Grimm, H., Kunz, U. /// Continuous Noble Metal Deposition on Carbon Based Supports for Preparation and Production of Fuel Cell Catalysts /// final report, Institute of Chemical and Electrochemical Process Engineering, TU Clausthal /// published 2018 (2015 in German language)

Grimm, Heiner
Kunz, Ulrich

Final report of the DFG sponsered research project

Continuous Noble Metal Deposition on Carbon Based Supports for Preparation and Production of Fuel Cell Catalysts

October, 15th, 2018

Index

1 Introduction

Nanosize dispersed platinum or platinum alloys on carbon based supports are established catalysts for fuel cells. As published, currently such catalysts are produced by batch processes solely. For this purpose, usually a dissolved platinum salt (platinum precursor) is reduced to platinum nanoparticles on the surface of the supporting carbon material. The results of this process (particle size and distribution, separation efficiency) depend substantially on the heating-up rate, which should be high to obtain advantageous product properties [sakthivel-2010]. Very high heating-up rates should be obtained in a directly electrically heated and continuously operated tubular reactor with appropriate dimensions. Such a process, already tested roughly at the Institute of Chemical and Electrochemical Process Engineering in Clausthal-Zellerfeld (ICVT) [aoun-2012; schlange-2011], has been advanced and its suitability for industrial production processes has been tested.

2 Basics

A common method to obtain carbon supported platinum catalysts is the so-called polyol reduction, where a platinum precursor, usually hexachloro platinic acid or one of its salts, is, in presence of dispersed support material, reduced at elevated temperature by ethylene glycol, which concurrently works as the solvent for the platinum precursor, the dispersing agent for the carbon support and the reducing agent.

The precursor reduction reaction proceeds as follows [aoun-2016; lee-2006; li-2005-1; schlange-2011]:

In the first step, ethylene glycol is converted to acetic aldehyde by elimination of water:

$C_2H_4(OH)_2 \rightarrow CH_3\text{-}CHO + H_2O$

The dissolved platinum(IV) is reduced to metallic platinum by the acetic aldehyde, which is oxidized to acetic acid:

$Pt^{4+} + 4\ CH_3\text{-}CHO + 4\ H_2O \rightarrow Pt(0) + 4\ CH_3\text{-}COOH + 4\ H^+$

With each mole of platinum reduced, 4 moles of H^+-Ions are generated, which cause a pH drop during this reaction.

The process is usually executed batchwise in a glass flask or similar. A certain amount of the platinum precursor is dissolved in water or ethylene glycol and, at room temperature, added to a stable support material dispersion in ethylene glycol, which is generally prepared by use of a strong ultrasonic device. The precursor-support ratio is calculated to obtain the desired platinum content in the product. A certain amount of sodium hydroxide, dissolved either in water or in ethylene glycol, is added to obtain a desired start pH value. Hereby either the NaOH solution is added until a certain pH value is displayed by the pH indicator, or a stoichiometric calculated NaOH amount is added, considering H^+-Ions of the precursor, if indicated. During the reaction the pH value decreases with increasing conversion.

The amount of added NaOH or the initial pH value have great influence on the size of the deposited platinum particles [li-2005-1], which should be smallest possible, because smaller particles usually show a better performance in oxygen reduction reaction [li-2005-2] (ORR).

At room temperature the reaction mixture is stable for at least some hours. Noticeable reaction rates are obtained only at higher temperatures. It can be assumed that also the reaction temperature influences the platinum nanoparticle generation and deposition. Furthermore, it can be expected that the evolution of the rates of nucleation and reaction with temperature are different, and therefore there should be a relationship between particle size and the development of the reaction temperature.

It is known that the size of the platinum particles is correlating with the specific surface of the catalytic active platinum and is therefore one of the most determining parameters for the catalytic activity.

On the other hand, the platinum particles should be distributed as unique as possible to minimize the average diffusion path length between the reactants and the catalytic active particles.

3 State of research

Most of the catalyst are produced in batch or semi-batch processes even nowadays, whereas continuous processes are rarely used for catalyst preparation. Results from various research about continuous catalyst production processes or nanoparticle precipitation are suggesting that in most cases the catalysts obtained from continuous processes will be more reproducible and active than catalysts prepared by the corresponding batch processes [aoun-2012; chen-2006; choi-2010; horn-2001; hung-2007; kaluza-2011; kawaguchi-1988; niesz-2008; sakthivel-2010, schlange-2011; schur-2003; yu-long-1996].

In the referring research studies various continuously operated reactors are examined, in particular stirred vessels [chen-2006], flame reactors [choi-2010], fluidized bed reactors [kawaguchi-1988], micro reactors or micro mixer cascades [horn-2001; hung-2007; kaluza-2011; niesz-2008; schur-2003] and tubular reactors [chen-2006; kunz-2009; yu-long-1996]. In some cases, the tubular reactor was used as deteriorating or post-conditioning down-stream equipment of another reactor type [chen-2006; kaluza-2011; kim-2002; schur-2003].

In further studies various heating-up methods, as microwave or directly electrically heated tubes, are compared with conventional heating methods [aoun-2012; deiwaraj-2003; sakthivel-2010; schlange-2011]. The results suggest that short heating-up periods can lead to catalysts with advanced properties.

In some cases continuously operated tubular reactors have already successfully been used for the determination of reaction parameters [kunz-2009; schüth-2001].

Only few of the mentioned studies deal with fuel cell catalyst preparation [aoun-2012; choi-2010; deiwaraj-2003; kunz-2009; sakthivel-2010; schlange-2011], some other deal with a continuous metal nanoparticle precipitation in general [chen-2006; choi-2010; horn-2001; hung-2007; niesz-2008].

Currently there are no known research projects about a fuel cell catalyst production using a directly electrically heated tubular reactor, besides of the publications and preliminary studies mentioned above, and the studies which are performed to obtain the present publication.

On the other hand, the importance and propagation of the so-called flow chemistry has increased severely during the last years, as well for laboratory purpose as for production processes for gram to kilogram scale. In this connection processes like blanding, separating or chemical reactions are performed in spaces continuously flowed through, usually performed as engraved channels or low diameter tubes. To simplify the handling of such equipment, standard operation units (mixers, heaters, coolers, reactors, separators) with standardized connections are used to install testing facilities as quickly and easily as conventional experimental set-up. Therefore, continuously operated catalyst preparation methods will coincide with the tendency to replace more and more of conventional laboratory batch processes by more efficient continuous ones.

4 CFCP (Continuous Fuel Cell Catalyst Production) test assembly

4.1 Setup and operation

Fig. 4-1 shows the CFCP test assembly setup.

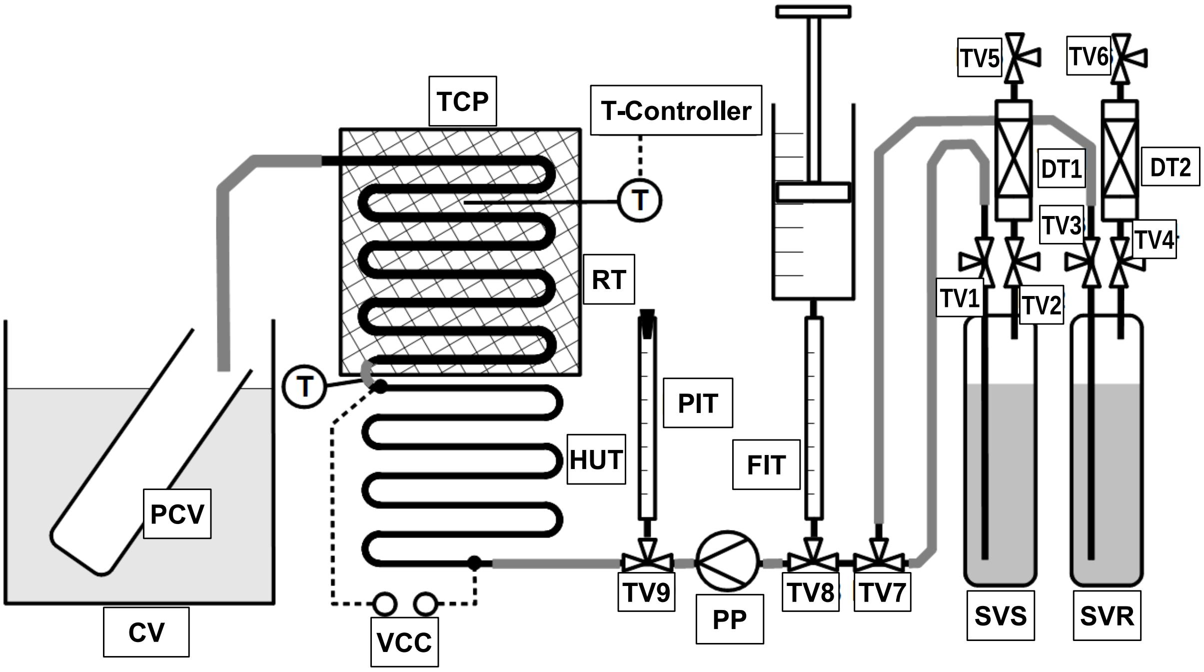

Fig. 4-1: CFCP test assembly (TV: three-way valve/cock; DT: drying tube; SVS: storage vessel for startup mixture; SVR: storage vessel for reaction mixture; FIT: flow indicator tube; PP: peristaltic pump; PIT: pressure indicator tube; HUT: heating-up tube; RT: reaction tube; TCP: temperature controlled plate; VCC: voltage and current controller (laboratory power supply); PCV: product collection vessel; CV: coolant vessel)

The CFCP test assembly substantially consists of a pumping assembly which, depending on the adjustment of TV7, forces the startup mixture or the reaction mixture from a storage vessel SVS or SVR through a directly electrically heated heating-up tube HUT and a downstream isothermic heated reaction tube RT into a cooled product collector vessel PCV. By using various heating-up tubes and various reaction tubes, and by adjusting various volume flows, heating-up times between about 5 s and 40 s could be achieved at reaction times which should be sufficient to obtain high conversion rates. The results of previous works [aoun-2012; sakthivel-2010; schlange-2011] allow to postulate that an almost complete conversion should be approached within some few minutes or even less. The product collector vessel was installed inclining in the coolant (cool tap water which was periodically replaced to keep its temperature low), because the product dispersion was expected to be rapidly quenched rather on the cooled wall of the vessel than on the surface of the liquid inside.

Because the used liquids were hygroscopic, the storage vessels were ventilated through silica filled drying tubes DT.

During startup operation the volume flow could be controlled by use of the volume flow indicator tube FIT. First, with all ways opened at TV8, the calibrated tube of the FIT could be filled up by slightly pulling the plunger of the syringe mounted above. After switching TV8 to left and up way opened, the liquid was temporarily pumped out of the calibrated tube only, while the time interval between two certain marks could be determined with a stopwatch. If necessary, the peristalting pump PP could be adjusted stepwise, in steps of 1 % of the maximal revolution speed.

In case of a beginning development of plugs, the increase of pressure drop in the tubular system was prematurely indicated by the pressure indicator tube PIT, to enable early counteractions, which usually was done by knocking on the assembly with a wooden stick or similar to disassociate the agglomerates, which was not always successful. Such pressure drops, however, only occurred during use of the thinner one of two used heating-up tubes.

4.2 Heating-up tubes

4.2.1 Dimensioning

4.2.1.1 Basics

The heating-up tube has to meet several special requirements and was therefore the first component of the CFCP assembly to be dimensioned. With respect to the comparably expensive reaction mixture the flow rates should be rather small, which will result in a laminar flow, especially in comparably viscous fluids like ethylene glycol. This means that the entire heat has to pass the liquid from the inner tube wall to the axis by heat conduction exclusively. To obtain the demanded heating-up periods of down to 10 s or even 5 s, the heating-up tube's inner diameter has to be small enough to enable a close-to-balance temperature distribution in the liquid from its core to its periphery over the entire tube length. On the other hand the inner diameter must be wide enough to reliably avoid pluggings by agglomerating catalyst support particles, even in the narrow gap between the end of the heating-up tube and an inserted coated thermocouple, which should be robust, and hence thick, enough to be handled easily. Such pluggings, even if quickly disassociated, would in any case disrupt the even flow and hence the steady-state operation, leading to unreliable test results. In addition, the inner diameter should be great enough to obtain a smallest possible pressure drop at the heating-up tube.

With respect to the directly electrically heating it is also to consider that for a given material the voltage-current ratio for the heating current will increase with decreasing material cross-section area and with increasing tube length. A not too low voltage-current ratio is important to realize an electrical contacting to the tube ends which matches the following demands:

- low heat branching-off from the tube
- low contact resistance to obtain a low additional heat generation at the contact point
- low additional heat generation in the supply line

The lower the heating current, the thinner the supply lines must be, which causes lower heat losses. As all common materials for electric lines have similar ratios for electrical and heat conduction, the choice of an optimal supply line material is not reasonable.

Lower material cross-section areas can be obtained either by a lower outer diameter or a lower wall thickness. Tubes with a low wall thickness to outer diameter ratio, however, tend to buckle or break when tried to be bent to a bow. To obtain a rather compact test assembly with encased heating-up tube, it was necessary to bend the heating-up tube to more or less wide loops.

For the reaction tube there were no serious restrictions referring to length, diameter or wall thickness.

4.2.1.2 Material

The heating-up tube material has to show a sufficient chemical persistence and elecrical conductivity. The electrical conductivity must be great enough to enable a heating voltage of only a few volts to avoid electrochemical by-effects, such as electrolysis. On the other hand, the electrical conductivity should be high enough to obtain a convenient voltage-current ratio, as explained in 4.2.1.1.

The chosen material was stainless steel 1.4301 (V2A), which, contrary to most other stainless steel types, is available as tubes in a great variety of dimensions. Its electrical resistivity meets the required range. The chemical persistance was proposed to be sufficient, though there were no experiences available at this time. All corresponding pilot tests had been performed with tubes of 1.4404 (X2CrNiMo17-12-2) [aoun-2012; schlange-2011].

4.2.1.3 Inner diameter determination

To evaluate the highest possible tube diameter to obtain an almost even temperature distribution in the flowing through liquid, a simple model was established to calculate the development of the radial temperature profile with time. Starting with the initial radial temperature profile of an evenly cold liquid in a hot tube, the radial heat exchange between very thin adjacent liquid layers and the resulting temperature changes were calculated in very short time intervals [grimm-2015], as described in the following paragraphs. The used equations correspond to the basic equations for heat transfer in solid cylindric objects.

For the calculations the tube and its liquid content was imaginated as a number g of thin-walled telescoped hollow cylinders [grimm-2015]. Each of these hollow cylinders is characterized by its inner and outer radius r_f and r_{f+1}. With $0 \leq f \leq g$, $r_{f,f+1}$ is the average value of r_f and r_{f+1}. The changing of the thermal energy $\Delta Q_{f,f+1}$ in the hollow cylinder between r_f and r_{f+1} is given by

$$\Delta Q_{f,f+1} = \Delta Q_{f+1} - \Delta Q_f \qquad (4\text{-}1)$$

For the inner cylinder directly around the tube axis is $\Delta Q_{f,f+1} = \Delta Q_{f+1}$, because there is no further material to exchange heat with. Similar, for the heating tube, which is imaginated as one single hollow cylinder, $\Delta Q_{f,f+1} = \Delta Q_f$, because in the present model it is not necessary to consider any heat loss from the tube to the ambience.

In equation (4-1) ΔQ_{f+1} and ΔQ_f represent the heat which is transferred in a very short interval Δt, therefore is

$$\Delta Q / \Delta t \approx \mathrm{d}Q / \mathrm{d}t \tag{4-2}$$

and hence, for both terms of equation (4-1) is given

$$\Delta Q_f \approx \Delta t \, L_{\mathrm{Tu}} \, K_f \, (T_{f,f+1} - T_{f-1,f}) \tag{4-3}$$

with L_{Tu} : tube length; T : average temperature of the referring hollow cylinder; K : heat transfer coefficient.

The heat transfer coefficient K_f can be calculated as follows:

$$K_f = \frac{2\pi}{\dfrac{\ln\left(\dfrac{r_f}{r_{f-1,f}}\right)}{\lambda_{f-1,f}} + \dfrac{\ln\left(\dfrac{r_{f,f+1}}{r_f}\right)}{\lambda_{f,f+1}}} \tag{4-4}$$

with: λ : thermal conductivity coefficient of the referring hollow cylinder.

Equation (4-4) considers, that adjacent hollow cylinders might have different thermal conductivity coefficients, as it is present for the tube and the adjacent liquid hollow cylinder.

For every hollow cylinder the ratio $\Delta T/\Delta Q$ between temperature increase and heat input is

$$\frac{\Delta T_{f,f+1}}{\Delta Q_{f,f+1}} = \frac{1}{\rho_{f,f+1} \, \mathrm{cp}_{f,f+1} \, L_{\mathrm{Tu}} \, \pi \, (r_{f+1}^{\;2} - r_f^2)} \tag{4-5}$$

with: ρ : density; cp : specific heat capacity.

Therefore, for every hollow cylinder the temperature change within the interval Δt can be calculated as follows:

$$\Delta T_{f,f+1} = \frac{\Delta T_{f,f+1}}{\Delta Q_{f,f+1}} \; \Delta t \, L_{\mathrm{Tu}} \left(K_{f+1} \left(T_{f+1,f+2} - T_{f,f+1} \right) - K_{f} \left(T_{f,f+1} - T_{f-1,f} \right) \right) \qquad (4\text{-}6)$$

The calculations for the evaluation of an appropriate inner tube diameter were carried out with an overall liquid temperature of 20 °C as start conditions and a constant tube temperature of 140 °C, which was scheduled as the optimal reaction temperature for the polyol reduction reaction with hexachloro platinic acid and ethylene glycol, as suggested in previous works [aoun-2012; sakthivel-2010; schlange-2011].

To keep a constant tube temperature during a calculation run, the heat capacity of the tube material was set to an extremely high value.

The development of the temperature profile for 4 tubes with different inner diameters is represented in Fig. 4-2. A diameter of 2.2 mm corresponds roughly to the inner diameter of the 1/8"-tube which had been used in previous tests with a directly electrically heated heating-up tube [aoun-2012; schlange-2011].

