

Spectroscopic studies on the formation of coke
on individual Fluid Catalytic Cracking particles:
the effect of poisoning metal compounds

Master thesis
Joris Goetze, student number 3018458

Supervisors: dr. ir. J. Ruiz-Martínez, prof. dr. ir. B. M. Weckhuysen
Group of Inorganic Chemistry and Catalysis, Utrecht University

Abstract

The formation of coke on individual Fluid Catalytic Cracking (FCC) catalyst particles was studied using UV/Vis microspectroscopy and confocal fluorescence microscopy, with n-hexane cracking as a model reaction. Bulk information was obtained with thermogravimetric analysis (TGA) and elemental analysis. To study the effect of metal poisons, four different catalyst particles were used: fresh particles and three kinds of deactivated particles, of which two had been treated with metal poisons (Ni, V). The microscopic measurements were performed using a specially designed quartz cell, which enabled studying individual FCC particles during hexane cracking. UV/Vis absorbance was found to be linearly related to the concentration of coke in the catalyst particles determined with TGA. The coke concentration was approximately 3 times higher for the particles deactivated with metal compounds than for the fresh particles after 2 hours of cracking. The UV/Vis data were fitted with a simplified kinetic model, which was able to explain the observed differences in UV/Vis absorbance between the different particles based on their deactivation treatments. Confocal fluorescence microscopy revealed the location of coke molecules within individual FCC particles.

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Chapter 1

Introduction

In oil refining, a large number of different processes are used to valorize the crude oil feedstock. Oil derivatives are used for a very wide range of applications: as fuels, feedstock for the production of plastics and of many other chemicals and products. Among the most important oil refining processes are cracking processes, which are used to convert long hydrocarbons (mostly alkanes) into smaller, more valuable chains (lighter alkanes, olefins, branched alkanes, etc.). The products from these cracking processes are very important for a number of applications, including transportation fuels and chemicals.

1.1 History

Already in the end of the nineteenth century, people were looking for ways to convert heavier oil fractions into products with a lower boiling point. In 1891 the first cracking process was patented in Russia by Vladimir Shukhov (Russian patent no. 12926). The developed process was a thermal cracking process, in which the oil feedstock is cracked using elevated temperature and pressure, but without the use of a catalyst. Later, in the first decades of the twentieth century, French engineer Eugene Houdry developed the first process of catalytic cracking, in which not only heat, but also a catalyst was used to perform the cracking reactions more effectively. The first commercial-scale catalytic cracking unit was built in 1937 in the United States, and many more were built in the early forties. Shortly after that, efforts were made by a consortium of a few large oil companies to develop a continuous process for catalytic cracking to compete with the fixed and moving bed reactors used in the process developed by Houdry. Their efforts resulted in the development of a process in which the vaporized oil feed is mixed with small catalyst particles in such a way that the mixture behaves as a fluid, leading to the name of the process: Fluid Catalytic Cracking (FCC). FCC is a continuous process, and proposed a few improvements compared the the fixed bed and moving bed Houdry cracking reactors. Since the first commercial run of an FCC plant in 1942, the FCC process has grown to be the most widely used process responsible for the conversion of heavy fractions of crude oil into more valuable gasolines and light fuel oil, with a daily capacity of over 2 million tons worldwide. [1] It is believed that in World War II the superior quality of aviation gasoline used by the Allied forces was one of the deciding factors

that contributed to winning the war. The development of both the Houdry and the FCC catalytic cracking processes have contributed to this, by being more effective in producing high octane number gasoline than conventional ways of producing gasoline, such as distillation and thermal cracking. [2]

1.2 FCC process

The reactions involved in the process of Fluid Catalytic Cracking are acid-catalyzed. In the early stages of the FCC process, until the early 1960's, the Brønsted acidity for the reactions was provided by amorphous silica-alumina catalysts. Later, these materials were replaced by zeolites, which offered a large improvement over the older amorphous materials in terms of activity, and mainly in selectivity. These improvements come from the tunable acidity and well-defined pore structure of zeolites. [3] Today, spherical catalyst particles of around 70 μm are used, containing zeolite domains, embedded in a matrix of clay, silica and alumina. The choice of zeolite is very important regarding the selectivity of the catalyst. Zeolite Y is used in all modern FCC units to provide the main cracking activity and selectivity towards gasoline-range hydrocarbons, but the particles containing Zeolite Y can be mixed with particles containing other zeolites. For instance, to selectively increase the amount of olefins produced at the expense of gasoline, catalyst particles containing ZSM-5 can be mixed with the particles containing zeolite Y. [1] The matrix is used to improve several features such as porosity, density and attrition resistance of the particles. Furthermore, matrices may provide catalytic activity for long hydrocarbons, which are limited to penetrate into the zeolitic micropore structure. [1]

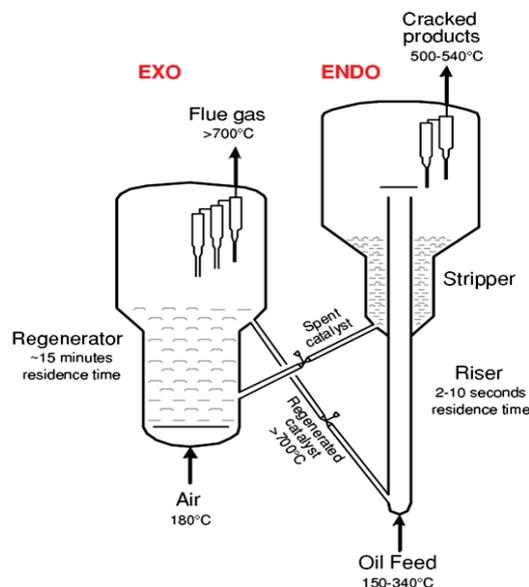


Figure 1.1: Schematic view of the different parts of an FCC unit. [4]

Figure 1.1 shows a simplified flow diagram of a modern FCC unit. The

actual cracking occurs when the catalyst particles and oil feed travel upwards in the riser. When the mixture enters the stripper, the cracked products leave the unit, whereas the deactivated catalyst particles are led to the regenerator. In the regenerator, oxygen is added, and the coke that has been formed on the catalyst particles is burned off. Subsequently, the regenerated catalyst particles are returned to the riser. The heat provided by the burning of coke is used to get the desired temperatures in the riser. This is also indicated in the figure: the left side, showing the regenerator which supplies heat is indicated with EXO (exothermic) and the right side of the diagram where heat is consumed in the reactor and stripper is indicated with ENDO (endothermic).

