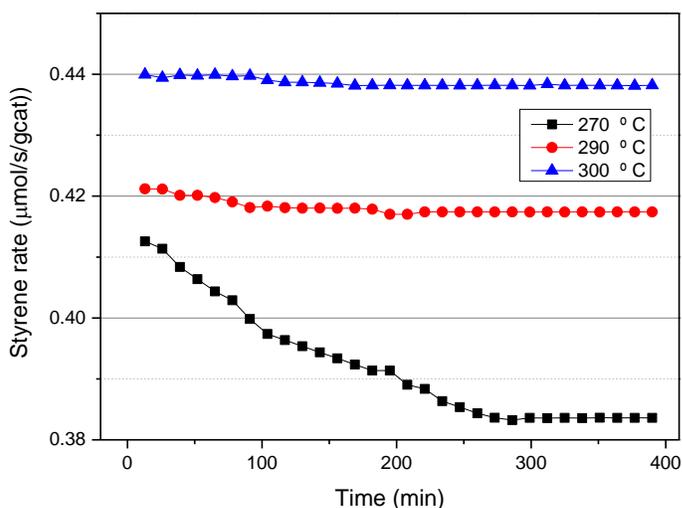


Figure 17: Deactivation in the initial experiments for the MWCNT-3 catalyst.

At 270 °C that which was the initial temperature of the experiments, the deactivation is clear. This may be explained due to the higher initial concentration of active functional groups located on the catalyst surface. Those active groups that are formed during the acid functionalization and by the ALD process are partly desorbed when the catalyst test starts to take place. Most likely the less stable

active sites are the ones that more easily desorb under the reaction atmosphere and thus the initial higher activity immediately decreases with time. However, it can be seen that for the next temperatures steps at 290 °C and 300 °C the deactivation is not that pronounced as at the initial temperature. This can be explained by the possible stabilization of the catalyst, where the less stable active groups decompose at 270 °C and the more stable groups remained on the catalyst surface and, thus, the activity became more stable for the further temperatures steps.

The most likely reason for the deactivation during the catalytic measurements is the initial carbon deposition on the catalyst surface that could appear at the beginning and then covering some of the active sites on the pristine surface. This deposition can come either from the ethylbenzene in the inlet stream or also from the styrene that is initially formed during the reaction that might partially polymerize. Therefore, there would be no desorption but rather carbon deposition on the catalyst surface that at the end could play a role in the catalyst deactivation with the reaction time.

During the deactivation period it was not possible to compare the catalytic activity of the materials tested, since the steady state in the system was not achieved. However, as mentioned before since the deactivation decreased dramatically in the next temperature steps, when the catalysts were tested by a second time with same conditions, it could be observed that the steady state in the system was reached, as seen in Figure 18.

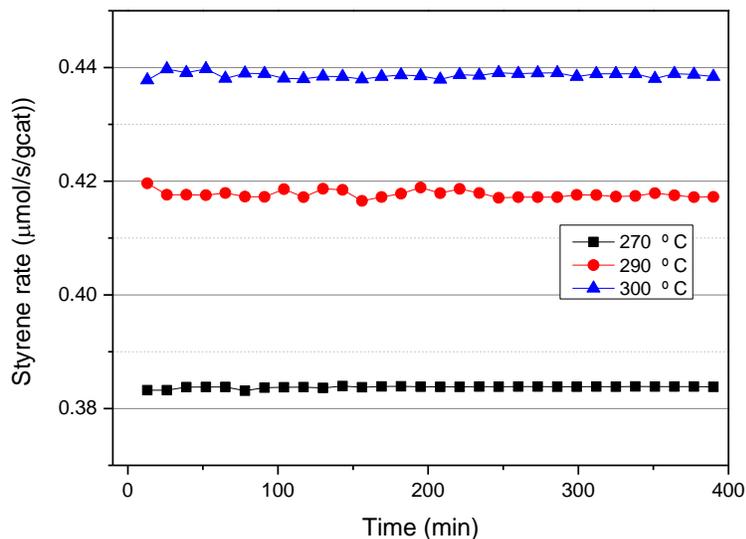


Figure 18: Catalytic stability after initial deactivation.

In Figure 18 the initial deactivation process seems to be over after the second measurements then, a steady state was reached with a constant styrene rate. Regarding the coke deposition that could initially deactivate the catalyst, it seems like this layer remain stable on the catalyst surface.

Only the results where the styrene rate got stable (steady state achieved) were taken into account to make a proper evaluation and comparison of all the catalyst tested.

After these results it can be demonstrated as expected, that the carbon nanotubes are very stable materials for the oxidative dehydrogenation reaction. At each temperature step the styrene rate basically remained constant after the initial deactivation period. This indicates that the functional groups that remained on the catalyst surface afterwards are very stable and the chemical properties and morphology stayed roughly the same during the whole reaction time at every temperature. It is also important to mention that the styrene selectivity was nearly

100% all the time and the possible by-products like toluene, benzene and methane were not detected at any time. This can also be related with the relatively low temperature during the catalytic test in comparison with previous studies. Furthermore, during the same measurements these materials showed high resistance toward combustion due to the low or even undetectable CO and CO₂ concentration in the outlet stream.

Additionally, by following the carbon balance results, they were always close to 100% during the whole measurements. This also confirms the high stability in the system, where after the first period of deactivation experiments, either the coke layer that could be formed on the surface became stable or the amorphous carbon likely produced during the pre-treatment easily desorbs at the beginning of the measurements and thus having a stable catalytic structure even at long time on stream.

Inside the stability of the catalysts is also important to mention the possibility of formation of active oxygen functional groups during the reaction, since it takes place under oxygen atmosphere. The constant styrene rate displayed in the Figure 18 is a clear evidence of the presence of stable functional groups that are continuously reduced and regenerated, similar to the red-ox mechanism proposed on the Langmuir-Hinshelwood model showed in chapter 1.

For all the catalysts the same procedure was applied where the already mentioned deactivation period took place and afterwards the stability and steady-state of the catalytic system was reached.

The pure MWCNT without ALD treatment was used as base materials for the catalytic measurements. Due to its availability in high amounts, this catalyst was tested many times by using the same experimental conditions, repeating the

measurements with the same batch and also by replacing the used catalyst with a fresh one. These measurements were made in order to verify the correct operation of the system and the reproducibility of the measurements. Additionally, by testing the same catalysts with long time on stream it was possible to evaluate the stability of the carbon material.

On the first measurement the reaction was tested with all the temperatures steps. Afterwards, the catalyst was replaced for a new batch and tested again with the same procedure and temperature steps. The results are shown in Figure 19.

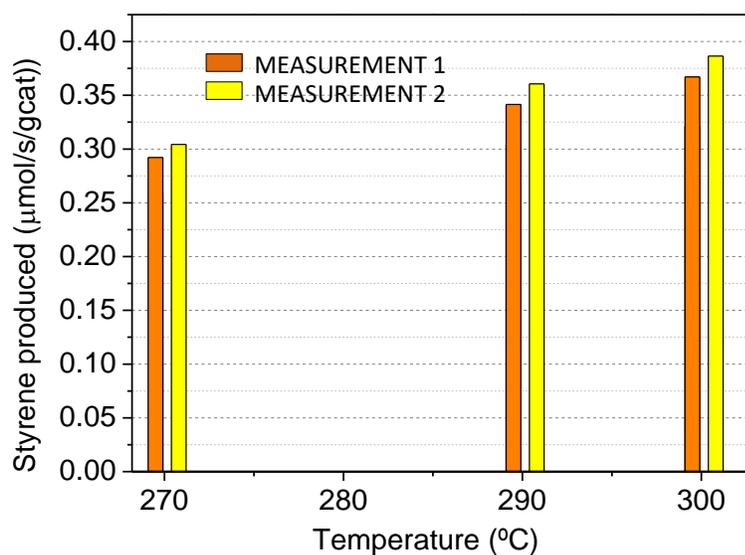


Figure 19: Reproducibility of the measurements for MWCNT-1.

It is important to mention that the values shown were the ones generated after the deactivation period took place. When the steady-state of the system was reached, the styrene rate became almost constant over long time on stream. Then, the average of the styrene rate for each experiment was then for comparison to create the Figure 19.

By comparing the results between the measurements it could be proven that when the catalyst bed was replaced by a fresh one, the styrene rates were roughly the same. Therefore, the system shows a high reproducibility. Just small differences on the styrene rate values between the measurements in every temperature step were observed. By seeing these results, good accuracy was guaranteed for the next measurements where the samples with vanadium deposited by the ALD treatment were used. Therefore, the experimental results obtained could be considered reliable without the need of many repetitions by using fresh batches that could be unnecessary also considering the much lower amount available for the carbon materials treated by the ALD.

Since 300 °C was the highest temperature for the catalytic test, it was considered the condition where the stability of the system could be affected the most, due to carbon deposition or simply catalyst burning. Therefore, an additional stability test was performed after the standard test. Here, the catalyst was kept at this elevated temperature for 20h. The results are shown in Figure 20.

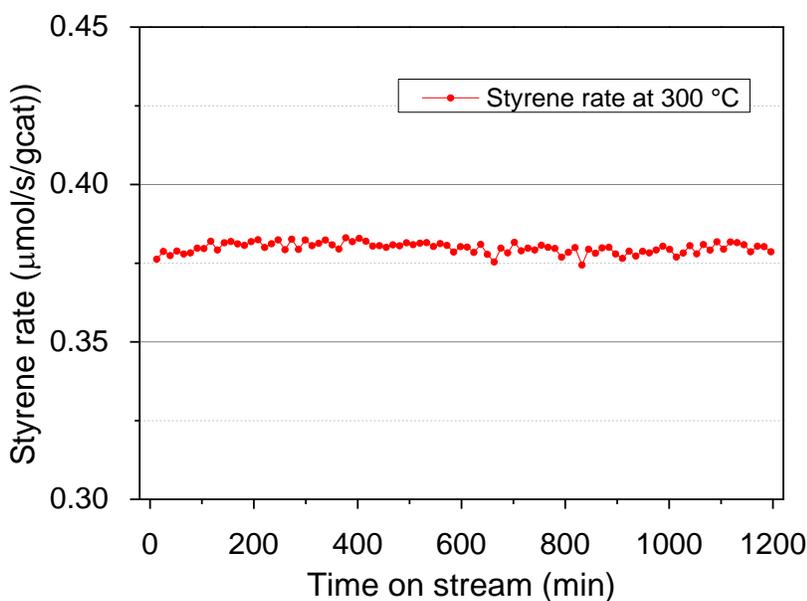


Figure 20: Stability of the MWCNT-1 catalyst at 300°C.

The main idea was to check the stability at 300 °C of the MWCNT that was used as based material for the catalytic test. As observed in Figure 20 this catalyst showed a high stability even at long time on stream. This was a very promising result to carry on with the V promoted MWCNT knowing already that the catalyst base material showed a high stability at the conditions chosen to perform the ODH reaction for the evaluation of the catalysts.

3.3 Vanadium-doped MWCNT for ODH reaction

Following the experimental procedure explained in the previous chapter, a complete evaluation of the MWCNT with different vanadium concentration, deposited by the ALD process, was performed. The catalytic activity of each material for the ethylbenzene ODH reaction was determined by using the setup explained in chapter 2 and afterwards a detailed characterization of the materials by using the methods also explained on the previous chapter took place. The main outcome of these experiments is shown next.

