

BSc Thesis Biotechnology

Selective carbohydrate oxidation on Pt/AC

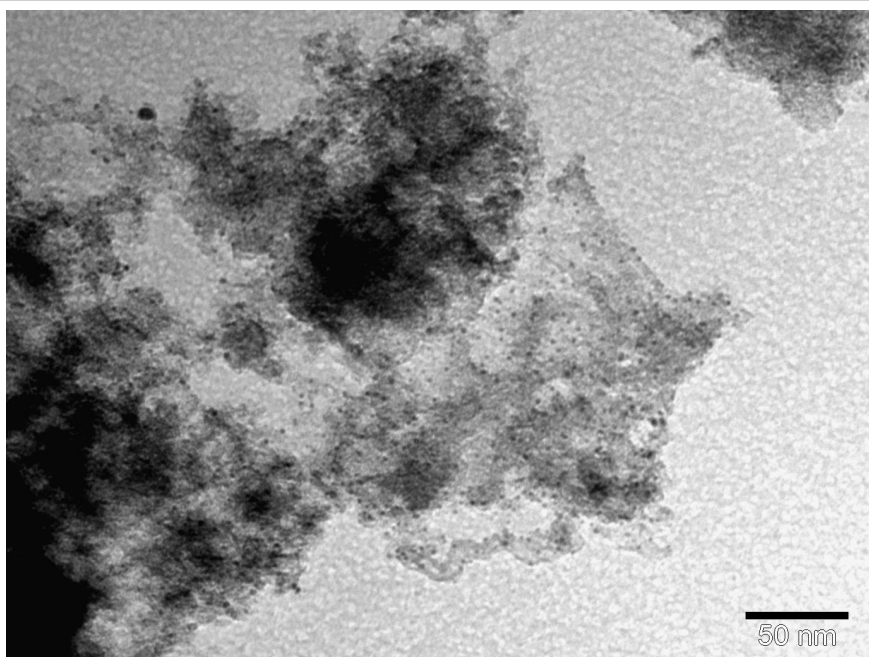
Marie-José Linders

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Supervisors:

EB (Evie) van der Wijst MSc

Prof. JH (Harry) Bitter



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Student : Marie-José Linders
Registration number : 940818521110
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Supervisor(s) : EB (Evie) van der Wijst MSc, prof. JH (Harry) Bitter
Examiners : Prof. JH (Harry) Bitter, dr. EL (Elinor) Scott
Group : Biobased Chemistry and Technology
Address : Bornse Weiland 9
6708 WG Wageningen
The Netherlands

Name course : BSc Thesis Biobased Chemistry and Technology

Abstract

The use of 1 wt.% platinum on activated carbon was investigated as a potential catalyst for starch oxidation, as gold catalyst was proven unsuitable in previous research. Three different preparation methods were used to synthesize the catalysts: incipient wetness impregnation, sol immobilisation and ion adsorption. The prepared catalysts were characterized using TEM, chemisorption, XRD and ICP-OES. A model oxidation was conducted to determine their catalytic activity, with glucose as substrate.

According to the TEM and chemisorption results, incipient wetness impregnation is the best technique to obtain a Pt/AC catalyst with a low average diameter size and a high metal distribution. However, the catalysts prepared with sol immobilisation had a higher catalytic activity when oxidising glucose. Therefore, bigger starch-like substrates such as maltose and maltotriose were oxidised on catalyst prepared with the sol immobilisation method as a model for starch oxidation. Methyl α -D-glucopyranoside, a glucose analogue without a reducing end, was oxidised with this catalyst as well.

The platinum performance was inferior when compared to the gold catalysts made in previous work. The conversions of glucose, maltose and maltotriose were about 8 times lower for the platinum catalyst than for the gold catalyst in the same amount of time. In contrast to the gold catalyst, a decrease in the catalytic activity was observed with increasing molecular weight for the platinum catalyst. As for the oxidation of methyl α -D-glucopyranoside, the platinum catalysts showed no activity, as was the case for the gold catalyst. According to literature, platinum has a lower selectivity for reducing ends than gold, making it a more appropriate catalyst for the oxidation of starch. This is why the research to a suited platinum catalyst should be continued.

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1 Introduction

In the last decennia concern about the exhaustion of fossil resources like oil and natural gas has grown rapidly. These compounds can have several applications such as energy source, polymers, pharmaceuticals, solvents, fertilizers, among other things. Because of our complete dependence on these resources and the fact that they are not renewable, finding a substitute is imperative.

One promising alternative is biomass, which has the advantage to be produced on a daily basis. Moreover, it has different components that could be interesting for further conversion into chemicals. The main products that can be obtained from biomass are carbohydrates, proteins, lipids and minerals in a smaller amount. Depending on the source, the content of these components will vary.

Cellulose, hemicelluloses and starch are the most abundant carbohydrates present in biomass, while pectin, inulin and sucrose are also present in smaller amounts. Glucose is the most important monosaccharide and monomer of polysaccharides in natural carbohydrates. Production of pulp from wood cellulose, applications of starch for paper making and in the food industry as well as uses of glucose and sucrose for fermentation are the most important chemical and technical uses of carbohydrates [1].

A more specific example of carbohydrate application is the use of oxidised or anionic starch. This molecule is obtained by selectively oxidising a part of the hydroxyl-groups of starch into carboxylic acids. An important feature of this negatively charged molecule is that it can be used as a sustainable replacement of polyacrylates and polyacrylamides, which are petroleum-based polymers. Anionic starch has applications in the paper, textile, laundry finishing and binding materials industry, but also in the food industry and in the preparation of biodegradable packaging [2].

In industry, the oxidation of starch is generally performed with sodium hypochlorite in stoichiometric amounts [2]. However, this method has the important drawback of producing a significant amount of sodium chloride as waste product, which makes the process unfriendly for the environment and very inefficient. Other methods to produce anionic starch are using H_2O_2 in high concentrations as the oxidant agent along with a copper sulphate catalyst, using O_3 as the oxidant in cooperation with silver(I) oxide and/or cobalt(II) acetate or by using different metal salts such as KMnO_4 or K_2FeO_4 [3].

To avoid the stoichiometric use of sodium hypochlorite and an undesired amount of waste product, a lot of research has been conducted on the use of homogeneous catalysts for the oxidation of starch. Some examples are the use of catalysts based on Cu and Mn [4] and the use of TEMPO as catalyst [5]. The drawback of these techniques and that of any homogeneous catalyst is the difficult separation of catalyst and product after the conversion.

A potentially more sustainable and environmentally friendly way to perform this oxidation is by using a heterogeneous supported catalyst. Separation of catalysts and products is not expected to be a problem here as the catalyst and the substrate are in different phases. Research on the use of heterogeneous catalysts for the selective oxidation of starch has not been conducted yet. However, it has been tested on other polysaccharides like inulin. In this experiment, the oxidation was performed with platinum on activated carbon as catalyst. Different substrates were used, e.g. inulin building blocks such as methyl α -D-fructofuranoside (degree of polymerisation DP1), sucrose (DP2) and nystose (DP4), but also inulin itself. The oxidation degree diminished with substrate size: methyl α -D-fructofuranoside was completely oxidized, whereas inulin with DP 30 had an oxidation degree of 20% [6].

Considering the size of starch, comparable results to those for inulin are expected. Polysaccharides generally tend to adsorb stronger to the catalyst surface than monosaccharides due to the higher amount of functional groups per molecule that can interact with the catalyst. Therefore, site-covering

and consequently deactivation of the catalyst may occur. Another common issue caused by large molecule size is diffusion limitation [7]. This is why the research done so far has been focused on the oxidation of starch building blocks like glucose and maltose. During this thesis mainly glucose will be used as model for starch. The focus will lie on the selection of the proper catalyst for the, in the end, oxidation of starch.

