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UNIVERSITY
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TWENTE

CATALYTIC PERFORMANCE OF ZEOLITE BASED MATERIALS

Study and optimization of catalytic performance of zeolites based catalytic materials towards microreactor applications

Bachelor assignment | R.A. Otter, s0208728

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1. Introduction

In 2011 Dr. Reyes Mallada visited the University of Twente as a researcher at the research groups Catalytic Processes and Materials (CPM) and Mesoscale Chemical Systems (MCS). She studied zeolites in microsystems and their catalytic performance.

This bachelor assignment continues on the work done by Dr. Reyes Mallada. The results of her experiments are used as a starting point for the settings. The assignment will start with a literature study, followed by studying the activity performance of a mordenite supported ruthenium catalyst in bromated reduction in a packed bed reactor, by using a portable UV-Vis spectrophotometer. Furthermore the residence time distribution in a packed bed of powdered ruthenium/mordenite catalyst and its subsequent influence on catalyst activity will be investigated. At last the important parameter values to establish the correlation or guidelines for studying ruthenium/mordenite coatings in pillared microreactor channels have to be identified and obtained.

1.1 Microreactors

Microreactors can stand high heat and mass transfer rates, due to a large surface area-to-volume, and are easy to scale up. By using microreactors there is a better way of using energy and materials, so the production will be more efficient and less polluting. Furthermore there will be a higher number of chemical conversions obtained, the process optimization is a simpler process, the design implementation is more rapid and there is a better safety. [1]

Most of the times a solid catalyst is used in microreactors, which should be deposited in the micro flow channel. [2] A catalyst reduces the activation energy of a reaction without being consumed, as shown in Figure 1.

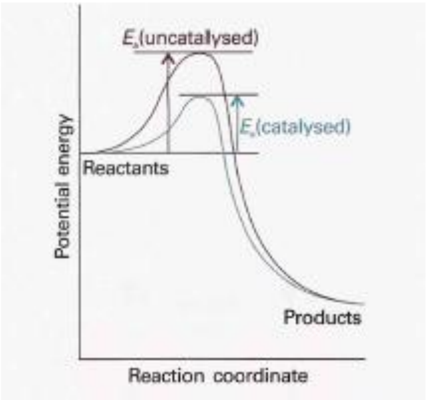

Figure 1. A catalyst reduces the activation energy of a reaction. [3]

When using a powdered catalyst in the microchannels there has to be coped with difficulties like pressure drop and flow distribution. Therefore, deposition of a thin uniform catalyst coating on the microchannel walls is a promising option. To achieve the best efficiency there has to be a thin and uniform catalyst deposition, which covers the microchannels and achieves a high exchange capacity. The catalytic coating should provide enough catalytic load, in a homogeneous way, with substantial mechanical stability and a good accessibility of the catalyst to the reactant molecules in order to improve the efficiency of the microcatalytic reaction system. A problem by using the thin coating is that it is hard to use the entire volume of the channel. [4] [5] [6]

1.2 Zeolites

Previously microchannels were coated with carbon nanofibers. The coating was used, for instance, as a support for the ruthenium catalyst. The advantage of the carbon nanofibers is the high accessibility for reactant molecules. On the other hand the stability of the catalyst under reaction conditions was not ideal.

Another option is to use a support material with a different surface chemistry than carbon nanofibers. Zeolites, like mordenite, are a promising option. Zeolites create a stable and high surface-area catalyst support layer on the microchannel walls. They have a good thermal stability and the synthesis process is reproducible. The ordered framework of the zeolitic structure is expected to contribute to stabilize the metal nanoparticles. [5]

1.2.1 What are zeolites?

Zeolites are microporous crystalline solids, which are composed of tetrahedral units of silica (SiO_4) and alumina (AlO_4). The pores, channels and cages are large enough to contain cations, water or other molecules. The pores of the zeolites act as molecular sieves. Due to a huge negative charge in the framework, catalytic and adsorption properties are present. Loosely held cations are in the cavities to preserve the electroneutrality of the zeolite. Some of those cations are able of cation exchange and are able to interact with polar molecules. [7] [8] [9] [10] [11]

1.2.2 What are zeolites used for?

Molecular sieves are used in different applications, like detergents, oil refining, petrochemical cracking, and agriculture. Zeolites are also used as an adsorbent or used by the separation of mixtures. They can be used in semiconductors or chemical sensors. [12]

In Figure 2 the estimated annual zeolite consumption can be seen.