3.3.1 Catalytic test results

The core of this work was the evaluation of the influence of vanadium species on the MWCNTs catalyst surface. Therefore, many catalytic measurements were performed in order to get kinetic results that allowed us to have a clear indication about the variation on the activity of the nanotubes with different vanadium concentrations that were deposited on the surface. The complete evaluation was performed with the already explained experimental procedure. The same procedure was applied for each catalyst. In cases where the amount of the catalyst was high enough, the measurements were repeated by replacing the catalyst bed with fresh material to check the reproducibility of the results.

After the measurements of all catalysts were completed, an average of the styrene rate for each catalyst at every temperature step was determined. They are shown in Figure 21. The initial deactivation period was also considered and, therefore, the values used for the comparison of the results were the ones after steady state was reached.

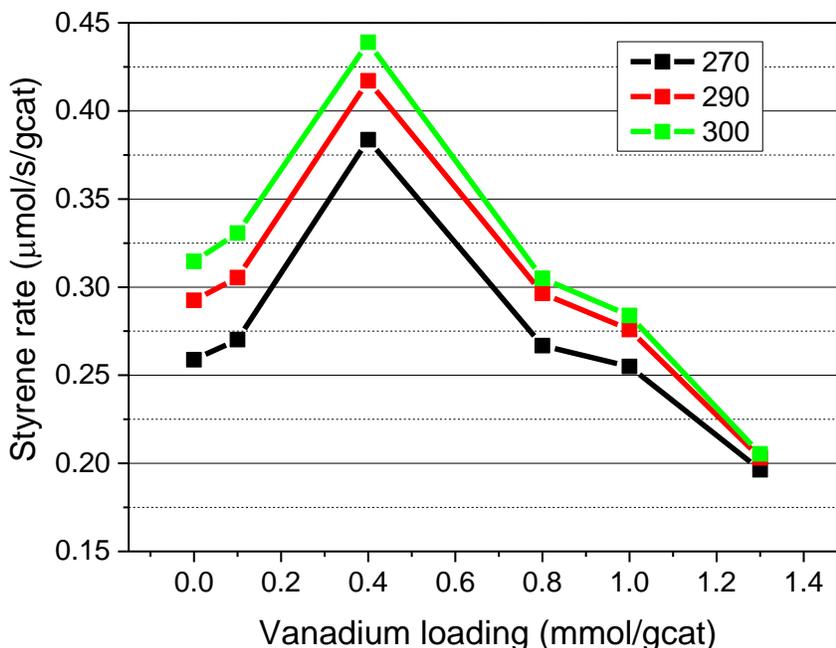


Figure 21: Comparison of the styrene rate for all evaluated catalysts.

As can be seen in Figure 21, there was certainly an influence of the vanadium concentration over the activity of the MWCNT. Comparing the results, the activity seems to slightly increase with even a small amount of vanadium, like 0.1 mmol/g_{cat} in case of MWCNT-2. However, a high increase of the styrene rate was observed when the vanadium concentration increases as seen in the results of the MWCNT-3 with 0.4 mmol/g_{cat}. This is probably due to a high availability of the vanadium active sites combined with the active functional groups already present in the carbon material.

On the other hand, an additional increase of the vanadium concentration changes the trend drastically. A clear decrease of the activity is present for catalysts with a higher vanadium loading. For the catalysts MWCNT-5 and MWCNT-6 that have the highest vanadium concentration (1 and 1.3 mmol/g_{cat}) the activity is even smaller than for the pure carbon sample without vanadium.

These results are somehow expected, since previous studies of catalyst with vanadium loadings as active sites, suggested that there is a possible agglomeration of the vanadium single sites.^[41] In these studies it was demonstrated that at low loadings of vanadium, isolated VO_x species that are believed to be active for the dehydrogenation reaction, are present with active V=O bonds, but at higher vanadium loadings these isolated vanadium species start to aggregate and form V-O-V bonds. These species are harder to reduce than the single sites and, furthermore, this leads to a catalyst deactivation because of the vanishing of the active single sites species and the formation of bulk vanadium V₂O₅ crystallites. Therefore, only well dispersed vanadium single sites species seems to be active for this reaction. The formation of bigger crystallites might delay the reduction of the V⁵⁺ active phase where the nucleophilic attack of ethylbenzene occurred and the styrene is formed.

Another common explanation the decrease of the activity with higher vanadium loading is the dropping of the catalyst surface area also caused by the covering of the porous materials by vanadium that agglomerates and might cover the pores where active sites are located.^[28,41,42]

However, in these studies the vanadium was deposited on other metal-based materials rather than carbon. Therefore, in case of the catalyst studied in this work, where the carbon support also acts as catalyst due to their active functional groups

that play a role in the dehydrogenation reaction, these agglomerates can also hinder the active sites present on the carbon structure.

It seems like there is optimal vanadium loading of around 0.4 mmol/g_{cat} as for the MWCNT-3 catalyst. At this concentration, probably three important aspects play a role in the reaction:

- The active functional groups (carbonyl) already present on the carbon surface of the support.
- The high density of active single sites of vanadium species.
- The formation of an active coke layer on the catalyst surface (as in metal oxides catalysts) that could be formed during the reaction.

The amount of active single sites with the highest oxidation state V⁵⁺ that are present on the surface of the MWCNT-3 catalyst is high enough to improve the activity of the catalyst in comparison with the pristine MWCNT-1. Furthermore, this loading is not so high so that the undesired agglomeration and formation of the much less active bulk V₂O₅ is avoided.

To find a clearer explanation regarding the different activities found during the catalytic tests, different characterization methods were applied on the materials before and after the reaction. These methods gave valuable information that helped us to understand what really happened on the catalyst structure and how it changed during the reaction. The main characterization results are shown later in this chapter.

The produced data from the catalytic measurements was used to determine the apparent activation energy (E_a) of the styrene formation. For all the materials the

activation energy was calculated by means of an Arrhenius plot. The E_a are shown in Figure 22.

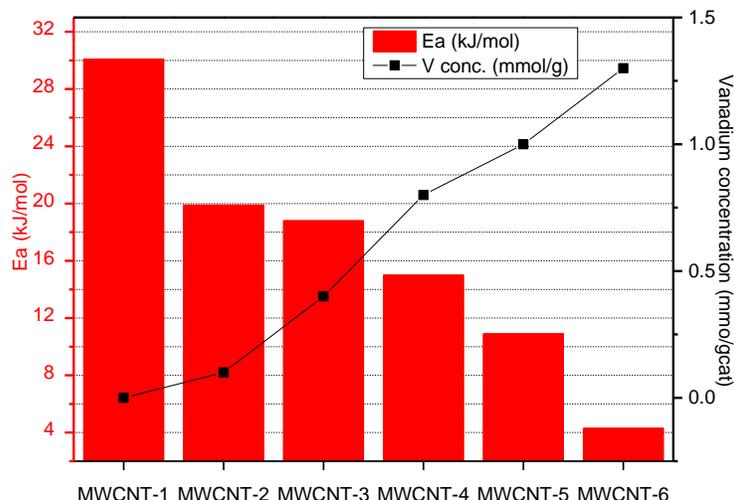


Figure 22: Determined activation energies for the tested catalysts.

In principle the values of the activation energy are low in comparison with values published in previous studies. One reason is the low temperature for the catalytic test. Usually, the temperatures used in previous experiments were around 500 °C. In this study the maximum temperature was 300 °C in order to avoid the problems of burning and deactivation of the catalysts as mention before. At low ranges, the increase of temperature does not seem to have a big influence on the reaction rate and, therefore, generating low values of the slope in the Arrhenius plots. Since the E_a is directly related with the slope, this explains the lower values. For example, in some cases like the MWNCT-6 where the reactivity was really low even at higher temperatures the slope value was really small which is reflected in the also really low E_a value.

It can be ruled out that our kinetic experiments were influenced by mass transport limitations, which usually might be a reason for the observation of low E_a (see Appendix 5.2)

However, it is also important to mention that in case of the most active catalyst (MWCNT-3) the E_a energy is smaller in comparison to the sample without vanadium (MWCNT-1). This could be also an indication of lowering the activation energy by adding V to the MWCNT and, therefore, a real catalytic influence.

Nevertheless, to analyze the catalytic influence by using the obtained E_a values might not be suitable. Due to the low values and low activity for most of the materials analyzed an evaluation of the catalytic impact is not appropriate.

3.3.2 Characterization of the catalysts

After the catalytic measurements were performed, the obtained results suggested a further and deeper analysis by means of different characterization methods. Those measurements gave valuable information for a better explanation of what happened with the materials by a comparison of the catalysts before and after the reaction took place. We focused on the morphology of the carbon materials and analyzed how it changed after the catalytic test in the dehydrogenation reaction.

From the catalytic results obtained, it was decided to choose three catalysts that showed a specific behavior. The catalysts to analyze are the following:

- MWCNT-1 since it was the pure carbon catalyst used as based material to compare with the vanadium-containing catalysts.
- MWCNT-3 as the most active catalyst with a vanadium loading of 0.4 mmol/g_{cat}.

- MWCNT-6 as the less active catalyst with the highest loading of vanadium of 1.3 mmol/g_{cat}.

By looking at the kinetic results the rest of the catalyst did not show big differences in activity in comparison with the MWCNT-1. Therefore, at these concentrations the influence of Vanadium is basically negligible. Consequently, these materials were not considered for a further characterization.

The TEM images showed valuable information about the initial state of the catalysts regarding their morphology and how their structure is modified during the reaction. In Figure 23 the images for the catalysts before and after the reaction are given.

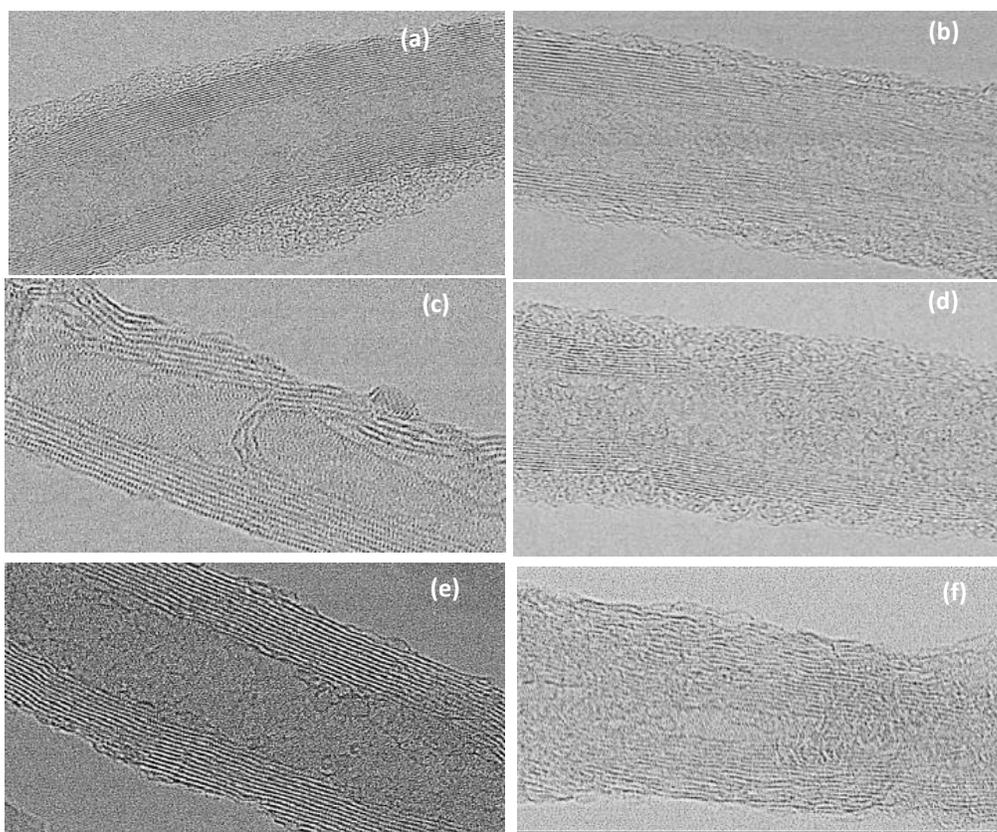


Figure 23: TEM images of MWCNT-1 before/after reaction (a)/(b), MWCNT-3 before/after reaction (c)/(d), MWCNT-6 before/after reaction (e)/(f).