1.1 Selection of a heterogeneous catalyst

1.1.1 Metal

Mostly noble metals like gold (Au), platinum (Pt), palladium (Pd) and combinations of the former have shown promising catalytic activity when it comes to selective oxidation of monosaccharides [8, 9]. When looking at monometallic catalysts on a carbon support, diverse outcomes can be found. Literature is particularly optimistic about Au catalysts because it has shown high conversion and 100% selectivity when it comes to glucose oxidation to gluconic acid (oxidation of the C-1) [10]. Furthermore, one of the big advantages Au has over other metal catalysts (such as Pt and Pd) is that it is almost immune to over oxidation, which prevents the catalyst from suffering deactivation [11]. This implies that the catalyst can be reused multiple times without the need of reducing it. Another article shows that Au has the highest turnover frequency (TOF) (17200 h^{-1}), followed by Pd (2000 h^{-1}) and Pt ($<500\text{ h}^{-1}$) [12] for the same reaction of glucose to gluconic acid under similar conditions¹. In yet another study, Pt and Pd catalysts were preferred because they were cheaper and easier to make, and their performance seemed comparable to the performance of gold. However, additional costs of pre-reducing Pt and Pd before every oxidation were not taken into account. The selectivity to gluconic acid did not overpass 77% with a TOF of 180 h^{-1} and 97% with a TOF of 4680 h^{-1} for Pt and Pd respectively [13].

All researchers seem to conclude that the use of promoters like Bi on Pt and Pd catalysts enhances the activity and selectivity in glucose oxidation; the rate of glucose oxidation was 20 times higher on a Pd-Bi/C than on a Pd/C catalyst [14]. For bimetallic systems, Au:Pt 2:1 seems to be the best combination to oxidize glucose (TOF 17600 h^{-1}) [12]. In general bimetallic catalysts show higher TOF-values than monometallic catalysts, as is the case when promoters are used. When made in the right ratio, the shortcomings of one metal are compensated with the strengths of the other. This phenomenon is known as synergetic effect [12].

Experiments conducted by my predecessor [15] using a gold catalyst on activated carbon (Au/AC) and gold on carbon nanofibers (Au/CNF) showed that, indeed, oxidation of glucose, maltose and maltotriose took place, but only at the reducing ends (Figure 1). This catalyst would be inefficient when used on starch, because there is only one reducing end present in this large molecule. An additional oxidation was conducted on methyl α -D-glucopyranoside, a derivative of glucose without a reducing end, in order to verify that only the reducing end was being oxidized in the previously mentioned carbohydrates. This experiment resulted in virtually no oxidation of the sugar, verifying the inability of Au catalysts to oxidize the hydroxyl groups of methyl α -D-glucopyranoside.

¹ T=323 K, pH 9.5, glucose/M = 1000, O₂-flow = 20 ml/min for [10]. T=323 K, pH 9.5, glucose/M = 3000, P(O₂) for [12]

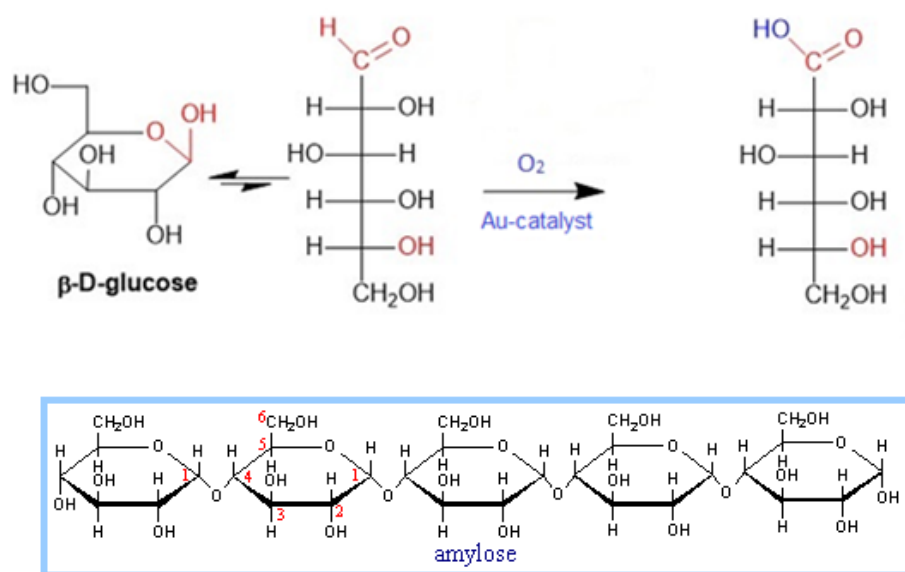


Figure 1. During the oxidation of glucose to gluconic acid the aldehyde on the C-1 (reducing end, depicted in red) of glucose is converted to a carboxylic acid. When a glucose molecule is a monomer in a starch molecule, the C-1 is making a glycosidic bond with the C-4 of the next glucose molecule, making this selective conversion impossible.

The selectivity of gold makes it an unviable catalyst for starch. Thus, an alternative for Au catalyst should be looked in to. Pt catalysts have shown interesting activity when it comes to oxidising different alcohols and aldehydes [11] and glucose [13]. The TOF of 5 wt.% Pt/C for the oxidation of glucose was calculated at 0.05 s^{-1} . Also, the redox potential of Pt is high compared to other metals used for oxidation (e.g. Pd) and is therefore less prone to over oxidation [16]. As mentioned before, the selectivity of platinum towards gluconic acid when oxidising glucose is lower than golds, but this is not necessarily an unfavourable property. Pt catalysts have shown the ability to oxidize glucose derivatives without reducing ends like methyl and n-octyl α -D-glucopyranoside [17] and methyl α -D-fructofuranoside [6]. In both cases mainly the C-6 alcohol was oxidised. This means that platinum is able to oxidise primary alcohols and not only the aldehyde on the reducing ends, as is the case with gold. This is of importance when applying a catalyst on starch. Another aspect that has to be taken into consideration is the support to which the catalyst is attached to.

1.1.2 Support

As mentioned before, undesired interactions between (large) molecules and the support can lead to catalyst poisoning and deactivation. Since carbohydrates are hydrophilic molecules, a hydrophobic support is preferred to prevent too strong interactions between the substrate and the catalyst. [18]. A widely used hydrophobic support that meets these requirements is carbon.

Some desirable properties of a catalyst support are: inertness², mechanical properties (attrition resistance, hardness), stability under reaction conditions, surface area. Carbon meets these properties for many catalytic applications [19].

There are different carbon materials available to prepare a support for a heterogeneous catalyst; graphite, carbon black, activated carbon and activated carbon fibres are some examples [20]. My predecessor used two common forms, activated carbon (AC) and carbon nanofibers (CNF). AC is usually derived from charcoal and has a porous structure with a relatively small amount of chemically bound heteroatoms (mainly oxygen and hydrogen). Additionally, AC may contain up to 15% of mineral matter

² The inertness of carbon for oxygen is restricted to temperatures below $\pm 150\text{-}200\text{ }^{\circ}\text{C}$.

(usually referred to as ash content). This composition depends on the precursor used and the treatment it undergoes to obtain the AC [20]. Oxygen surface groups are by far the most important in influencing the surface characteristics adsorption behaviour of AC [21]. This influence extends to two important stages: during the preparation of the catalyst, to bind the metal precursors to the support as well as during the reaction itself, to have a successful interaction between catalyst and substrate.