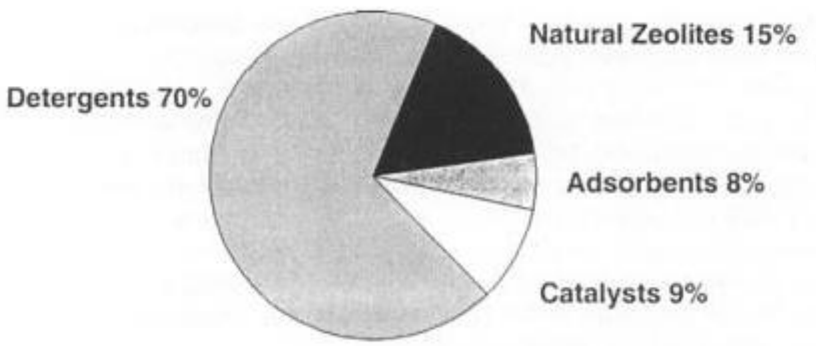

Figure 2. Estimated annual zeolite consumption (wt-% of total) by the major individual applications [9]

Detergents

One of the most common uses of zeolites is in detergents. Synthetic zeolites with an equal number of aluminium and silicon atoms have a maximum cation exchange capacity. This means that each oxygen atom is linked to an aluminium and silicon atom and the cavities contain the maximum density of exchangeable cations. The higher the cation exchange capacity the better the zeolite can replace the calcium and magnesium cations in the water with sodium cations. [9]

A few of the applications of zeolite films at microscale are pictured in Figure 3.