It can be seen that the MWCNT-1 before reaction has a clear amorphous carbon layer. This layer could be formed during the functionalization by acid treatment. As shown in previous studies, the treatment of MWCNT with acids (nitrosulfuric in our case) can modify the initial graphitic structure of the nanotube. Specifically when nitrosulfuric acid is used, there is a clear decomposition not only on the surface layer but also in the inner structure, increasing the number of defect sites on the catalysts. Consequently, this can explain the roughness of the catalyst before the reaction.^[60]

After the reaction, the catalyst seems to get partially “clean”. The structure of the nanotubes looks cleaner and a big portion of the amorphous layer that appeared before the reaction is no longer laying on the surface. This is a good indication that the catalyst is modified during the reaction. Primarily, the amorphous carbon decomposed since it was the less stable part of the catalyst. With the presence of oxygen at relatively high temperatures, decomposition of this layer is somehow expected. It can also be seen that not only the disordered carbon on the surface decomposes, since the inner the part of the nanotubes also looks better defined after the reaction.

The decreasing of the amount of amorphous carbon on the catalyst after the reaction, can also explain the deactivation period mentioned before. Knowing that the functional groups are formed mainly on the defect sites, this amorphous carbon formed during the acid treatment normally contains a high amount of the functional groups active for the ODH reaction. Therefore, the deactivation occurs partly because that “active” layer of amorphous carbon is decomposing gradually during the reaction time.

Finally, although the structure of the catalyst seems to be more graphitic after the reaction, there is still an amorphous layer on the surface. Since the activity after long time on stream became stable, it might be that this coke layer is also stable and the functional groups located on it are being reduced and oxidized constantly (as shown in the reaction mechanism, see chapter 1) in a steady way.

For the MWCNT-3 at a first glance the differences between the catalysts before reaction in comparison with MWCNT-1 are clear. The initial amorphous layer formed during the acid treatment is gone. Most likely, decomposition of this disordered carbon occurred during the ALD treatment. It looks like the conditions during the ALD procedure with temperatures of 150 °C are high enough for decomposition of the amorphous carbon already present in the catalyst. Therefore the surface and structure of the nanotubes before the reaction looks clean.^[59]

However, the deactivation period was also present in this catalyst. This can be explained by the presence of less stable functional groups located not only on the amorphous carbon layer, but also on the nanotube surface. Some of these active groups could decompose in the initial catalytic test since they are located on the more graphitic sites. Normally, the bonds between the functional groups on graphitic carbon are weak, so the stability of these groups is really low. Therefore, the initial decomposition of these groups and, accordingly deactivation occur.^[16]

Big changes on the MWCNT-3 catalyst structure takes place during the reaction. By looking at the TEM images a thick layer of amorphous carbon is deposited on the nanotube surface during the reaction. Since this was the most active catalyst, it is clear that this layer plays a crucial role on the catalytic activity. Possibly the activity of the catalysts is partly due to this coke formation on the surface. The vanadium species could also play a role by inducing the coke formation that is

active for the reaction. This behavior is not so different from the metal-oxide based catalysts that were explained in the introduction part.

By comparing the behavior of the pure carbon MWCNT-1 and MWCNT-3, it seems like two important facts play a role to obtain a high catalytic activity. One is, that active groups already present in the MWCNTs, formed during the pretreatment by both acid to form the carbonyl groups, and the vanadium active species through the ALD process in addition. The second fact is the coke layer formation during the reaction which is active and eventually gets stable due to the steady state reached on the reaction.

In case of the MWCNT-6, the catalyst with the highest vanadium concentration, the vanadium seems to inhibit the activity of the nanotubes. The activity of this catalyst was the lowest and even below than the sample MWCNT-1 without vanadium.

Some similarities in the structure with the MWCNT-3 catalyst before reaction can be observed. Again the material gets cleaned during the ALD treatment, since almost no amorphous carbon can be observed on the catalyst before the reaction test.

Nevertheless, the image of the catalyst after the reaction show that besides some differences on the nanotubes shapes, the morphology did not change so much after the reaction. As mentioned in previous chapters there are many studies that explained the influence of high concentrations of vanadium on the catalyst. Normally the catalytic activity drops down when high amounts of vanadium are used.^[41,42] The agglomeration of the V species leads a to reduction of the most active species (V^{5+}) and crystal formation, that does not show any activity for the ODH reaction.^[19] These agglomerates could even cover the active sites present on

the carbon material, which explains the lower activity compared to pure carbon sample.

However, another key fact of the catalytic activity that was mentioned before is the coke layer formation. The MWCNT-6 had a really low or even none amorphous carbon formation on the surface. This confirms the important role of the coke layer in the catalytic activity. Probably the vanadium crystallites besides covering the active groups for the ODH reaction also hinder the active coke formation during the reaction. On the other hand it seems that only vanadium single sites induce the coke formation.

In order to confirm the differences in the catalyst structure before and after the reaction observed in the TEM images, TPO experiments were performed. The main idea was to analyze the stability of the MWCNTs under oxygen atmosphere and, thus, detect whether the morphology actually changed during the reaction as shown on the TEM images.

All the TPO profiles give valuable information regarding the burning resistance of the catalysts. However, in order to have a better and easier comparison of the catalyst behavior during these experiments, a calibration method was used (see chapter 5.5 in the appendix) in order to quantify the CO and CO₂ desorbed during the measurement. The amount of CO and CO₂ can be seen in figure 24.

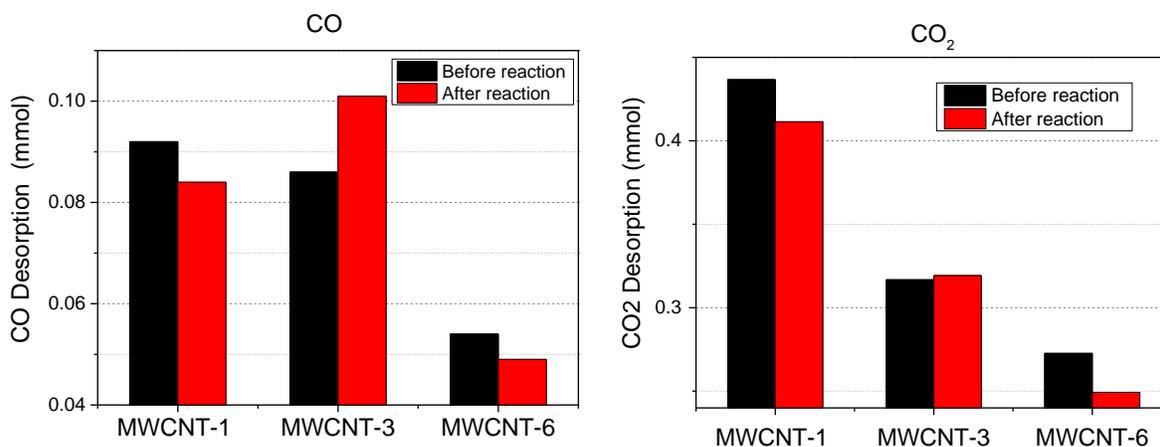


Figure 24: CO and CO₂ evolution during TPO measurements.

By looking at the Figure 24 comparing the amount of CO and CO₂ evolved during the TPO, the catalyst before reaction showed higher amounts for both. This could also be linked to the presence of more disordered carbon in the whole structure of the pristine nanotubes.

In the TPO profiles for the MWCNT-1 (Figure 25) it can be seen that the fresh catalyst starts to burn earlier. This can be related with the already mentioned presence of the amorphous carbon that was formed in the acid treatment.

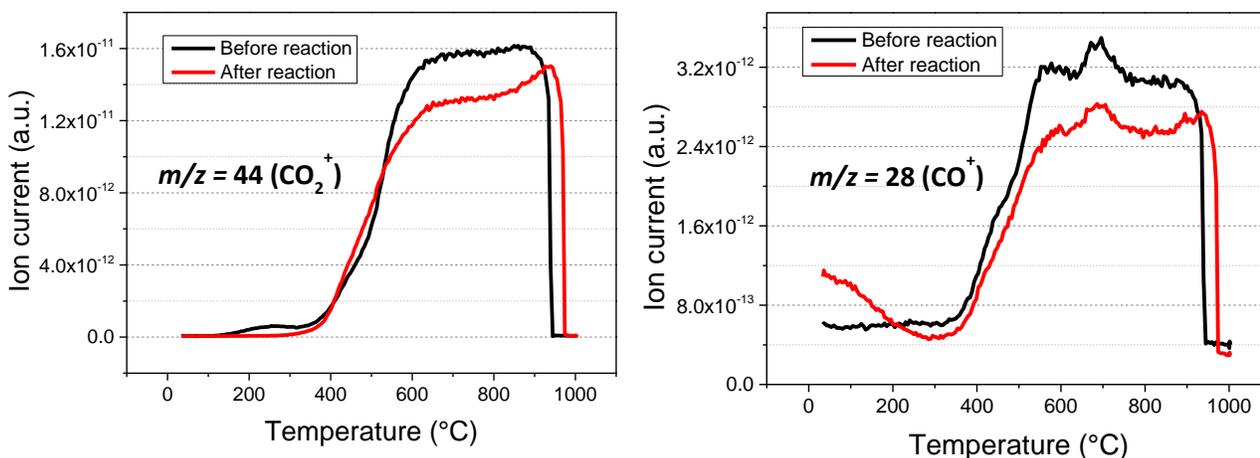


Figure 25: Profiles of CO₂, and CO during TPO analysis for MWCNT-1, fresh and used catalysts

The TPO profiles on Figure 25 for the MWCNT-1 catalysts are in good agreement with the expected behavior. Therefore, it was confirmed that the fresh catalyst has a more disordered structure, and it gets clean during the reaction. However, also a constant and stable layer of amorphous carbon remained on the surface after the reaction which appears to be active for the ODH reaction.