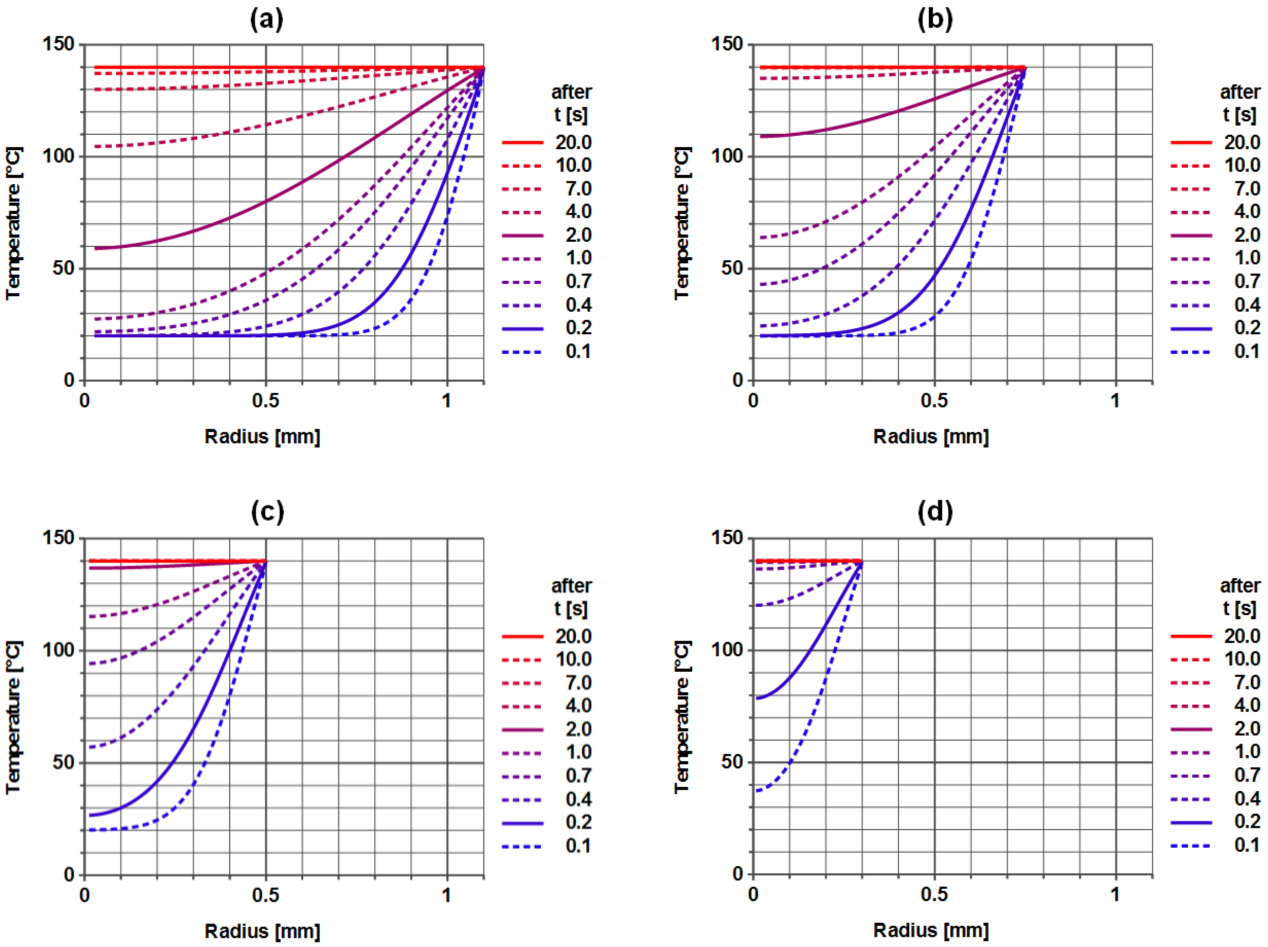

Fig. 4-2: Development of the radial temperature profile in ethylene glycol in various stainless steel tubes whose temperatures are abruptly raised to 140 °C and then remaining constant (inner diameter is a: 2.2 mm; b: 1.5 mm; c: 1.0 mm; d: 0.6 mm)

The displayed graphs are allowing a rough estimation of the highest suitable inner diameter, if the time interval to obtain an almost even temperature profile is considered as about 1/5 to 1/10 of the retention time. By this, it is taken into account that in the continuously operated tube the wall temperature will not be constantly 140 °C, but will increase from room temperature to 140 °C. For a retention time of 10 s the so estimated inner diameter should not be more than about 1 mm.

To verify this coarse estimation, the model was modified to calculate the temperature profile development in a fluid which is plug-flowing through a tube, where the tube temperature is uniformly increasing over the tube length from 20°C at the inlet to 140 °C at the outlet. This easier to install plug-flow model does not really represent a laminar flow, but should result in at least similar results. An uniform temperature increase over the tube length can be proposed because of adequate measurement results from previous works [schlange-2011].

The results for heating-up tubes with different inner diameters plug-flowed through by ethylene glycol at a retention time of 10 s are represented in Fig. 4-3.

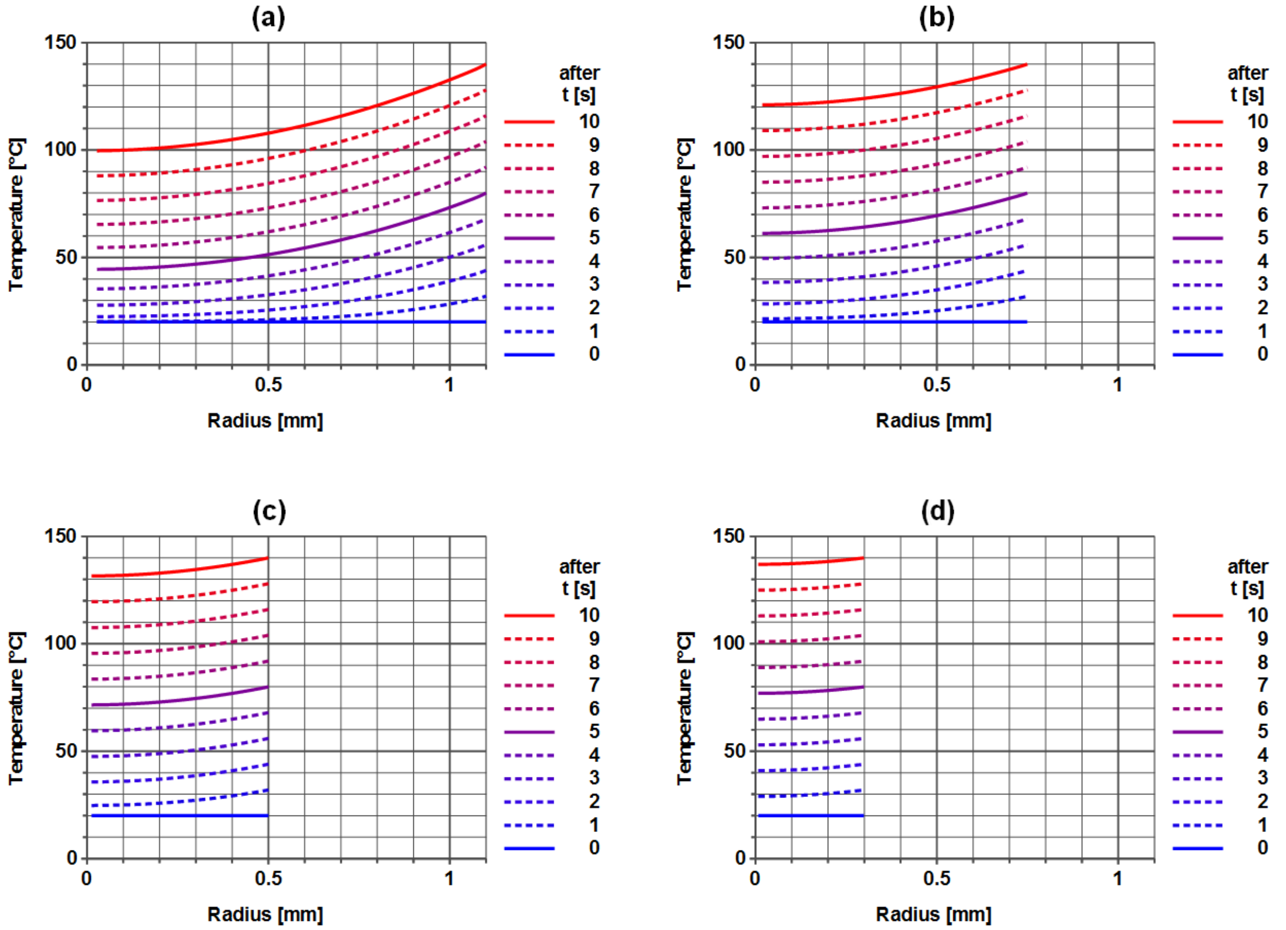

Fig. 4-3: Development of the radial temperature profile of plug-flowing ethylene glycol over time (which is corresponding to the covered distance) in various stainless steel tubes with temperatures uniformly increasing from 20 °C at the inlet to 140 °C at the outlet, during a retention time of 10 s each (inner tube diameters: a: 2.2 mm; b: 1.5 mm; c: 1.0 mm; d: 0.6 mm)

In a laminar flowing liquid, the liquid near the tube axis should be heated up less, because of the lower retention time there. Which flow type really would appear, however, could not be predicted at the time when the calculations were done. Because of the dispersed, but probably more or less agglomerated support material, the flow could as well be supposed as approaching plug-flow or approaching laminar flow. Therefore, a further, time intensive model development was disclaimed.

Some investigation about the retention time profile at real test assembly operation was executed in a late phase of the project, in the context of a student research project [kongolo-2016].

Referring to Fig. 4-3(c), the highest inner diameter of 1 mm for 10 s retention time, as was proposed from Fig. 4-2(c) can be confirmed. In a heating-up tube of 1 mm inner diameter it should be possible to heat up a flowing-through ethylene glycol based liquid up to about 130 °C at the axis and by guess >135 °C on the average.

The heating-up tube with 2.1 mm inner diameter, used in preliminary tests [aoun-2012; schlange-2011], however, would not have been suitable to approach a uniform temperature level within periods much shorter than 1 minute, but was sufficient for the tests with heating-up times of downto 50 s (Fig. 4-4), which in fact was the lowest retention time performed with this tube.

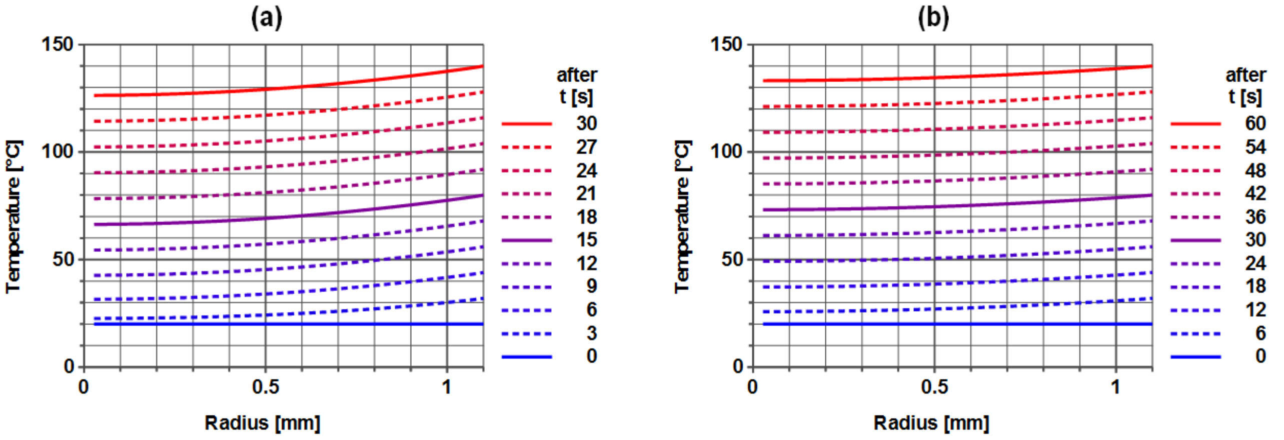

Fig. 4-4: Radial temperature gradient development in ethylene glycol flowing through a stainless steel tube, whose temperature increases linearly over its length, at different retention times (a: 30 s; b: 60 s); pseudolaminar flow with uniform velocity distribution

4.2.2 Setting up

To obtain an optimal current-voltage ratio for the heating current, thin walled tubes were used to set up two different heating-up tubes with the properties represented in Tab. 4-1.

Heating-up tube	HUT-1	HUT-2
Material	1.4301	1.4301
Inner diameter (mm)	0.8	1.0
Wall thickness (mm)	0.2	0.1
Length of heated zone (mm)	500	318
Volume of heated zone, calculated (mL)	0.251	0.250
Volume of heated zone, measured (mL)	-	0.258

Tab. 4-1 Materials and properties of the heating-up tubes

Due to the disadvantageous diameter wall thickness ratio, bending the tubes appeared to be difficult. As there was no adequate tool commercially available, a simple self made improvisational bending tool (Fig. 4-5) was used, which can easily be fitted to different outer tube diameters by variation of the distance between the washers. By using screws with various diameters it is also possible to variate the bending radius. To avoid direct contact between tube and screw gearing a short piece of a PTFE tube around the screw was mounted between the washers.

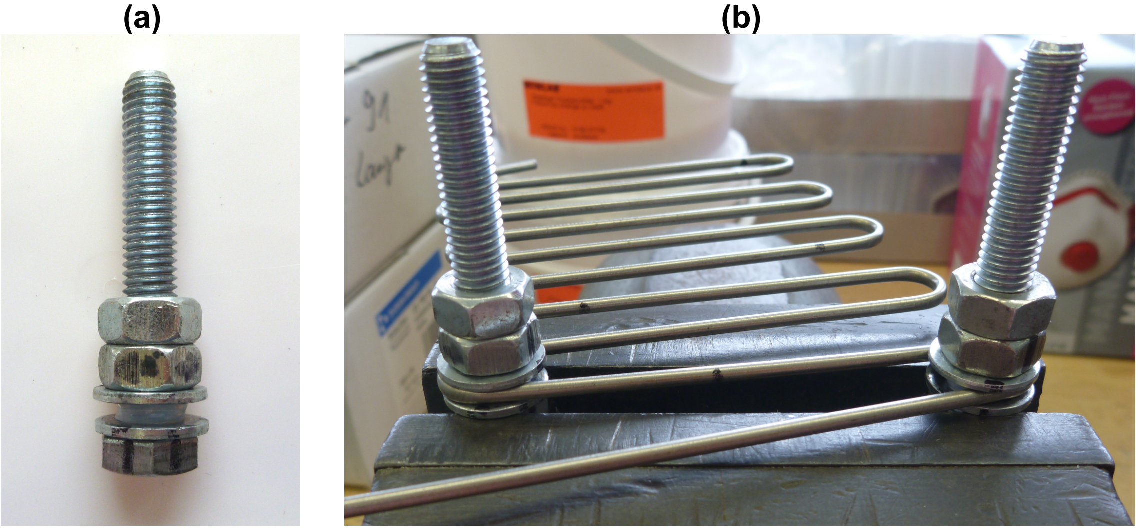

Fig. 4-5: Improvisational bending tool for thin-walled tubes with low diameters, which can be adjusted exactly to the desired diameter; (a): adjustable bending element; (b): bending of a tube by help of two bending elements fixed in a bench vice

With bending tools like this, the heating-up tube HUT-1 could easily be bended to the form shown in Fig. 4-6(a), so it could fit into its housing to be protected against air movement.

The second heating-up tube HUT-2 with an extremely thin wall of 0,1 mm could not be bended properly even with the tool, but could be bended to a wide S, bare-handed (Fig. 4-6(b)).

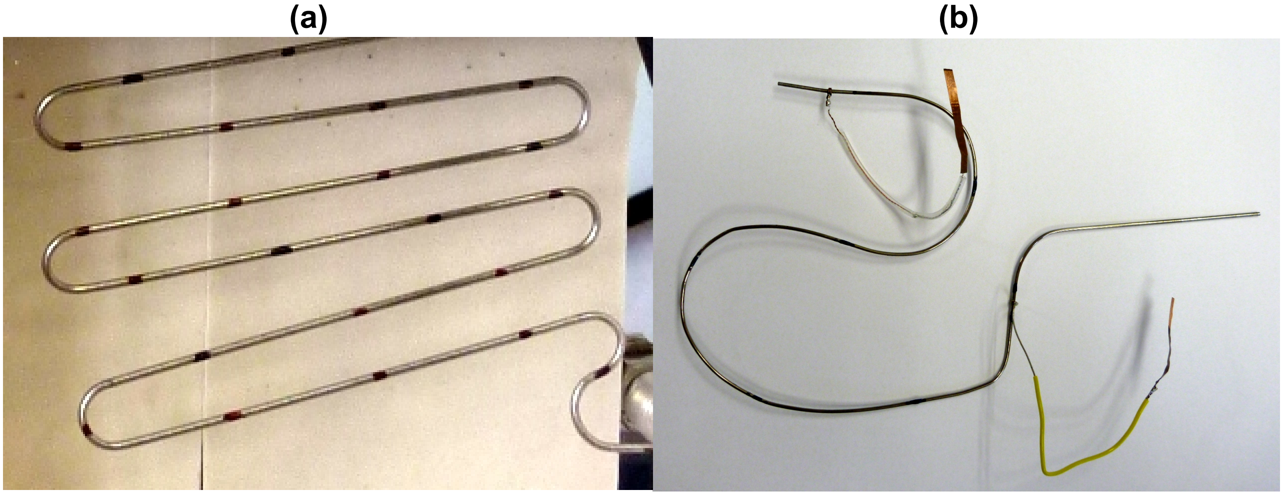

Fig. 4-6 (a) HUT-1, installed inside its housing (with marks every 2 cm), and (b) HUT-2, equipped with electrical contact wires

4.2.3 Electric contacts and mechanical fixing

At the feed end, the heating-up tube will be cooled down to about room temperature by the incoming liquid. Therefore there will be no noteworthy heat dissipation at this end, and there is no need for a special dimensioning of the contacting wire. In contrast to this, the wire and contacting at the tube outlet side must be dimensioned carefully to approach a good balance between heat evolved in the contact and heat dissipating through the contact wire. This could approximately be achieved by wrapping a copper wire of suitable strength around the tube, optimize the contact by intruding tin solder and connect a thin supply line by soldering, as shown in Fig. 4-7(c).