The present groups on the AC can have different influences during the preparation of the catalyst. Acidic groups on the surface decrease the hydrophobicity of the carbon support, which leads to an easier interaction between the surface and the aqueous metal precursors. The less acidic groups increase the interaction of the supported metal particles with the AC, which minimizes the sintering propensity of metal on carbon [22]. The presence and nature of the groups can also influence how the substrate binds (or is repelled). In the case of carbohydrates, having many hydrophilic groups on the surface can have different influences in the interactions between substrate and support. They are beneficial when the substrate's interaction with the active catalyst is promoted. However, these interactions can also be too strong, leading to the substrate not desorbing from the surface and causing catalyst poisoning.

Carbon nanofibers are prepared in a special manner, whereby the structure and the groups present are steerable. This gives more control over the presence of hydrophobic or hydrophilic groups and over the interactions between support, metal precursor and substrate [23].

According to my predecessor's results, Au atoms supported on AC performed better than Au atoms supported on CNF. The influence of the nature of the support was also compared with Pt on AC and on graphite in another study, although this research was focused on catalyst deactivation. No dependence of the deactivation on the type of carbon support was observed. However, the activity of the graphite supported catalyst was low compared to the AC support when oxidizing methyl α -D-glucopyranoside. A reaction temperature difference of 20 K was necessary to obtain comparable reaction rates for both catalysts. No clear explanation of why this is necessary was given by the authors [24]. Given these outcomes, continuing the experiments with AC supported Pt seems reasonable.

1.2 Reaction mechanism on Pt catalyst

It has been suggested that the oxidation of alcohols and related compounds on metal surfaces can proceed via two different mechanisms [25]. The first mechanism involves the reaction of the organic substrate with oxygen, both adsorbed on the metal surface. This results in the formation of a peroxide intermediate which decomposes to yield an aldehyde and hydrogen peroxide. The second and most accepted mechanism is a dehydrogenation mechanism involving hydrogen transfer to the platinum surface followed by the oxidation of the adsorbed hydrogen atom with adsorbed oxygen [11, 25]. This suggestion is supported by kinetic modelling of glucose oxidations [26] and by measuring the hydrogen that was formed from aldose aqueous solutions at basic pH (>11) in the presence of a platinum or a rhodium catalyst [27]. Further experiments supporting the dehydrogenation mechanism are the oxidation experiments of ethanol and 2-propanol conducted with $^{18}\text{O}_2$, where it was shown that this isotope was not incorporated into products of the reaction [28]. This means the molecular oxygen from the gas flow reacts with the H-atom adsorbed to the Pt surface. In another experiment [29], measurements of the electrode potential showed that the potential of the platinum catalysts in alcohol solutions was similar to that of the hydrogen electrode, which suggests that the surface of the Pt catalyst was mostly covered by adsorbed hydrogen.

A schematic outline of the dehydrogenation mechanism is showed in Figure 2. This reaction can be divided in two steps. First, the substrate is ionized by the abstraction of a proton by a OH^- ion. At the same time, a H^+ ion is transferred to the Pt surface or to an adsorbed oxygen atom. In both cases the H^+ reacts with an oxygen atom to form OH^- .



In water, aldehyde groups are in equilibrium with their corresponding hydrate (geminal diol). This diol-group reacts into a carboxylic acid in the same way as described above for a single alcohol and as depicted in Figure 2 [30]. When the reducing end is being oxidised, the reaction as depicted in step 2 can be assumed.

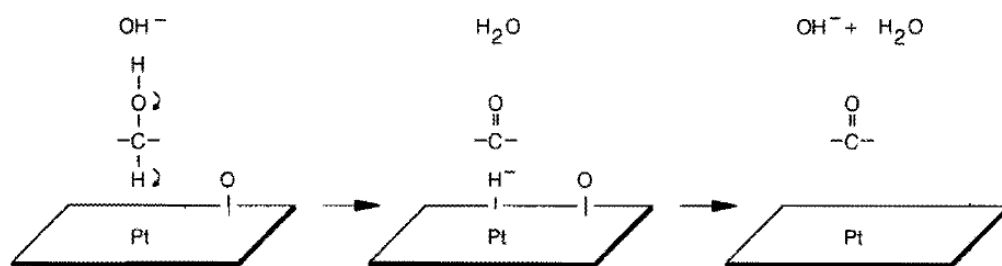
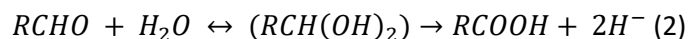


Figure 2 Schematic outline of the reaction mechanism involved in the oxidation of hexoses and related compounds [30]

After a thorough study of the oxidation of hexoses, Heyns et al. [25, 31, 32] concluded that the dehydrogenation mechanism is the most plausible one on Pt catalysts, and proposed the following order in oxidation rate of hydroxyl groups:



Glucose, maltose, maltotriose and starch all have one hemiacetal group, whereas methyl α -D-glucopyranoside only has one primary hydroxyl group and three secondary hydroxyl groups. Since the vast majority of the hydroxyl groups present on starch are secondary hydroxyl groups, a rather slow reaction rate for the oxidation of these groups is anticipated. Primary hydroxyl groups are also present in the carbohydrate, but in a much smaller amount.

Considering the proposed reaction mechanism, a strong influence of pH is expected. The use of different pH values for the oxidation of glucose was investigated [33]. Poisoning of the catalyst by the reaction products in neutral and acidic medium was observed. Basic pH seems to favour the oxidation of glucose to gluconate. An increase in pH is accompanied by an increase of the glucose anion concentration, which results in an increase in the reaction rate [30].

1.3 Research objectives

The goals of this study are to make a platinum catalyst that closely resembles the physical properties (particle size/loading) of the Au/AC made in earlier experiments and to compare their catalytic performances. In order to achieve this, the amount of active Pt atoms in each Pt particle should have to be similar to the amount of active Au atoms in each Au particle. Since the molecular weights of gold and platinum are very similar (196.966 and 195.084 g/mole, respectively), applying the same Pt-loading (1 wt.%) should give a comparable catalyst. Also, the particle size and dispersion have to be similar.

Only the sol immobilisation technique was performed by my predecessor, because this technique has the advantage of obtaining highly dispersed metal catalyst [34]. This is of great importance for Au since its catalytic activity diminishes drastically with particle size over 10 nm [35]. In this approach, impregnation and ion adsorption will be performed as well, in order to investigate which method is the most interesting when making a Pt catalyst as regards the particle size distribution and the metal loading on the surface.

There are four main research questions:

- 1. Which technique is the best to prepare a Pt/AC catalyst suitable for the oxidation of starch?**
- 2. Is this Pt/AC catalyst physically similar to the Au/AC catalyst made in previous work?**
- 3. How does the Pt/AC catalyst perform compared to the Au/AC catalyst when oxidising glucose, maltose, maltotriose and methyl α -D-glucopyranoside?**

Methyl α -D-glucopyranoside was not oxidised by Au/AC, which was also in accordance with previous studies which stated that only reducing ends could be oxidised by Au/AC. According to the background information in this document, Pt can oxidise this monosaccharide. Performances of the two metals will be compared.

My predecessor's research was focussed on the influence of molecular weight of the substrate on the catalyst performance. This is why glucose (DP1), maltose (DP2) and maltotriose (DP3) were used (Figure 3). As stated before, a decrease in catalytic performance is expected with increasing molecule size. The results from my predecessor were somewhat unclear: when performing the oxidation on Au/CNF a clear dependence on molecule size was observed, with a decrease in performance coupled to an increase in molecular weight. For the Au/AC no relation could be observed between the catalyst's performance and the substrate's size.