For the most active catalyst MWCNT-3 with 0.4 mmol/g_{cat} of vanadium, when the amount of CO and CO₂ produced are compared, the differences became very clear. The profiles are shown in Figure 26

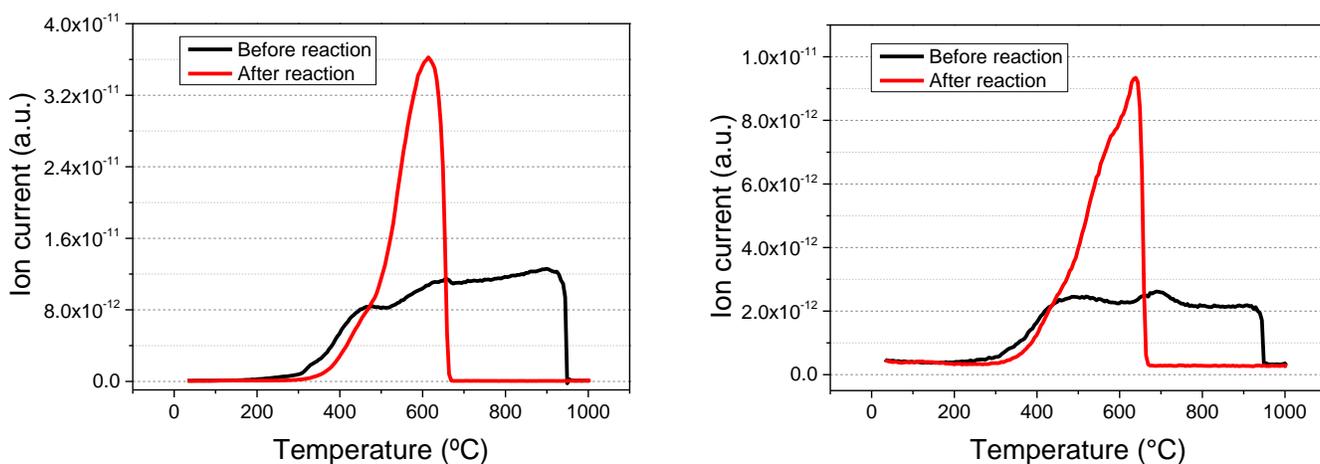


Figure 26: Profiles of CO₂ and CO during TPO analysis for MWCNT-3, fresh and used catalysts

The catalyst after reaction showed higher amounts for the CO and CO₂ probably due to the presence of more disordered carbon on the surface. This can be explained by the thick layer of amorphous carbon that was formed during the reaction as observed in the TEM images.

Since this catalyst was the most active, these profiles again corroborate the explanations given before. The MWCNT-3 has a high activity mainly due to the active amorphous carbon layer formed during the reaction that is steadily laying on the surface while the reaction is taking place.

This coke layer, besides being active is very stable during the reaction, by looking at the profiles on Figure 26 these results also confirm the stability of the amorphous carbon layer at the reaction conditions (below 400 °C and 2% of oxygen). The CO and CO₂ evolution starts later for the catalyst after reaction. The fresh catalyst start to burn a bit earlier, probably due to the presence of unstable amorphous carbon that is laying in the fresh material even after the ALD treatment. This amorphous carbon desorbed completely during the catalytic test. Then, the active coke layer that is deposited on the surface during the experiments showed high stability at the reaction conditions (below 300 °C). This can explain the evolution of CO and CO₂ at higher temperatures for the catalyst after reaction.

Finally, by comparing the TPO measurements for the MWCNT-6 the differences are very clear with the other two catalysts. In Figure 27, it can be observed that the amount of CO and CO₂ that evolved from the sample is considerably smaller due to the much lower presence of amorphous carbon on the surface even after reaction.

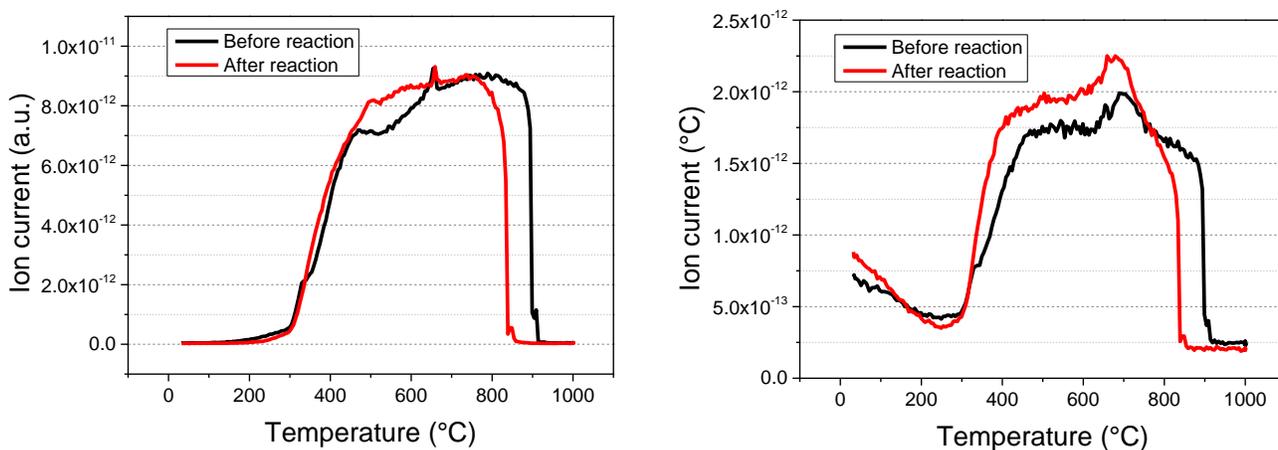


Figure 27: Profiles of CO₂, and CO during TPO analysis for MWCNT-6, fresh and used catalysts.

Since this is the catalyst with the highest amount of vanadium it means, that it stayed longer in the ALD device, and the amorphous carbon removed almost completely after this treatment. Furthermore, after the reaction took place, as observed on the TEM images, no coke layer was formed during the reaction and the catalyst even has less disordered carbon after reaction as seen in Figure 24, were the amount of CO and CO₂ decreased after the kinetic measurements.

These results highlight again the importance of the active coke layer on the nanotube surface that is being formed on the sample during the reaction. When this layer is not present the activity is very low like in the case of MWCNT-6

Afterwards, in order to identify the functional groups present on the catalysts TG-MS measurements were performed. A detailed analytic procedure of the oxygen functional groups by TG-MS was developed previously in our research group.^[50] The same method has been applied in this study.

As mentioned in the introduction part, the TG-MS analysis is an accurate tool to identify the presence of different oxygen functional groups in the catalyst. The functional groups decompose at different temperatures forming CO and CO₂ depending on the group (see Table 5). With the method applied in this study by using isothermal steps, it was possible to get a clear separation of the groups that evolve during the heating.

Table 5. Oxygen functional groups present on carbon materials.^[50]

Functional group	Temperature (°C)	Detected species
Carboxyl	275	CO ₂ + H ₂ O
Anhydride	435,460	CO ₂ + CO
Lactone	650	CO ₂
Phenol	735	CO
Ether	735	CO
Carbonyl/Quinone	920	CO

Due to the specific interest of the CO and CO₂ evolution, the results are focused on the ion current of CO₂⁺ (m/z 44) and CO⁺ (m/z 28) detected by the mass spectrometer. All the MS profiles of these TG-MS experiments are given in chapter 5.3 in the appendix.

The main reason of these measurements was to determine the exact amount of the active functional groups that were present during the reaction. Therefore, the peak areas of the MWCNT-1, MWCNT-3 and MWCNT-6 were determined and by means of the same calibration used for the TPO measurements the total amount of the functional groups were obtained. The amount of each functional group for the three catalysts and their comparison before and after reaction can be seen in the Figure 28.

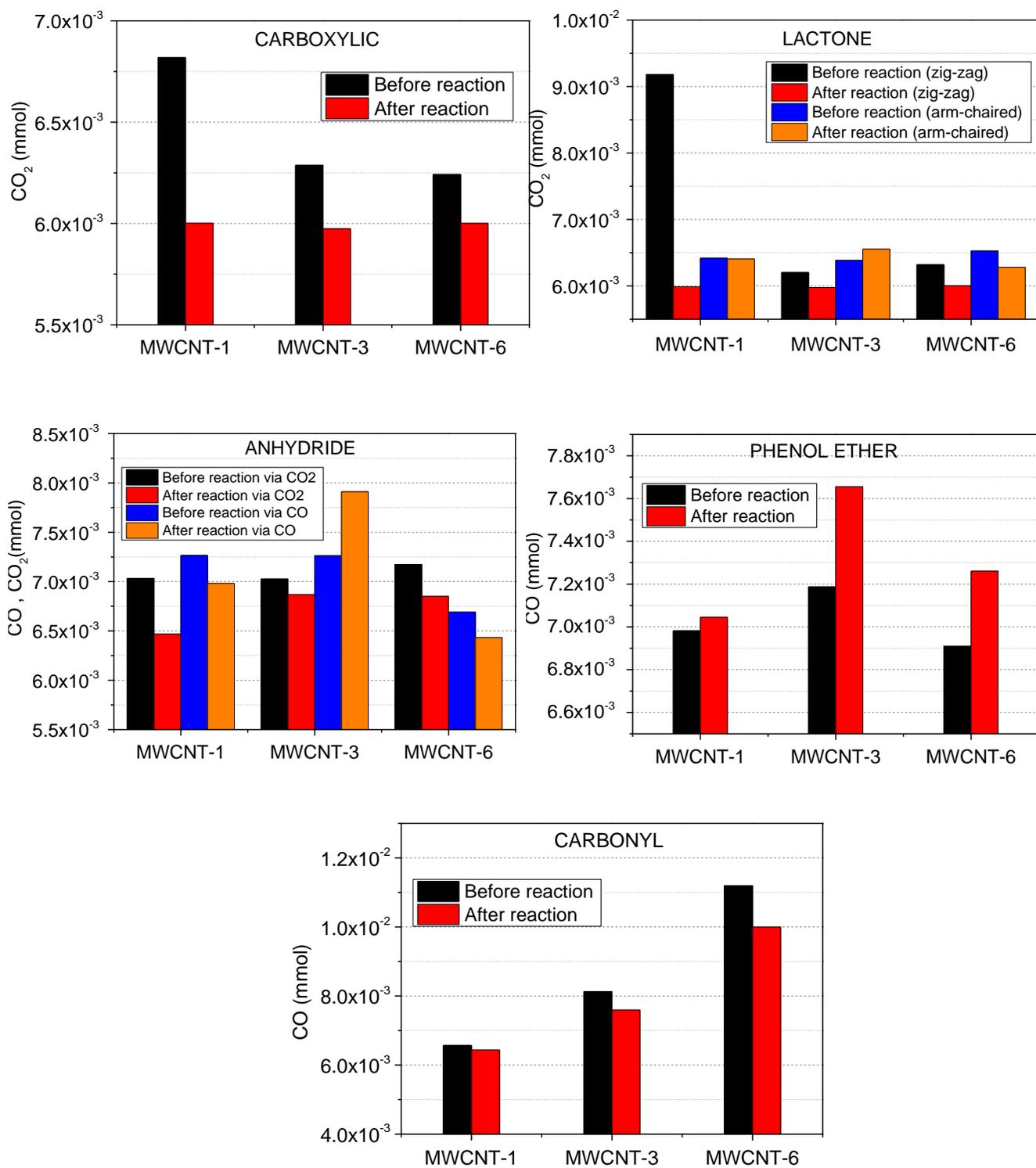


Figure 28: Amount of functional groups contained on the tested catalysts before and after the catalytic test.

By analyzing each of the functional groups in Figure 28, that are located on the catalyst, it can be confirmed that in the case of the most active catalyst the concentration of some of the functional groups increased during the reaction. Probably, as mention before, most of these functional groups are then located in the active amorphous carbon layer that was formed during the catalytic test.