To get a suitable wire strength, different wires were tested and the corresponding temperature profiles around the contact were observed and estimated by help of a thermocamera. To increase the emission coefficient to a value around 0.95, the contact and the adjacent part of the tube were coated with a matt paint.

One additional advantage of the tin solder connection was an intrinsic safety. In any case of overtemperature at the heating-up tube outlet, caused by e.g. a decreasing flowrate or any other lack of liquid feed, the solder at the contact melted at once to disconnect the line. Due to the melting point of usual tin solder of about 180 °C and the boiling point of ethylene glycol of 197 °C, there was no possibility to evolve any dangerous situation from evaporating liquid. This safety function was successfully tested several times, and worked properly at an accidentally air intrusion caused by pitting corrosion at an upstream stainless hollow needle tube.

For the heating-up tube HUT-1, which at first was used for a number of test runs, a removable contacting by using a narrow copper strip in a silicon tube (Fig. 4-7(a) and (b)) was tested, but did not work properly, because of an unstable contact resistance which forced to numerous readjustments of the voltage supply. Because of these problems, and because of severe plugging problems, this heating-up tube was replaced by HUT-2, which was better contacted and a bit wider in inner diameter, so there were no more pluggings during use of this tube.

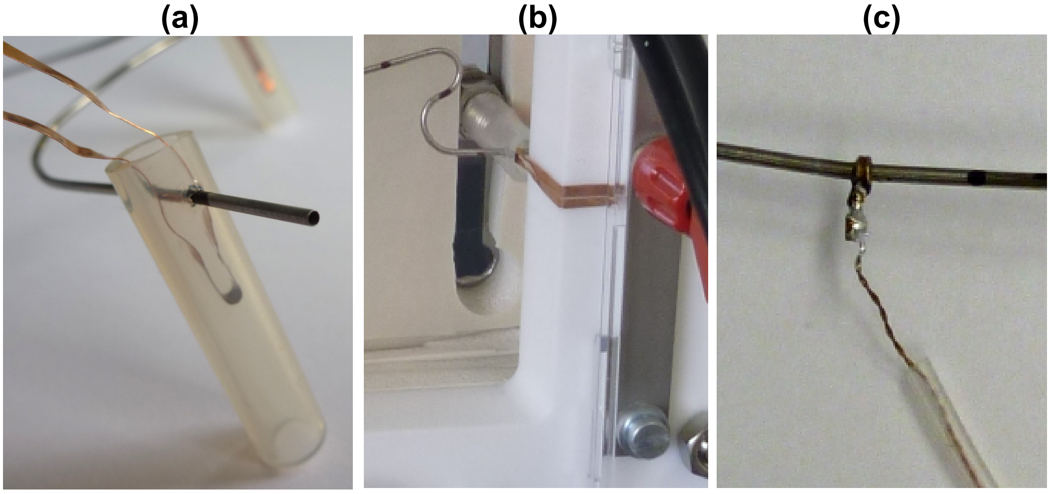

Fig. 4-7: Electric contacting and mechanical fixing of the heating-up tube; (a), (b): preliminary version at first test runs; (b): installed; (c): finally used version

4.2.4 Ensuring constant flowrates

At constant voltage supply, any accidental volume flow change will lead to a temperature profile change along the heating-up tube. Reasons for too high temperatures of the heating-up tube and its liquid content by an accidentally flow decrease may be:

- Pumping failure (e. g. by a broken peristaltic pump tube)
- Plugging
- Air intrusion through an upstream leakage

To avoid pumping tube damages, these tubes were frequently renewed by way of precaution. Pluggings were observed only during use of HUT-1, in most cases it was possible to resolve the plugging by knocking on the test equipment housing. After installing of HUT-2 there were no more pluggings.

4.3 Reaction Tubes

4.3.1 Material

Mainly because of the large number of available sizes, tubes of 1.4301 were used to prepare the reaction tubes, too.

4.3.2 Setting up

To obtain different retention times at a certain heating-up tube and a certain heating-up time, different reaction tubes were prepared with 2.0 mm inner diameter and 2.6 mm outer diameter. To get these tubes installeable, they were bended, as shown in Fig. 4-8, by use of the self-made bending tool.

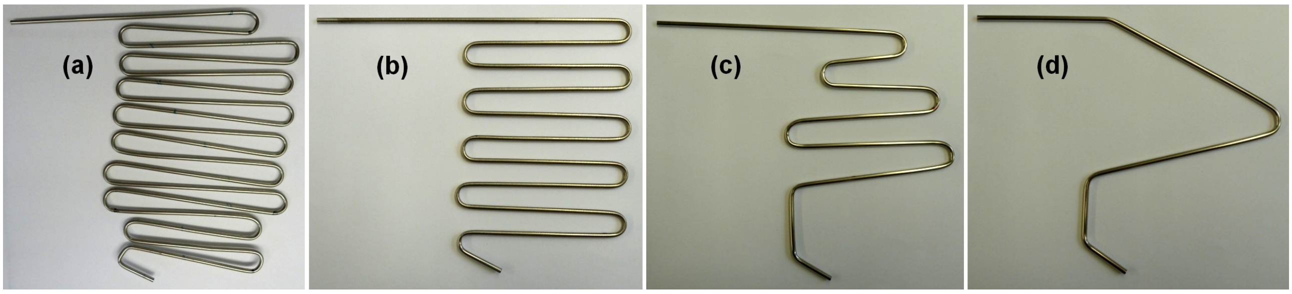

Fig. 4-8: Reaction tubes with different length; (a): 2000 mm; (b): 1000 mm; (c): 600 mm; (d): 300 mm

To determine the real volume, flat-seating plugs were prepared for both tube ends, and weighed both empty and completely filled with water. The determined tube volumes are 6.048 mL, 3.255 mL, 1.787 mL and 0.965 mL. Because the reaction line effectively begins at the end of the heating-up line, the volumes of the end of the heating-up tube (downstream from the electrical contact point) and the silicon tube connecting heating-up tube to reaction tube, were added to obtain the effective reaction volumes of 6.085 mL, 3.292 mL, 1.824 mL and 1.002 mL.

4.3.3 Isothermic heating

In each case, the current reaction tube was pressed on an isothermic heatable aluminum plate by a thermal resistive isolating silicon foam sheet which was fixed by a metal plate attached by screws. At the backside of the heatable plate and around, silicon isolating pads were applied, too.

4.4 Fluid management

4.4.1 Fluid pipes, connectors and valves

Because of their chemical inertness, and because very flexible and easy to use, silicon tubes were used to build the flow paths and to connect the metal tubes with one another. The standard tube size was 1 mm inner and 3 mm outer diameter. Downstream the pump, the tubes were secured against slipping by wrapping a thin wire around and drilling its ends.

To block, to switch or to branch flow paths, small three-way cocks were installed, which are of the type usually used for medical purposes. The connectors were made by fitting short stainless steel tubes of 1.2 mm outer diameter to the openings, as can be seen in Fig. 4-9.

These three-way cocks are pressure resistant up to some 100 kPa and of very low capacity. Two or more three-way cocks can directly be connected with each other.

Fig. 4-9 exemplifies a part of the fluid system. The stainless tube connectors were installed to the cock openings by help of improvisational tube fittings, made of the cock plugs and some small pieces of silicon tube as compression sealings, which were designed to minimize dead volumes.

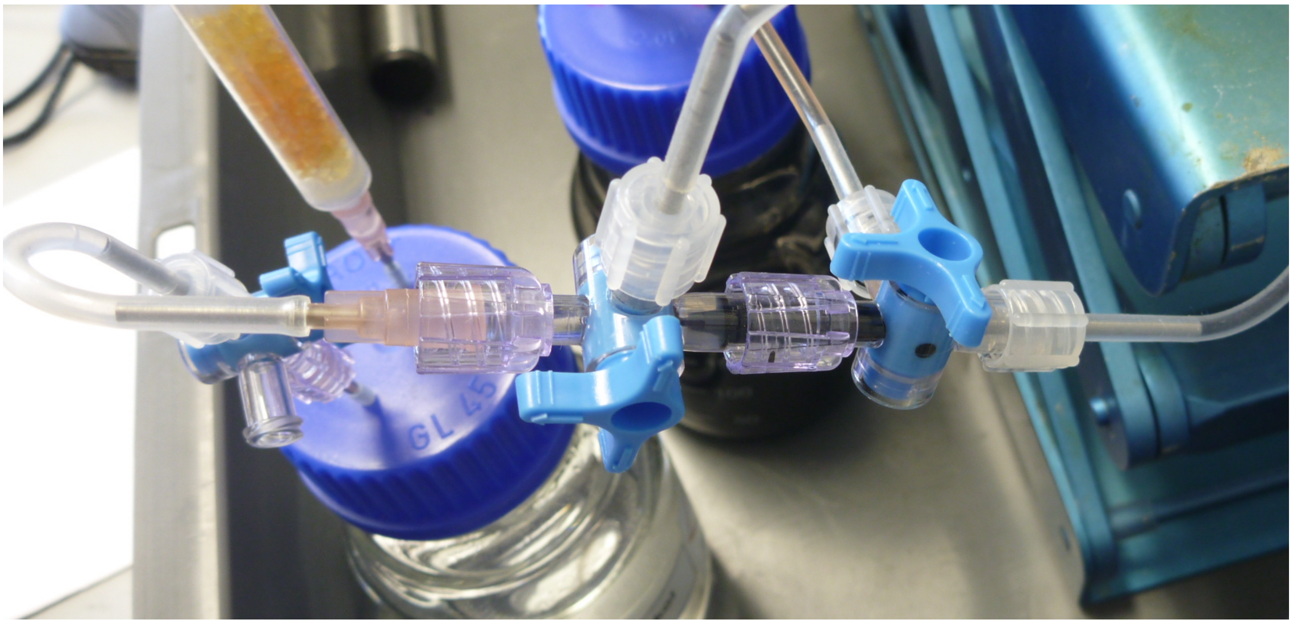

Fig. 4-9: Part of the fluid system of the test equipment with three-way cocks; at the left hand side as a cutoff valve, in the middle and at the right hand side as 2 coupled switching valves

4.4.2 Pumping equipment

The used pump was a peristaltic pump (Ismatec; ISM 796C). The peristaltic tube was a silicon tube of 1 mm inner and 3 mm outer diameter, as was used for the overall fluid mamagement of the equipment, too. With this peristaltic tube, volume flows of 0.3 mL/min up to 3.0 mL/min could be obtained with sufficient accuracy by adjusting the pump frequency between 8 % and 80 % of its frequency range.

4.4.3 Measuring devices

4.4.3.1 Volume flow

To obtain the desired volume flow, the equipment was operated with startup mixture (pure ethylene glycol) before every test run to adjust the test system to the desired operation parameters. The volume flow was measured during this startup mode, by switching TV8 that way that the fluid was pumped out of the filled calibrated pipe, which allowed to measure the time between two marks to determine the volume flow. The desired volume flow could then be adjusted by an adequate increase or decrease of the pump frequency.

The exact actual average volume flow was determined after every test run by weighing the obtained product dispersion and by division of the calculated volume by the corresponding time interval. The density of the liquid was assumed to be 1.024 g/cm³ (density of ethylene glycol at 140 °C [vdi-2006]).

4.4.3.2 Pressure

The pressure indicator tube was installed as a safety control only, to detect pluggings inside the reaction system as a corresponding pressure increase. No high accuracy was necessary, but the amounts of fluid branching into the indicator and getting back into the reaction system should be minimized, to minimize volume flow changes in the reaction system and hence minimize changes in the steady-state conditions. A simple solution was to install a short, one end closed thin pressure indicator tube, which works by compressing the air in the tube depending on the pressure of the fluid which can be indicated by the fluid's level in the calibrated tube. The amount of liquid temporarily branched-off was 0.02 mL at 100 kPa. The three-way cock allowed to uncouple the pressure indicator tube, if required.

4.4.3.3 Temperature at heating-up tube outlet

The directly electrically heated heating-up tube was powered by an adjustable laboratory power supply (McPower; Digi 30-5) with controls for coarse and fine adjustment, at voltage limitation mode, which was sufficient to obtain a widely constant temperature during operation, if there were no violations of the steady-state conditions. Once in a while, a fine voltage readjustment could be required. An additional precondition to obtain a constant temperature was a housing around the heating-up tube to be prevented from air movements, e. g. by the running fume hood, moving persons or opening doors.

The connection between heating-up tube and reaction tube was performed by a piece of silicon tube with integrated thermocouple for the measurement of the temperature of the heated up liquid. This improvisational part is, compared with a conventional tube fitting, much more slim and lightweight, to minimize problems which could derive from heat dissipation. To prepare this connection tube, it first had to be wrapped some times with PTFE tape, then the thermocouple was carefully sticked through the wrapped part of the tube and fastened and additionally sealed by wrapping some more PTFE tape around (Fig. 4-10(a)). The 0.25 mm thermocouple is rather damageable by sharp bendings, especially at the transition to the connected cable. As a protection against sharp bendings at any position, the thermocouple was placed inside a silicon tube, as shown in Fig. 4-10(b).

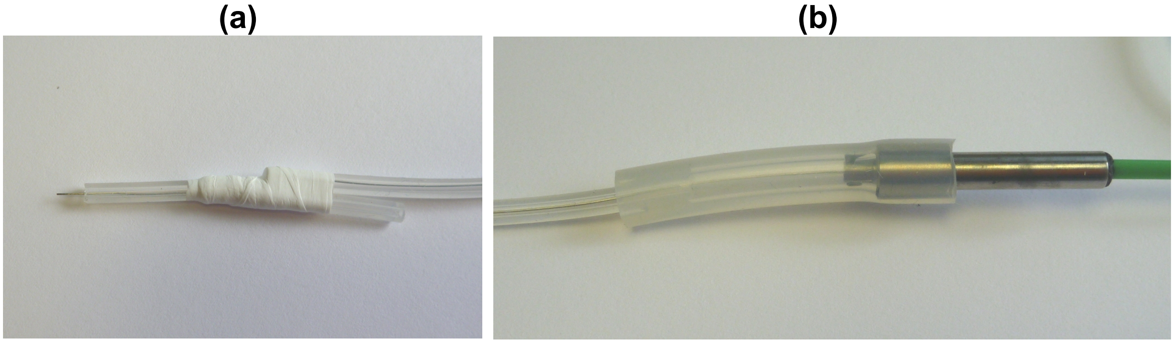

Fig. 4-10: Connector between heating-up tube and reaction tube (a) and protection for the weak 0.25 mm thermocouple (b)

4.5 General operation mode for the CCP initialization

To start the test equipment, first the vessels for the startup mixture and the reaction mixture were filled, the product collection vessel was set to its position, and the corresponding cocks were switched into the right positions to run the equipment with startup mixture. The pump was adjusted to slow revolution and switched on. The heating plate controller was switched on, then it had to be waited until its desired temperature had been approached. Then the pump revolution was adjusted to approximately the desired flow, the power supply for the heating-up tube was adjusted to zero volts and switched on. The voltage was then carefully raised until the desired temperature at the heating-up tube outlet was approached. Then, the volume flow was determined by using the volume flow indicator, and, if required, readjusted. After switching to the reaction mixture, the heating-up voltage was carefully readjusted and a time interval estimated to be sufficient for a complete change from startup mixture to reaction mixture had to be waited, before the actual test run was started by changing to a new, empty collector vessel.

The test run was usually finished after the reaction mixture had been used up. Then it was switched back to startup mixture and the end point of the test run was defined by the exchange of the filled collector vessel by a new one.

After every test run, the liquid flow system was cleaned by intermediately pressing air and water through the reaction system by use of a syringe. At this junction, some material which had been remained in the tubes, was driven out. After some single test runs, this residual material was collected and examined, as described in chapter 7.7.

4.6 Batch process operation

To perform the batch preparation tests, the reaction mixture was filled into a reaction vessel (glass flask or big test tube, which allows a faster heating-up) with magnetic stirrer and a PTFE coated thermocouple (delivered by Omega) positioned inside and a hose to purge with nitrogen fastened at the neck. At start time the vessel was put into a heating bath filled with silicon oil which was preheated to 160 °C. After approaching 140 °C, the reaction mixture was kept at this temperature for a certain additional time, then removed from the heating bath and allowed to cool down.

During the process, the temperature in the reaction vessel was monitored.

5 Preparation

5.1 Reaction mixtures

The main component of the reaction mixtures was ethylene glycol, which worked as solvent, dispergent and reductant. Additional ingredients were fine dispersed carbon as catalyst support material, hexacloroplatinic acid (HPA) and sodium hydroxide. In some cases, a certain amount of water was added, too. The standard support material was hydroxy-carboxy-functionalized carbon nanotubes (oxCNTs), in particular cases, Vulcan-XC-72R carbon black was used, which is a standard electrocatalyst support for commercial purposes.

The oxCNTs had been preparated by treating MWCNTs (Bayer Material Science, BayTubes® C150HP) during 5 hours with boiling hydrochloric acid to remove cobalt residues, and subsequently with boiling concentrated nitric acid during 5 hours to oxidise a part of the carbon atoms to alcoholic or carboxylic groups, mainly at point defects of the graphene structure.

To obtain the desired amount of reaction mixture, the required weights of the ingredients were calculated to approach a composition as follows:

- 1.8 g carbon based support material per kg of reaction mixture (= 2.0 g per 1 L of reaction mixture, like in preliminary works [schlange-2011])
- The theoretically required content of HPA to obtain a catalyst with the desired platinum content (Note: because of a possible, more or less pronounced elimination of functional groups during the reaction, the platinum content in the prepared catalysts might be higher than the theoretical maximum!)
- The required amount of a 0.2 M NaOH solution in ethylene glycol to obtain the desired NaOH Pt ratio for pH control

A possible support material weight decrease by elimination of functional groups during the reaction was not known by value and therefore could not be considered.