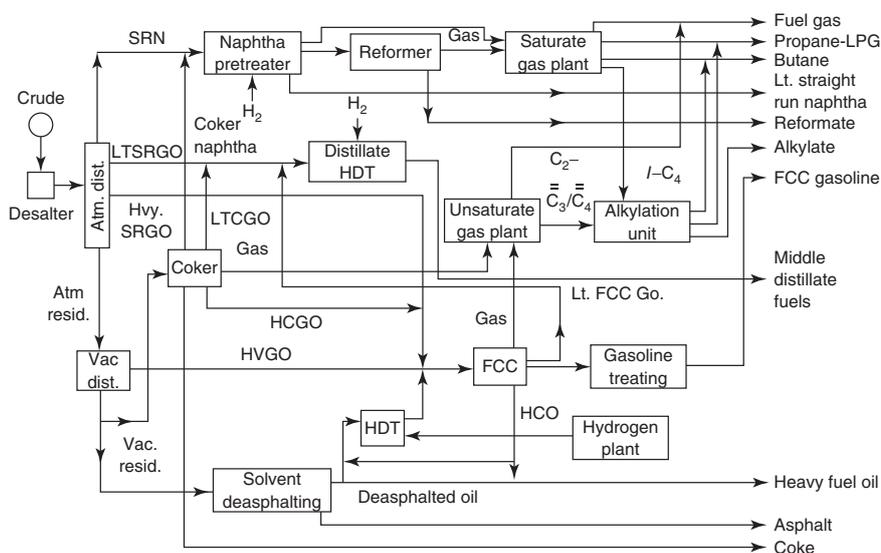


Figure 1.2: Position of the FCC unit within the overall process of oil refining. [1]

The position of the FCC unit within the overall process of oil refining is shown in Figure 1.2. The main feedstock for the FCC process is heavy vacuum gas oil (HVGO), the overhead product of vacuum distillation. But also other feedstocks can be used: heavier oil fractions such as the bottom product of vacuum distillation (resid) and lighter fractions are sometimes used as feed. This has influence on the FCC process: not only are there different hydrocarbons in the different oil fractions, but there are also differences in the amount and type of contaminating compounds, such as metal- or nitrogen compounds which can be found in different oil fractions. Depending on the feedstock, different ratios of zeolites have to be used in order to perform the cracking effectively. [1, 3, 5]

1.3 Zeolites

In the 1960's zeolites replaced the amorphous silica-aluminas used before in catalytic cracking. Zeolites are crystalline aluminosilicates with a well-defined pore structure. The primary building blocks for zeolites are tetrahedrons of

one silicon or aluminum atom surrounded by four oxygen atoms. These tetrahedrons are interconnected, forming secondary building blocks such as 5- and 6-membered rings, from which many different ordered 3-dimensional pore structures can be formed. As of today, over 200 different zeolite frameworks are known. [6] The two types of zeolite that are used extensively in Fluid Catalytic Cracking are zeolite Y and ZSM-5. [1, 7] Zeolite Y has the same structure as the naturally occurring faujasite zeolite, with cavities of 12 Å, interconnected by pores with a diameter of 7.4 Å. ZSM-5 exhibits the MFI framework, and has intersecting straight and zig-zag channels, both with diameters of ca. 5.5 Å. These differences in pore size and pore geometry result in difference in selectivity between these zeolites. Another important property of zeolites is the ratio between silicon- and aluminum atoms in the zeolite framework. This Si/Al ratio is one of the factors that defines the acid site strength and -density and can be tuned to get zeolites with desired properties. The Si/Al ratio has effect on the acidity because Al tetrahedrons provide a negative charge to the zeolite framework, which has to be compensated for by positively charged atoms. Most zeolites are nowadays synthesized in an alkali environment, which results in sodium cations compensating for the negative charge in the framework coming from the aluminum atoms. To make the zeolites catalytically active, Brønsted acid sites are introduced on the zeolite surface by exchanging the sodium cations for ammonium ions by treating the synthesized zeolites with ammonium salts. This is followed by a calcination which causes the ammonium ions to decompose and a hydrogen atom binds to the oxygen, creating a Brønsted acid site (Figure 1.3). [3]

Zeolites introduced improvements over the amorphous catalysts, by providing much higher activity, and even more important, better selectivity than the catalysts commercially available before. These beneficial effects are caused by the high acid site density and well-defined pore structure of zeolites compared to their amorphous predecessors. Also, the properties of the zeolites are tunable to a great extent. Controlling the acidity during zeolite synthesis and choosing zeolites or zeolite mixtures with the desired pore structure are done to make catalyst particles that are suitable for the cracking of specific oil fractions. [1, 3, 8]

1.4 Deactivation and coke formation

There are a number of different deactivation mechanisms that can occur during FCC operation. The main reason for deactivation, however, is the formation of carbonaceous deposits, coke, on the catalyst particles. During cracking coke molecules block the access to Brønsted acid sites either by being absorbed on the active sites, or by blocking the zeolite pores (Figure 1.4), thereby also causing the the active sites to be inaccessible. [1, 7, 8] In principle this deactivation by coke is reversible, because the coke can be burned off in the regenerator. However, the hydrothermal conditions in the regenerator also cause a second, irreversible deactivation effect. During regeneration, dealumination of the zeolite framework occurs, resulting in destruction of the framework and the decrease of the acid site density. [9] However, the regeneration process also plays an important role in the heat balance of an FCC unit: the heat coming from the exothermic regeneration process is used to provide heat for the endothermic cracking reaction. [7, 10] This means that insight in the formation of coke is important, because it plays an

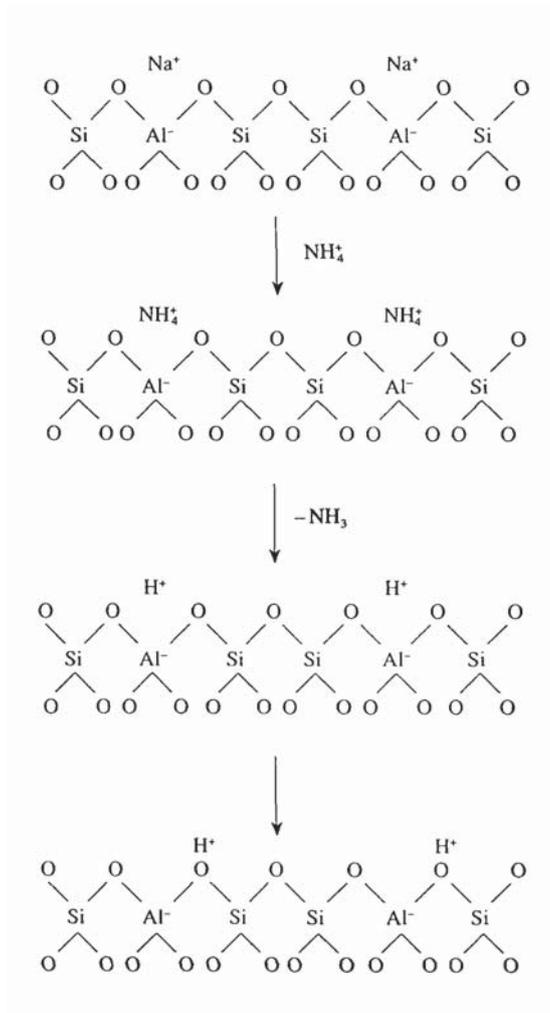


Figure 1.3: The formation of Brønsted acid sites. [3]

important role in the overall FCC operation, in terms of deactivation and heat balance. Because coke formation is a cause for deactivation in many different catalytic processes, the formation of coke on heterogeneous catalysts has been studied to a large extent. Coke formation is the result of a large number of different processes, such as hydrogen transfer, dehydrogenation, condensation, and rearrangement reactions. [3, 11] The formation and composition of coke depends on many factors, such as feedstock composition, nature and structure of the catalyst, temperature, etc. At low temperatures, "soft"-, or "soluble" coke is usually formed. The formation of this soft coke is the result of mainly hydrogen transfer and rearrangement steps, and the structure of the coke molecules is very much dependent on the structure of the reactant. The coke molecules are usually not polyaromatic. These products have some mobility through the pores of the catalyst and can be extracted from the catalyst by dissolving them in CH_2Cl_2 . [11] At higher temperatures which are used in the FCC process, other reactions such as condensation and dehydrogenation become increasingly important, resulting in the formation of "hard" coke, which can be polyaromatic or even graphitic in nature. These coke species must be removed by oxidative regeneration at temperatures of above $550\text{ }^\circ\text{C}$. [8, 11, 12]