By comparing the functional groups in the samples before the catalytic test, the presence of a high concentration of some functional groups for the untreated sample MWCNT-1 is observed. These functional groups (carboxylic and lactone) are considered the less stable ones since they evolved at the lowest temperatures. Therefore, a part of these functional groups were located in the amorphous carbon that is formed during the acid pretreatment and most of them easily evolved during the catalytic measurement. Likewise, this explanation is also confirmed by looking at the much lower concentration of these groups for the ALD treated samples were most of the amorphous carbon layer generated during the acid treatment is also removed. With these results one can conclude that the carboxylic and lactone group do not seem to play an important role for the catalytic activity since there are no big differences on the concentration of them if we compare the most and less active samples (MWNCT-3 and MWNCT-6).

On the other hand, for more stable functional groups like anhydride (via CO) and phenol ether the trend changes. The concentration of the phenol ether groups is increase after reaction. For the most active sample even the anhydride via CO increased and it can be seen, that the concentration of these groups together with the phenol group are the highest. This can be a good insight that these groups participate on the reaction and have an influence on the catalytic activity. Most likely these “new” groups formed during the ODH reaction are located on the

active coke layer observed in the TEM images. This result emphasizes even more the importance of this coke layer for improving the catalytic activity.

Although it is in general believed, that only carbonyl groups are active for the ODH reaction these results suggest that also other oxygen functional groups can play a role on the activity of the catalysts. Some previous studies also explained how some functional groups beside the carbonyl groups also could be modified during the reaction and be transformed into a quinone-ketone like active group. Most of the groups that contain hydroxyl, carboxylic acid, and anhydride groups on the CNT surface would convert to ketonic or quinoidic carbonyl groups during the reaction which have a higher thermal stability.^[18,50]

Finally, the presence of the most stable functional group (carbonyl) which is also believed to be the active group for the ethylbenzene ODH reaction, seems to increase when the concentration of vanadium increases as well. This can be explained by the inactivity of this functional group on the ALD process as mentioned before and its high stability that makes that this group stays in the material during the ALD treatment. However, it is important to mention that although the MWCNT-6 was the catalyst with the highest concentration of the carbonyl group, it was also the less active. This can be explained first by the high vanadium concentration and formation of vanadium agglomerates that inhibit the activity of the catalyst. Furthermore, as seen in previous studies where vanadium species on nanotubes are analyzed, the reduction of vanadium on MWCNT are reflected on a rise of the CO⁺ signal at the same temperature where the carbonyl groups are identified.^[50] Therefore, most likely the quantification of these groups is not reliable due to the overlapping of the CO evolution of both vanadium reduced species and carbonyl groups. This concept can be confirmed by the signals of the CO desorption at 900°C for the catalysts with vanadium deposited in comparison

to the pure carbon material (MWCNT-1). Likewise, the catalyst with most vanadium deposited (MWCNT-6) showed the highest “carbonyl” amount since also has the highest reduced vanadium species that agglomerate and deactivate the catalyst as explained before.^[50]

The application of this method in order to identify the oxygen functional groups can be very effective for graphitic materials like carbon nanotubes. However, the accuracy of the method can be affected when high amounts of amorphous carbon are present in the material. Since some of the catalysts showed coke layer formation after reaction, the results reflected here could be affected by this carbon deposition. Nevertheless, we consider this method as an attractive tool to give insights regarding the presence and modification of the active functional groups during the reaction.

3.3.3 Proposed mechanism of vanadium species

In previous studies it was demonstrated that at low loadings of vanadium, isolated VO_x species that are believed to be active for the dehydrogenation reaction, are present on the surface as V⁵⁺. As the Langmiur-Hinselwood mechanism suggests, in case of the carbon active groups, on the first step the ethylbenzene molecule is activated by the extraction of the alkyl hydrogen atom by the contact with the C=O (carbonyl) bond located on the carbon material, to form styrene. After the dehydrogenation step the C=O is being reduced forming hydroxyl C-OH species. Afterwards, the hydroxyl species are re-oxidized to form again the carbonyl bonds by means of the oxygen which is the other reactant. This functional group does not react with the vanadium precursor during the ALD process and thus remains on the nanotube surface before the reaction takes places. The presence of both active

groups from vanadium and carbon cause an improvement of the activity as observed for the catalyst with 0.4 mmol/g_{cat} (S-3).^[41]

On the other hand, in case of the vanadium active sites, the mechanism may occur in a different way. It could happen that the oxygen activation occurs first and afterwards the ethylbenzene dehydrogenation step takes place. A schematic representation of the proposed reaction mechanism is shown in Figure 29.

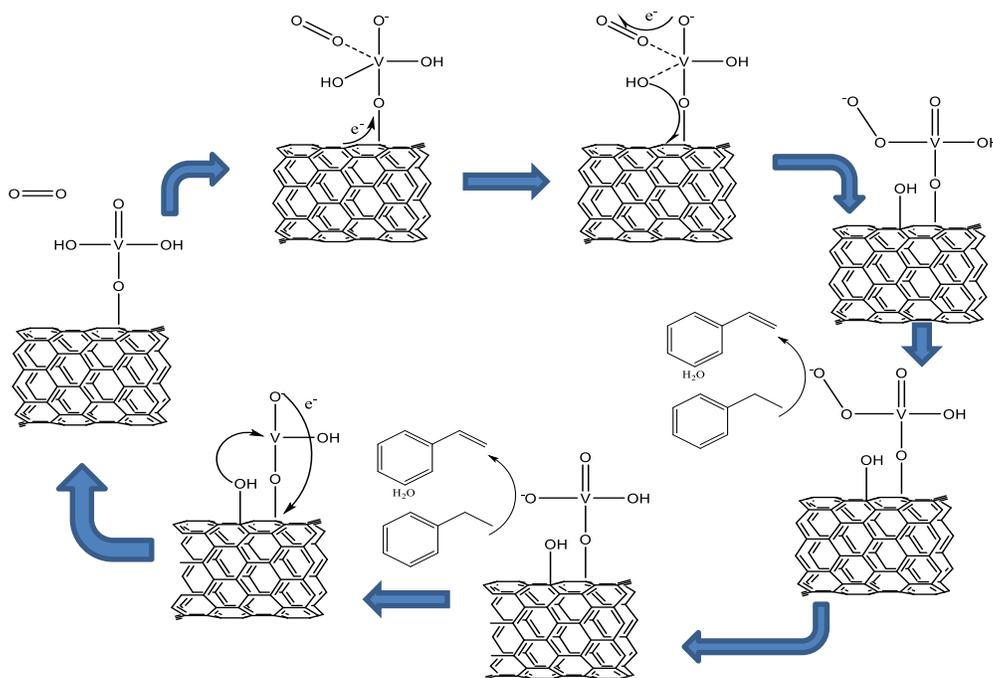


Figure 29: Proposed mechanism for the ethylbenzene ODH reaction, on Vanadium modified carbon supports.

First, the activation of oxygen takes place by means of the active vanadium specie attached on the nanotube surface. The oxygen interacts with vanadium after an electron transfer from the carbon support (MWCNT) to the double bonded oxygen. The electron migrates through the oxygen atom that is bridging the carbon support and the vanadium specie (V-O-C). On the next step, one electron is transferred from the V=O bond and is then reduced forming the O⁻ specie. Afterwards, the

migration of the initial –OH bond to the carbon surface takes place. After that, the O^- specie formed during the oxygen activation is in charge of the reaction of the ethylbenzene molecule that is dehydrogenated to form styrene and water as products, generating the desorption and electron transfer from this O^- to the neighbor O specie. The regeneration of the active vanadium specie takes place after a second consecutive dehydrogenation step where again styrene and water are formed thanks to the extraction of the other O^- specie left. Finally, an electron transfer from O^- to form again the $V=O$ bond and the OH placed on the carbon surface to the vanadium restore the active vanadium group to the initial state.

This mechanism highlights the interaction between the carbon nanotube and the vanadium species deposited. During the reaction the nature of the carbon support also played an important role on the activity of the catalyst when active vanadium species are present.

On the other hand, as mentioned before, at higher vanadium loadings the isolated vanadium species start to aggregate and the link with the carbon support gets lost due to destruction of the C-O-V bond. Therefore, no electron transfer is possible between the carbon support and the vanadium specie. Furthermore, the formation of polymeric V^{5+} with bridging V–O–V bonds hinders the oxygen activation step due to the absence of OH- species. The V-O-V bonds are harder to reduce than the single sites, and lead to a catalyst deactivation also due to the vanishing of the active V^{5+} species.

4. Conclusions

A detailed evaluation of MWCNTs for the oxidative dehydrogenation of ethylbenzene (ODH) was performed. It was possible to study the influence of vanadium that was deposited by the ALD process on the functionalized MWCNTs. The main approach of this study was to focus on the catalyst structure and how it is modified during the reaction. Different characterization methods like TEM, TG-MS and TPO were applied to the catalysts before and after reaction in order to get information regarding their morphology and the active site.

The catalytic evaluation for each catalyst showed an initial deactivation that was caused by the evolution of the less stable active groups that occurred at the initial temperature steps. Nevertheless, in the following temperature steps all the catalysts showed high stability with constant styrene rate at each measurement with the temperature steps.

It was possible to find an influence of the vanadium that was deposited on the functionalized MWCNT by the ALD process. At low concentrations there was a positive influence by enhancing the catalytic activity in comparison with the pure carbon catalysts. The availability of active vanadium single sites in parallel with the active groups placed on the carbon surface seems to improve the styrene formation up to optimum concentration of 0.4 mmol/g_{cat}. However, when the vanadium concentrations are higher (above 0.8 mmol/g_{cat}) the activity is negatively affected. The active vanadium single sites agglomerate at higher concentrations and become inactive for the ODH reaction and even hinder the activity of the nanotube itself by blocking the functional groups, having lower activity than the

pure carbon catalyst as seen for the material with highest vanadium concentration (1.3 mmol/g_{cat}).

On the other hand, TEM and TPO analysis proved the big influence of the amorphous carbon deposited on the catalyst surface on the activity. This coke which is formed during the reaction seems to play a crucial role, having a direct relation between catalyst activity and coke formation. This layer seems to become the main active site while the reaction is taking place and this could be explained by the big differences on the coke layer between the most and the less active catalysts. Whereas, the MWCNT that showed the highest activity contents a thick layer of active coke as seen in the TEM images and further confirmed by means of TPO measurements. The same methods indicated that the less active catalyst had almost no disordered carbon on its surface.

Therefore, the influence of the active coke on the activity is very important and most likely the role of vanadium is partly to enhance this coke formation on the nanotube surface. When the vanadium concentration gets too high, the coke formation did not occur and the catalyst is basically inactive for the ODH reaction.

Finally, a detailed analysis of the functional groups content on the catalysts by means TG-MS was performed. In principle, by comparing the samples with vanadium and the pure carbon sample, as expected, the consumption of some of the oxygen functional groups takes place during the ALD process. Those functional groups react with the vanadium precursor to generate the vanadium sites chemically adsorbed to the nanotube surface. Furthermore, it was also possible to corroborate by comparing the most active catalyst before and after the ODH reaction that the active coke formed during the reaction holds a higher content of

some active groups. This result supports the idea of a higher catalytic activity when coke layer is present.

However, a direct relation between catalytic activity and carbonyl groups that is active for the ODH reaction was not possible to determine. The catalyst with the highest vanadium loading had also higher carbonyl content but it was almost inactive in the ODH reaction. This is due to the probed vanadium agglomeration that hinders the activity of carbon active sites besides the reduction of these agglomerates that overlap the peak of carbonyl groups analyzed by the TG-MS method.

Additionally, those results also support the indication that other functional groups play a role on the reaction, and some of them are presumably modified to carbonyl groups while the reaction is taking place. Although, to have a better insight regarding the alteration of functional groups while the reaction is taking place, in-situ analysis methods must be developed.