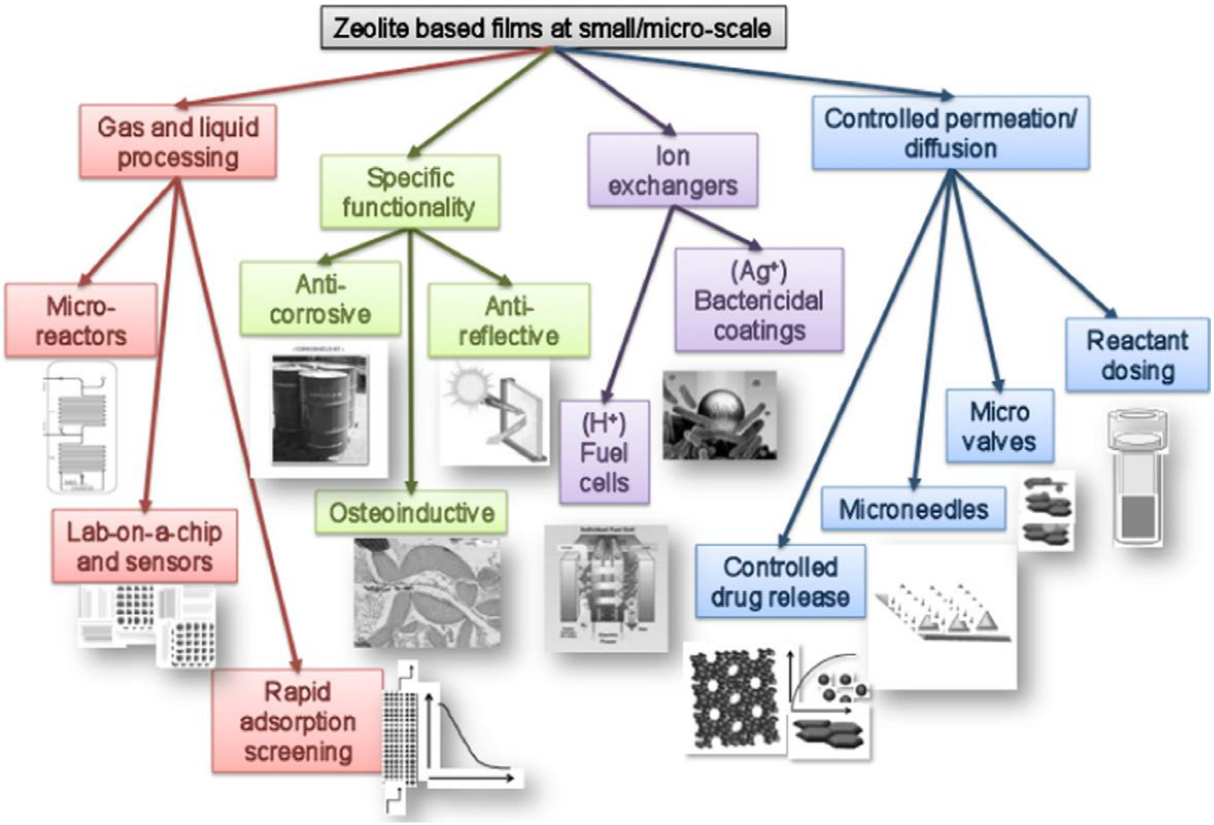

Figure 3. Some emerging applications of zeolite films at small/micro-scale [4]

Zeolite films can be grown on different, inorganic and organic, supports. By growing these films some of the characteristic properties of zeolites can be transferred to a 2-dimensional structure, with potential applications like reactor engineering and chemical analysis. There are a couple of applications for zeolite films, like zeolite membranes, which are used for separation and delivery of molecules, zeolite coating, used in microreactors, and zeolite-based gas sensors. [4]

Microreactors which are coated with zeolites are capable of a higher productivity than conventional packed bed reactors. If the channels in the microreactor are coated with a layer of zeolite almost everything of the catalyst is available for reaction. The large surface-to-volume ratio of zeolite-coated microchannels provides a great contact between reactants and catalyst and a better approach to matching permeation and reaction rates. Furthermore, the mass transport rate is higher than in a packed bed reactor. [13] [14]

1.2.3 Mordenite

Mordenite is a zeolite with the chemical formula $(Na_2,Ca,K_2)Al_2Si_{10}O_{24}\cdot nH_2O$, the ideal composition is $Na_8Al_8Si_{40}O_{96} \cdot 24H_2O$. [15] A representation of mordenite is shown in Figure 4.

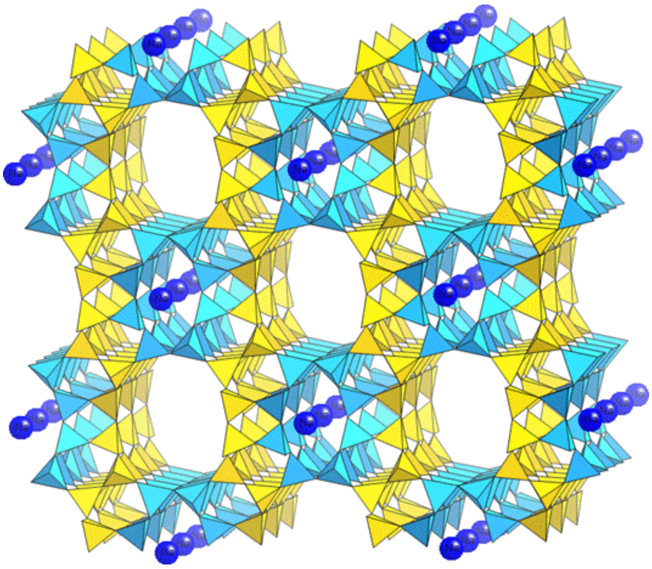

Figure 4. Mordenite: the SiO4 polyhedra are represented as yellow tetrahedra; AlO4 polyhedra are aqua tetrahedra. [16]

Mordenite is known as a zeolite whose needles grow perpendicularly to the support. There is almost no crystal intergrowth, so the individual crystals offer a high accessibility to the reactants. [17] Furthermore, mordenite can be used as a carrier of catalysts up to temperatures of 500 °C. [18]

Mordenite has a high thermal and acid stability. Mordenite has a Si/Al-ratio ≥ 5, which makes the material resistant to several chemical and thermal treatments. [15] Due to these characteristics mordenite is used in several applications like cracking, alkylation, polymerizations, the isomerisation of xylenes and cyclohexane. [19]

Two SEM images of the mordenite structure are shown in Figure 5 and Figure 6.