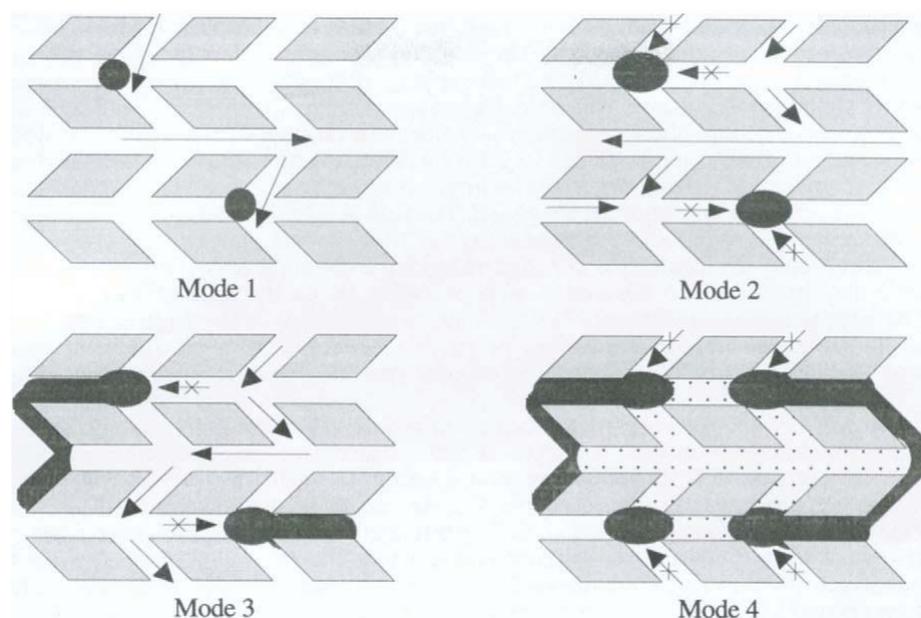


Figure 1.4: Schematic of pore blocking by coke molecules in HZSM-5. [8]

The choice of feedstock for the FCC process has a great influence on the activity and selectivity, but also on the deactivation of the catalyst particles. Depending on the crude oil source and the oil fraction used as feedstock, the reaction mixture can contain various poisoning metal- (Ni, V, Na, Fe), and nitrogen compounds, which can have a detrimental effect on the performance of the catalyst. For instance, when resid, which contains relatively large amounts of these poisoning compounds, is used as feedstock, a decrease in activity and increase in coke formation can be expected. [1, 7]

Poisoning metals such as Ni and V are present in the oil feed mainly as

porphyrins and naphthenates and are adsorbed in the meso- and macropores of the matrix of FCC catalyst particles. They are known for deactivating FCC particles in various ways. The metal compounds act as a catalyst mainly in dehydrogenation and condensation reactions, two important reactions for the formation of coke, thus increasing the coke formation in FCC particles. Also, V compounds are mobile over the surface of FCC particles, and can move into the zeolite domains. There they have a destructive effect on the zeolite structure, by enhancing dealumination. [7, 13]

Also, other poisons, such as nitrogen compounds that are present in the oil feed can have an effect on FCC operation and deactivation of the catalyst particles. Nitrogen compounds are present in the feed as basic and non-basic molecules. The basic compounds include alkyl derivatives of pyridine and quinoline, while the non-basic are present as pyrroles and carboxamides. Basic nitrogen components are thought to deactivate FCC catalysts by adsorbing strongly to the zeolite acid sites, which are responsible for most of the cracking activity. Furthermore, when basic nitrogen compounds are present during cracking an increase in coke formation is observed, which also leads to deactivation of the catalyst particles. [12, 14] Ho et al. have shown that the higher the proton affinity of the nitrogen base is, the stronger its deactivating power. [15]

1.5 Objective and approach

In this master thesis, the effect of poisoning metal compounds on the formation of coke on individual FCC particles will be studied. Much catalytic data is available on the effect of these compounds on bulk activity and selectivity of the catalyst. However, detailed insight on the rate of coke formation and its location within individual FCC catalyst particles is relatively scarce. For that reason, an important part of this master thesis consists of microspectroscopic analysis on individual FCC particles using UV/Vis microspectroscopy and confocal fluorescence microscopy. Cracking experiments will be done, in which n-hexane will be used as model feedstock. The effect of the presence of metal poisons in the catalyst particles on coke formation will be studied in-situ. In addition, other techniques such as thermogravimetric analysis and elemental analysis will be used to quantify the microspectroscopic data and relate it to bulk properties of the catalyst.

Chapter 2

Experimental

2.1 Laboratory deactivation methods

The catalyst particles used in the experiments consist of zeolite Y domains, embedded in a matrix of silica, alumina and clay. Four types of catalyst particles in different deactivation stages were used in all the experiments: Fresh (FR), Steam deactivated (ST), Mitchell impregnated-steam deactivated (MI) and Cyclic deactivated (CD). Steam deactivation, Cyclic deactivation and Mitchell impregnation-steam deactivation are three laboratory deactivation methods, which are used to simulate the influence of steam, coke formation and metal deposition on the activity of a working catalyst under operating conditions, the so-called equilibrium catalyst (ECAT). [1] The deactivation procedure of fresh FCC catalyst particles by these three different methods was always preceded by sieving the materials between 38 and 125 μm . The following descriptions of the deactivation methods are reproduced from the article written by Buurmans, Ruiz-Martínez et al. [16]

Steam deactivation

Steam deactivation occurred by first preheating and drying the FCC material in air to 873 K for 1 h followed by a treatment at 1061 K for 20 h in 100% steam.

Mitchell impregnation-steam deactivation

Mitchell impregnation-steam deactivation is a two-part method: First, an incipient wetness impregnation was done with metal naphthenates dissolved in hexane (7500 ppmwt atomic Ni, 3000 ppmwt atomic V as measured by X-ray fluorescence spectroscopy on catalyst). Subsequently, the samples were dried in air, after which a multistep calcination was performed, heating in air (2 h each at 473, 673 and 873 K). Secondly, a steam deactivation, as described for the ST sample, was performed for 10 h. [17]

Cyclic deactivation

Two-step cyclic deactivation was performed on an Imtech Cyclic Deactivation unit (CDU) with 20 cycles of alternating cracking-regeneration (step 1) followed

by 120 cycles of alternating oxidation-reduction (step 2) to achieve 7500 ppmwt Ni and 3000 ppmwt V on the catalyst material. Each sieved catalyst was pre-heated and dried to 873 K for 1 h prior to loading in the CD unit. A single cycle in step 1 consisted of fluidizing the catalyst in N₂ to crack a vacuum gas oil (VGO) spiked with metal naphthenates at 773 K for 5 min, stripping hydrocarbons from the catalyst pores with N₂ for ~ 7 min, while heating from 773 to 923 K, and regenerating the catalyst at 923 K for 30 min in a O₂/N₂ mixture (40:60 mol%). A single cycle in step 2, conducted continuously at 1043 K in steam, consisted of oxidation in H₂O/O₂/N₂ (40:25:35 mol%) for 2 min, stripping in H₂O/N₂ (40:60 mol%) for 1.5 min, reduction in H₂O/H₂/N₂ (40:25:35 mol%) for 7 min, and stripping in H₂O/N₂ (40:60 mol%) for 1.5 min. Reaction temperatures in the CDU were measured in the fluidized catalyst bed by using a thermocouple.

By comparing the three types of deactivated samples with fresh samples it is possible to determine both the role of metal compounds and hydrothermal conditions in deactivation during the cracking process.