In this experiment, the influence of molecular weight will be investigated as well, in order to compare the influence of molecular weight on Pt/AC with Au/AC. This leads to the fourth research question:

- 4. How does molecular weight of the substrate influence the performance of the Pt/AC catalyst?**

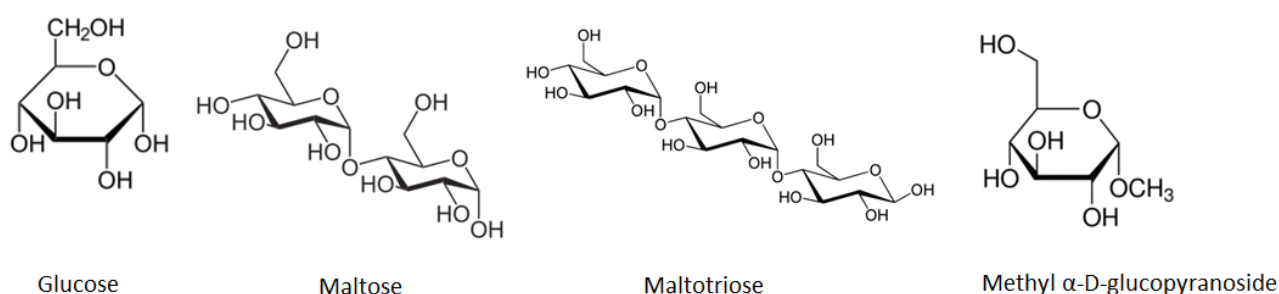


Figure 3. Substrates to be oxidised with Pt/AC

The research can be divided into two stages. During the first stage, meant to answer the first two research questions, 14 platinum catalysts will be made with three different techniques. These catalysts will be compared to each other on different aspects. Based on those comparisons, one catalyst will be chosen and used in further oxidations. Stage two, meant to answer the third and fourth research questions, will be conducted with only the chosen catalyst.

2 Materials and methods

2.1 Preparation of 1 wt.% Pt catalysts on AC

Three methods were used to make the Pt/AC catalysts: impregnation, ion adsorption and sol immobilisation. Norit SX ULTRA activated carbon was used as support. Two different platinum precursors were used, tetraammineplatinum(II) nitrate ($[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$, 99.995%) and chloroplatinic acid hydrate ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, $\geq 99.9\%$), both from Sigma Aldrich. A 5 wt.% Pt/AC bought from Sigma Aldrich was used as reference.

2.1.1 Incipient wetness impregnation

Firstly, the pore volume of the support was determined experimentally by adding Milli-Q water (MQ) until saturation of the activated carbon was reached. The determined porosity for Norit SX ULTRA AC was 0.88 ± 0.04 g/g (mass water per mass support).

Once the porosity was known, an accurate stock solution of the two precursors could be made, in order to reach a Pt loading of 1 wt.%. These stock solutions were added dropwise while shaking vigorously to 2 gram of support each, until the support was saturated. After this, the catalyst was left in the 60°C oven overnight.

Three different batches of impregnations were made. In batch 1 and 2 the point of zero charge of the support was not taken into account. Therefore, the pH of the stock solutions was not adjusted; the stock solution of $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ had a pH of 1.02 and the $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ solution a pH of 3.88. The catalysts made in batch 1 were only reduced in 30 mL/min H_2 and 63 mL/min N_2 atmosphere at 300°C. The catalysts made in batch 2 were calcined for two hours at 250 °C in static air in Nabertherm P 330 calcination oven with a heating ramp of 5 °C/min. This step was done in order to determine the influence of calcination on the catalysts properties and performance. Afterwards, the catalysts were reduced in 30% H_2 and 26% N_2 atmosphere at 300°C.

The point of zero charge of Norit SX ULTRA activated carbon is 8.1 [36]. In the third batch the pH of the $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ solution was adjusted to 9.23 with diluted 25% ammonia solution. The pH of the $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor was not adjusted. No calcination took place, only a reduction in 30% H_2 and 26% N_2 atmosphere at 200°C. The reduction temperature was adjusted because it is suggested in many different studies that Pt/C should be reduced around 150-200°C [37, 38]. A temperature programmed reduction (TPR) was attempted, but did not give any useful information.

An overview of the procedure steps is given in Table 1.

Table 1. Conditions of impregnation preparation

	Both precursors used?	pH adjusted?	Calcined?	Reduction temperature
Batch 1	Yes	No	No	300°C
Batch 2	Yes	No	Yes, at 250°C	300°C
Batch 3	Yes	Yes	No	200°C

2.1.2 Sol immobilisation

Sol immobilisation following Pazhavelikkakath Purushothaman et al. [39] was performed. The two different platinum precursors were used to make Pt-colloid suspensions in parallel. A 2 wt. % PVA-solution was made to function as stabilizer of the colloidal particles. 4.75 mL of this PVA solution was brought in each reactor and added up with MQ to get a total volume of 350 mL in both of them. The

two different precursors were added to the reactors in order to get a suspension of 1 wt.% Pt under magnetic stirring at 400 rpm. The platinum precursors in the solutions were reduced with the slow addition of 5 mL of a 0.1 M NaBH₄ solution. A copper colour was observed for the H₂PtCl₆·xH₂O precursor solution, while a pale greyish colour was observed by the [Pt(NH₃)₄](NO₃)₂ precursor solution. It took around 2 hours for the [Pt(NH₃)₄](NO₃)₂ precursor sol to get this colour, while the copper colour of the H₂PtCl₆·xH₂O precursor sol appeared immediately after adding the reductor. The pH of the Pt-colloids was brought to 2.5 with 0.2 M H₂SO₄.

Two support suspensions of 2 gram activated carbon in 20 mL MQ were sonicated in a VWR™ ultrasonic bath for 30 minutes. The support suspensions were then added to the Pt-colloid suspensions and stirred with a magnetic stirrer at 400 rpm for 3.5 hours.

After this, the catalyst was filtered with a Buchner funnel connected to a vacuum pump using Whatman™ 50 hardened filter paper and washed with 1 L MQ. The filtrate of both precursors was colourless, which indicated that there was little or no platinum particles left in the solution. The catalyst cake was left in Nabertherm P 330 calcination oven at 105 °C for 16 hours. Finally, the catalyst was refluxed for one hour in 300 mL MQ in an oil bath at 90 °C, to eliminate the remaining PVA. After the refluxing step the catalyst was filtered and washed again, and left in the calcination oven at 105 °C for 16 hours.

2.1.3 Ion Adsorption

Ion adsorption following Toebes et al. [40] was performed. Again the two precursors were used to make 2 gram of catalyst each, so 4 gram in total. The mass of precursor required to get 1 wt. % Pt was dissolved in 500 mL demi water at 90 °C under magnetic stirring. The previously weighed support was added to the solution and the pH was adjusted with diluted ammonia. The point of zero charge of Norit SX ULTRA is 8.1 [36]. For the [Pt(NH₃)₄](NO₃)₂ precursor the pH was brought to 10, the pH of the H₂PtCl₆·xH₂O precursor solution was not adjusted since it was already pH 3, the desired pH. The suspension was left under vigorous mechanical stirring for 18 hours.

The catalyst was filtered with Whatman™ 50 hardened filter paper and washed with 500 mL demi water using a Buchner funnel and a vacuum pump. The cake was left in the 60 °C oven overnight. Half of the batch was calcined at 200 °C in static air to see if this step is necessary, as was the case with the impregnated catalysts. After this, the catalysts were reduced in hydrogen at 200 °C. The other half was only reduced in hydrogen at 200 °C.