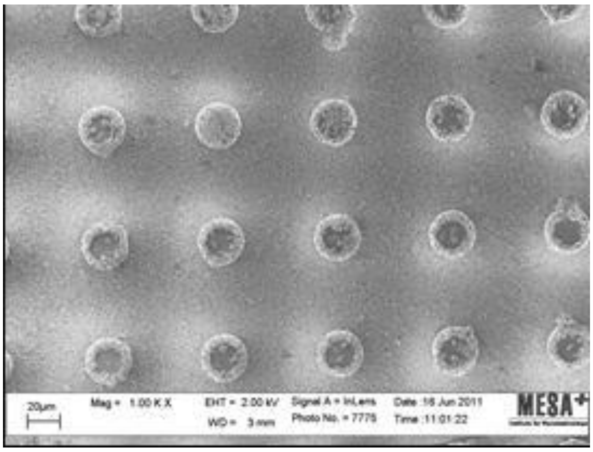

Figure 5. SEM image of pillared channels seeded with mordenite nanocrystals layer

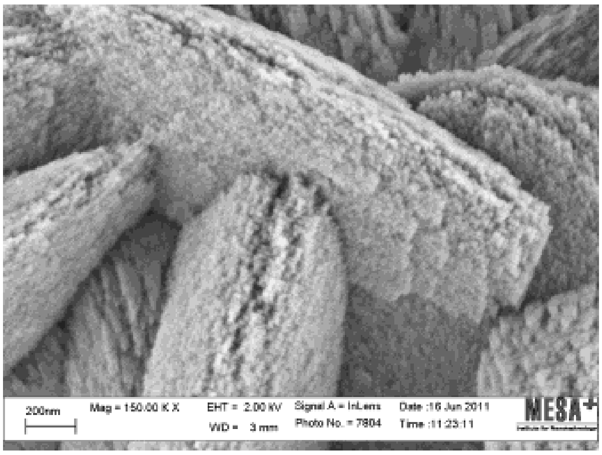

Figure 6. SEM image of a detail of the morphology of the mordenite crystals

1.3 Bromate reduction

One way catalysts can be used is for the reduction of the bromated contaminants in drinking water. Drinking water could contain bromate, which is potential carcinogen to humans. Therefore the World Health Organization has restricted the bromate level in drinking water to 0.01 mg/L. In the Netherlands the bromate content is restricted to 0.001 mg/L or 0.005 mg/L in disinfected water in the *Drinkwaterbesluit* (23 May 2011). [20]

There are a couple of ways contaminated drinking water can be disinfected; chlorine was used a lot in the past. UV-light is used as well to disinfect contaminated drinking water. Nowadays ozone (O_3) is a popular disinfectant for drinking water instead of chlorine, because it avoids the chlorination by-products, like trihalomethanes and haloacetic acids, which are potentially carcinogen. Furthermore ozone is very effective at removing pesticides and other unwanted constituents of water. But when ozone reacts with naturally occurring bromide, bromate can be formed. Bromate is very difficult to remove because it has a high solubility, stability and non-biodegradation in water. [21] [22] [23] [24] [25] [26]

The BrO_3^- decomposition is possible via the following redox reactions: [27]

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E = 1.23-0.059\ pH$$

$$BrO_3^- + 6H^+ + 5e^- \rightarrow \tfrac{1}{2}\ Br_2 + 3H_2O \qquad E = 1.49-0.071\ pH$$

$$BrO_3^- + 6H^+ + 6e^- \rightarrow Br^- + 3H_2O \qquad E = 1.44-0.059\ pH$$

However, the kinetics of the bromate reduction via these reactions is very slow. But, when there are organic fluids like methanol or ethanol in the reaction medium, the rate of bromate reduction increases rapidly, because those are more easily oxidised than water by bromate ions. When there is MeOH present the rate of bromate conversion is forty times as high as when there is only water present. [22] [27] [28]

1.4 Guaiacol

During one of the meetings Prof. Dr. K. Seshan came up with the idea to try to break down guaiacol into methanol and phenol by using high-performance liquid chromatography (HPLC), as shown in Figure 7.