2.2 Microspectroscopic techniques

To study the formation of coke on individual FCC catalyst particles, cracking of hexane was chosen as a model reaction. Two in-situ microspectroscopic methods were used: UV/Vis microspectroscopy and confocal fluorescence microscopy. The spatial resolution of these techniques enables the study of the catalyst at single particle level during the cracking reaction. This allowed us to visualize both the rate and the location of the coke formation in individual FCC particles.

For both methods, the cracking reaction took place in a specially designed quartz reactor cell (Figure 2.1), mounted on the heating stage of a Linkam Scientific Instruments FTIR 600 cell, which was attached to a Linkam TMS 94 temperature controller. In a typical experiment, 0.015 g of catalyst particles was placed in the cell and the cell was mounted on the heating stage. The temperature was set at 500 °C, with a ramp of 15 °C per minute. Setting the temperature at 500 °C on the temperature controller resulted in a temperature of around 500 °C at the surface of the heating stage onto which the quartz cell was mounted. However, inside the quartz cell, the temperature was notably lower, ~400 °C, measured with a thermocouple. At this temperature, the catalyst was calcined and activated in a gas stream of 50 % of N₂ and 50 % of O₂ at 120 mL min⁻¹. After one hour at 500 °C, the flow was switched to 60 mL of N₂. Subsequently, n-hexane (Acros, 99+%) was introduced in the cell at a rate of 10 μL min⁻¹ using a needle, attached to a syringe pump. The close contact of the needle with the hottest part of the in-situ cell ensured that the n-hexane was in the gas phase during the reaction. The syringe pump allowed us to control the reactant rate with high precision. During cracking individual particles were monitored using UV/Vis microspectroscopy or confocal fluorescence microscopy for 2 h. After 2 h of cracking, the addition of hexane was stopped and the cell was cooled down, while the flow of 60 mL min⁻¹ N₂ was maintained. In all experiments, individual particles from the same position in the cell were studied. This was done in order to avoid the influence of a non-homogeneous distribution of hexane in the cell on the results.

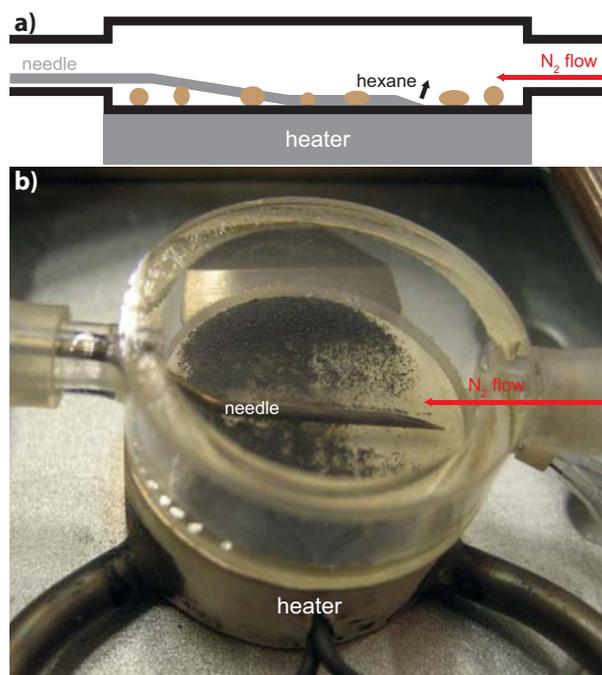


Figure 2.1: a) Schematic representation of the quartz reactor cell; b) Photograph of the reactor cell. The cell has a diameter of 3 cm.

UV/Vis

For the UV/Vis experiments, the cell was placed on an Olympus BX41M optical microscope attached to an Avantes AvaSpec-2048TEC UV/Vis spectrometer using optical fibers (Figure 2.2, left). When coke was formed, the absorption of visible light by the catalyst particles changed, which was monitored using the UV/Vis spectrometer. This effect of coke formation could also be seen without using a UV/Vis spectrometer: the catalyst particles became visibly darker when coke was formed.

Confocal fluorescence

Identical experiments were performed with a confocal fluorescence microscope (Figure 2.2, right). The quartz cell was placed on a Nikon Eclipse 90i upright microscope with a $\times 50$, 0.55 NA dry objective lens. Confocal fluorescence images were collected by a Nikon A1-SHR A1 R scan head connected to a Melles Griot laser light source with an emission wavelength of 561 nm (yellow diode-pumped solid-state laser, 50 mW). The emission was detected by a A1-DU4 4 unit. The detection range was 570–620 nm. The fluorescent nature of the coke species makes the coke formation visible with fluorescence microscopy, which enables time- and spatially-resolved visualization of the formation of fluorescent coke species with submicron resolution. The confocal microscope encloses a pin-hole to cut off the out of focus light, making it possible to visualize single planes of the catalyst particle in a non-destructive way (Figure 2.3).

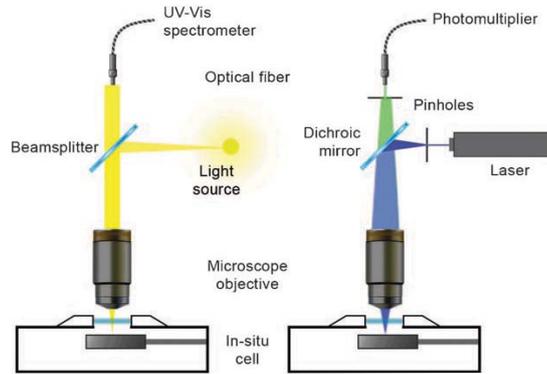


Figure 2.2: Schematic representations of the UV/Vis microspectroscopy (left) and confocal fluorescence microscopy (right) setups. [18]

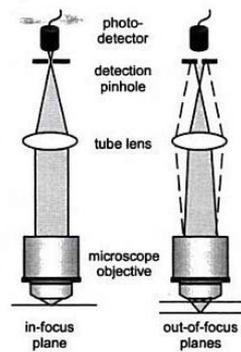


Figure 2.3: Schematic picture of the pinhole in the confocal microscope, allowing for high axial resolution. [19]

2.3 Bulk techniques

To support and to quantify the results obtained with the microspectroscopic techniques, bulk techniques were also applied to get information about the nature and composition of the coke.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed to quantify the amount of coke and to get information on the composition (C/H ratio) of the coke molecules using a PerkinElmer Pyris 1 TGA attached to a mass spectrometer. 5–10 mg of spent catalyst was dried under N₂ flow of 10 mL min⁻¹ at 300 °C for 60 min after which the gas flow was switched to oxygen (10 mL min⁻¹). Subsequently, the temperature was raised to 950 °C at a rate of 10 °Cmin⁻¹.

Nitrogen physisorption

Nitrogen physisorption was performed on the catalyst particles before and after cracking at 77 K using a Micromeritics ASAP 2020 instrument. The change in micro- and mesopore volume after cracking can be used to get information on the location of coke formation within the catalyst particles. [20]

Elemental analysis

To obtain information about the composition and C/H ratio of the coke, some samples were sent to Mikroanalytisches Laboratorium Kolbe (Germany) for elemental analysis.

Chapter 3

Results and Discussion

3.1 Rate of coke formation

In the UV/Vis measurements, individual particles were followed for 2 hours, during the cracking of n-hexane. The absorbance in the UV/Vis region gives an indication of the amount coke that is deposited on the catalyst particles. During all experiments, the absorbance increased during the cracking reaction, indicating that coke was formed. This effect could also be seen without the use of a microscope: the particles became visibly darker during cracking (Figure 3.1). In a typical experiment, UV/Vis absorbance spectra showed no clear bands in the region between 400 and 700 nm. Rather, an increase in absorbance was seen over the whole range between 400 and 700 nm (Figure 3.2).