This study reveals the good properties of the MWCNTs for the ODH reaction and the positive influence of vanadium when low concentrations are used. The results shown here also suggest that not only the pre-treatment to form functional groups is necessary, but also how the catalysts characteristic can be adjusted to enhance the active coke formation. This is where the vanadium played a role in our case.

5. Appendix

5.1 Initial deactivation of tested catalysts

As explained in the chapter 3, the initial deactivation period was present for all the catalysts tested in our project. The rest of all the plots can be seen next.

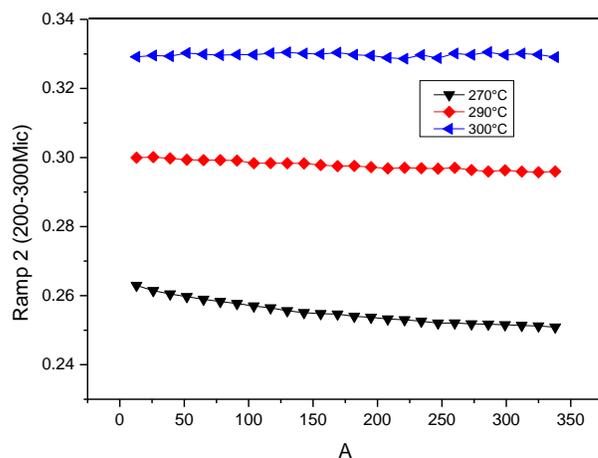


Figure 1A: Catalytic deactivation in the initial experiment for MWCNT-1 (pure carbon) catalyst.

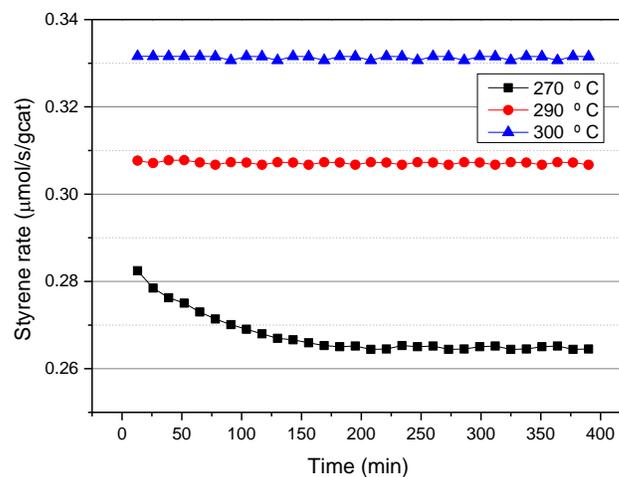


Figure 2A: Catalytic deactivation for initial experiment for MWCNT-2 (0.1 mmol/g_{cat}) catalyst.

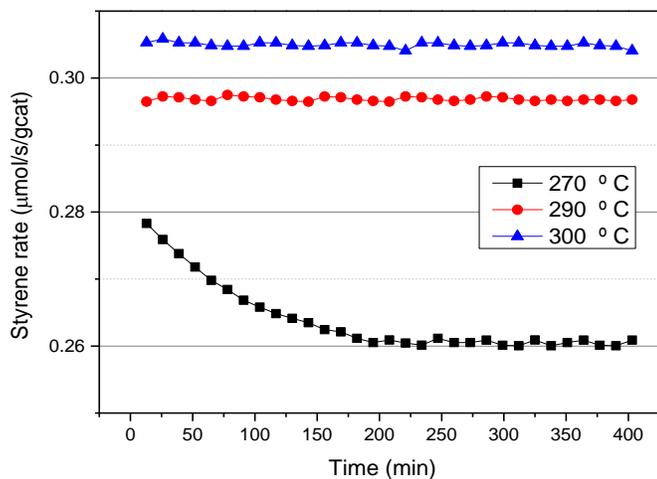


Figure 3A: Catalytic deactivation for initial experiment for MWCNT-4 (0.8 mmol/g_{cat}) catalyst.

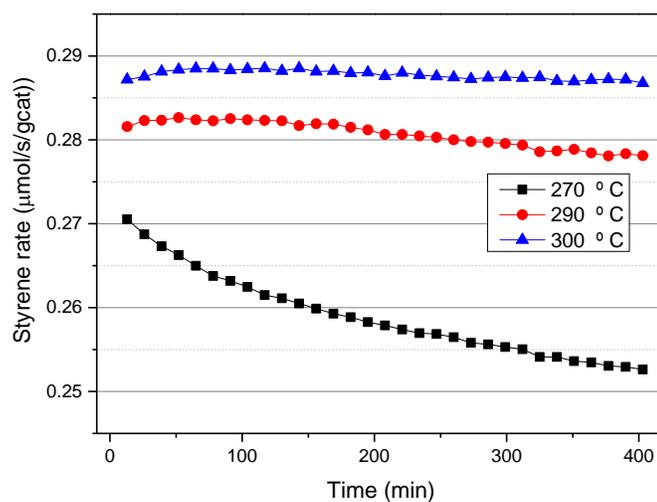


Figure 4A: Catalytic deactivation for initial experiment for MWCNT-5 (1 mmol/g_{cat}) catalyst.

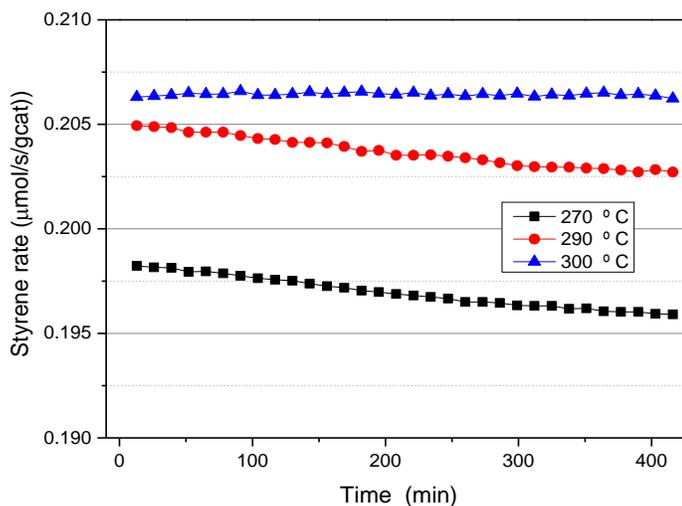


Figure 5A: Catalytic deactivation for initial experiment for MWCNT-6 (1.3 mmol/g_{cat}) catalyst

5.2 Mass transfer limitation experiments

Mass transfer limitation can play an important role in the reaction kinetics, either in the conversion or in the product formation. In homogeneous reactions this effect is almost negligible since all the components are in the same phase and well mixed. However, in heterogeneous reactions where usually the catalyst is in a solid phase and the reactants are in liquid and gas phase the reaction rate can have a big dependence on the mass transfer diffusion between the phases.

Something to take into consideration before performing kinetic measurements is to exclude the possibility of having limitations by mass transfer. This is possible when the rate of the mass transfer to the active sites is less than the rate of the reaction. In order to test whether this phenomenon is present in our system, different experiments were performed. The results are shown next.

5.2.1 Mass transfer limitation by pore diffusion

In heterogeneous reactions the catalysts are normally porous solids with really high surface area. This area is mainly located in the inner part of the solid and corresponds to the walls of pores. In order to reach the active sites located inside the pores the reactants have to diffuse inside them. In the case of high reaction rates this diffusion can cause a gradient of concentration inside the pores. The main idea of performing these experiments is to verify if with the chosen experimental conditions these concentration gradients are considerably small.^[62]

One of the more used methods to determine experimentally the effects of the pore diffusion limitation, is changing the particle size of the catalyst and perform experiments at same conditions. In case of diffusion limitation present in the system the utilization of the catalyst particle is incomplete and, therefore, leads to

different results in conversion and selectivity with the change of the mentioned particle size.

Multiwalled carbon nanotubes without any atomic layer deposition treatment but functionalized by means of nitrosulfuric acid was used for the experiment (MWCNT-1). The main results are shown in Figure 6A.

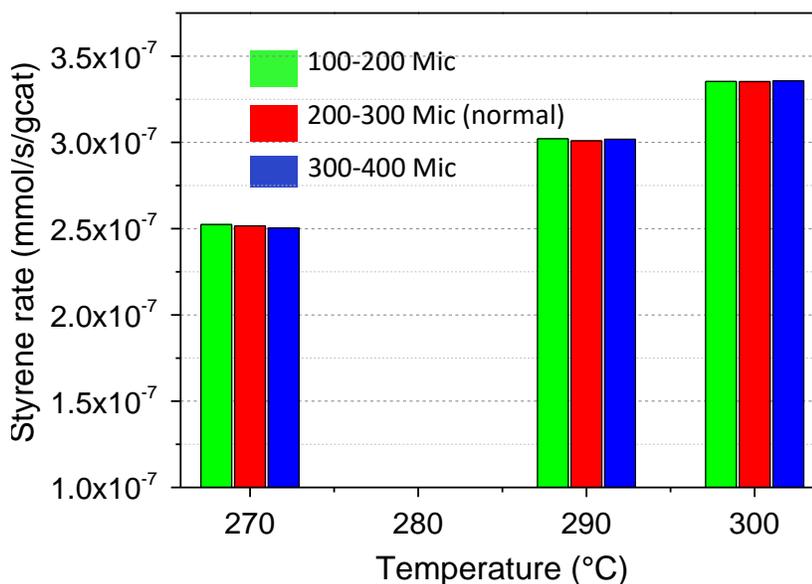


Figure 6A: Results of the test for mass transfer limitation by pore diffusion comparison.

The experiment was performed by using three different particle sizes of the catalyst. First the particle size used at normal conditions (200-300 μ m) and two more batches of catalyst with smaller (100-200 μ m) and bigger (300-400 μ m) fractions of the particle size. According to the results shown in Figure 6A, there are no bigger differences on the styrene rates between the experiments by changing the particle size. Seeing these results, it is possible to say that the influence of the particle size is negligible and internal gradients are absent even with finer particle sizes of the catalyst. Therefore, there is no limitation caused by pore diffusion for the chosen reaction conditions.

5.2.2 Mass transfer limitations by external diffusion

The stream concentration around the catalyst sites normally should be the same from the particle surface to the active sites of the pores. This kind of limitation can be present when the diffusion from the bulk phase to the surface of the catalyst is slow. Then the external mass transfer resistance can get really high and could be considered as an important factor. The resistance can be controlled by the reaction conditions like pressure, temperature and particle size of the catalyst.^[62]

This phenomenon is related to the linear velocity dependence from the system and explained the possible rate variation by the intraparticle diffusion. If the conversion changes by varying the linear velocity while the residence time is kept constant, it means that the rate is being affected by external mass transfer. The mass transfer resistance must be small compared to the surface reaction resistance.^[62]

A usual way to rule out the presence of external mass transfer limitation is by varying the fluid velocities of the reactants with a fixed amount of catalyst and then repeating the experiment with a different amount of catalyst. Another good way is by varying both the flow rate and the catalyst mass and for a second experiment use a different amount of catalyst but also change the flow rate to keep the same residence time of the initial experiment. In either ways the results should be similar in the absence of external mass transfer limitation.