The HPA is strongly hygroscopic and was therefore weighed inside a glove bag under dry nitrogen. For the first tests, a HPA solution in ethylene glycol with known Pt content was prepared and used for several tests. After it had been observed that the use of such solutions older than about 1 month results in a very low deposition efficency, even if stored in a refrigerator and optically seemed unaltered, no more prefabricated HPS solution was used.

The support material was applied as a prefabricated dispersion with solid contents of around 5 g/kg. For the prefabrication, about 1 g of solid was weighed exactly and sonicated in about 80 mL to 100 mL ethylene glycol in a 100 mL test tube by an ultrasonic horn (Bandelin Sonopuls 2070 with KE76 sonotrode). After having obtained a stable, cluster-free dispersion, it was diluted with ethylene glycol to a solid content of 5.0 g per 1 kg of dispersion. No disadvantages of the use of these prefabricated dispersions were observed, even after use of some dispersions which had been stored for several months.

Nevertheless, at least the procedure was changed to prepare only the required amount of carbon dispersion for every single test run, because it appeared to be easier to prepare a higher number of small amounts than a lower number of large amounts. The extremely dusty Vulcan-XC-72R carbon black, however, was dispersed in one single batch, to avoid to have to handle this material, followed by elaborating cleaning procedures, more than one single time.

The NaOH solution in ethylene glycol was prepared by dissolving the calculated amount of small NaOH perls (1 mm diameter) in a certain quantity of dry ethylene glycol by stirring over night. Larger NaOH pellets would dissolve extremely slowly, therefore the use of them is not recommended for the purpose described. The exact NaOH concentration was determined by titration with HCl solution.

For the first test runs, a 1.0 mole/kg NaOH solution was used, which by time got more and more brown, possibly caused by an alcaline catalysed reaction with ambient oxygen. For further tests, a 0.2 mole/kg NaOH solution was used, which never was observed to change its colour.

In opposite to preliminary tests [schlange-2011], no aqueous NaOH was used, on the one hand to avoid a possible steam bubble evolution in the hot reaction system, and on the other hand to avoid a possible unwanted influence of water on the size of the deposited platinum particles, which had been described in some publications [knupp-2008; lee-2006].

For the preliminary tests at the Institute of Chemical Process Engineering (ICVT), the NaOH solution was added until a certain pH was displayed on a usual pH meter with a glass membrane electrode designed for aqueous solutions. [schlange-2011] added aqueous NaOH up to a displayed pH of 10, while [sakthivel-2010] added NaOH in ethylene glycol to obtain a displayed pH between 10 and 11. For the current project, a calculated stoichiometric amount of NaOH, dissolved in ethylene glycol, was added. To neutralize 2 protons per Pt from the HPA and 4 protons evolving during reaction, a NaOH Pt ratio of 6 should be approached, theoretically. This is fitting rather well with the ratio 6.07 which was obtained in a test where NaOH solution was added up to a displayed pH of 10.0.

The standard NaOH Pt ratio for the first tests was 6.0, whereas some of these tests were performed with ratios of 4.0 or 8.0 to examine the pH influence on the test results. Later tests, especially those to examine the influence of heating-up time and reaction time, were performed at a NaOH Pt ratio of 5.0, because the previous test results suggested sufficient results at this NaOH Pt ratio, rather than at 6.0 or 4.0. Similar had been reported by [aoun-2016] for the batch preparation of Pt-oxCNT catalysts by polyol reaction.

A NaOH Pt ratio between 4 and 6, which seems to be optimal for 40 % Pt catalyst preparation, is not supposed to be optimal for the preparation of catalysts with much higher or lower Pt contents, as suggested by results from tests to prepare 60 % Pt catalysts.

To prepare the reaction mixture, a certain amount of HPA was dissolved in a small amount of ethylene glycol, then the carbon support dispersion, the NaOH solution, the water, if indicated, and finally pure ethylene glycol, were subsequently added in the calculated amounts, while the mixture was stirred.

An addition of surfactants, as described as positive in adequate, microwave heated reaction mixtures [sakthivel-2010], was disclaimed, because preliminary tubular reactor test results [schlange-2011] are suggesting, that surfactants are unassential in continuously operated tubular reactors.

5.2 Catalyst samples

5.2.1 Separation and Purification

Because of the severe efforts for separation and purification of the catalyst samples from the product dispersion, it was examined in a project borne bachelor thesis, if these efforts could possibly be minimized [genthe-2015].

Usually purification is performed by washing the solid with a good solvent for both ethylene glycol and sodium chloride, like water or a water alcohol mixture. For the solid-liquid separation filtration and centrifugation are established methods.

By centrifugation in a laboratory centrifuge, a rapid sedimentation of the catalyst is possible. Frequency and separation time have to be well adjusted to obtain a sediment which clearly separates from the liquid, but can be redispersed easily. The most problematic step was the redispersion, because it is extremely difficult to control if there are no more lumps of solid left, which would drop the washing effectivity [genthe-2015]. In addition, the same procedure has to be done in more than one centrifuge vessel.

Dispersions from different test runs showed different behaviour. In some cases, there was no proper separation, the liquid remained dark or dull. The yield losses, however, were small and not serious in laboratory tests [genthe-2015].

If larger amounts of liquid have to be centrifugated, the capacity of the centrifuge might be exceeded, which would force to spend more time to run several passages per washing step.

By vacuum filtration through a 45 μm membrane filter, a complete separation of the solid phase could be achieved in all cases. The main filtration problem was that the primary product dispersion passed through the membrane very slowly, because of the high viscosity of ethylene glycol [genthe-2015]. To increase the filtration rate by dissolving the primary product dispersion with water was found to be useless, because the filtration rate increase was more or less overcompensated by the increase of the dispersion volume. As a result, it seemed recommended first to centrifuge the primary dispersion and then filtrate the second and the following dispersions, whose main component is water [genthe-2015].

A fundamental problem with the filtration and the washing of the filter cake by batchwise application of fresh washing liquid is that the filter cake may not be flown through evenly and therefore the contaminants from the less perfused areas are washed out very slowly. In fact, after the stirring up of a filter cake which, by a filtrate analysis, had already been judged to have been largely purified, a considerable increase in the concentrations of impurities in the filtrate was detectable [genthe-2015]. In particular, in the case of a dry falling of the filter cake this will be rinsed very unevenly due to the cracks formed therein. Although a repeated intermediate re-stirring of the filter cake during the wash resulted in an improvement in the washing result, the stirring inside the filter device, down to the sensitive membrane filter, occasionally resulted in a membrane damage by the used spatula [genthe-2015].

Since neither the centrifugation nor the filtration nor their combination in the form described were found to be completely satisfactory, an alternative method of product preparation was tested, doing completely without a centrifuge and characterized by only little required effort and low costs, both in laboratory and production scale.

Hereby, the primary product dispersion is infused into a stirred vessel filled with a larger amount of water (at least 10 times the amount of product dispersion). The agitating is then stopped and the solid, which has formed weak agglomerates, is allowed to settle overnight, or at least 1 hour. After decanting off the supernatant liquid, the weak sediment sludge can be easily redispersed by fresh water, without clumping. Settling, decanting and redispersing of the sediment is repeated more or less often, depending on the required purification grade. The final sediment sludge is filtered and the filter cake is washed several times with water, avoiding dry cracking, and finally dried at elevated temperature (60 °C to 80 °C) in a gentle nitrogen stream.

The method described normally will take about one to ten days until a catalyst sample is available for further investigation or a production lot can be ready for shipment, depending on the number of purification steps, if settling takes place overnight. Upscaling can easily be performed either by use of larger vessels and suction strainers or by a larger number of vessels and suction strainers. The required effort is extremely low and the equipment costs are almost negligable. For most laboratory purposes, only one larger beaker is required for the main cleaning steps which will take less than 10 minutes for each manual operation. Almost any number of catalyst samples can be processed in parallel without any problems. The method can as well be used for the purification of product dispersions from discontinuous processes.

Nevertheless, it has to be considered that the settling appears to be uncomplete. After 24 hours, up to about 10 mg of several 100 mg of total solid remained in the supernatant liquid as very small agglomerates, and remarkably more at settling times of one or few hours, which might be required to obtain samples or product within a short time. In case of laboratory studies the corresponding yield loss might be tolerable. If not, or for industrial purposes, a yield loss can easily be avoided by operating as follows: The decanted liquids of all purification steps are not discarded but collected and, when the final product slurry is getting ready to be filtrated, the decanted liquids are filtered before. This will not take much time, in spite of the comparably large quantity of the collected liquid, because these solid-depleted liquid will pass the filter membrane rather quickly. Subsequently the thin material layer on the membrane shall be rinsed with water, and thereafter the slurry with the main part of the product, which has been washed several times, shall be filtrated through the same membrane, to get the complete amount of product.

After having been successfully tested, the method described was used to separate and refine all catalyst dispersions obtained thereafter. It proved to be convenient for Pt catalysts on oxCNT supports as well as Pt catalysts on Vulcan-XC-72R carbon black.

5.2.2 Drying and breaking

Since Pt-C catalysts tend to spontaneous ignition at higher temperatures, especially if they should be impurified by ethylene glycol residues, all washed and filtrated catalyst samples were transferred into a round bottom centrifuge tube of thick walled glass which was equipped with a nitrogen passage and heated to 75 °C in a thermostat. After drying, the material was crushed using the same centrifuge vessel as a mortar and a stainless steel bar with rounded end as a pestle, which was plunged through a pierced silcon sheet which was imposed on the centrifuge tube to prevent the material inside from skipping out. Initial tests with an agate mortar had shown an intensive tendency of the catalyst product to be spewn out of the mortar during crushing.

In contrast to conventional methods, the described use of one single vessel for both drying and crushing is advantageous, because both impurification and loss of sample material are minimized by avoiding unnecessary material transfer and crushing inside a closed compartment, respectively.

5.2.3 Yield determination

The crushed samples were filled into tared vials and weighed. Small residues remaining at the used equipment (centrifuge tube, pestle, funnel) were considered by weighing the equipment both in clean and in used state, and added to the weighed mass of the sample.

The theoretical 100 % yield value was calculated from the measured total amount of the corresponding product dispersion, its support material content and the actual platinum content of the product was determined by TGA analysis. In general, yields in the range between 85 % and 90 % were achieved, but significantly less in some cases. Since the support material may possibly have lost a significant extent of functional groups during the platinum deposition process, the actual yields might be larger than the calculated values.

5.3 Sample carrier for transmission electron microscopy (TEM)

The preparation of the TEM samples was executed by performing the following procedure: Some crumbs of the sample (about 1...3 mg) were mixed in a small vial with a few mL of isopropanol and treated in an ultrasonic bath (Bandelin; Sonorex Super) for about 1 min. Subsequently, a small but sufficient proportion of the sample was dispersed to finer particles. The dispersion was then left for some hours to separate the troublesome coarser particles by settling down. Then the sample carrier (PLANO GmbH, Wetzlar, S162-3, Formvar / Kohlefilm auf 3.05 mm Cu) was grasped with tweezers and briefly drawn through the supernatant dispersion for wetting, resulting in a visible lens of liquid on the metal grid. The wetted sample carrier clipped by the tweezers was then introduced into a moderate nitrogen stream where it dried within a few minutes to be ready for TEM analysis.

This procedure requires less efforts than other TEM sample preparation procedures which at the institute were commonly used at the corresponding time, lead to better results, too, and was therefore made to the standard procedure lateron.

6 Characterisation

6.1 Platinum content of the catalysts

The platinum content of the catalyst samples was determined by thermogravimetric analysis (TGA) (Mettler, TGA 860, 50 ml/min air, 20 K/min to 900 °C). The sample mass at the final temperature was divided by the sample mass at a given $T_{100\%}$ temperature, considered to represent the dry mass of the sample.

Since carbons may typically contain adsorbed water at temperatures above 100 °C, but the elimination of functional groups from hydroxylated and carboxylated CNTs (oxCNTs) does not occur below 200 °C, $T_{100\%}$ was determined to be 180 °C, based on the TGA curves obtained from the first 4 samples available. Obviously, two of these samples had accidently been dried very poorly, proven by the referring TGA results. Due to the high water content of these two samples, the temperature range where water desorption occurs was clearly identifiable at temperatures up to about 150 °C to 160 °C, followed by an almost horizontal TGA curve section up to about 190 °C to 220 °C.

To estimate the influence of the $T_{100\%}$ choice on the resulting platinum content values, the average deviations between the results based on $T_{100\%}$ of 150 °C instead of 180 °C, and $T_{100\%}$ of 210 °C instead of 180 °C were calculated for 10 TGA curves which were randomly selected from the TGA curves obtained during the entire project. The relative deviations were -0.7 % for 150 °C and +1.1 % for 210 °C.

6.2 Platinum particle size and specific surface area

6.2.1 Methods

A basic requirement for a high activity of a catalyst is a large specific surface of the active component, which in this case is the platinum. To determine the specific platinum surface for the catalysts prepared in context to the project, the following methods were applied:

- Transmission electron microscopy (TEM): On the basis of TEM images with sufficient magnification, the size of a large number of individual particles was determined, as far as appropriate, for all samples. The calculated surfaces and volumes of every considered particle of a certain catalyst were summed and the resulting sums used to calculate the specific Pt surface area.
- Chemisorption measurements: By help of chemisorption measurements the specific Pt surface could be measured directly, without regard to the particle size.
- X-Ray diffractometry (XRD): Using XRD the average particle size was determined for a few samples using the Scherrer equation [allmann-2003]. From the average particle size a specific surface area value was roughly estimated.

In the following text the expression "Pt particle diameter" means the diameter of a sphere with the same volume as the particle.

6.2.2 Transmission electron microscopy (TEM)

All the TEM pictures were obtained using a JEM 2100 from Jeol company, at 160 kV.

As one advantage of the TEM based particle size determination this method will provide not only an average value but the particle size distribution which is required to calculate a correct value for the specific surface area. In contrast, the specific surface area calculated from the average particle size will, in almost all cases, deviate more or less from the correct value.

To determine the individual particle sizes, TEM images with a comparatively high magnification and good contrast were selected, which in the ideal case depicted individual CNT fibers or soot particles, respectively. In general, however, several fibers or soot particles were partially superimposed or arranged vertical to the image plane. In these cases an increased probability is assumed, that accidentially two or more Pt particles are arranged one above the other to give a TEM image that seems to represent one single Pt particle, usually bigger than any of the included particles alone. Therefore, image sections like this were excluded from particle size examinations.

To determine the particle sizes, the freeware program Lince (http://www.mawi.tu-darmstadt.de/media/naw/software/Lince242e.exe), which is designed especially for this purpose, was used. To evaluate a particle size, two points on the boundary of a particle image were set, whose distance between in the opinion of the executing person corresponds to the diameter of a sphere which has the same volume as the particle. One shortcoming of the particle size determination by TEM recording is that currently there is no procedure rule which is both practicable and applicable exactly and involuntary. In addition, because a TEM particle image is only a shadow of the corresponding particle, the dimensions of the particle which are perpendicular to the image plane can not be examined.

But because the very most of the observed particle shadows are something between circular and oval, the usual form of the particles is supposed to be something like an ellipsoid of rotation. If the deviation from a sphere is not very important, the surface volume ratio of an ellipsoid of rotation will be similar to that of a sphere.

Fig. 6-1 shows the particle shadows which typically can be observed. As mentioned above, all zones of the picture where two or more of the nanotubes are superimposed have to be excluded from particle size examinations.

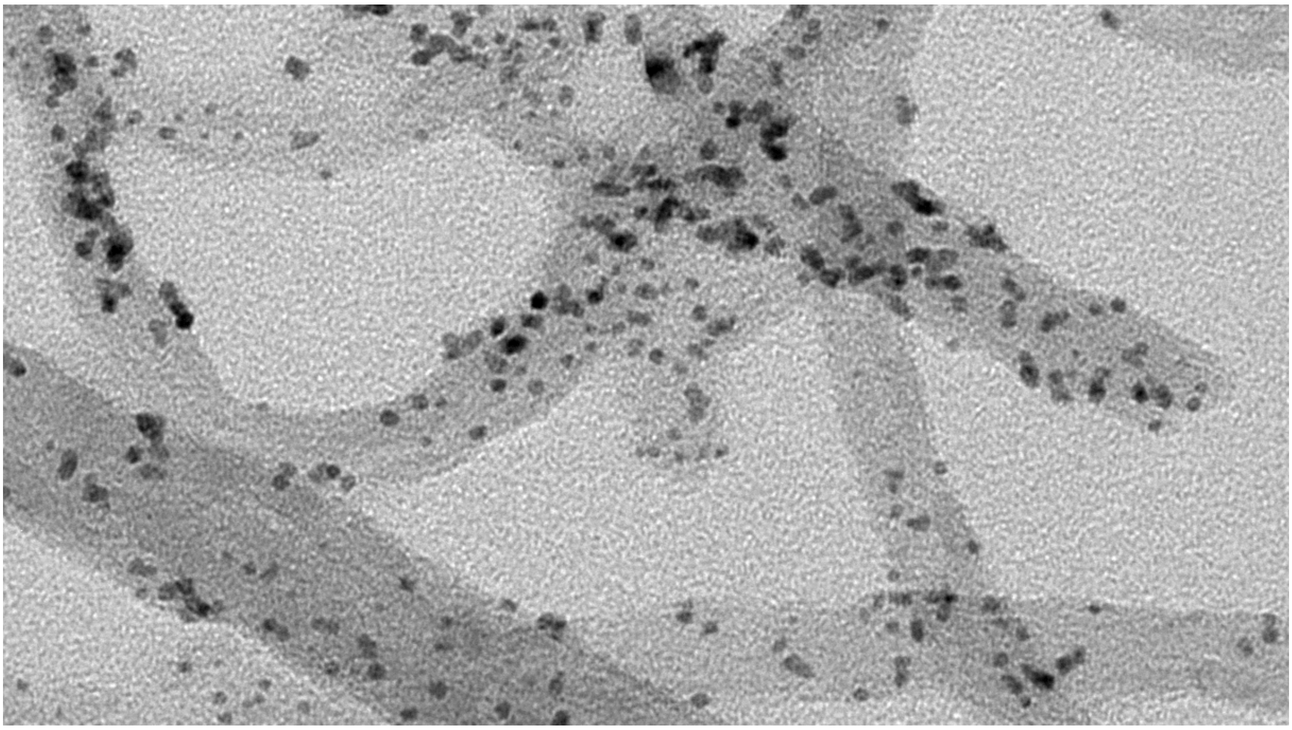

Fig. 6-1: Typical example of a TEM image with high magnification which could be used for a particle size examination

In Fig. 6-1 it is visible that not in every case a clear boundary between the particle and the environment is visible. In addition, very small particles could exist that can not be distinguished from the background noise. On the other hand very small particles might be pretended by the background noise.