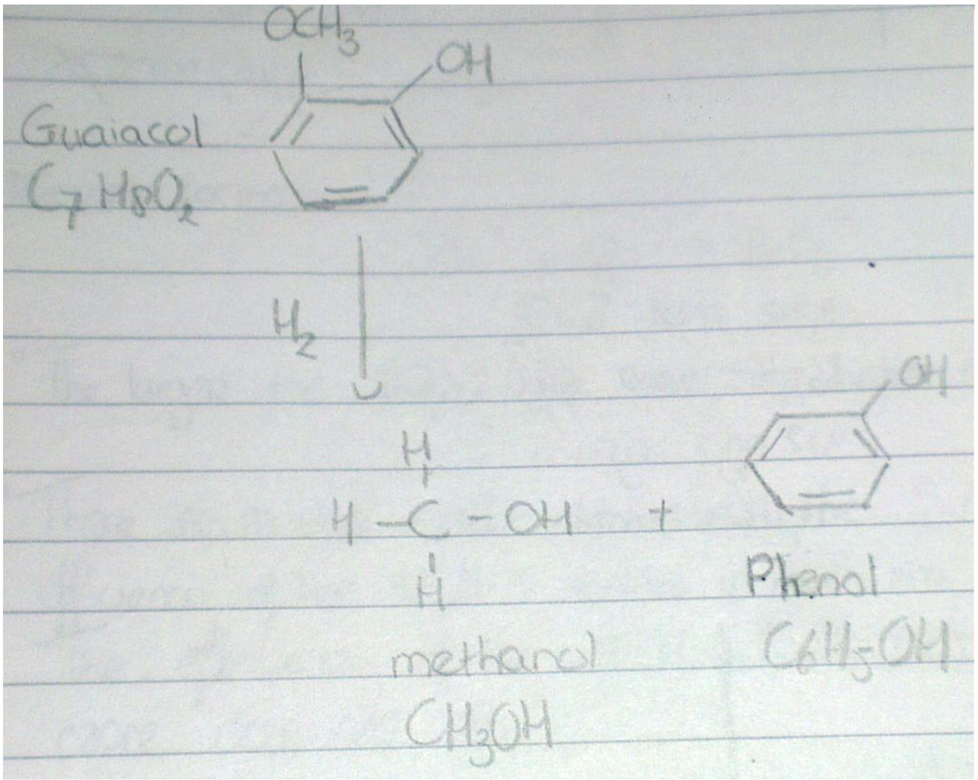

Figure 7. Schematic overview of the breaking down of guaiacol

Unfortunately, during the start of this idea it turned out the HPLC was broken. There was decided to concentrate at the bromate experiments and not to work on the guaiacol experiments.

2. Experimental

2.1 Catalyst preparation

There are two ways the catalyst could be made, using ion-exchange or evaporation.

Ion-exchange

Dr. Reyes Mallada used the following ion-exchange procedure:

1. Calculate the amount of 5 mM ruthenium solution needed for the desired wt% of ruthenium.
2. Put the, calculated amount of, mordenite powder + 5 mM ruthenium solution in a vial.
3. Immerse the vial in an ultrasounds bath at 80 °C for 2 hours.
4. Separate the solid from the solution by centrifugation. The solution will be clear, so all ruthenium has been ion-exchanged.
5. Wash the powder with water and centrifuge at least three times.
6. Dry the solid in the oven at 100 °C.
7. The solid reduced in a 90% N_2/10% H_2-stream with a flow rate of 100 ml/minute using the following program:

- Room temperature → 275 °C, 0.5 °C/minute;
- Stay at 275 °C for 30 minutes;
- 275 °C → 400 °C, 0.2 °C/minute;
- Stay at 400 °C for 30 minutes;
- 400 °C → room temperature, 1 °C/minute.

Evaporation

It is also possible to prepare the catalyst by evaporation:

1. Calculate the amount of precursor ruthenium nitrosyl nitrate needed for the desired wt% of ruthenium.
2. Put the, calculated amount of, mordenite powder + ruthenium nitrosyl nitrate in a vial.
3. Dilute the powder with water.
4. After vaporisation for 2.5 hours all the water is evaporated.
5. Dry the powder in the oven overnight.
6. Sieve the pellets within a diameter of 400-600 micron, 1/10 of the diameter of the packed bed reactor.
8. The solid reduced in a 90% N_2/10% H_2-stream with a flow rate of 100 ml/minute using the same program Reyes used.

2.2 Fluidic set-up and procedure

Fluidic set-up

In

Figure 8 there is a schematic overview of the set-up used for the experiments. A syringe pump is connected to the packed bed reactor, where filters were used to prevent the catalyst to go out of the reactor. The packed bed reactor is connected to the flow cell, where light is send in by a light source via an input fiber. The light interacts with the sample and the output fiber carries the light from the sample to the spectrometer, which is connected to the computer. On the other side of the flow cell the sample will be collected in a beaker.