The main idea of this experiment was to evaluate the possible presence of external mass transfer limitation. Three experiments were performed, one with the normal chosen experimental conditions of catalyst mass (100mg) and total flow (40 ml/min) and the other two by varying proportionally the total flow rates and the catalyst mass for each experiment. For the first experiments the total flow and the catalyst mass were reduced to half of the normal conditions (20 ml/min of total

flow and 50 mg of catalyst) compared to and in the other experiment the flow and catalyst mass were increased by 1.5 times (60 ml/min of total flow and 150 mg of catalyst) the normal conditions. The main results are shown in the Figure 7A.

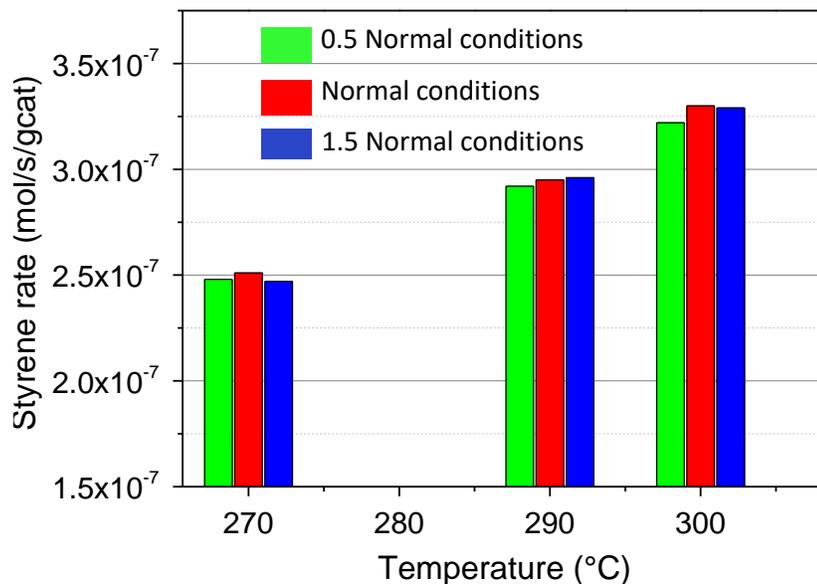


Figure 7A: Results of the test for mass transfer limitation by external diffusion comparison.

As can be seen in the Figure 7A although there are some small differences between the experiments in comparison to the results of the internal diffusion experiments, there is not a real trend of a higher styrene rate with higher flows and anyways those differences are not that high enough to consider a real presence of external mass transfer limitation.

Considering the results of both internal and external mass transfer diffusion experiments, a reaction performed at the chosen conditions is not limited by any of these effects. These results are very important to verify whether the reaction conditions and reactor design were correct to make a good and comparable evaluation of the performance of the different catalysts that are object of this work.

The system that was chosen for the kinetic analysis seems to be the right one and starting from these results it was possible to carry on with the experiments and make a proper evaluation by excluding side effects that could appear.

5.3 Liquid feeding of EB to the system

Since the ODH set-up used in this project was a self-made device, some challenges took place in order to achieve a reliable system able to perform good experiments with high precision and reproducibility. One of the main challenges we had to face in this work was to get the right system for delivering of liquid ethylbenzene to the reactor. This was a critical step since having a stable concentration of EB in the inlet stream was essential for a proper catalytic evaluation.

Primarily, it was intended to use a syringe pump that dose the liquid ethylbenzene to an evaporator where it would be vaporized and mixed with the O₂ and N₂. In principle the idea of using this system was to have an appropriate control of the liquid EB dosing by adjusting the flow of the syringe pump. However, this kind of system is very sensitive to ambient temperature fluctuations since the liquid EB density changes with temperature and although the volume injection can be always the same the real mass injection varied. Furthermore, the small amounts of injection could produce pulsing of EB injected. The room temperature in our laboratory was not possible to control and, therefore, to obtain a stable ethylbenzene concentration in the main stream was very difficult. Although there were many attempts to optimize the system, the stability was only achieved for short reaction times (Figure 8A). Therefore, since we wanted to perform stability tests continuously for even more than one day the option of using this system was ruled out.

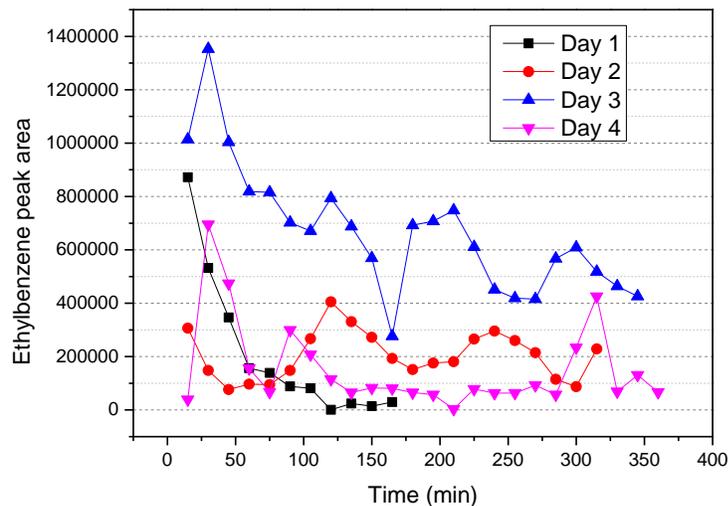


Figure 8A: Ethylbenzene peak areas vs time on stream with the syringe pump system.

Later, another system for the EB delivering was installed in the setup. In this case the injection consisted on a pressurized vessel where the ethylbenzene was placed inside and nitrogen was used as an inert gas to keep the right pressure inside. Then, a liquid mass flow controller (LMFC) was directly coupled to the vessel and the EB flow was controlled by this device. Afterwards, the EB flow went to the same evaporator used for the syringe pump system. One disadvantage of using this system was the low volume capacity of the vessel and the long time required to refill it that might interrupt the measurements.

Again, as can be seen in Figure 9A the stability of EB in the inlet stream to the reactors was very low. Therefore, this system was also excluded to perform catalytic measurements.

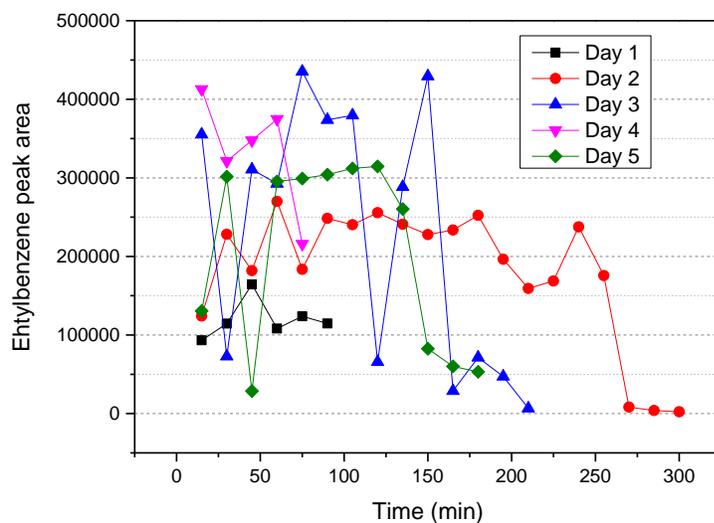


Figure 9A: Ethylbenzene peak areas vs time on stream with the pressurized system.

Finally, it was decided to use a saturator system. A saturator is a device usually made of glass that consists of two concentric tubes. The liquid (ethylbenzene) is located in the inner tube. Then, the permanent gas mixture (O_2 : N_2) get in contact with the liquid and it carries part of it. The desired concentration of the EB in gas phase depends on its vapor pressure. A thermostat is used in order to control the temperature in the inner pipe where the mixture of EB with the permanent gases takes place. This is possible by circulating a cooling liquid which temperature is then controlled by the thermostat.

For this system the stability was much higher (see Figure 10A) and longer than for the other devices used before. Therefore, this was the system chosen to perform all the experiments described in this thesis.

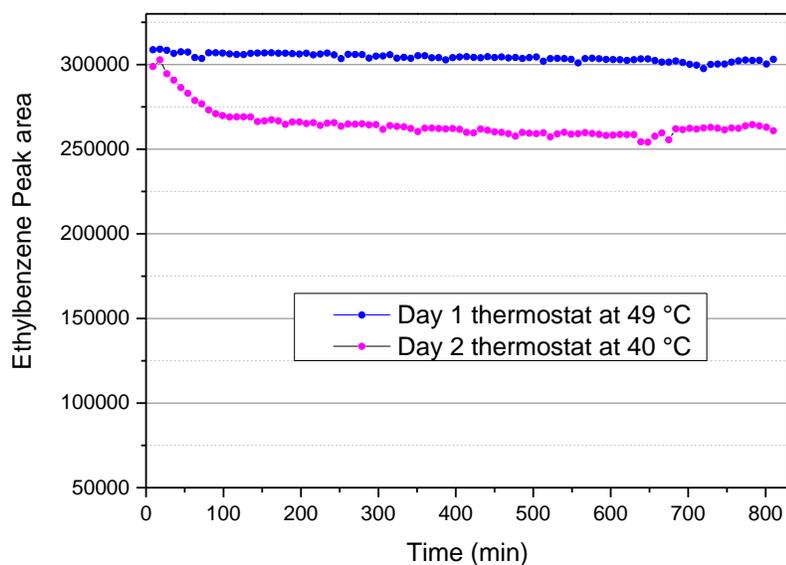


Figure 10A: Ethylbenzene peak areas vs time on stream with the saturator system.

5.4 Thermogravimetric mass spectrometry (TG-MS)

The Figure 11A showed the MS profiles for the MWCNT-1. In each profile there is a comparison of the catalyst before (black line) and after reaction (green line).

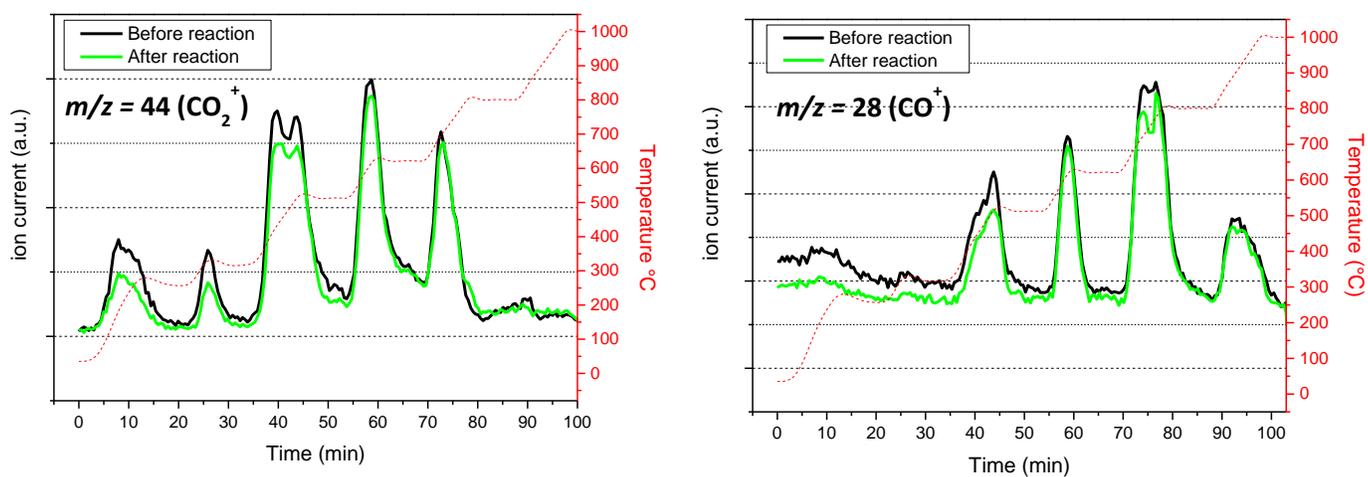


Figure 11A: Ion currents of CO₂ (m/z 44) and CO (m/z 28) for MWCNT-1.