Based on a model assumption that the particle is a cylinder with a hemisphere attached on both sides, aligned parallel to the image plane, it has been shown that a good way to construct an equivalent spherical diameter is to draw the diagonal for the cylindrical part, which is imaged as a rectangle. It is proved by calculations that with increasing length-to-diameter ratio there is a serious increase of the deviations between both volume and surface of the particle and volume and surface of the calculated equivalent sphere, but only a moderate deviation between the surface-volume ratios of model particle and sphere, which is lower than 10 % at a particle length-to-diameter ratio of 2. Particle images with a length-to-diameter ratio of more than 2 were not found in a noteworthy number and besides might be effected by several particles arranged in a row.

The particle size determinations were made by considering the results of the described model as much as possble.

For the determination of the Pt particle diameter of a certain sample, usually at least a few 100 particles were considered. For 3 samples, however, the dimensions were first determined on a lower number of particle images, and later a second particle size determination was made on the basis of further TEM images. In Table 6-1, for the 3 referred samples the number of particles considered in the first and second pass, the corresponding mean particle diameters and the weighted average of both values are represented. These values might be regarded as representing the reproducibility of the results from the TEM-supported Pt particle size determination.

Sample	n_1	n_2	D_1 [nm]	D_2 [nm]	D_{1+2} [nm]
34P	74	78	2.14	2.24	2.19
36R	89	138	2.30	2.35	2.33
36U	140	164	2.44	2.35	2.39

Tab. 6-1: Comparison of the results from TEM supported particle size determination passes using different TEM images of the same sample (n_1, n_2: number of particles examined during 1st and 2nd pass)

6.2.3 Chemisorption

The principle of the pulsed chemisorption measurement is to precondition a known mass of the sample at elevated temperature in an inert gas stream to remove adsorbed substances and then, at a lower temperature, treat this sample with a series of well known amounts of a gas to be sorbed by the sample (pulses). With a suitable detector, the remaining portion of every amount of gas to be sorbed is determined. As soon as the sample is saturated, after every pulse detected signals of constant magnitude are obtained, which can be related to the pulse quantity of the gas to be sorbed. The sorbed amount can be determined from the summed differences between the measured remaining quantities at every pulse and the constant remaining quantities after sample saturation.

Considering the corresponding stoichiometry, the active surface area can be calculated from the masses of the adsorbed gas and the active substance. Knowing the molar mass of the active substance per surface unit and the density of the active substance, the equivalent diameter for spherical particles of the active substance can be calculated, assuming that all these particles are of the same size. Due to the actually given particle size distribution, this value inevitably differs more or less from the actual mean particle size.

During the measurements, it was found that for the used gases to be adsorbed, carbon monoxide and hydrogen, there is a non-negligible desorption rate from the examined platinum-carbon catalyst samples. This fact is not described or considered in the operating manual for the chemisorption device used, so that it seemed to be necessary to develop an operation and evaluation mode suitable to take into account the desorption effects to obtain correct results. This operation and evaluation mode was developed on the basis of model calculations and subsequently applied to the performed pulse chemisorption measurements. A publication on this topic is planned.

The chemisorption measurements were carried out with a BELCAT-M (BEL Japan, Inc), generally with CO, or, in single cases H_2, as the gas to be sorbed.

6.2.4 X-ray diffraction analysis (XRD)

The XRD device available (Siemens; D5000 Kristalloflex; $\vartheta/2\vartheta$ mode; Co-Kα, 0.1789 nm; 40 kV; 40 nA) required a sample mass of several g to obtain best performance. The actual sample mass was in no case more than some 100 mg, in some cases even less than 100 mg. Nevertheless, some samples were examined by the XRD device as good as possible, to calculate the average Pt particle size from the Pt-(111) peak half-value width by use of the established Scherrer equation.

6.2.5 Method comparison

The results obtained by the different methods are not easily comparable. By chemisorption, the primary result is the overall Pt particle surface in a certain sample amount, which, considering the referring Pt mass, allows to calculate the diameter of assumed spherical Pt particles of uniform size. This diameter differs more or less from the average diameter of the same mass of spherical Pt particles of distributed sizes. Therefore, differences between particle sizes from chemisorption and TEM are anticipated. The Pt particle diameters from XRD are average particle sizes [allmann-2003] and should therefore match or correlate to the TEM results in some degree.

In Tab. 6-2, the results obtained from the different methods are compared with each other.

	Average Pt particle diameter [nm]		
Sample	TEM	XRD	Chemisorpt.
17	2.5		3.13; 3.94
18	1.87		3.60; 3.67
19	2.62	3.7	3.90; 6.28
20	2.16	3.6	2.75
22	2.27	4.1	
23	1.84	4.2	
24	2.12	3.7	3.64
25	2.03	2.4	4.67

Tab. 6-2: Comparison of the average Pt particle diameter obtained from the different methods

The XRD values are greater than the TEM values, and a correlation apparently does not exist. Because of the much too small XRD sample mass, the XRD values are seeming not to be very reliable, a further discussion of this indication was resigned.

Three of the chemisorption measurements were repeated, which in two cases lead to a severely increased diameter result. Possibly every sample pretreatment (at 350 °C, under hydrogen flow) had caused a decrease of the active Pt surface, e.g. by particle coalescence. A further examination was not possible, because the corresponding samples had already been lost during cleaning of the sample tubes.

It can be proved by calculations that, at the same overall specific surface, the average size of uniform sized spherical particles is greater than the average size of spherical particles with a size distribution. The differences, however, are not great enough to be proposed as the only reason for the observed differences between chemisorption and TEM results.

Compared to the chemisorption results, the TEM generated specific Pt surfaces are much higher, as shown in Tab. 6-3.

	Specific surface [m²/g]	
Sample	TEM	Chemisorpt.
17	90	45; 36
18	116	39; 38
19	93	36; 22
20	101	51
22	92	
23	128	
24	102	38
25	108	30

Tab. 6-3: Comparison of the specific Pt surface values obtained from TEM and chemisorption measurements

Because of the direct particle visibility, and because of the circumstances mentioned above, in the present case the TEM method was supposed to be more reliable than the chemisorption and XRD method, and therefore only the TEM results are considered for the discussion below.

6.3 Spatial distribution of the platinum particles on the support material

Assuming a high catalytic activity of the platinum, the reaction rate depends on short diffusion distances between the reactants and the Pt particles. Therefore the macroscopic catalytic activity should increase with increasing uniformity of the spatial Pt particle distribution.

To evaluate the grade of distribution uniformity, a simple method was developed which allowed to obtain an estimated value which could be used to compare the different catalyst samples with each other. The procedure for each sample was as follows:

Several TEM images of lower magnification (showing a range of some 100 nm to about 1000 nm) were selected and rated by grouping each of them to one of five distribution grades, where the discrete values 0 to 4 are meaning distributions from almost uniform to widely concentrated within a few clusters. The average value of the obtained estimates was named uniformity number UN. Because of the severe standard deviations found (about ±0.8 on average) for almost every sample, it should be considered that a comparison of the UN values of different samples is reliable only in case of sufficient differences.

7 Experiments, results and conclusions

7.1 First operation experience and modifications of the test assembly

The first experimental phase was characterised by the fact that both the pilot plant and the procedures for reaction mixture preparation and product dispersion refining were not fully developed and had to be adapted to recent knowledge several times. Therefore, the experimental results obtained in this stage should be considered with a certain reservation. Consequently, mainly the test results from the subsequent project phases were considered.

The plant was initially operated with the 0.8 mm heating pipe, the 0.5 mm thermocouple and the 1000 mm reaction tube, usually at a flow rate of approximately 1.5 mL/min, which corresponds to an averge retention time of about 10 s in the heating pipe and about 120 s in the reaction tube. During these tests pressure increases were observed in irregular time intervals, obviously caused by pluggings of agglomerated solids. Usually, the pluggings could be disassociated by tapping on the system, if not short-term self-disassociated. Although only a few test operations had to be shut down because of exceptionally persistent pluggings, it has to be assumed that there had been a substantial temporary disruption of the steady-state operation at every pressure increase.

The particle agglomerates formed in the test assembly were rather coarse-grained, as shown in Fig. 7-1. Such agglomerates were not formed when a CNT dispersion without platinum precursor was used.

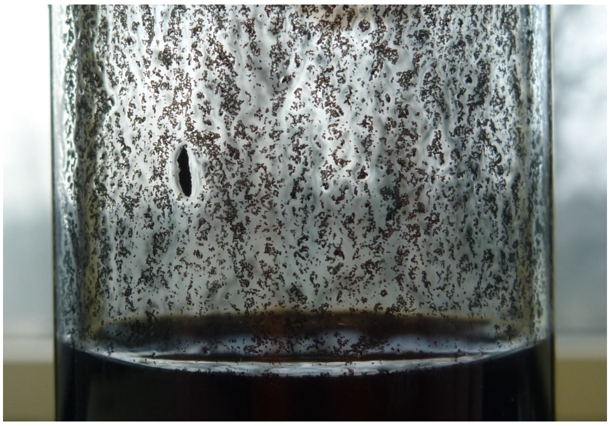

Fig. 7-1: Product agglomerates at the wall of the collector vessel (diameter 33 mm)

Furthermore, in some cases an alternating outflow of clear and black fluid was observed (Fig. 7-2). Probably this is caused by a temporary sticking of agglomerate plugs in the reaction system which first can easily be passed through by the fluid, but are released after a short time when their compaction has increased sufficiently to be pushed forward by the fluid again and then move up to the exit of the reaction system.

Fig. 7-2: Clear liquid, followed by a compacted agglomerate plug, at the reaction tube exit

In some test runs with unheated heating-up tube, no such compacted plugs and clear outflow were observed. Probably the generation of these plugs takes place in the narrow gap between the end of the heating-up tube and the thermocouple, but, off course, only at elevated temperature, which is necessary for the formation of particle agglomerates in the used reaction mixture. It can also be concluded that the particle agglomeration, at least partly, already takes place during the 10 s when the fluid passes the heating-up tube.

After replacement of the 0.8 mm heating-up tube by the 1.0 mm one, pluggings were observed only in a few cases, causing only low pressure increases. After replacement of the 0.5 mm thermocouple by a 0.25 mm one, too, neither pressure increases nor clear outflow segments were observed any longer.

7.2 Variation of the reaction mixture

7.2.1 Variation of the support material

Only one single catalyst sample with Vulcan-XC-72R carbon black was prepared with the CFCP equipment. A comparation of the results with those of an oxCNT supported catalyst sample, prepared under similar test conditions, is shown in Tab. 7-1. In both cases the platinum is deposited on the carbon support nearly completely.

Support material	oxCNTs	Vulcan-XC-72R
NaOH Pt ratio	5.0	5.0
Retention time in the heating-up tube [s]	9.4	12.7
Retention time in the reaction tube [s]	223	299
Pt mass fraction (desired)	0.40	0.40
Specific surface of the Pt-particles [cm²/g]	115	115

Tab. 7-1: Comparation of catalyst samples on oxCNT and Vulcan-XC-72R support; the specific surface is determined from TEM images and refers to the mass of the deposited platinum

Fig. 7-3 shows TEM images of both catalysts at comparable magnification. The particle distribution on the Vulcan based catalyst is almost perfect and much better than on any of the oxCNT based ones. This is probably caused by different surface properties of the support materials.

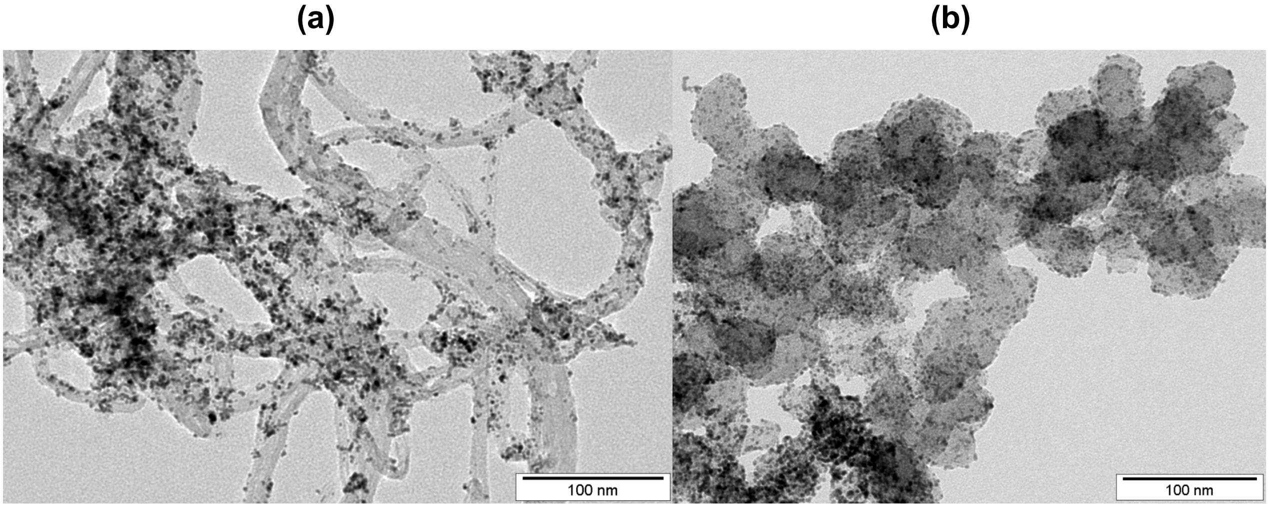

Fig. 7-3: TEM images of an oxCNT based (a) and a Vulcan carbon black based (b) platinum catalyst

7.2.2 Variation of the NaOH Pt ratio

Tests with NaOH Pt ratios of 4.0 up to 8.0 were performed. Among the performed tests with NaOH Pt ratios of 4.0, 5.0, 6.0 and 8.0, there are considerable results of two test runs in each case, which are shown in Fig. 7-4.

All of the tests were performed at retention times around 10 s in the heating-up tube and around 240 s in the reaction tube. Each of the reaction mixtures was designed to obtain up to 40 % Pt in the product, except of one reaction mixture, which was designed to obtain 41.5 % Pt, by cause of a calculation error. In this case, a Pt content of 42.9 % was determined, which at the same Pt deposition rate would be 41.3 % if the reaction mixture composition would have been set up correctly. Instead of the determined value, the adapted value 41.3 % is used below, to make it to some degree comparable to the other values.

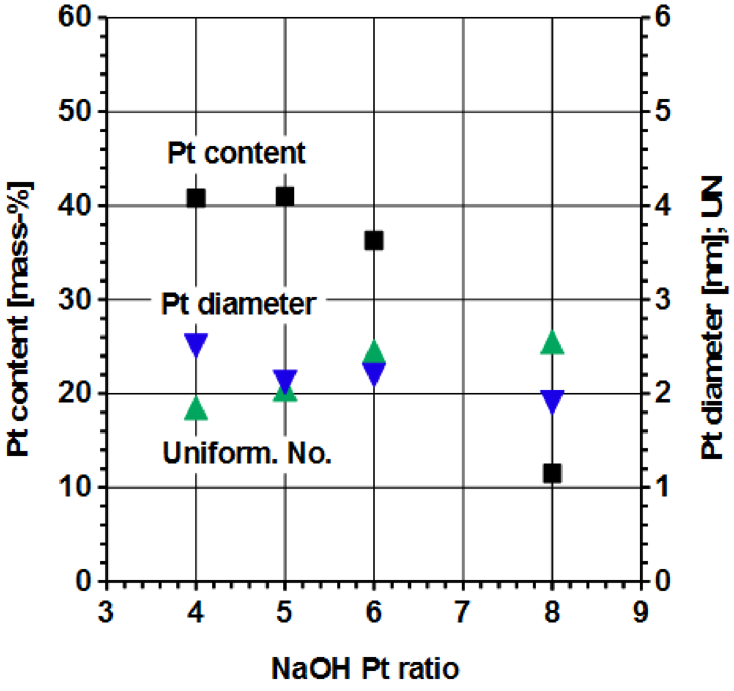

Fig. 7-4: Platinum content, average Pt particle diameter and uniformity number of catalyst samples from reaction mixtures with different NaOH Pt ratio

At a NaOH Pt ratio of greater than about 5 % the Pt deposition is incomplete and decreases strongly with increasing NaOH Pt ratio, whereas there seems to be a slight decrease of the Pt particle diameter with increasing NaOH Pt ratio. Both tendencies are similar to results described in [li-2005-1] and [aoun-2016]. However, the influence of the NaOH Pt ratio on the Pt particle size seems to be lower at the continuous preparation than at the batch preparation described in [aoun-2016]. The differences might be caused by the use of NaOH in ethylene glycol instead of aqueous NaOH as used in [aoun-2016], where an increasing NaOH content is linked to an increasing water content. But it is unlikely that the increasing water content is the only reason for the different results, because of a not very pronounced dependency between water content and Pt particle size [lee-2006] (increase from 2.0 nm at 0 % H_2O to 2.5 nm at 5 % H_2O). The water content of a reaction mixture as used in the tests described above, which is alcalized by adding 1.0 molar aqueous NaOH, will be 3.6 % at a NaOH Pt ratio of 6.0. About the uniformity number, there might be a slight increase (which means: spatial distribution becoming worse) over NaOH Pt ratio, but not significant, regarding the great deviation of these values.