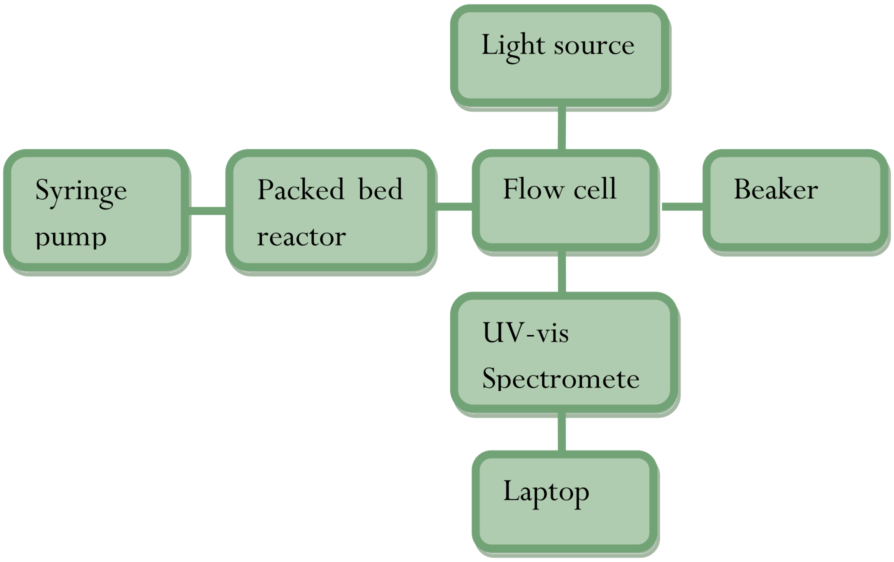

Figure 8. Schematic overview of set-up

By using this set-up there can be made absorbance spectra, by using the following instructions:

1. Set data acquisition parameters (e.g. integration time, scans).
2. Let the feed concentration flow to the cell, while taking the dark spectrum.
3. Take the dark spectrum: press the 'S' and 'dark lamp' icon.
4. Switch on the deuterium lamp.
5. Warm up for at least 1 hour.
6. Take the reference spectrum: press the 'S' and 'yellow lamp' icon.
7. Press 'A' icon to chose the absorbance spectra to measure the samples.

Procedure

The outcomes of Dr. Reyes Mallada were used as a starting point:

- With 47 mg of catalyst, a feed concentration of 5 mM BrO3- and 50 mM EtOH with 50 µl/min no conversion was present
- With 45 mg of catalyst, a feed concentration of 10 mM BrO3- and 50 mM EtOH with 50 µl/min there was activity present, but there are no conversion numbers

In the experiments 47 mg catalyst will be used. The integration time is 100 ms and the scans are set to 20. Several parameters will be changed during the experiments:

Temperature

- Room temperature
- 50 °C
- 80 °C
- 120 °C

Feed concentration

- Blank
- 5 mM BrO_3^- / 50 mM MeOH (CH_3OH)
- Formic acid (HCO_2H)

Flow rate

The experiments will start with a flow rate of 50 µl/min. If these experiments succeed the flow rate will be differed from 50 µl/min till some ml/min.

3. Results and discussion

An overview of the work and experiments done during the bachelor assignment is shown in Table 1.

Date	Work
07-02-2012	Start bachelor assignment – literature study for two weeks.
15-02-2012	New idea: breaking down guaiacol into methanol and phenol by using high-performance liquid chromatography (HPLC). It turns out the HPLC is broken, so there was decided to focus on the bromate reduction experiments and not to work on the guaiacol.
24-02-2012	End literature study
27-02-2012	Starting with preparation of 3 wt% Ru-catalyst, using the ion-exchanging method of Dr. Reyes Mallada.
29-02-2012	During the meeting there is decided to not make the catalyst with ion-exchange, but with evaporation.
29-02-2012	Make Ru-catalyst by using the method of evaporation.
06-03-2012	Finished making Ru-catalyst.
15-03-2012	Results of XRF by Louise Vrielink, the catalyst has 2.366 wt% ruthenium. This is not the 3% as hoped for; this can be explained by some mistakes in the measurements.
15-03-2012 till 11-04-2012 **20-04-2012 till 16-05-2012**	From this moment on there were schedules for the experiments made. First the fluidic set-up was flushed with water, which worked well; there was a good flow and no leaking. After this the packed bed reactor is filled with catalyst. When the set-up is run with water, it starts leaking at the fluidic components or the syringe pump got stalled. This can be explained by a big pressure inside the reactor, which the syringe pump could not handle. There is made use of filters to prevent the catalyst to leave the reactor, which can cause this pressure. The leakage can be caused by this pressure, fluidic components which were broke or by the O-rings, which close off the reactor, whose did not fit properly. All the fluidic components, the O-rings and the filters were changed, but this did not result in a non-leaking reactor.
13-07-2012	Results of chemisorptions by Karin Altena-Schildkamp.
02-08-2012 till 03-08-2012	Last attempt to gather results with packed bed reactor. One of the capillaries broke so no results.