2.2 Characterization of the different Pt/AC catalysts

2.2.1 TEM

A Transmission Electron Microscope (TEM) was used to visualise the different catalysts and determine the size of the active particles. In order to prepare the samples for the TEM analysis, 10 mg catalyst was suspended in 1.5 mL absolute ethanol and sonicated in a ultrasound bath for 30 min. A droplet of this suspension was placed on a carbon-coated copper grid. JEOL JEM-1011 Electron Microscope was used for this analysis.

For each catalysts an approximate of 20 pictures were taken on different magnifications. The program FIJI (ImageJ) was used to determine the diameter size of the Pt particles (d). With d the dispersion of the platinum particles could be calculated with the following equations [41]:

$$Metal\ dispersion\ (D_M) = \frac{6 * M_{Pt}}{\alpha_{Pt} * \rho_{Pt} * N_A * d_{vs}} \quad (3)$$

With d_{vs} , the average volume-surface diameter of Pt particles:

$$d_{vs} = \frac{\Sigma d^3}{\Sigma d^2} \quad (4)$$

Where M_{Pt} is the molar mass of Pt (195.084 g/mole), α_{Pt} is the average effective area of Pt atom on the support ($1 \times 10^{-19} \text{ m}^2$), ρ_{Pt} is the density of platinum ($21.45 \times 10^3 \text{ kg/m}^3$) and N_A is the Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$).

2.2.2 Chemisorption

Pulse chemisorption was used to determine the Pt surface-area on the catalyst and the metal dispersion. The measurements were carried out with two different gases: H_2 and CO. For each measurement, approximately 200 mg sample was introduced in the micrometrics AutoChem II Chemisorption Analyzer. Firstly, the catalysts were heated with $10^\circ\text{C}/\text{min}$ rate in a hydrogen atmosphere until 200°C . This temperature was held for 90 minutes in order to reduce the platinum on the catalyst. Afterwards, the sample was cooled to 35°C and an inert gas was flowed to remove any impurities that might be left over due to the reduction. Then the pulse chemisorption took place. The dispersion of metal particles in the catalysts was estimated under the assumption of $CO:Pt = 1:1$ and $H_2:Pt = 1:2$ stoichiometry.

The software of micrometrics AutoChem II Chemisorption Analyzer used equations 5 and 6 to calculate the metal dispersion and the active particle size:

$$D_M = 100 \left(\frac{V_s * SF_{calc}}{SW * 22414} \right) GMW_{calc} \quad (5)$$

Where D_M is the metal dispersion, V_s is volume adsorbed (cm^3 at STP), SF_{calc} is the calculated stoichiometry factor, SW is the sample weight (g) and GMW_{calc} the gram molecular weight (g/mole).

$$Active \text{ particle size} = \frac{6}{D_{calc} * \left(\frac{SW}{GMW_{calc}} \right) * 6.023 * 10^{23} * SA_{calc}} \quad (6)$$

Where D_{calc} is the calculated metal density (g/cm^3) SW is the sample weight (g), GMW_{calc} the gram molecular weight (g/mole) and SA_{calc} is the calculated specific surface area (per gram of metal).

2.2.3 XRD

X-ray Diffraction was performed using Philips XRD in order to get an insight of the crystalline structure and the size of the Pt particles. For this analysis, a commercial 5 wt.% Pt/C was firstly measured, in order to create a method suitable for the made catalysts. Approximately 200 mg of each sample was brought into the XRD. The samples were scanned from 10° to 80° 2-theta.

2.2.4 ICP-OES

Inductively coupled plasma optical emission spectrometry (ICP-OES) Vista-MPX CCD Simultaneous was used to measure the platinum loading on the catalysts. Around 50 mg of each catalyst was weighed in order to get on the 1 – 5 mg Pt/L calibration curve. A harsh environment is created to dissolve the Pt, but also the activated carbon. For this, 4 mL nitric acid, 1 mL perchloric acid, 1 mL hydrogen peroxide and 1 mL MQ were added to the weighed catalyst. After this, the samples were microwaved in Ethos 1 microwave at 220°C for one hour and 20 min. After the samples were cooled down, they were diluted to 100 mL with MQ in a volumetric flask. Some of the samples needed a filtration step, because not all the AC had dissolved. 10 mL from this dilution was taken with 50 μL Yttrium as internal standard and analysed in the ICP-OES.

2.3 Heterogeneous oxidation of carbohydrates with Pt/AC catalysts

The substrates for the oxidations D-(+)-glucose ($C_6H_{12}O_6$, $\geq 99.5\%$), D-(+)-maltose monohydrate ($C_{12}H_{22}O_{11} \cdot H_2O$, $\geq 99\%$), and methyl α -D-glucopyranoside ($C_7H_{14}O_6$, $\geq 99\%$) were bought from Sigma-Aldrich. Maltotriose ($C_{18}H_{32}O_{16}$, $>95\%$) was bought from Megazyme. The oxidation of glucose was used as a model reaction; all catalysts oxidised this substrate. Only the chosen catalyst was used to oxidise the bigger substrates.

The oxidation reactions took place at the same conditions used by my predecessor, in order to be able to compare the performance of the Pt/AC catalysts with the Au/AC catalyst. This means: 50°C (323 K), pH 9 kept constant with pH stat Ω Metrohm 800 Dosino³ with a 0.5 M NaOH solution, O_2 -flow = 300 mL/min and substrate/metal ratio = 900 mole/mole with a 0.1 M substrate concentration. Demi water is used as solvent in a 150 mL volume.

Samples of 500 μL were taken during the reaction with a 1 mL Eppendorf volumetric pipette after 0 min, 15 min and 60 min for all reactions, and at the time the reactions were stopped. In order to filter the remaining catalyst from the samples, 1 mL Terumo[®] syringes with BD Microbalance[™] 3 needles were used in combination with a Phenomenex RC membrane 0.2 μ filter.

2.4 HPLC analysis of oxidation samples

In order to evaluate the performance of the catalyst, the samples taken during the oxidation were analysed with Dionex UltiMate 3000 RS autosampler HPLC on an Aminex HPX-87H, 300x7.8 mm (Bio-Rad 125-0140) column at 35°C . Both substrate and acid products can be measured with this column. All samples were diluted to a maximal concentration of 5 g/L. Calibration curves of the substrate and the main product were taken into each measurement, with concentrations of 0.1, 0.5, 1 and 5 g/L. The eluent used is 5 mM H_2SO_4 with a flow of 0.5 mL/min. 250 mM propionic acid in 1 M H_2SO_4 was used as internal standard.

There were no standards available for the oxidation products of maltose, maltotriose and methyl α -D-glucopyranoside. Therefore, a LC-MS analysis on Dionex UltiMate 3000 in combination with Thermo Scientific LCQ FLEET was performed in order to determine which product(s) was formed during the oxidation reactions. No quantitative measurements could be performed.

With the HPLC data of glucose, conversion, selectivity and the specific reaction rate of each catalyst could be calculated according to the following equations [41]:

$$\text{Conversion} = \frac{\text{initial [substrate]} - [\text{substrate}]_{\text{at } t}}{\text{Initial [substrate]}} * 100\% \quad (7)$$

$$\text{Selectivity} = \frac{\text{amount of main product at } t}{\text{initial amount of substrate} - \text{amount of substrate at } t} * 100\% \quad (8)$$

$$\text{Specific reaction rate} = \frac{\text{mole substrate converted at } t}{\text{gram metal present} * t} \quad (9)$$

In combination with the TEM and chemisorption data, the turnover frequency (TOF) could be calculated according to the following equation [9]:

$$\text{Turnover frequency} = \frac{\text{moles of substrate converted}}{\text{moles of surface metal} * \text{time}} \quad (10)$$

³ Ω Metrohm 877 Titrino plus was used for a part of the glucose oxidations because of a malfunction of Ω Metrohm 800 Dosino

With moles of surface metal defined as [13]:

$$\text{Moles of surface metal} = \text{moles}_{Pt} * \omega_{Pt} * D_{Pt} \quad (11)$$

Where moles_{Pt} is the total amount of Pt moles present in the reactor, ω_{Pt} is the Pt loading of this catalyst and D_{Pt} is the dispersion of the Pt particles on the catalyst.