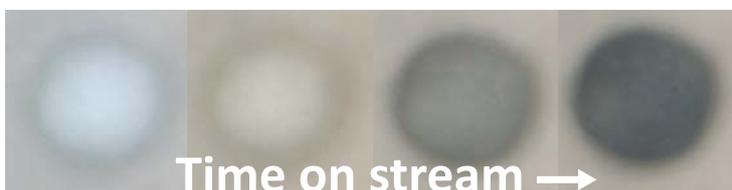


Figure 3.1: An individual FCC particle becomes darker during cracking.

Because no clear bands appeared between 400 and 700 nm, a single wavelength ($\lambda = 580$ nm) was chosen and the absorbance at that wavelength was plotted versus time. 580 nm was chosen because of the good signal to noise ratio at that wavelength. The resulting absorbance vs. time plots give information about the rate of coke formation. For the four different particles absorbance vs. time plots are shown in Figure 3.3. The absorbance is higher for all deactivated particles (ST, MI and CD) than for the FR particles. The highest absorbance is seen for the particles with metal compounds (MI and CD). These results can be explained by the different deactivation treatments that were used (Table 3.1). As a result of their deactivation treatments all deactivated particles have larger zeolite pores than the fresh particles. This results in more coke formation, because the coke molecules have more space to grow in these larger pores. An additional effect causes the higher absorbance for the MI and CD particles. In these particles, metal compounds that can act as active sites towards coke

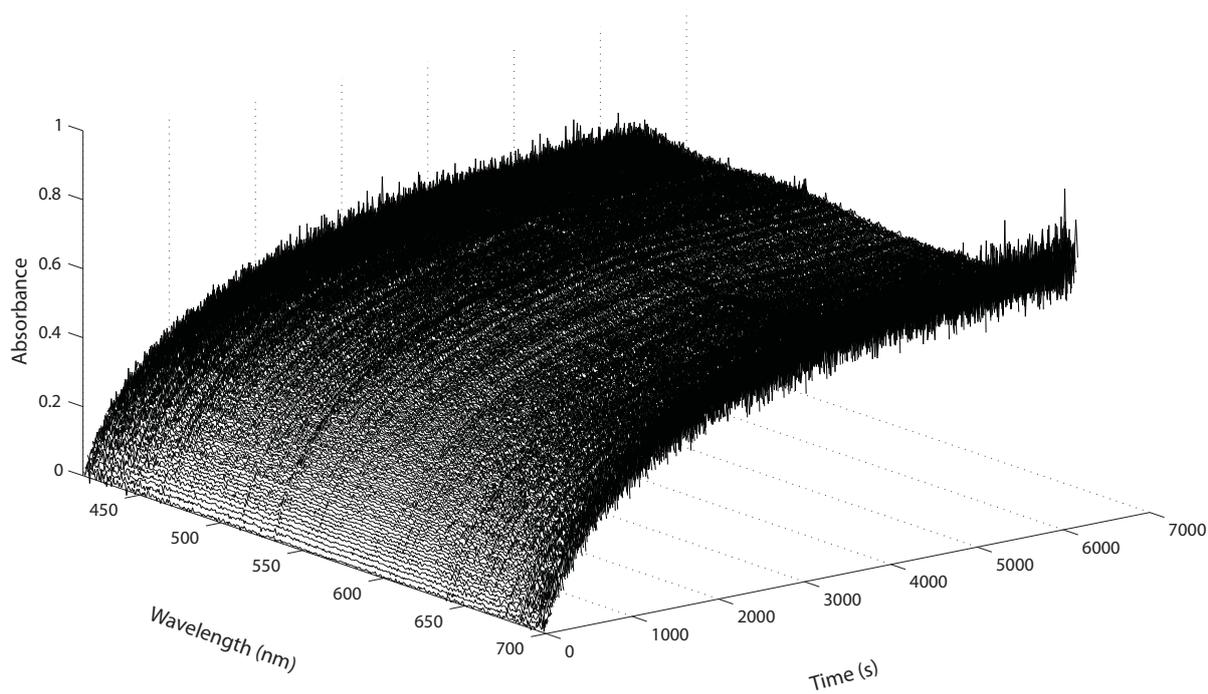


Figure 3.2: Absorbance between 400–700 nm of a CD catalyst particle during cracking.

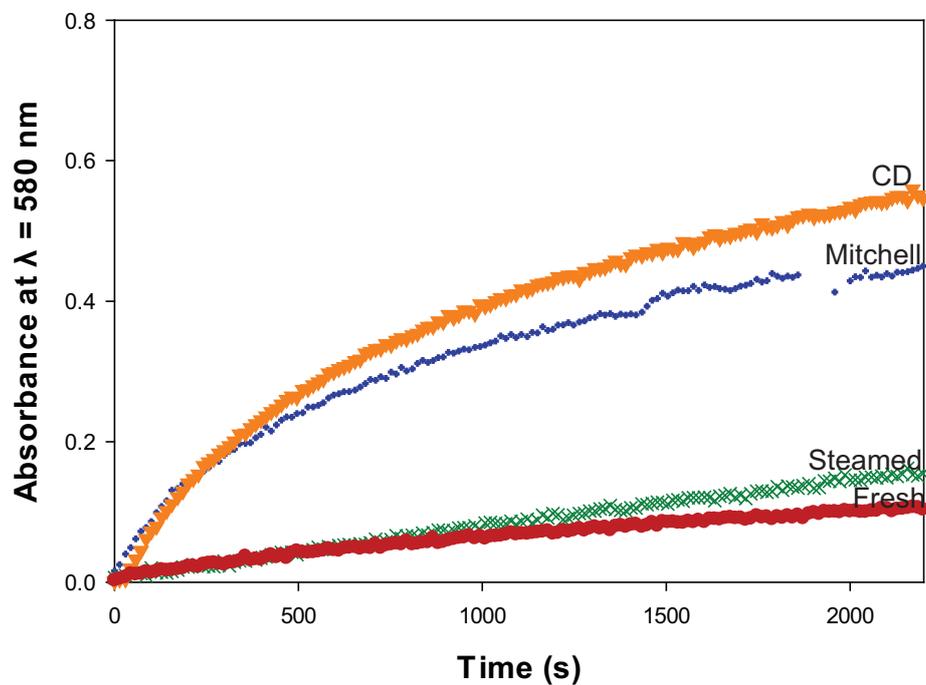


Figure 3.3: UV/Vis absorbance plotted against time for the four different FCC particles.

formation are present in the meso- and macropores of the material, leading to more coke formation and higher UV/Vis absorbance.

Table 3.1: Different deactivation methods and their effects on the FCC particles.

particles	deactivation method	effects
Fresh (FR)	-No deactivation	
Steamed (ST)	-Steam treatment	-Zeolite framework destroyed: larger zeolite pores
Mitchell (MI)	-Impregnation with metal compounds -Steam treatment	-Metals present in meso- and macropores -Zeolite framework destroyed
Cyclic deactivated (CD)	-Cracking/regeneration with metals present	-Metals present in meso- and macropores -Zeolite framework destroyed

In order to obtain quantitative information about the formation of coke from the UV/Vis results, it is of key importance to know how the UV/Vis absorbance relates to the amount of coke deposited on the catalyst particles. The Beer-Lambert law states that absorbance is linearly related to the concentration of an absorber in solution. However, these cracking experiment differ from the conditions of the Beer-Lambert law on two points: the absorbance is measured from reflected light instead of transmitted light, and the FCC particles are solid. To determine whether in this case the measured UV/Vis absorbance is linearly related to the amount of coke deposited on the particles, the UV/Vis results were compared to the coke concentration on the particles after cracking, determined with thermogravimetric analysis (TGA). In TGA measurements, the coke deposited on the particles is burned off at high temperatures. The weight loss during this process is monitored, and this indicates how much coke was deposited on the particle. The absorbance at the end of the cracking process of 2 hours was compared to the percentage of coke determined with TGA analysis, and the results show that the absorbance is indeed linearly related to the concentration of coke (Table 3.2, Figure 3.4). The coke percentage in the FR particles was not taken into account, since it is expected that high the weight loss observed with TGA is not only accounted for by the burning of coke; the FR particles have not been subjected to hydrothermal conditions before the TGA measurements, and under these conditions, phase changes in the clay can lead to considerable weight loss due to dehydroxylation.