Table 1. Journal of work done

In Appendix A the quantification of the Ru-MOR sample and in Appendix B the results of the chemisorption can be found. There was lots of trouble with the packed bed reactor in the experiments. The reactor was leaking, we tried to solve this by changing all possible components of the reactor, including all fluidic components and O-rings, but this did not work out.

Which could be done in future experiments to prevent the syringe pump getting stalled is using filters with a bigger pore diameter. When using these filters, there will be less resistance to the flow, which could prevent the syringe pump stalling. Also there can be made use of other kind of filters, like steel wool.

4. Conclusions

Unfortunately my bachelor assignment did not work out as I hoped for. There were a lot of problems with a leaking reactor, which I tried to solve for many weeks. I, with help of Roald and Vijay, could not find the problem and the reactor kept on leaking. I am disappointed I did not receive any results on the packed bed reactor, even though I put a lot of time in it.

Acknowledgements

I would like to thank my daily supervisors Vijay Thakur and Roald Tiggelaar for their help during my bachelor assignment and Prof. Dr. K. Seshan for his clear explanations. Also I would like to thank the research groups Catalytic Processes and Materials (CPM) and Mesoscale Chemical Systems (MCS).

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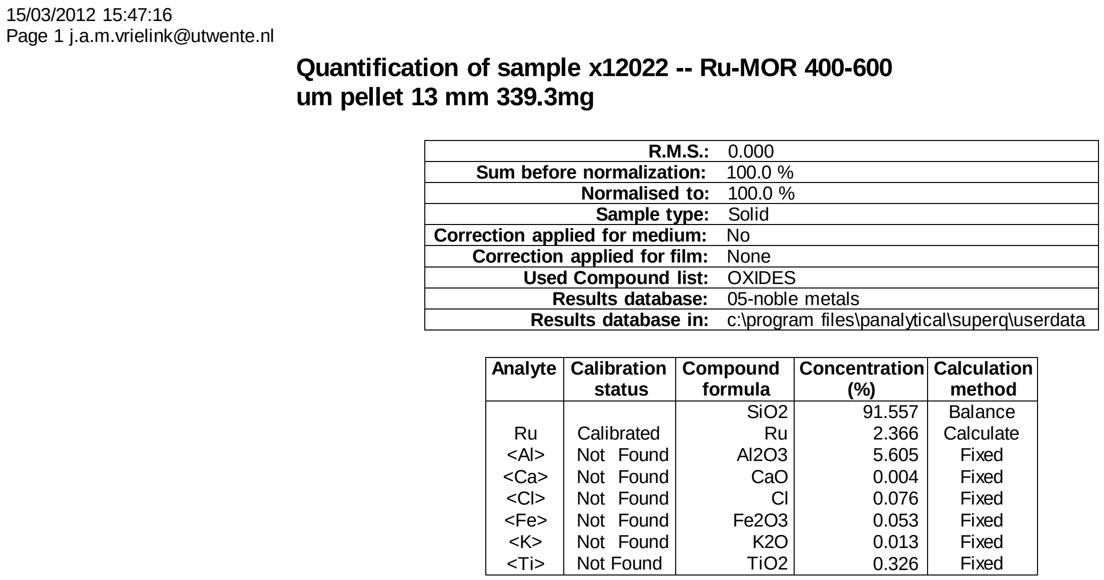
Appendix A - Quantification