If an almost complete deposition of the available Pt on the support material is required, a NaOH Pt ratio of about 5 seems to be the optimum. This result was found also by [aoun-2016] for the batch procedure. How far this result can be extended to other desired Pt contents than 40 %, is not surely investigated. Two tests designed to theoretically obtain 60 % Pt catalysts were performed, but showed quite inconsistent results (Pt content determined = 36 % and 54 %; average Pt particle size = 2.16 nm and 1.84 nm, respectively). In addition, both samples are suspect to low reliability. One reaction mixture had been prepared with a lower oxCNT content (1.66 g/kg instead of 1.80 g/kg) by mistake, with correct ratios between HPA, oxCNTs and NaOH, however. At the other test, the product yield was only 45 %, whereas it normally was somewhere between 85 % and 90 %.

7.2.3 Addition of water

Two tests were performed using reaction mixtures with the same contents of HPA, oxCNTs and NaOH (NaOH Pt ratio = 6.0) as used to obtain a 40 % Pt catalyst, but, in addition, had a water content of 2.0 % and 5.0 %, respectively. The retention times were around 10 s in the heating-up tube and around 240 s in the reaction tube.

At a water content of 5 % no stable operation of the test assembly was possible, because of the generation of large amounts of water vapor, which violently drove the reaction mixture out of the reaction system. Therefore, neither a steady state operation nor a determination of the retention times was possible. However, a product sample could be collected, with a Pt content of about 23 %, which was estimated from XRD data. There was no more sample available for a more accurate TGA based Pt content determination.

At 2 % water in the reaction mixture, a steady state operation was possible. Only some small vapor bubbles could be observed, which are not supposed to be able to substantially influence either the retention times or the steady state condition, because of their low size and number. On the other hand, on their way through the tubes of the reaction system these bubbles can act similar to pigs in a pipeline, and therefore can make the retention time spectrum much more narrow. If so, the retention time spectrum should modify aperiodically, because of the irregular occurrence of the vapor bubbles.

The obtained Pt content of the referring catalyst sample of 28 % is much lower than the Pt contents of more than 35 % of samples prepared with water free reaction mixtures from comparable tests. The average Pt particle size of the 2 % water test product (2.26 nm), however, is absolutely comparable with the Pt Particle size of test products from water free feeds (2.27 nm and 2.12 nm), which cornforms to the results of other authors [lee-2006].

7.3 Comparation of continuous operation versus batch process

To compare the CFCP procedure with a conventional batch procedure, some batch tests were performed. For the batch tests, the heating-up time was defined as the time period between start of heating up and the approach to 135 °C, and the reaction time was defined as the time period between the end of the heating-up time and the time after the begin of cooling down when 135 °C is approached again.

The most relevant test results were obtained in the later project phases, when both the test assembly and the test procedure were optimized to a high grade. In these project phases, the batch tests were performed in slim reaction vessels (100 mL test tubes), which allow shorter heating-up times than the round bottom flasks which are commonly used in laboratory batch operations. Fig. 7-5 shows the temperature trends during the referring tests.

These batch tests were performed with a reaction mixture designed to obtain a 40 % Pt catalyst on oxCNTs, with a NaOH Pt ratio of 5.0.

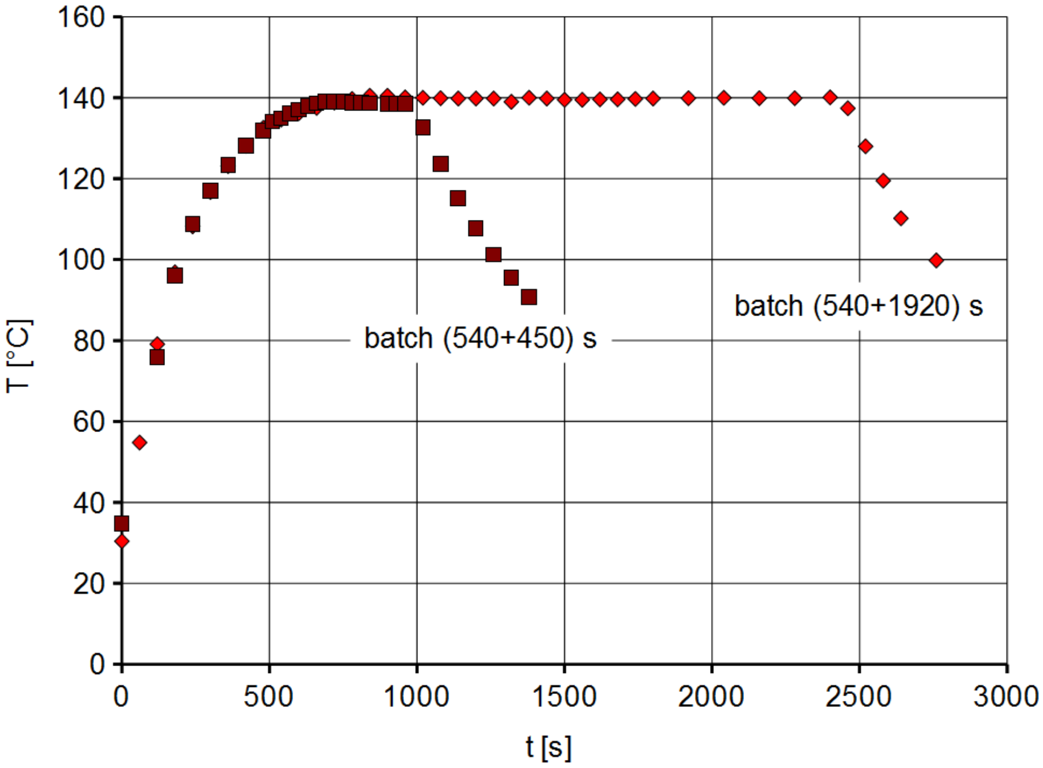

Fig. 7-5: Temperature trends in the reaction mixtures during the batch tests. The reaction time was variated between both tests and much shorter than 3 hours, which is a reaction time commonly chosen for polyol reduction batch tests.

Tab. 7-2 shows the results of the batch tests described above, in comparison to the results of three continuous tests which were operated with reaction mixtures of the same composition.

Sample	32	31	29	28	27
Operation type	contin.	contin.	contin.	batch	batch
Average heating-up duration [s]	10.7	10.2	9.5	540	540
Average reaction duration [s]	253	242	223	450	1920
Pt content [mass-%]	40.9	41.0	46.6	41.8	42.7
Av. Pt particle diameter [nm]	2.37	2.18	2.06	2.66	2.60
Uniformity number UN	1.9	2.4	1.7	1.8	1.9
Comments	1	1	2		

Tab. 7-2: Properties of catalyst samples prepared with reaction mixtures of same composition, but either in a continuous or in a batcg process (NaOH Pt ratio = 5.0; reaction mixture designed for 40 % Pt content) (1: Operation interchanging between normal, KCl free, and KCl containing reaction mixture; 2: The stated Pt content of 46.6 % may be distorted by a measurement error)

In all cases the available Pt was largely or entirely deposited on the support material. The Pt content of the batch made catalysts seem to be slightly higher than those of the continuously made ones, which might be caused by the much longer reaction time, which might have caused an elevated separation of functional groups from the supporting oxCNTs.

The Pt particle size is considerably lower in the catalyst from the CFCP test assembly than in the catalysts from the batch processes, in accordance to results from other publications [aoun-2012; schlange-2011].

The spatial distribution of the Pt Nanoparticles on the support material is roughly the same at all of the referred samples and corresponds to the moderate distribution grade which was observed at most of the samples obtained during the project.

Further two batch tests were performed with a NaOH Pt ratio of 6. The test results and the results from comparable continuous tests are shown in Tab. 7-3. These batch tests were performed "as usual" in a round bottom flask, causing longer heating-up times than in the batch tests described above, the reaction times were, "as usual", 3 hours.

Sample	24	22	17	9
Operation type	contin.	contin.	batch	batch
Heating-up time [s]	9.8	9.9	960	840
Reaction time [s]	230	233	11000	10100
Pt content [mass %]	37.0	35.6	35.0	21.6
Aver. Pt particle diameter [nm]	2.12	2.27	2.50	2.08
Uniformity number UN	2.2	2.7	1.5	1.5
Comments			1	2

Tab. 7-3: Properties of comparable catalyst samples from continuous and batch tests (NaOH Pt ratio = 6.0 and 6.07; reaction mixture designed for 40 % Pt content) (1: reaction mixture prepared with HPA solution which had been stored longer than 3 weeks; 2: NaOH Pt ratio = 6.07; possibly malfunctioning nitrogen purge)

With the low reliability of these batch test results (see note 1 and 2) in mind, there shall be no further discussion.

7.4 Comparison of a continuous process generated catalyst with a commercial product catalyst

For a comparison with a commercially available fuel cell catalyst which was present at the Institute of Chemical and Electrochemical Process Engineering from earlier studies (BASF, 60 % Pt on Vulcan-XC-72R carbon black), a catalyst with 40 % Pt on the same support material was prepared in the continuously operated test assembly. Tab. 7-4 and Fig. 7-6 show an overview over the two catalysts and their properties.

Catalyst	Sample 30	BASF-C1-60
Operation type	contin.	batch, supposedly
Heating-up time [s]	12.7	unknown
Reaction time [s]	299	unknown
Pt content [mass-%]	39.6	0 (supplier's declaration)
Aver. Pt particle diameter [nm]	2.07	4.93
Uniformity number UN	1.1 ± 1.1	0.6 ± 0.9

Tab. 7-4: Comparison of the properties of a continuously preparated fuel cell catalyst with a commercially available one with the same support material

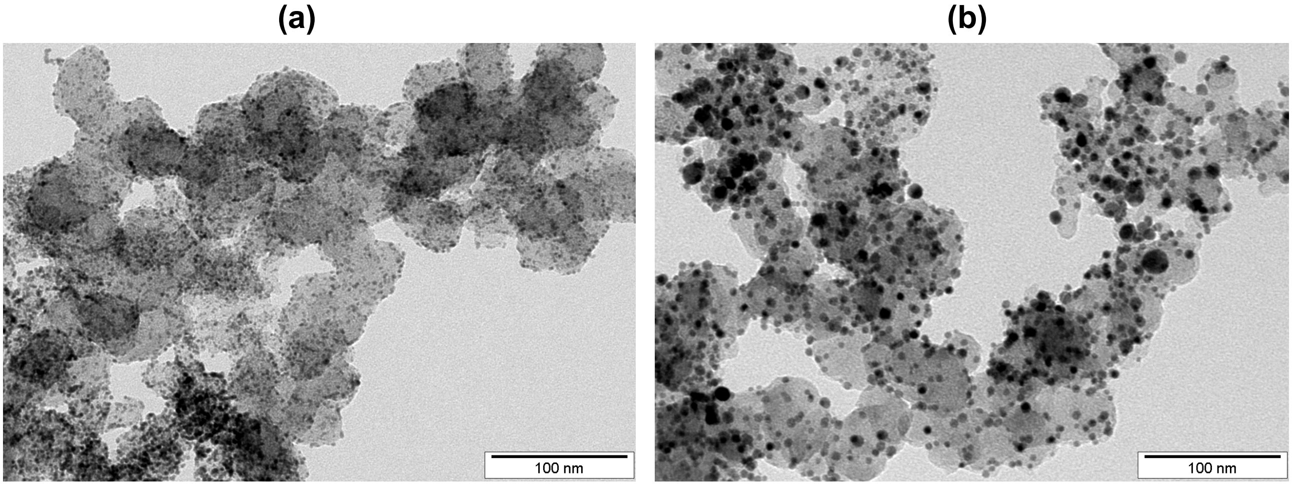

Fig. 7-6: TEM images of (a) a continuously preparated Pt catalyst and (b) a commercially available Pt catalyst with the same support material (Vulcan-XC-72R carbon black)

Between both catalysts there is a huge difference in particle size. Both particle size distributions, visualized over a logarithmic scale, are similar, but for the commercial product shifted to higher size values (Fig. 7-7). The spatial particle distribution (UN) is excellent for both catalysts.

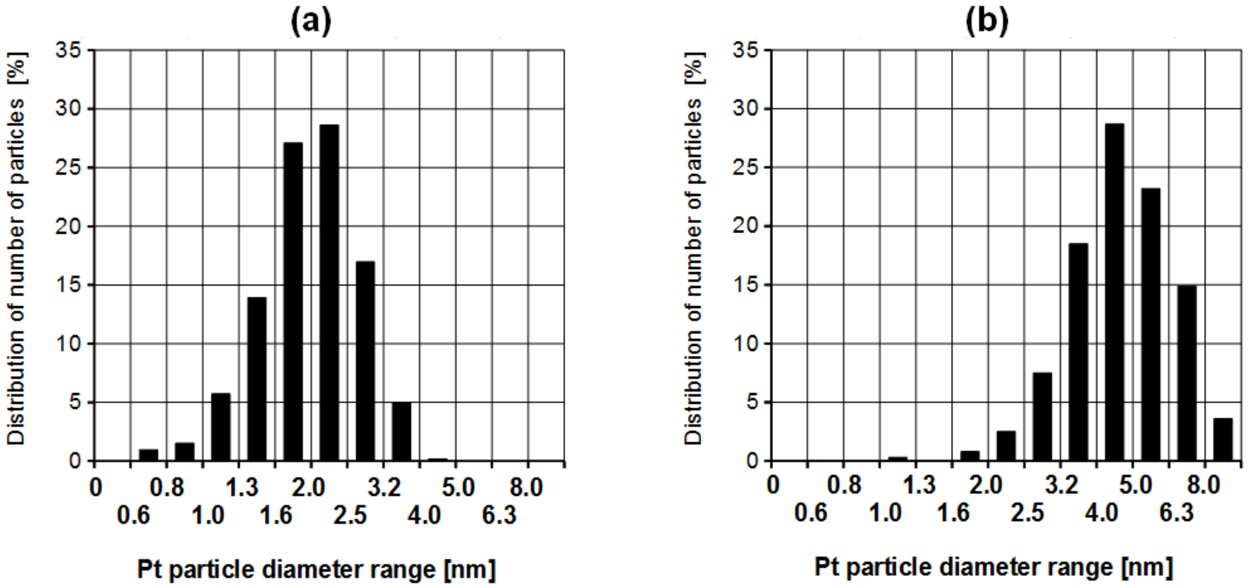

Fig. 7-7: Comparison of the Pt particle size distributions of a continuously prepared catalyst (a) with that of a commercially available one (b) with the same support material

7.5 Tests without directly heated heating-up tube

Three tests were performed where the heating-up tube was deactivated and therefore the heating-up of the reaction mixture had to take place in the reaction tube, whose temperature was kept constant at 140 °C. The main aim for these tests was to prove that the observed pluggings, as supposed, take place in the heating-up tube range. Indeed, no pressure increases during any of these tests were observed.

The 3 tests with deactivated heating-up tube were performed with different retention times, which was put into practice by volume flow variation. The NaOH Pt ratio was 6.0 each, the reaction mixtures were designed for a 40 % Pt catalyst each, though one of the reaction mixtures by mistake contained a little more support material, corresponding to a Pt content of 38.5 %. The results of the described tests are shown in Tab. 7-5 and Fig, 7-8.

Sample	7	5	6
Reaction time [s]	66	122	245
Pt content [mass-%]	28.6	32.1	38.1
Aver. Pt particle diameter [nm]	2.10	2.74	3.74
Uniformity number UN	1.6 ± 0.7	2.4 ± 1.1	1.3 ± 1.0
Comments		1	

Tab. 7-5 Results of the continuous operated tests with deactivated heating-up tube (reaction tube only) (1: reaction mixture by mistake designed for 38.5 % Pt content)

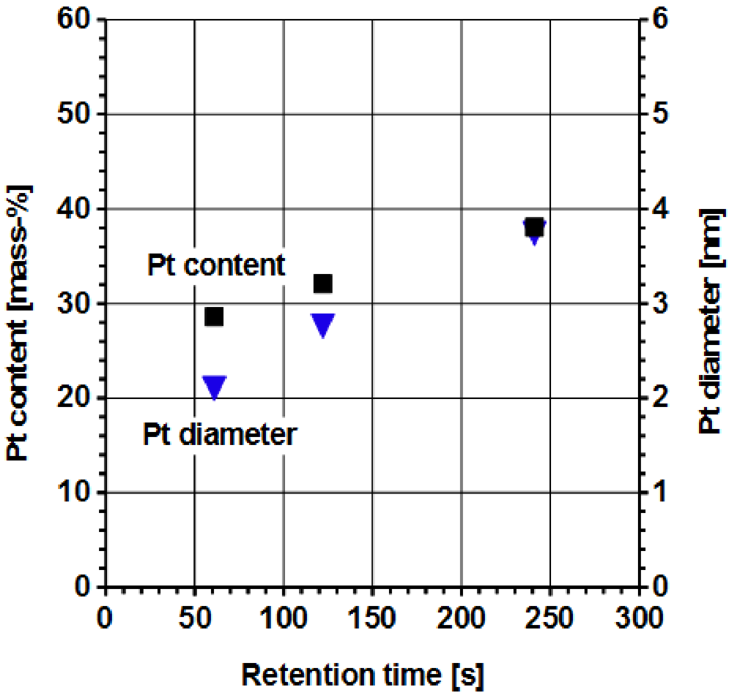

Fig. 7-8 Results of the continuous operated tests with deactivated heating-up tube (reaction tube only)

The Pt content in the produced catalysts increases with increasing retention time. For a retention time of 245 s, the Pt content corresponds approximately to the results of comparable experiments with activated heating-up tube at similar retention times. When the heating tube is deactivated, the Pt particle diameter strongly increases at rising retention time, and is almost twice as large as in comparable experiments with activated heating-up tube at a retention time of 245 s. The increasing Pt particle size can also be seen directly in Fig. 7-9.