3 Results and discussion

3.1 Stage 1: Finding the best technique to prepare a 1 wt.% Pt/AC suitable for starch oxidation

The first stage of this thesis consisted of preparing 14 catalysts with 3 different techniques: incipient wetness impregnation, sol immobilisation and ion adsorption. A summary of the preparation conditions is given in Table 2.

Table 2. Summary of the preparation condition of the different Pt/AC catalysts. The batches shown in orange were selected for the comparisons between the different preparation methods.

[Pt(NH ₃) ₄](NO ₃) ₂ and H ₂ PtCl ₆ ·xH ₂ O precursors used with all techniques							
Technique	Impregnation			Sol immobilisation		Ion adsorption	
Batch	1	2	3	1	2	1	
Calcination step	No	Yes	No	Not applicable	Not applicable	Yes	No
Reduction temperature	300°C	300°C	200°C	Not applicable	Not applicable	200°C	200°C

Only the data of the calcined and reduced at 300°C impregnated Pt/AC catalysts (batch 2), the with H₂PtCl₆·xH₂O prepared sol immobilisation catalysts and the non-calcined ion adsorption catalyst are shown in this chapter (shown in orange in Table 2). Two batches prepared with the same precursor are shown for sol immobilisation because no successful catalyst was obtained when using this technique in combination with the [Pt(NH₃)₄](NO₃)₂ precursor (see Section 3.1.1.2). These catalysts were chosen as a representation of their preparation method, as they showed the highest activity of the batches made. Looking back, a more logical choice would have been to select impregnation and ion adsorption catalysts made under the same conditions (calcination and reduction temperature). A commercial 5 wt.% Pt/AC was also tested, in order to have a reference. The data of the rest of the prepared catalysts is available in the Appendix.

3.1.1 Characterization of catalysts

The prepared catalysts were analysed with four characterization methods: TEM, chemisorption, XRD and ICP-OES, as described in Section 2.2.

3.1.1.1 Diameter of platinum particles

TEM

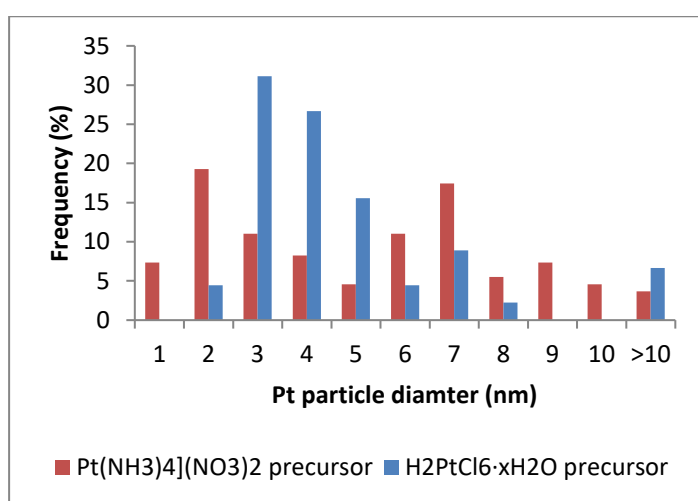
In order to measure the diameter of the platinum particles, calculate the average volume-surface diameter of the particles and to get an idea of the metal dispersion, the selected catalysts were observed with TEM. The commercial 5 wt.% Pt/AC was also analysed as reference.

Particle size distribution

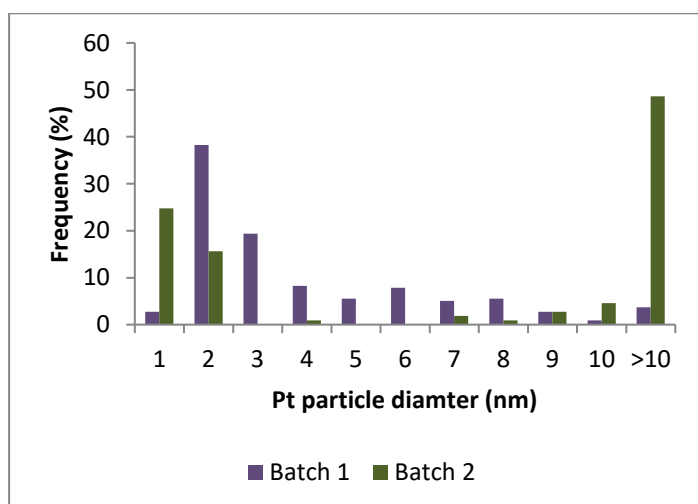
In Table 3 a summary of the particle analysis results is shown. The results are based on the TEM pictures, which can be found in Appendix I. The distribution of the particle size is depicted in Graph 1, Graph 2, Graph 3 and Graph 4 for each preparation method and the commercial catalyst.

Table 3. Particle analysis results from TEM photos

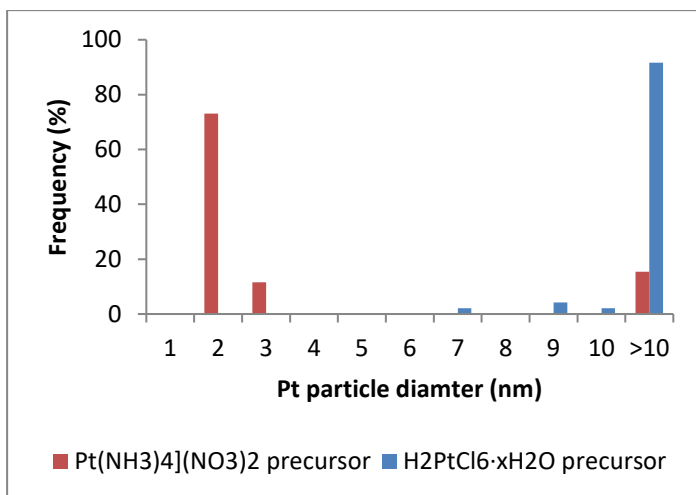
	Incipient wetness impregnation, calcined		Sol immobilisation		Ion adsorption		5 wt.% Pt/AC commercial catalyst
Precursor	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O	H ₂ PtCl ₆ ·xH ₂ O, batch 1	H ₂ PtCl ₆ ·xH ₂ O, batch 2	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O	
Average d (nm)	5.3	4.9	3.6	4.6	6.4	19.4	4.7
Standard deviation (nm)	2.2	2.4	2.4	3.2	3.6	6.9	8.4
Minimum d (nm)	1.2	1.8	0.8	0.7	1.5	7.3	0.9
Maximum d (nm)	12.7	16.0	19.7	22.3	78.5	39.0	99.3
Number of particles measured	109	45	217	109	26	48	485



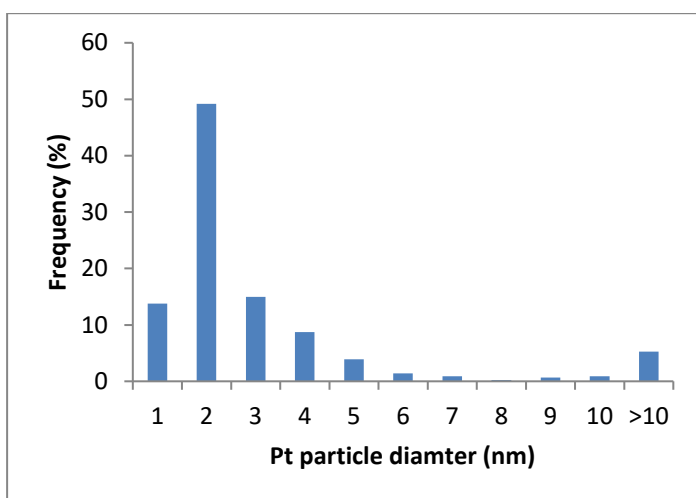
Graph 1. Particle size distribution of impregnated Pt/AC catalysts based on TEM images