The linear correlation between absorbance and coke percentage indicates that UV/Vis absorbance can be used as a quantitative measure for the concentration of coke in the FCC particles. As a consequence, this allows for the absorbance vs. time plots to be fitted with kinetic formulas describing the rate of coke formation, in which the UV/Vis absorbance represents the amount of

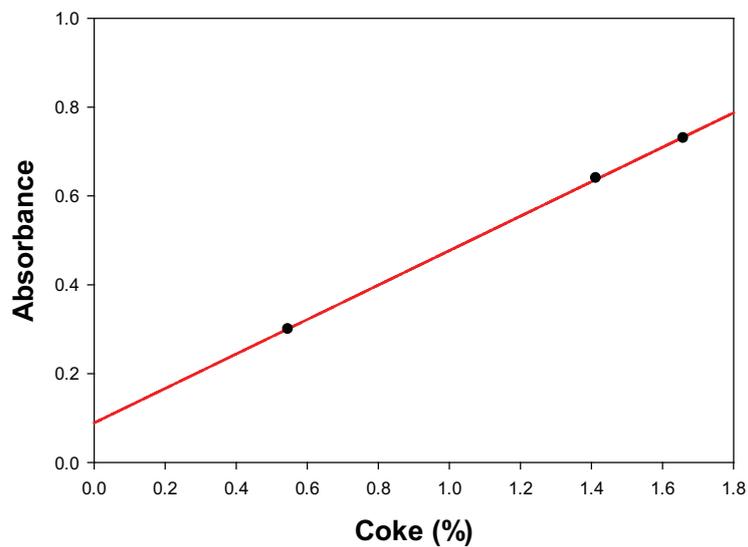


Figure 3.4: UV/Vis absorbance after 2 h of cracking versus coke concentration determined with TGA.

Table 3.2: Coke concentration after 2 h of cracking determined with different methods

Particles	Absorbance	TGA	Elemental analysis C
FR	0.2	2.81%	0.17%
ST	0.3	0.55%	0.13%
MI	0.65	1.41%	0.87%
CD	0.73	1.66%	1.12%

coke deposited on the particles.

A detailed study on the kinetic model of coke formation was beyond the scope of this thesis, so a simplified model based on the kinetic model of Beirnaert et al. [21] was chosen to describe the coking process during the cracking of hexane. In this model, the overall coke formation is described by two mechanisms, which are assumed to follow first-order kinetics. The first mechanism describes the formation of coke molecules on the active sites of the catalyst, whereas the second accounts for the growth of coke molecules. With those two mechanisms combined, the equation describing the kinetics of coke formation is as follows:

$$[Coke] = a(1 - e^{-bt}) + c(1 - e^{-dt})$$

In this equation, a is the maximum absorbance that can be reached through the first mechanism (i.e. formation of coke on active sites) and b is the apparent rate constant for the first mechanism. In the second part of the equation, c is the maximum absorbance that can be reached through the second mechanism (i.e. coke growth) and d is the apparent rate constant for the second mechanism. An overview of these constants for the four different FCC particles is given in Table 3.3. Graphs of the fitted UV/Vis data can be found in Appendix A. The differences in these constants between the different catalyst particles can be explained by the deactivation treatments to which the particles were subjected. First of all, the maximum amount of coke that can be formed on active sites (a) is the highest for the fresh particles. This result can be explained by the higher amount of Brønsted sites acid sites in the fresh particles caused by the fact that the amount of Brønsted acid sites decreases because of deactivation treatments. Secondly, the rate of coke formation on active sites (b) is much larger for the particles with metal compounds (MI, CD) than for the particles without metals. This can be explained by the fact that the poisoning metal compounds act as active site in the process of coke formation, as they enhance dehydrogenation reactions. These metal active sites only have activity towards the formation of coke, and not towards other (cracking) reactions, which can explain the observation that the rate of coke formation on active sites is much higher for the metal-poisoned particles. Thirdly, the maximum amount of coke that can be formed during coke growth (c) is much larger for the deactivated particles (ST, MI, CD) than for the fresh particles. This results can be explained by the physico-chemical changes upon deactivation and the location where coke is formed. The steam treatment that the deactivated particles are exposed to damages the the zeolite framework, creating large cages in which much larger coke molecules can grow than in the FR zeolite framework. In the MI and CD particles, the metal compounds are present in the mesopores of the matrix, which also allows the coke molecules to grow to a large extent. These trends show that this simplified kinetic model for coke formation is able to accurately explain the observed differences in UV/Vis absorbance between the different particles using knowledge of the different deactivation methods.

Table 3.3: Kinetic constants for the fitted UV/Vis absorbance plots.

Particles	a	$b (s^{-1})$	c	$d (s^{-1})$
FR	0.35	0.0001	0.03	0.0020
ST	0.21	0.0002	0.25	0.0002
MI	0.18	0.0029	0.43	0.0004
CD	0.13	0.0052	0.57	0.0007

3.2 Location of coke formation

Confocal fluorescence microscopy experiments were performed to locate fluorescent coke domains within the particles. Figure 3.5 shows fluorescent images of a single FR particle after 2 h of cracking, at different depths. At depths larger than $\sim 7 \mu\text{m}$, fluorescence can not be measured because of the attenuation of light in the particle. The image shows regions of intense fluorescence of 2–3 μm . These regions were not visible in the particles before cracking (Figure 3.5 d), which means that the fluorescence comes from the coke that is formed during the cracking reaction.

When fluorescent images of the four types of particles are compared (Figure 3.6), it can be seen that the particles deactivated with metal compounds (MI, CD) and to a lesser extent also the ST particles show much less fluorescence than the fresh particles. This is remarkable, because UV/Vis, TGA and elemental analysis show that more coke is formed in the deactivated FCC particles. This means that the fluorescence intensity can not be used as a measure for the amount of coke produced. An explanation for the lower fluorescence observed in the deactivated particles can be found in the nature of the coke, which will be discussed below. However, the fluorescence images can be used to get information about the location of the coke that is fluorescent. For instance, the fluorescent domains appear to be larger for the deactivated particles than for the fresh particles, which is expected, since there is more space for the coke molecules to grow in the deactivated particles than in the fresh particles.

Nitrogen physisorption was used to provide more information about the location of the coke. By comparing the micro- and mesopore volume of the particles before and after cracking, nitrogen physisorption could possibly reveal where the coke is mainly located, in the zeolite micropores or in the larger mesopores in the matrix of the particles. However, nitrogen physisorption measurements showed only very small changes in pore volume before and after cracking and the results could not be used to reveal the location of coke.