By looking at the plots for the pure carbon material, there is a presence of all the oxygen functional groups.

Additionally, the same measurement procedure was applied for the most active sample (MWCNT-3), the results are shown in the Figure 12A.

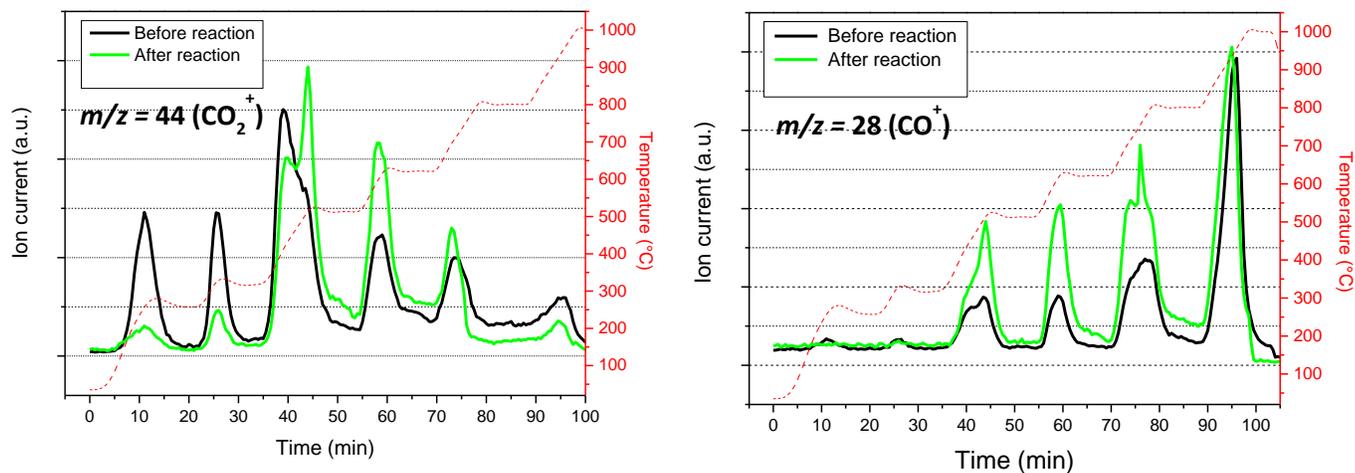


Figure 12A: Ion currents of CO₂ (m/z 44) and CO (m/z 28) for MWCNT-3.

The same analysis was then applied for the less active catalyst MWCNT-6. The main results are shown in Figure 13A.

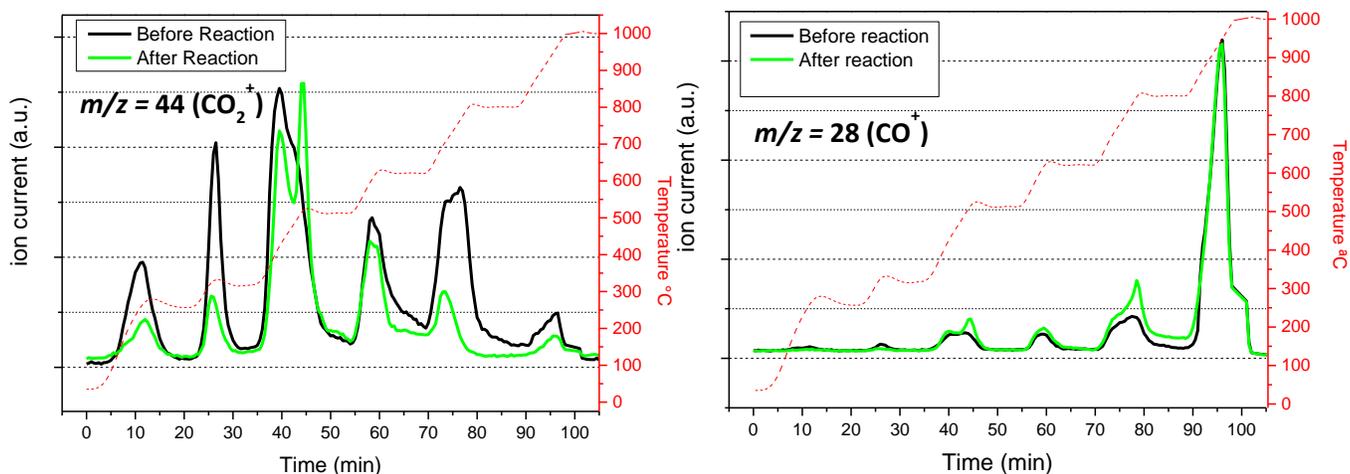


Figure 13A: Ion currents of CO₂ (m/z 44) and CO (m/z 28) for MWCNT-6.

5.5 TG-MS calibration

The TG-MS analysis performed to determine the presence of the oxygen functional groups is a useful technique that gives valuable information regarding the activity of the catalysts. However this method does not give exact values of the amount of those functional groups. Then, in order to get those values a further calibration of the TG-MS device was performed and the exact amount of each functional group was then determined.

The calibration procedure applied is explained in detailed elsewhere and used calcium oxalate as reference material.^[63] The reason of using this compound is due to its thermal decomposition that takes place in three different steps. CO and CO₂ are desorbed separately as shown on the reactions bellow.

1. $\text{CaC}_2\text{O}_4 \bullet \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$ (loss of water)
2. $\text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3 + \text{CO}$ (loss of carbon monoxide)
3. $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ (loss of carbon dioxide)

Therefore, knowing the exact mass of calcium oxalate by the thermogravimetric measurements it is possible to obtain stoichiometrically the mass of CO and CO₂ by analyzing the ion current data from the MS signal. Knowing this, three different measurements were performed by varying the mass samples of carbon oxalates, getting three different peak intensities for CO and CO₂ while the samples are heated until 1000 °C. The main results of the calibration are shown in Figure 14A.

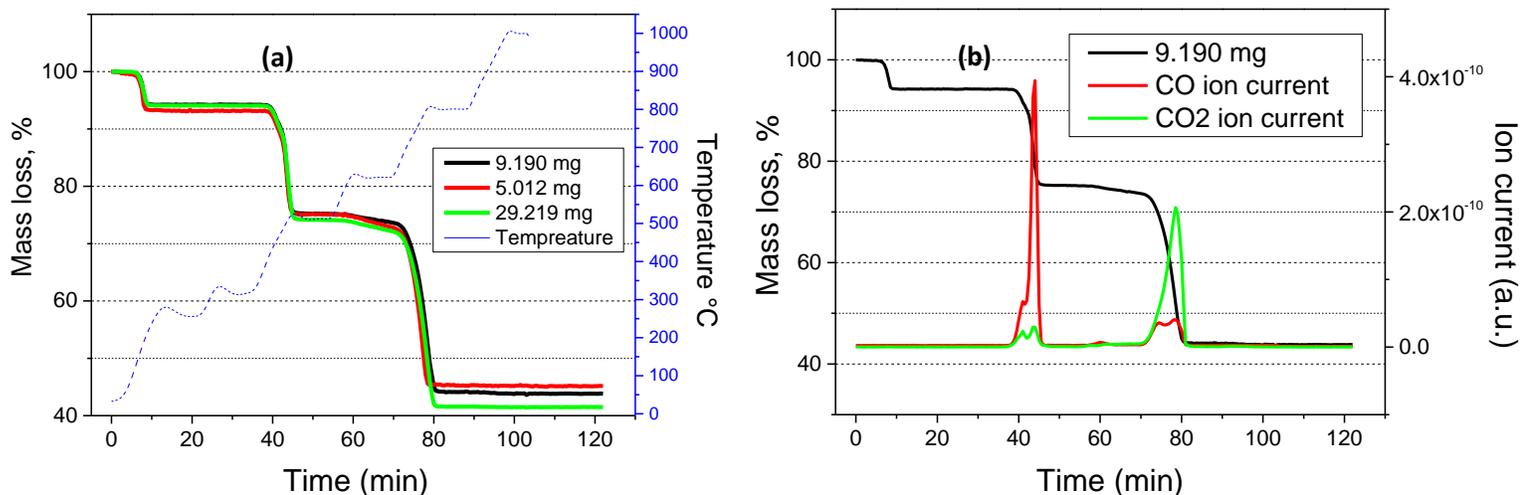


Figure 14A: TG-MS calibration with calcium oxalate. (a) TG profile of all samples; (b) TG, CO and CO₂ profile for one selected sample.

As seen in Figure 14A, there are three different steps: the first step is desorption of water and the second and third steps are the decomposition of CaC₂O₄. The steps can be correlated to water, CO and CO₂. The Figure 17A shows the mass loss and desorption of CO and CO₂ measured in the MS for one of the samples. The same behavior was observed for the other two samples.

Finally, the masses of CO and CO₂ generated on each measurement were calculated by stoichiometry and correlated with the peak intensities in the MS. The calibration curves were built as seen in Figure 15A.

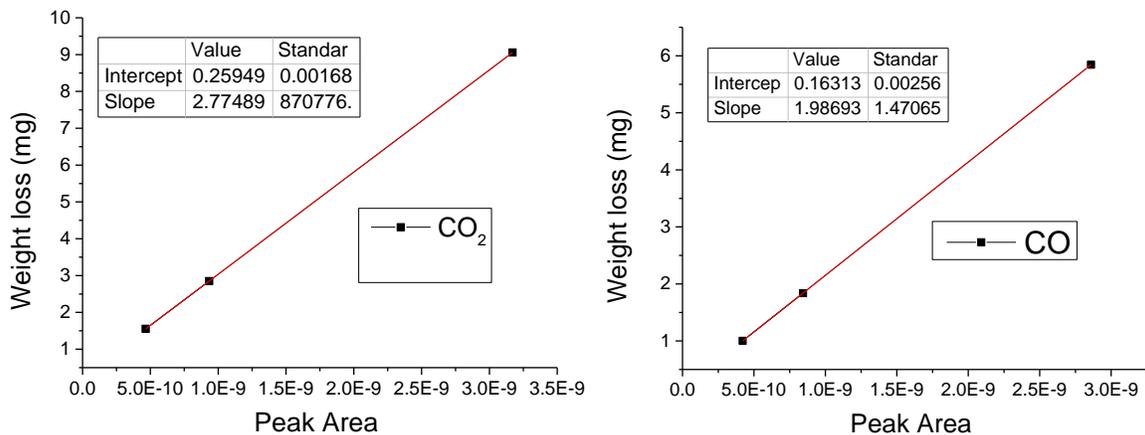


Figure 15A: TG-MS calibration for CO and CO₂.

5.6 Lebenslauf (Curriculum Vitae)

Is not in the online version

5.7 Erklärung (statement)

Hiermit versichere ich, dass ich die vorliegende Arbeit mit dem Titel

„Ethylbenzene ODH as a test reaction for carbon-based catalyst“

selbst verfasst und keine außer den angegebenen Hilfsmitteln und Quellen benutzt habe, und dass die Arbeit in dieser oder ähnlicher Form noch bei keiner anderen Universität eingereicht wurde.

Essen, im Oktober 2019

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