Graph 2. Particle size distribution of sol immobilisation Pt/AC catalysts based on TEM images



Graph 3. Particle size distribution of ion adsorption Pt/AC catalysts based on TEM images



Graph 4. Particle size distribution of commercial 5 wt.% Pt/AC catalyst based on TEM images

The two impregnated catalysts have an irregular particle size distribution, independent of the precursor used. For the two different batches of sol immobilisation, made with the same precursor under the same conditions, a significant difference in particle size is observed. The second batch has a bimodal distribution, with almost 50% of its particles above 10 nm and the other half around the 2 nm, whereas only about 5% of the first batch's particles are above the 10 nm. This could indicate that the samples were not very representative or that the sol immobilisation technique is hard to reproduce. It is however rather unusual for a catalyst prepared with the sol immobilisation method to display particles larger than 10 nm [34].

The catalysts made with ion adsorption and [Pt(NH₃)₄](NO₃)₂ precursor had a few very large particles, but the vast majority is around 2 nm. As for the H₂PtCl₆·xH₂O precursor catalyst, mostly particles above the 10 nm were observed. The commercial catalyst had many small particles (2 nm) and a some big ones (50-100 nm), which was rather unexpected.

Average volume-surface diameter and dispersion calculation of platinum particles

The average volume-surface diameter (d_{vs}) is calculated according to Equation 4 shown in Section 2.2.1. With d_{vs} , the metal dispersion of the catalysts was calculated following Equation 3 (Section 2.2.1). The results are depicted in Table 4. For the calculation of d_{vs} , the bigger particle diameters d (above 20 nm) were left out, since they do not contribute to the active surface of the catalyst due to their size.

Table 4. Calculated average volume-surface diameter and calculated metal dispersion from TEM data

	Incipient wetness impregnation, calcined		Sol immobilisation		Ion adsorption		5 wt.% Pt/AC commercial catalyst
Precursor	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·x H ₂ O	H ₂ PtCl ₆ ·xH ₂ O, batch 1	H ₂ PtCl ₆ ·xH ₂ O, batch 2	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·x H ₂ O	
Average volume-surface diameter of platinum particles d _{vs} (nm)	8.0	9.3	9.6	14.7	12.9	15.9	9.2
Metal dispersion	11.3%	9.7%	9.4%	6.2%	7.0%	5.7%	9.8%

The lowest average volume-surface diameter is observed for the impregnated with [Pt(NH₃)₄](NO₃)₂ precursor catalyst. For impregnated Pt/AC catalysts reduced at 300°C, a particle size of 2-17 nm is expected [42], this corresponds with the found values. The average diameter (d) of the platinum particles obtained with sol immobilisation should not overpass the 10 nm [34, 43]. The values encountered are not as expected for this technique. This also seems to be the case for the ion adsorption catalysts, where an average of 1-2 nm is ordinary [40]. Why these big differences in particle size were obtained is not known.

According to Equation 3 (Section 2.2.1) the dispersion of the particles is indirectly proportional to the average volume-surface diameter of the particles. In general a low particle dispersion is observed for all samples measured. Another definition of dispersion is:

$$D = \frac{N_S}{N_T} \quad (12)$$

Where N_S is the number of surface atoms and N_T the total number of atoms present. Hence, a low dispersion indicates a low number of surface atoms. The surface atoms are the ones in contact with the substrate and therefore responsible for the catalytic activity. According to TEM data, incipient wetness impregnation seems to give the lowest average volume-surface diameter and the highest metal dispersion of all techniques.

Chemisorption

As described in Section 2.2.2, pulse chemisorption with CO and H₂ was carried out. However, the measurements with CO chemisorption gave rather doubtful results. Because of this, it was decided to leave these values out of the Results and discussion chapter. The comparison between H₂ and CO chemisorption can be found in Appendix II. The results of the calculations on the H₂ chemisorption are shown in Table 5.

Table 5. Average diameter of platinum particles according to H₂ pulse chemisorption results

H ₂ chemisorption	Incipient wetness impregnation, calcined		Sol immobilisation		Ion adsorption		5 wt.% Pt/AC commercial catalyst
Precursor	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·x H ₂ O	H ₂ PtCl ₆ ·xH ₂ O, batch 1	H ₂ PtCl ₆ ·xH ₂ O, batch 2	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·x H ₂ O	
Metal dispersion	20.2%	35.6%	2.4%	1.8%	3.2%	20.8%	36.8%
Average diameter (hemisphere) of Pt particles (nm)	5.6	3.2	48.2	61.7	35.1	5.5	3.1

What stands out immediately is the big particle size of the sol immobilisation catalysts. When looking at the H₂ uptake graph of these two catalysts (not shown), a negligible absorbance was observed. This

probably means that the catalysts did not absorb any H_2 and the numbers shown are a result of poor integration. A reason for the reduced absorption could be PVA-chains attached to the Pt atoms that were not washed off during the refluxing step (see Section 2.1.2).

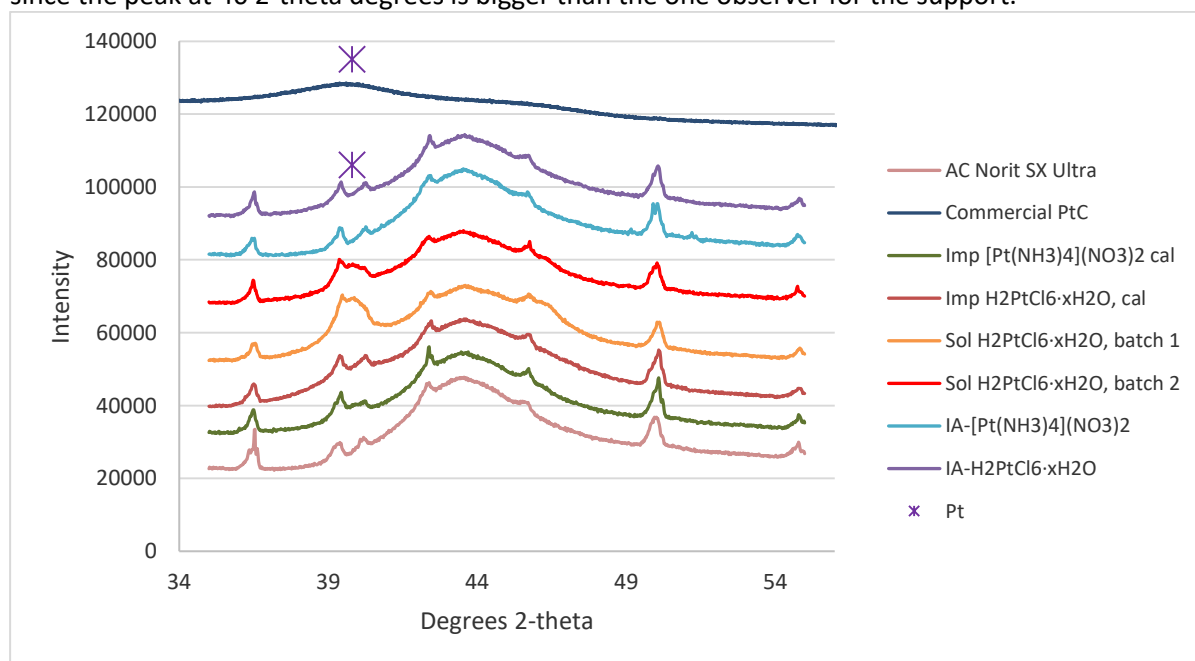
These catalysts were characterized right after they were prepared. Since the sol immobilisation catalysts did have a good oxidation performance (see Section 3.1.3), it was assumed that, if there were PVA-chains still attached to the Pt atoms, they got de-attached during the reaction. This is why the spent sol immobilisation catalysts were also measured, but without any better chemisorption. An explanation could be the adsorption of the substrate on the catalyst. The spent sol immobilisation catalyst from batch 1 was washed with 1 L demi-water, in an attempt to de-attach the substrate. Again, no better chemisorption was obtained. (See Appendix II for results).