3.3 Nature of coke

To explain the large differences in fluorescence intensity observed with confocal fluorescence measurements, the nature of the coke was studied. Elemental analysis was used to determine the C/H ratio of the coke molecules. The results are shown in Table 3.4. It is clearly visible that the C/H ratio is higher for the ST particles, and much higher for the MI and CD particles. This observation supports the conclusion that the nature of the coke is responsible for the observed fluorescence intensity discussed in the previous section. When the C/H ratio

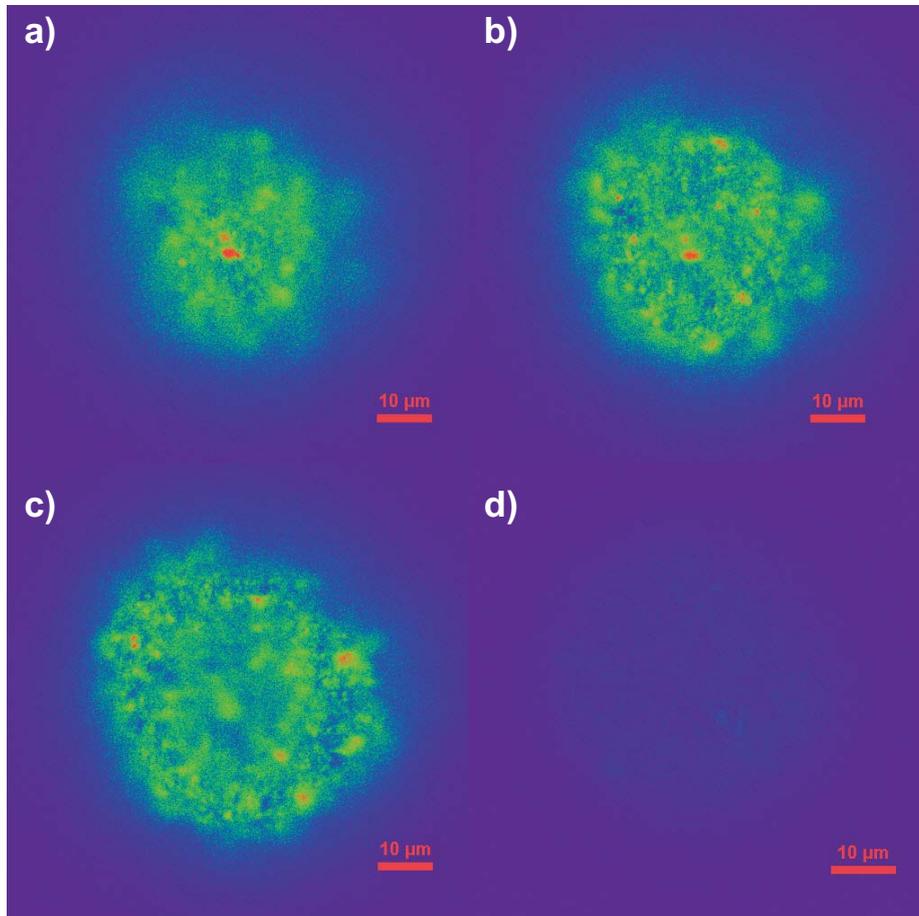


Figure 3.5: Fluorescent images of a single FR particle after 2 h of cracking at depths of a) 0 μm , b) 3.5 μm and c) 7 μm (right). d) Fluorescent image of a single FR particle before cracking, when no coke is present. Very little fluorescence is observed.

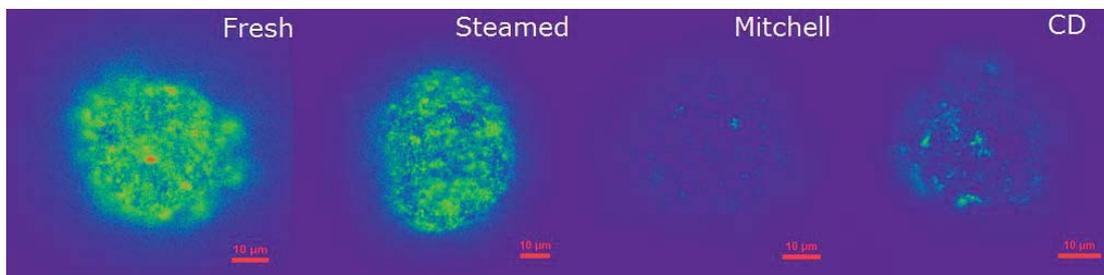


Figure 3.6: Fluorescent images of the four different particles after 2 h of coking.

increases, i.e. when the coke becomes more graphitic rather than polyaromatic, the fluorescence intensity decreases. Previous studies also show that graphitic molecules exhibit low fluorescence. For the FR particles, the C/H ratio is remarkably low, and suggests that the coke that is being formed is aliphatic in nature rather than aromatic. This is highly unlikely, as coke formation at the temperatures used usually results in polyaromatic coke molecules. [11] Similarly to the high TGA weight loss observed in the FR particles, we expect that H atoms from hydroxyl groups present in the FR particles contribute to the high percentage of H in the elemental analysis and thus the low C/H ratio observed.

Table 3.4: C/H ratios for the different FCC particles after cracking determined with elemental analysis

Particles	C/H ratio
FR	0.41
ST	1.25
MI	9.18
CD	13.78

Chapter 4

Conclusions

The specially designed quartz cell, combined with the injection of hexane using a needle and syringe pump provided the possibility to study individual FCC particles during hexane cracking. Using UV/Vis spectroscopy and confocal fluorescence microscopy the coke formation on individual particles was studied. In the UV/Vis experiments, the increase of absorbance with time on stream was much higher for the deactivated particles. This was especially the case for the particles with metal compounds, with absorbances of three times higher than fresh particles after two hours of cracking. Comparing the UV/Vis absorbance after cracking with the percentage of coke determined with TGA, it was concluded that the UV/Vis absorbance can be directly related to the amount of coke on the catalyst. This allowed for fitting of the UV/Vis data with a simplified kinetic model. With this model, the differences in the rate and amount of coke formation could be explained physically using the differences in the deactivation procedures.

Confocal fluorescence microscopy revealed the location of coke molecules within the FCC particles. Also, large differences were seen in fluorescence intensity for the different particles. The deactivated particles, and especially the particles with metals compounds, showed much less fluorescence. Elemental analysis showed that the carbon to hydrogen ratio was higher for the deactivated particles, i.e. the coke was more graphitic in these particles. This accounts for the lower fluorescence intensity observed in the deactivated particles.

The microspectroscopic techniques used in this research can also be used as a powerful analytic tool for studying other poisons for the FCC process such as nitrogen compounds, as well as a wide variety of other catalytic systems, in which more insight in the behaviour of individual particles is desired.

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Appendix A

Fitted UV/Vis graphs

Below, absorbance vs. time plots of the four different particles are shown, fitted with the simplified kinetic formula described in Chapter 3:

$$[Coke] = a(1 - e^{-bt}) + c(1 - e^{-dt})$$

The black dots represent the measured UV/Vis data points, the red line represents the first part of the kinetic formula (i.e. formation of coke on active sites) and the dark blue line represents the second part of the kinetic formula (i.e. coke growth). The total concentration of coke as calculated with the kinetic model is represented by the light blue line.