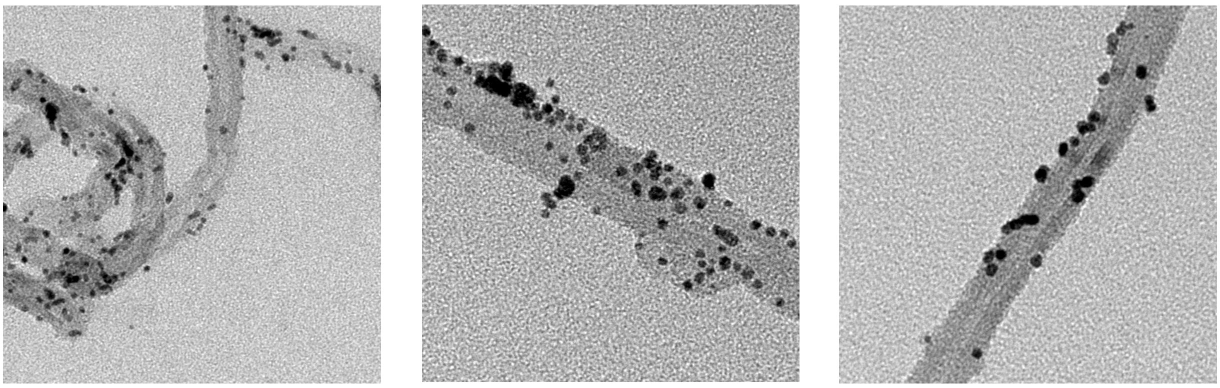

Fig. 7-9: TEM-Images of same magnification, showing samples from test operation 7 (left hand side), 5 (middle) and 6 (right hand side), representing the results from a continuous operation at deactivated heating-up tube at retention times of 66 s, 122 s and 245 s, respectively.

The strongly increasing particle size can not be explained by the idea that after a certain reaction time no new particles are formed and Pt is deposited on already existing particles only, because after about 60 s the remaining dissolved Pt(IV) of about 1/3 of the initial amount could be sufficient for a particle diameter increase by up to 14 % only. On the other hand, a redistribution of Pt from smaller particles to larger particles appears very unlikely within the very short time available. The yet most likely explanation for the great dependency between Pt particle size and retention time is that a higher flowrate, which is given at shorter retention times, will favor the Pt particle nucleation process. Appropriate tests with similar volume flows but different lengths of post-reaction tubes to obtain different retention times might provide further information about this, but were not performed at deactivated heating-up tube.

Fig. 7-10 shows the particle size distributions of the samples from the corresponding tests. With increasing retention time the entire curve is shifted to larger particle sizes. Why the middle curve shows a more narrow distribution is not known.

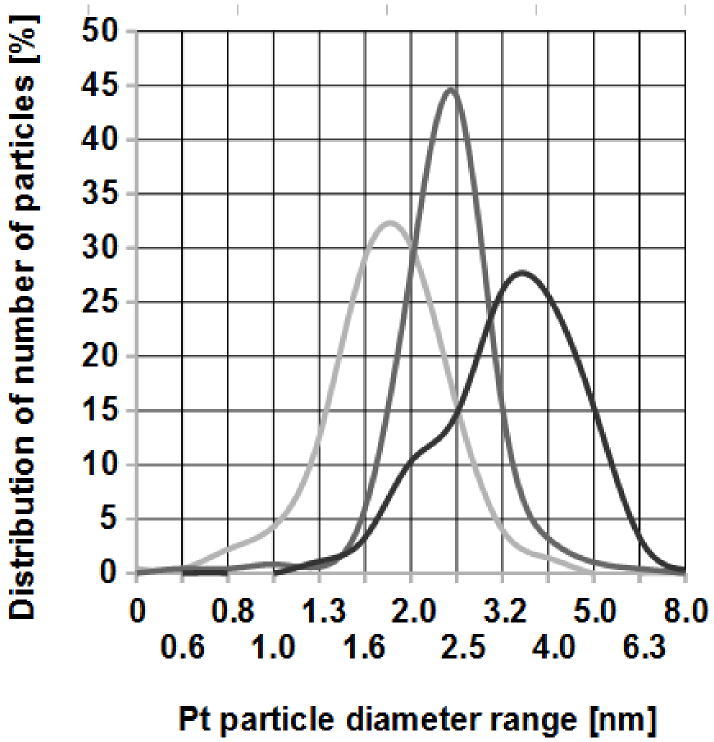

Fig. 7-10: Pt particle size distribution for the catalyst samples from the continuous mode experiments with deactivated heating-up tube (retention times: light gray: 66 s, medium gray: 122 s, dark gray: 245 s), representation as smoothed lines; the abscissa is divided logarithmically

7.6 Different combinations of retention times in heating-up tube and reaction tube

The influence of the average retention time in both the heating-up tube and the reaction tube was investigated on three test series with different reaction tube lengths at a NaOH Pt ratio of 5.0 and a reaction mixture designed for a 40 mass-% Pt catalyst. For a given reaction tube length, the retention time variations were achieved by appropriate variation of volume flow and heating-up tube length. The latter was achieved by either deactivating the heating-up tube heating (effective retention time = 0) or by clamping a temporary contact half way between the 2 permanent contacts and conduct the electric current through this temporary contact instead of the contact at upstream position, which in fact results in a halved length of the heated heating-up tube section.

Fig. 7-11 and Fig. 7-12 show the dependencies of the parameters Pt content, Pt particle diameter and uniformity number from the retention time in the reaction tube and the heating-up tube. The reaction tube retention time variation is represented at heating-up tube retention times of around 5 s and around 10 s. Because the volume flow had been used as a parameter to adjust retention time, the values are representing results from tests with various volume flows, which are reckognizable by the size of the referring symbols. To obtain diagrams with a sufficient number of values, the samples from tests with retention times in the other tube within a range of 37 s up to 41 s and within a range of 74 s up to

157 s were selected to be represented in Fig. 7-12(a) and Fig. 7-12(b), respectively.

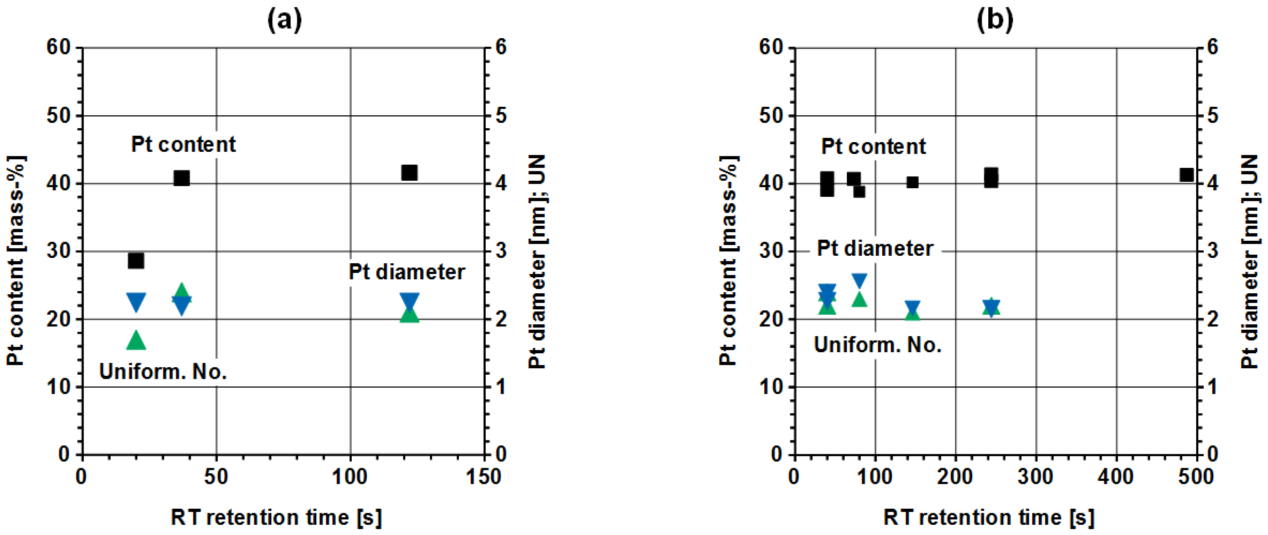

Fig. 7-11: Retention time variation in the reaction tube at two different retention times in the heating-up tube (a): approx. 5 s, (b): approx. 10 s; tests performed at volume flows of (a): about 3 mL/min; (b): about 1.5 mL/min and about 0.75 mL/min (volume flow indicated by size of the symbols: 3.0 mL/min = largest symbol); reaction mixture designed for 40 % Pt content and a NaOH Pt ratio of 5.0, each

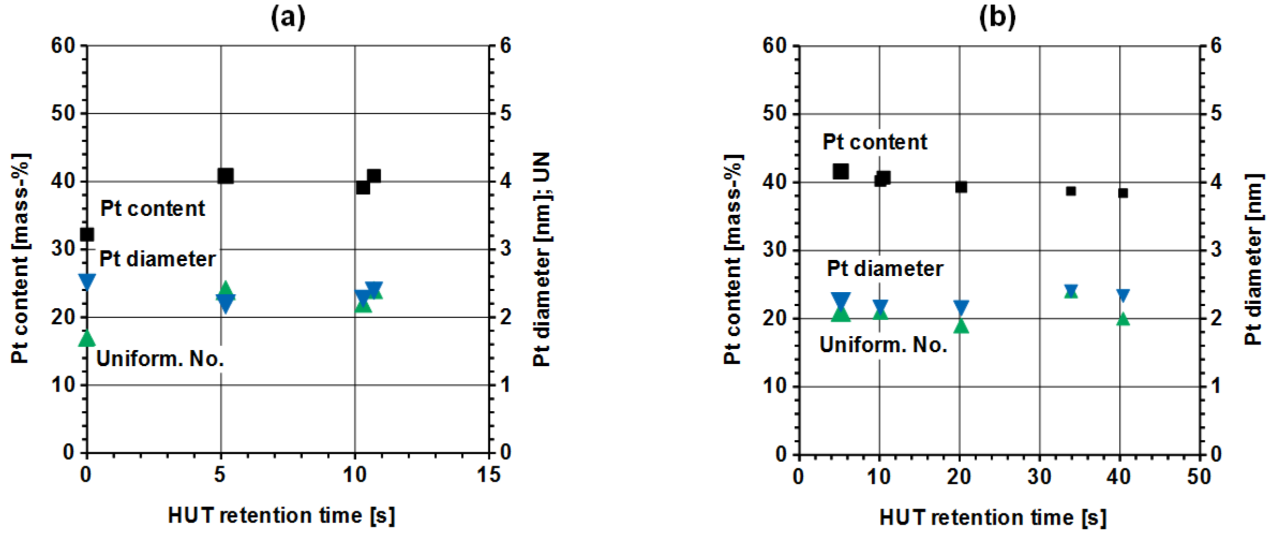

Fig. 7-12: Retention time variation in the heating-up tube at two different retention time ranges in the reaction tube (a): retention times between 37 s and 41 s; (b): retention times between 74 s and 157 s; at different volume flows (volume flow indicated by size of the symbols: 3.0 mL/min = largest symbol); with a reaction mixture designed for 40 % Pt content and a NaOH Pt ratio of 5.0, each

It is noticeable that with the continuous operated test equipment a complete or almost complete Pt deposition can be achieved at rather short retention times. Even a retention time of only 25 s (heating-up tube and reaction tube summarized) is already sufficient to obtain a deposition grade of about 70 %, and after less than 50 s the Pt deposition is almost complete. The Pt particle diameter is similar in all cases, which seems to be the same for the particle uniformity, considering the huge tolerances of these values.

In any case represented, a short retention time in the heating-up tube, and supposedly a higher volume flow, too, seems to favorize a complete Pt deposition on the support, if the heating-up tube is in operation. If not, characterized as retention time 0, the deposition grade was nonsatisfying, though the total retention time in the reaction system was not much lower than during the tests with running heating-up tube.

In summary, the use of a directly electrically heated heating-up tube is necessary to obtain a good Pt deposition performance within a very short total retention time. In addition, it is advantageous to run the test equipment at a high flowrate.

7.7 Catalyst residues from reaction system cleaning

After each testing day, the reaction system of the CFCP test equipment was cleaned. For this purpose, the supply hose to the pump from the switching valve (TV7 in Fig. 4-1) was decoupled and, by use of a syringe, alternately water and air were alternately squeezed and sucked through the reaction system at the highest flow rates obtainable by this method. During every cleaning operation, a noticeable amount of catalyst which had adhered to the tube walls and remained in the reaction system, was detached from the tube walls and flushed out.

These catalyst particles had been in contact with reaction mixture, which contained more or less residual Pt precursor, during much longer time intervals than the matter which had passed through the reaction system without stopover, and therefore might contain higher Pt contents than calculated from reaction mixture composition. This was examined in 3 cases, after tests with reaction mixtures designed for a 40 % Pt product with a NaOH Pt ratio of 5.0. The amount of the purged material was some 10 mg in each case. The samples were cleaned and dried as well as the regular samples and examined by TGA and TEM analysis. The results are shown in Tab. 7-6.

Sample	32-Z	33-Z	34-Z
Reaction tube volume [mL]	6.048	6.048	1.824
Reaction tube retention time [s]	253	variable	variable
Pt content [mass-%]	79.6	90.6	88.9
Aver. Pt particle diameter [nm]	2.62	2.24	1.99
Uniformity number UN	1.0 ± 0.8	1.9 ± 1.3	2.2 ± 1.3

Tab. 7-6: Properties of catalyst residues purged out of the reaction system during daily cleaning operations after one or more tests

Each sample had a very high Pt content, up to more than 90 %. The spatial Pt particle distribution varies from sample to sample, and seems to be excellent in sample 32-Z, as is shown by the TEM images in Fig. 7-13, which represent typical TEM images of this sample. In contrast, the TEM images of the two other samples are showing a wide range of Pt particle spatial distribution qualities, as shown in Fig. 7-14 and Fig. 7-15 by example. For both these samples, there are TEM images showing a very good Pt particle distribution, as well as Images showing a very bad one.

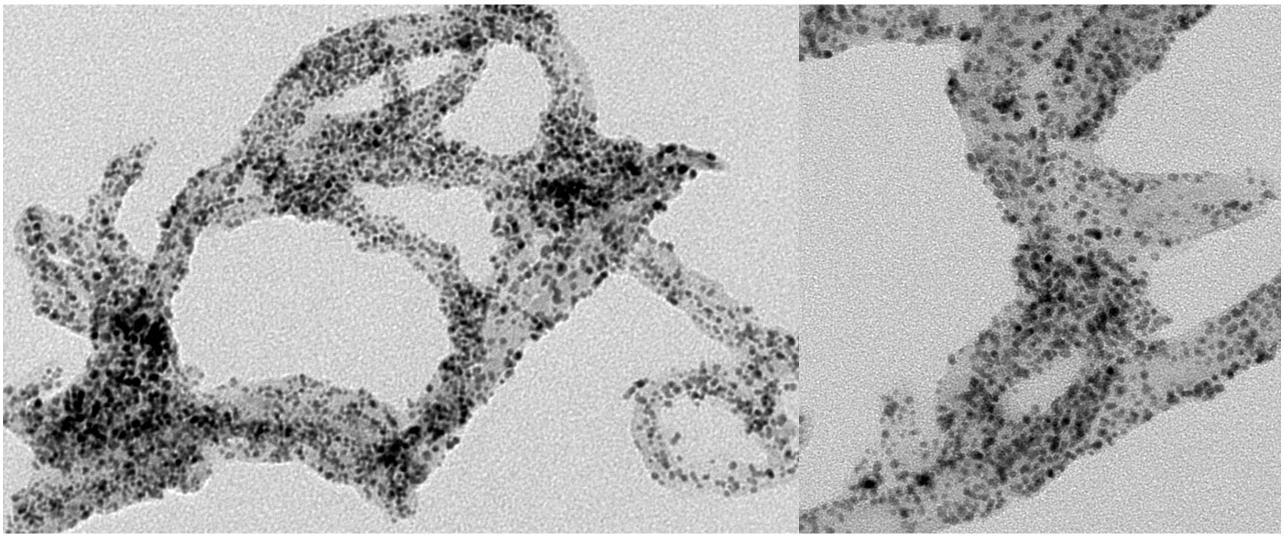

Fig. 7-13: Examples of the Pt particle spatial distribution on the support material at sample 32-Z

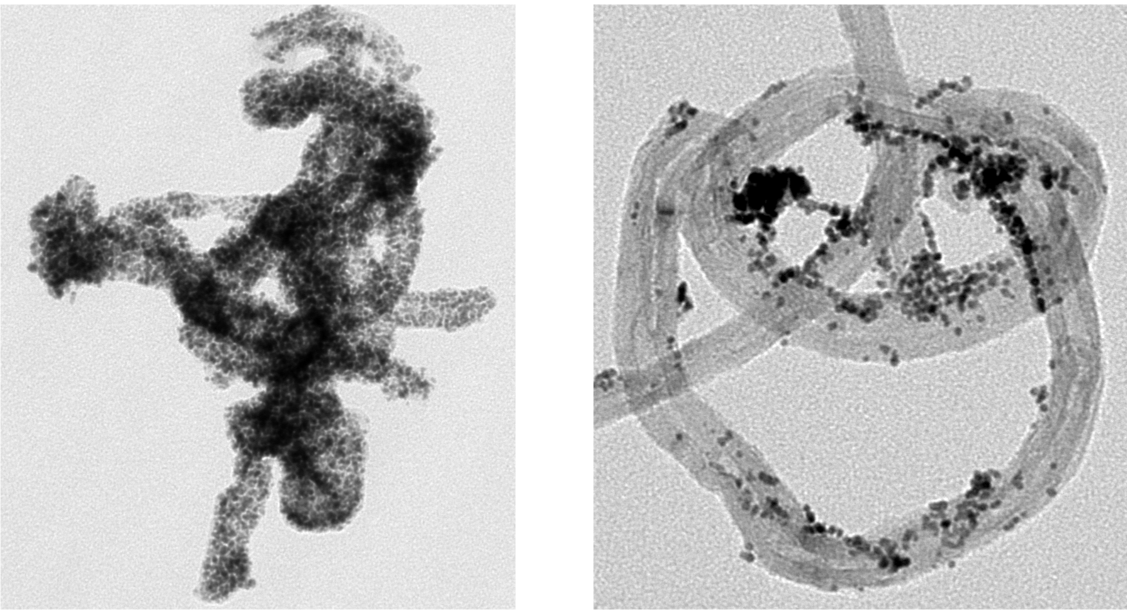

Fig. 7-14: Examples of the Pt particle spatial distribution on the support material at sample 33-Z

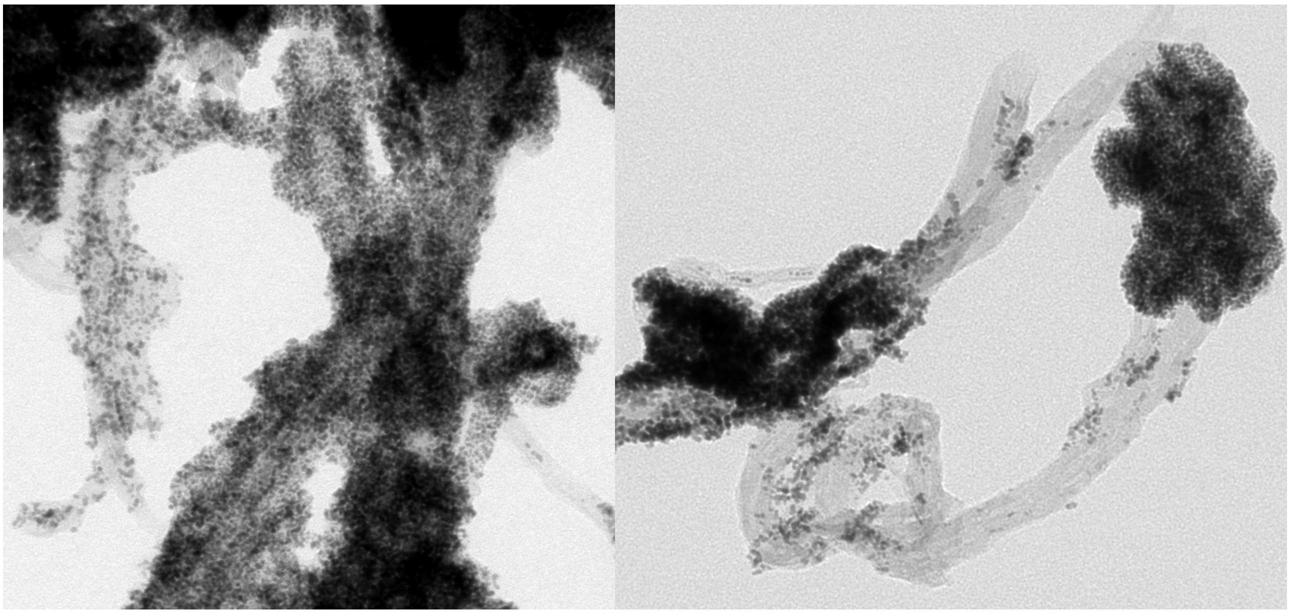

Fig. 7-15: Examples of the Pt particle spatial distribution on the support material at sample 34-Z

To obtain Pt catalysts with a very high Pt content as production residues does not seem to be a suitable method for the production of appreciable quantities. However, it may be possible to develop a suitable process for producing such catalysts, based on the continuous process described in this publication.