15/03/2012 15:47:16
Page 1 j.a.m.vrielink@utwente.nl

Quantification of sample x12022 -- Ru-MOR 400-600 um pellet 13 mm 339.3mg

R.M.S.:	0.000
Sum before normalization:	100.0 %
Normalised to:	100.0 %
Sample type:	Solid
Correction applied for medium:	No
Correction applied for film:	None
Used Compound list:	OXIDES
Results database:	05-noble metals
Results database in:	c:\program files\panalytical\superq\userdata

Analyte	Calibration status	Compound formula	Concentration (%)	Calculation method
		SiO2	91.557	Balance
Ru	Calibrated	Ru	2.366	Calculate
<Al>	Not Found	Al2O3	5.605	Fixed
<Ca>	Not Found	CaO	0.004	Fixed
<Cl>	Not Found	Cl	0.076	Fixed
<Fe>	Not Found	Fe2O3	0.053	Fixed
<K>	Not Found	K2O	0.013	Fixed
<Ti>	Not Found	TiO2	0.326	Fixed

Appendix B - Chemisorption

Chemiesorption experimental data sheet

Name:Ria Otter	Date 06-07-2012	Ofi-nr:
Sample:Ru / Mordenite	wt% metal: 2,366	Total sample weight:

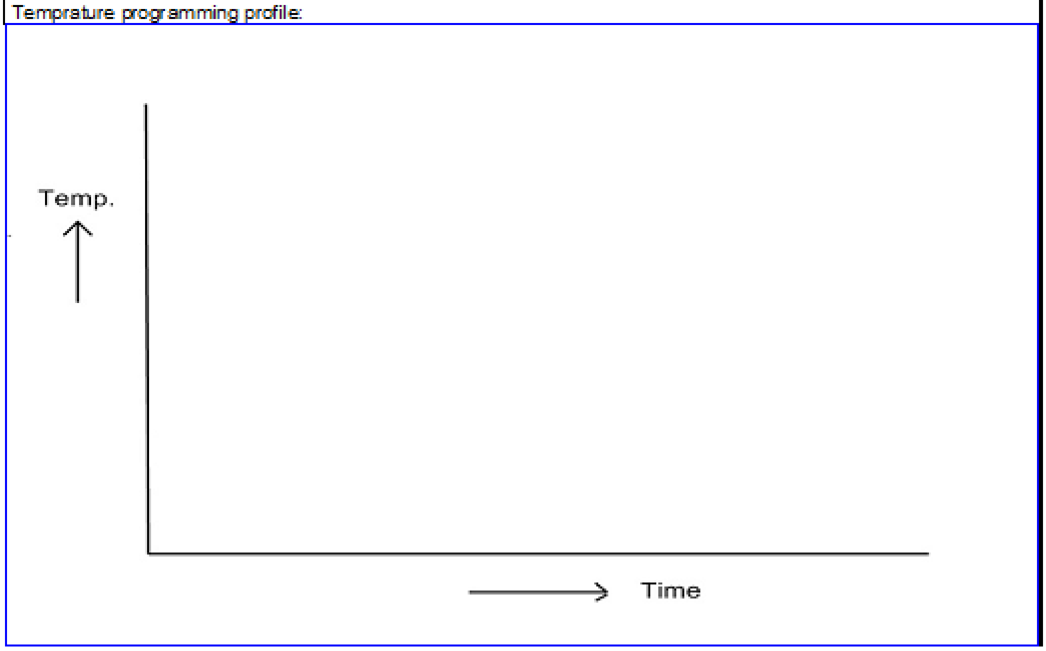
Sample Ru-Mor

T max. reductie: 300	T max. oxidation:400	T max reaction:300

Estimated adsorption based on 100% dispersion: $ml^{(H2/CO)}/g$

Prep gasses: He/H2	Sorbent gas:CO

Temprature programming profile:



To be filled in by Karin:

Date of experiment 10-07-2012

Filename:002-419

Sample name Ru-Mor

Temp during adsorption: 22,6 °C	Weighed in: 0,1461 gram
Metal disperion: 4,9618 %	Metallic surface area: 0,4442 m²/g sample
Metallic surface area: 18,7762 m²/g metal	Active particle size: 25,7705 nm

Comments:
1) Sample flushed for 20min with He 5.0
2) Heated up Sample with 5°C/min to 300°C with H2 5.0
3) Sample reduced for 1h at 300°C with H2
4) Sample cooled down with 5°C/min with He to R.T.
5) Sample measured with CO

The peaks heights are really close to each other, the results are laying in the detection limit of the detector!