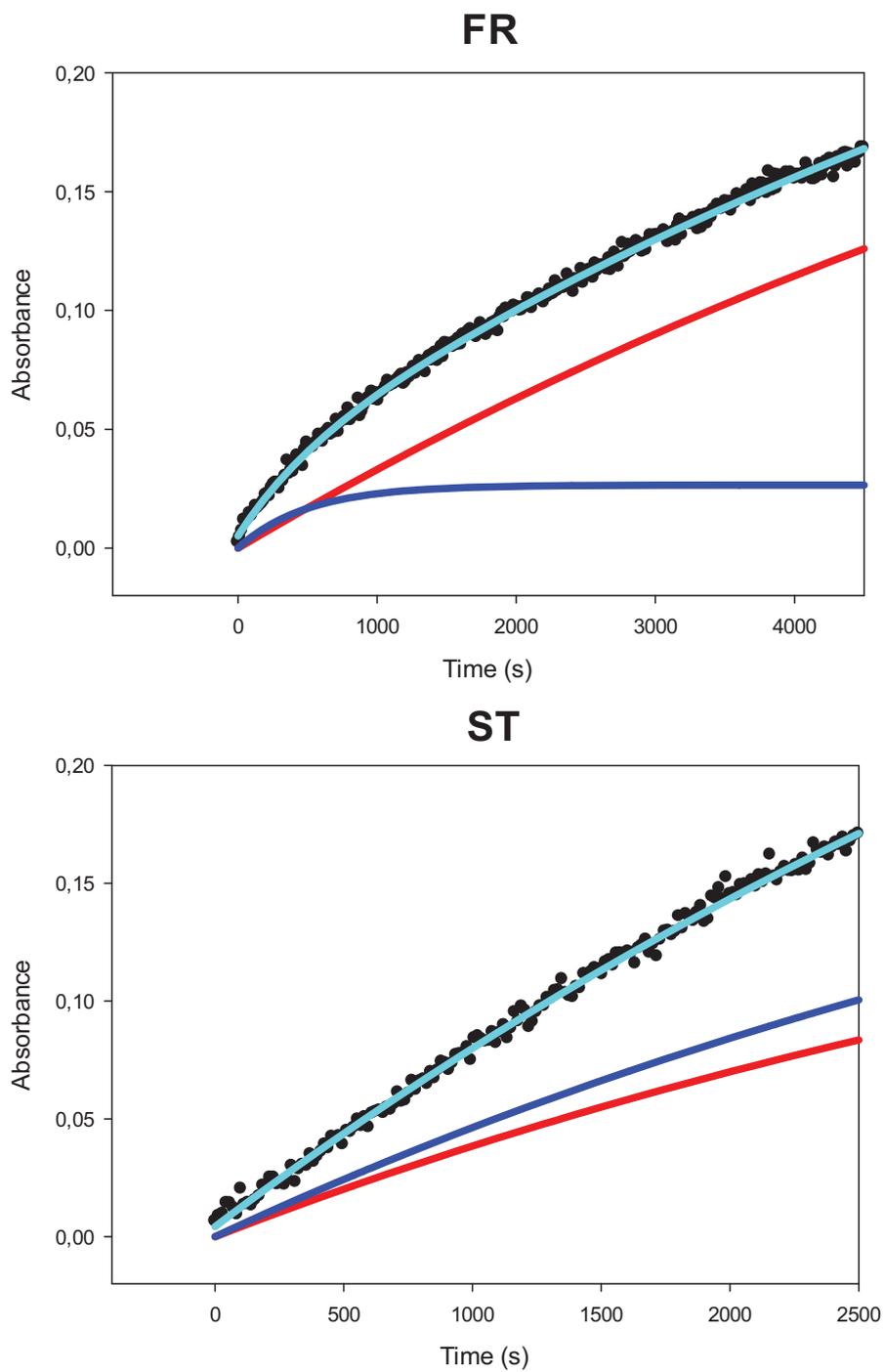


Figure A.1: Absorbance vs. time plots of the FR and ST particles, fitted with the simplified kinetic formula.

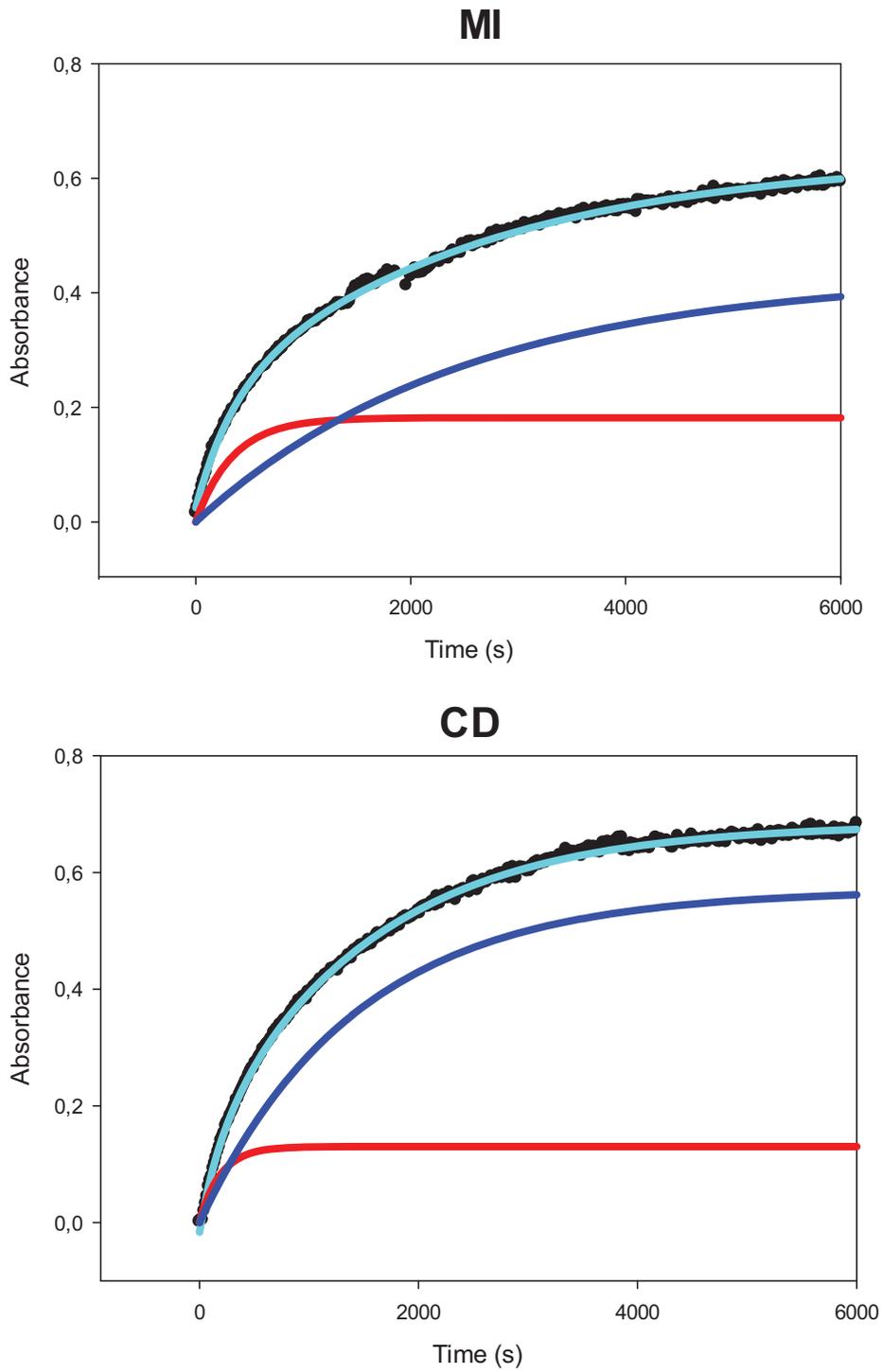


Figure A.2: Absorbance vs. time plots of MI and CD particles, fitted with the simplified kinetic formula.