7.8 Corrosion effects

No noticeable changes were observed regarding the hose assemblies and joints made of ordinary silicone rubber (LEZ-SIL-60-TF, AET Lezaud GmbH) which were not replaced during the entire project period. Even the thermally loaded silicon tube connection between heating-up tube and reaction tube did not show any degradation, as e. g. a lowered elasticity. However, this tube connection, which included the thermocouple inlet, had to be renewed each time the thermocouple was changed, so the operation duration did not cover the entire project period. The silicone peristaltic pump hoses did not show any special failure phenomena in excess of the usual degradation by the perpetual deformations during pumping. As a usual precaution against mechanical degradation induced leakages, the peristaltic tubes were replaced at regular intervals. In the intervals between the test operations, the system was usually filled with pure ethylene glycol.

There were no leakages at the used heating-up tubes and reaction tubes, both of stainless steel 1.4301, in spite of long operation intervals at elevated temperature in some cases, and in spite of the thin tube walls. The second heating-up tube, which had been in use during almost the entire project time, had a wall thickness of only 0.1 mm.

In contrast, some of the stainless hollow needles, which were designed for medical purpose and slightly modified to fit the requirements of the test equipment, had to be replaced because of pitting corrosion induced leakages. This is noticeable, because these needles should be made from the same material (1.4301) as the reaction system tubing, and none of these needles had been contact to hot reaction mixture. On the other hand, at least one of the corrupted syringes had been in contact to cold reaction mixture residues over long time periods.

8 Summary

It has been validated that carbon supported platinum catalysts can be prepared by polyol reaction method in a continuously operating reaction system consisting of a directly electrically heated heating-up tube and an isothermic heated reaction tube. The results are clearly worse if the directly electrically heated heating-up tube is removed or deactivated. Platinum contents of up to at least 60 % are proved to be obtainable. In the used equipment, a complete deposition of the platinum, dissolved as a hexachloroplatinate salt in almost anhydrous ethylene glycol, takes place within very short reaction times of lower than 1 minute, provided that the heating-up time is very short, within a range of 5 s to 20 s. The average platinum particle size obtained is generally between 2 nm and 2.5 nm. In comparison to samples obtained from the same reaction mixture by a conventional batch process, the catalysts produced in the continuous process have noticeably higher specific areas. The continuous process is suitable as well for CNT based catalysts as for carbon black based ones. It seems that carbon black as support allows a more even spatial distribution of the platinum nanoparticles, which might be caused by an uneven distribution of functional groups in the functionalized CNTs. On the other hand, the wide range of particle distribution qualities observed indicates possible influences also from operation

To be able to heat up an ethylene glycol based liquid reaction mixture within 10 s by passing it through a heated tube, the tube diameter must not exceed 1 mm, as was calculated by numerical modelling. Such a tube allows a volume flow of at least 3 mL/min, corresponding to a production of more than 0.5 g/h of catalyst. In principle, higher flowrates should be possible if the correspondent pressure drop can be managed, this had not been investigated.

For the separation and purification of the catalysts a cheap and simple procedure was developed, which is suitable for both laboratory and production scale and allows high material throughput without centrifuges and other expensive equipment, which requires only a low labour input.

A heating-up interval decrease downto 10 s seems to increase product quality, probably due to the comparably high volume flow which seems to favor a good product quality, whereas a further heating-up interval decrease does not seem to result in a further quality increase.

Some observed corrosion problems referring to stainless steel hollow needles have indicated, that 1.4301 stainless steel probably will not be a suitable material for long time used reaction tubes and reaction mixture piping in commercial production equipment which is based on the continuous method described above.

9 Future prospects

There is a good chance to build up and run a commercial scale test plant based on the research results discussed. To perform higher production rates than in the test assembly, however, a system of parallel directly electrically heated heating-up tubes will be required, with high requirements concerning the even distribution of heating currents and flowrates between the lines. The development and testing of such a system, as well as the testing of corrosion resistant electrical conductive materials, is a possible issue of a continuative research project.

The cheap and easy separation and purification process for the polyol process catalysts can be used in both laboratory and production scale, probably without high efforts. As commercial processes are seldom described in detail, however, the described procedure or a similar one might already be in use in one or another production process or laboratory procedure.

10 Appendix

10.1 References

[allmann-2003]
Allmann, Rudolf:
Röntgenpulverdiffraktometrie: rechnergestützte Auswertung, Phasenanalyse und Strukturbestimmung
2. Auflage, Springer, 2003
ISBN 978-3-540-43967-7
ISBN 978-3-642-56079-8 (eBook)
DOI 10.1007/978-3-642-56079-8

[aoun-2012]
Aoun, N.; Schlange, A.; dos Santos, A. R.; Kunz, U.; Turek, T.
Continuous preparation of highly active Pt/CNT catalysts
Vortrag, Saarbrücken, 2012

[aoun-2016]
Aoun, N.; Schlange, A.; dos Santos, A. R.; Kunz, U.; Turek, T.:
Effect of the OH-/Pt Ratio During Polyol Synthesis on Metal Loading and Particle Size in DMFC Catalysts
Electrocatalysis (2016) 7:13–21
DOI 10.1007/s12678-015-0275-9

[chen-2006]
Chen, R.; Du, Y.; Xing, W.; Zhang, L.; Xu, N.
Continuous production of nano-sized nickel based on ceramic membrane filtration
Nanoscience 11 (2006) 131-136

[choi-2010]
Choi, D.; Lee, H.; Shim, Y.-B.; Lee, D.
A One-Step Continuous Synthesis of Carbon-Supported Pt Catalysts Using a Flame for the Preparation of the Fuel Electrode
Amer. Chem. Soc. (2010)
doi: 10.1021/la1005264

[deiwaraj-2003]
Deivaraj, T. C.; Chen, W.; Lee, J. Y.
Preparation of PtNi Nanoparticles for the Electrocatalytic Oxidation of Methanol
J. Mater. Chem. 13 (2003) 2555-2560
doi: 10.1039/B307040A

[genthe-2015]
Genthe, N.
Abtrennung und Reinigung von kohlenstoffgeträgerten Platinkatalysatoren aus Dispersionen in Ethylenglykol zur Probengewinnung im Labormaßstab
Bachelorarbeit; Institut für Chemische und Elektrochemische Verfahrenstechnik; TU Clausthal

[grimm-2015]
Grimm, H.; Kunz, U.
Continuous Fuel Cell Catalyst Preparation in a Directly Electrically Heated Tubular Reactor
Chem. Eng. Technol. 2015, 38, No. 10, 1758–1764
DOI: 10.1002/ceat.201400767

[horn-2001]
Horn, D.; Rieger, J.
Organische Nanopartikel in wässriger Phase - Theorie, Experiment und Anwendung
Angew. Chem. 113 (2001) 4460-4492

[hung-2007]
Hung, L.-H.; Lee, A. P.
Microfluidic Devices for the Synthesis of Nanoparticles and Biomaterials
Journal of Medical and Biological Engineering 27(1) (2007) 1-6

[kaluza-2011]
Kaluza, S.; Behrens, M.; Schiefenhçvel, N.; Kniep, B.; Fischer, R.; Schlçgl, R.; Muhler, M.
A Novel Synthesis Route for Cu/ZnO/Al 2 O 3 Catalysts used in Methanol Synthesis: Combining Continuous Consecutive Precipitation with Continuous Aging of the Precipitate
ChemCatChem 3 (2011) 189 – 199
doi: 10.1002/cctc.201000329

[kawaguchi-1988]
Kawaguchi, T,; Wakasugi, T.
Continuous Preparation of Activated Carbon Supported Zinc Acetate Catalyst and Industrial Synthesis of Vinyl Acetate from Acetylene
J. Chem. Tech. Biotechnol. 42 (1988) 113-127

[kim-2002]
Kim, K. D.; Kim, H. T.
Synthesis of titanium dioxide nanoparticles using a continuous reaction method
Colloids and Surfaces A: Physicochemical and Engineering Aspects 207 (2002) 263–269

[kongolo-2016]
Kongolo, K. N.
Rechnerische Verknüpfung der Verweilzeitcharakteristiken hintereinandergeschalteter durchströmter Anlagenteile
Studienarbeit; Institut für Chemische und Elektrochemische Verfahrenstechnik; TU Clausthal

[kunz-2009]
Kunz, U.; Turek, T.
Flow through reactors for organic chemistry: directly electrically heated tubular mini reactors as an enabling technology for organic synthesis
Beilstein Journal of Organic Chemistry 2009, 5, No. 70.
doi:10.3762/bjoc.5.70

[lee-2006]
Lee, K.; Zhang, J.; Wang, H.; Wilkinson, D. P.:
Progress in the synthesis of carbon nanotube- and nanofiber-supported Pt electrocatalysts for PEM fuel cell catalysis
Journal of Applied Electrochemistry (2006) 36, 507–522
DOI: 10.1007/s10800-006-9120-4

[li-2005-1]
Li, X.; Chen, W.; Zhao, J.; Xing, W.; Xu, Z.:
Microwave polyol synthesis of Pt/CNTs catalysts: Effects of pH on particle size and electrocatalytic activity for methanol electrooxidization
Carbon 43 (2005) 2168–2174

[li-2005-2]
Li, W. Z.; Song, S. Q.; Zhou, W. J.; Sun, G. Q.; Xin, Q.; Poulianitis, C.; Tsiakaras, P.:
Direct Methanol Fuel Cells: The Influence of Methanol on the Reduction of Oxygen Over Pt/C Catalysts with Different Particle Sizes
Ionics 11 (2005) 112-119

[niesz-2008]
Niesz, K.; Hornyak, I.; Borcsek, B.; Darvas, F.
Nanoparticle synthesis completed with in situ catalyst preparation performed on a high-pressure high-temperature continuous flow reactor
Microfluid Nanofluid 5 (2008) 411–416
doi: 10.1007/s10404-008-0257-9

[sakthivel-2010]
Sakthivel, M.; Schlange, A.; Kunz, U.; Turek, T.
Microwave assisted synthesis of surfactant stabilized platinum/carbon nanotube electrocatalysts for direct methanol fuel cell applications
J. Power Sources 195 (2010) 7083-7089
doi: 10.1016/j.jpowsour.2010.05.002

[schlange-2011]
Schlange, A.; Dos Santos, A.R.; Kunz, U.; Turek, T.
Continuous preparation of carbon-nanotube-supported platinum catalysts in a flow reactor directly heated by electric current
Beilstein J. Org. Chem. 7 (2011) 1412-1420
doi:10.3762/bjoc.7.165

[schüth-2001]
Schüth, F.; Bussian, P.; Aagren, P.; Schunk, S.; Linden, M.
Techniques for analyzing the early stages of crystallization reactions
Solid State Sciences 3 (2001) 801–808

[schur-2003]
Schur, M.; Bems, B.; Dassenoy, A.; Kassatkine, I.; Urban, J.; Wilmes, H.; Hinrichsen, O.; Muhler, M.; Schlögl, R.
Kontinuierliche Cofällung von Katalysatoren in einem Mikromischer: nanostrukturierte Cu/ZnO-Komposite für die Methanolsynthese
Angew. Chem. 115 (2003) 3945 –3947
doi: 10.1002/ange.200250709

[vdi-2006]
VDI-Wärmeatlas; 10. Auflage; 2006
Springer-Verlag, Berlin, Heidelberg, New York
ISBN-10 3-540-25504-4
ISBN-13 978-3-540-25504-8

[yu-long-1996]
Yu-Long, Z.; Zhou, C.-R.; Su, X.-L.
Unsupported precipitated Fe-Cu-K catalysts used for the slurry fischer-tropsch synthesis
Journal of Natural Gas Chemistry 5 (1996) 97-106

10.2 List of symbols

Symbols:

cp	Specific heat capacity
D	Particle diameter
g	Number of hollow cylinder type layers, one inside the other
K	Heat transition coefficient
L	Length
n	Number of particles or particle images
Q	Heat quantity
r	Radius
t	Time
T	Temperature
Δ	Difference
λ	Heat conductivity coefficient
ρ	Density
ϑ	Bragg angle

Indices:

f	Number of a hollow cylinder type layer
Tu	Tube

10.3 List of abbreviations

CFCP	Continuous fuel cell catalyst production
CNTs	Carbon nanotubes
CV	Coolant vessel
DFG	Deutsche Forschungsgemeinschaft
DT	Drying tube
Fig.	Figure
FIT	Flow indicator tube
HPA	Hexachloro platinic acid hexahydrate
HUT	Heating-up tube
ICVT	Institute of Chemical and Electrochemical Process Engineering
MWCNTs	Mutiwalled carbon nanotubes
ORR	Oxygen reduction reaction
oxCNTs	Oxigenized funktionalized carbon nanotubes
PCV	Product collection vessel
PIT	Pressure indicator tube
PP	Peristaltic pump
PTFE	Polytetrafluoroethylene
RT	Reaction tube
SVR	Storage vessel for reaction mixture
SVS	Storage vessel for startup mixture
Tab.	Table
TCP	Temperature controlled plate
TEM	Transmission electron microscopy
TV	Three-way-valve/cock
UN	Uniformity number
VCC	Voltage and current controller
XRD	X-ray diffractometry

10.4 List of publications derived from the project

10.4.1 Peer reviewed publications

- Grimm, H.; Kunz, U.:
  Continuous Fuel Cell Catalyst Preparation in a Directly Electrically Heated Tubular Reactor
  Chem. Eng. Technol. 2015, 38, No. 10, 1758–1764
  DOI: 10.1002/ceat.201400767

10.4.2 Other publications, in addition to the present final report

- Grimm, H.; Kunz, U.
  Continuous Fuel Cell Catalyst Preparation in a Tubular Reactor With Directly Heated Heating-Up Section
  Posterpräsentation, 47. Jahrestreffen deutscher Katalytiker, 12.-14.03.2014, Weimar
- Grimm, H.; Kunz, U.
  Rohrreaktor mit direktbeheizter Aufheizstrecke zur kontinuierlichen Herstellung von edelmetallbasierten Katalysatoren für Brennstoffzellen
  Posterpräsentation, ProcessNet-Jahrestreffen Reaktionstechnik 2014, 28.-30.04.2014, Würzburg
- Grimm, H.; Kunz, U.
  Directly electrically heated tube for rapid heating-up of fluid reactant mixtures
  Posterpräsentation, 5th Conference of the FCS (Flow Chemistry Society), 17.-18.02.2015, Berlin
- Genthe, N.:
  Abtrennung und Reinigung von kohlenstoffgeträgerten Platinkatalysatoren aus Dispersionen in Ethylenglykol zur Probengewinnung im Labormaßstab
  Bachelorarbeit, TU Clausthal, 2015
- Grimm, H.; Kunz, U.:
  Kontinuierliche Edelmetallabscheidung auf kohlenstoffbasierten Trägermaterialien zur Herstellung von Katalysatoren für Brennstoffzellen
  Ausführlicher Ergebnisbericht zum DFG-geförderten Projekt KU 853/9-1
  http://www.icvt.tu-clausthal.de/forschung/publikationen/grimm-kunz-2016_kontinuierliche-herstellung-von-brennstoffzellen-katalysatoren_bericht-dfg-projekt.pdf
- Kongolo, K. N.:
  Rechnerische Verknüpfung der Verweilzeitcharakteristiken hintereinandergeschalteter durchströmter Anlagenteile
  Studienarbeit; Institut für Chemische und Elektrochemische Verfahrenstechnik; TU Clausthal

10.5 Acknowledgement

The authors would like to thank the Deutsche Forschungsgemeinschaft DFG for their support of the project.