Another catalyst with big average particle size is the with $[Pt(NH_3)_4](NO_3)_2$ prepared ion adsorption, in contrast to its counterpart with $H_2PtCl_6 \cdot xH_2O$ prepared catalyst. The smallest average particle size was observed by the commercial catalyst. According to the chemisorption data, incipient wetness impregnation seems to be the best technique if one intends to obtain particles below the 10 nm, regardless of the precursor.

XRD

The catalysts, as well as the support (AC Norit SX Ultra) were analysed with XRD from 10 to 80 degrees 2-theta. In general the XRD couldn't measure much platinum because of the low loading of the catalysts; most of the catalysts' diffractograms are similar to the support's diffractogram. The major platinum peak was found at 40 degrees 2-theta, which is why a deeper scanning of the region from 34 to 55 degrees 2-theta was conducted. The results are shown in Graph 5.

There were several peaks encountered in the support's diffractogram, which was unexpected since activated carbon is usually an amorphous compound. These peaks correspond to graphite peaks. Unfortunately, one of these peaks overlaps with the platinum peak at 40 degrees 2-theta, making it difficult to make calculations from these data. The results of these calculations are shown in Table 6. It is visible in Graph 5 that the two sol immobilisation batches have relatively large platinum particles, since the peak at 40 2-theta degrees is bigger than the one observed for the support.



Graph 5. XRD diffractograms of differently prepared Pt/AC catalysts. The purple star indicates the platinum peak for the commercial catalysts and one time for one of the prepared catalysts. Imp=impregnated, Sol= sol immobilisation, IA=ion adsorption, cal=calcined.

The diameter of the platinum particles on the two ion adsorption catalysts could not be determined with this technique, because the amount of platinum present was not enough to produce a clear peak. The difference in diffractograms was too low to give a significant value. It is important to mention this apparatus is not able to measure particles below the 3 nm, the values given are an average of all the particles above this value. As was visible from the diffractograms, the average size of the platinum particles is bigger for the sol immobilisation catalysts.

Table 6. Particle size obtained from XRD diffractogram

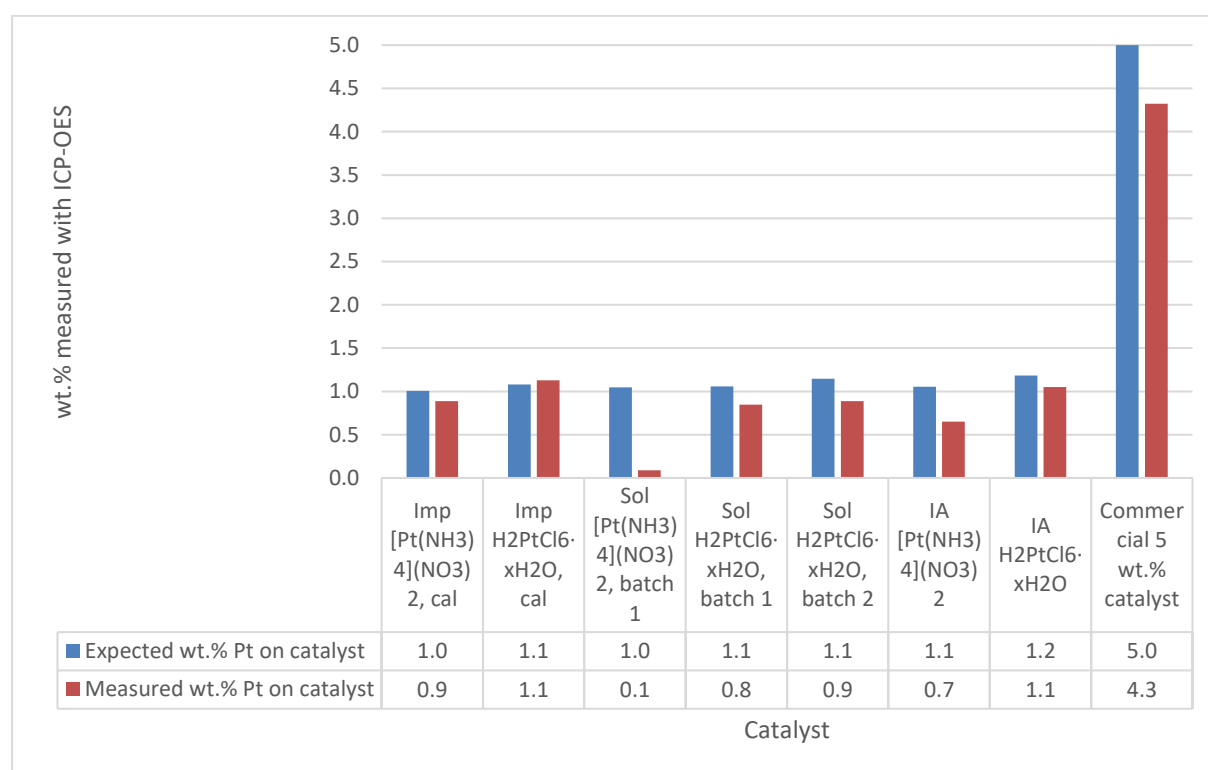
	Incipient wetness impregnation, calcined		Sol immobilisation		Ion adsorption		5 wt.% Pt/AC commercial catalyst
Precursor	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O	H ₂ PtCl ₆ ·xH ₂ O, batch 1	H ₂ PtCl ₆ ·xH ₂ O, batch 2	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O	
Average diameter of Pt particles (nm)	7	3	6	8	Not possible to determine	Not possible to determine	Not determined

3.1.1.2 Pt-loading

ICP-OES

With ICP-OES the success of the different preparation techniques could be verified, by comparing the theoretical with the actual platinum loading of the catalysts. The theoretical loading is based on the platinum added during the preparation of the catalyst, it is the maximum loading possible. Except for one catalyst, the prepared catalysts had a loading very similar to the theoretical one. The results of the measurements are shown in Graph 6.

The platinum content of the H₂PtCl₆·xH₂O precursor is somewhere between the 37-40% according to Sigma Aldrich. A platinum content of 40.4% was measured with ICP-OES. This value was assumed for the calculation of the theoretical loading of the with this precursor made catalysts.



Graph 6. Expected loading and loading measured with ICP-OES on Pt/AC. Imp=impregnated, Sol=sol immobilisation, IA=ion adsorption, cal=calcined.

In general the loading measured with ICP-OES was closer to the theoretical loading when using the $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor, independent of the technique used.

The sol immobilisation prepared with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ had a neglectable loading measured with ICP-OES. A second sol immobilisation batch was prepared, without better outcomes for this precursor. Apparently, the platinum sol formed (if there was a sol formed at all) from $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ via the method of Pazhavelikkakath Purushothaman et al. [39] does not have a high affinity for the support.

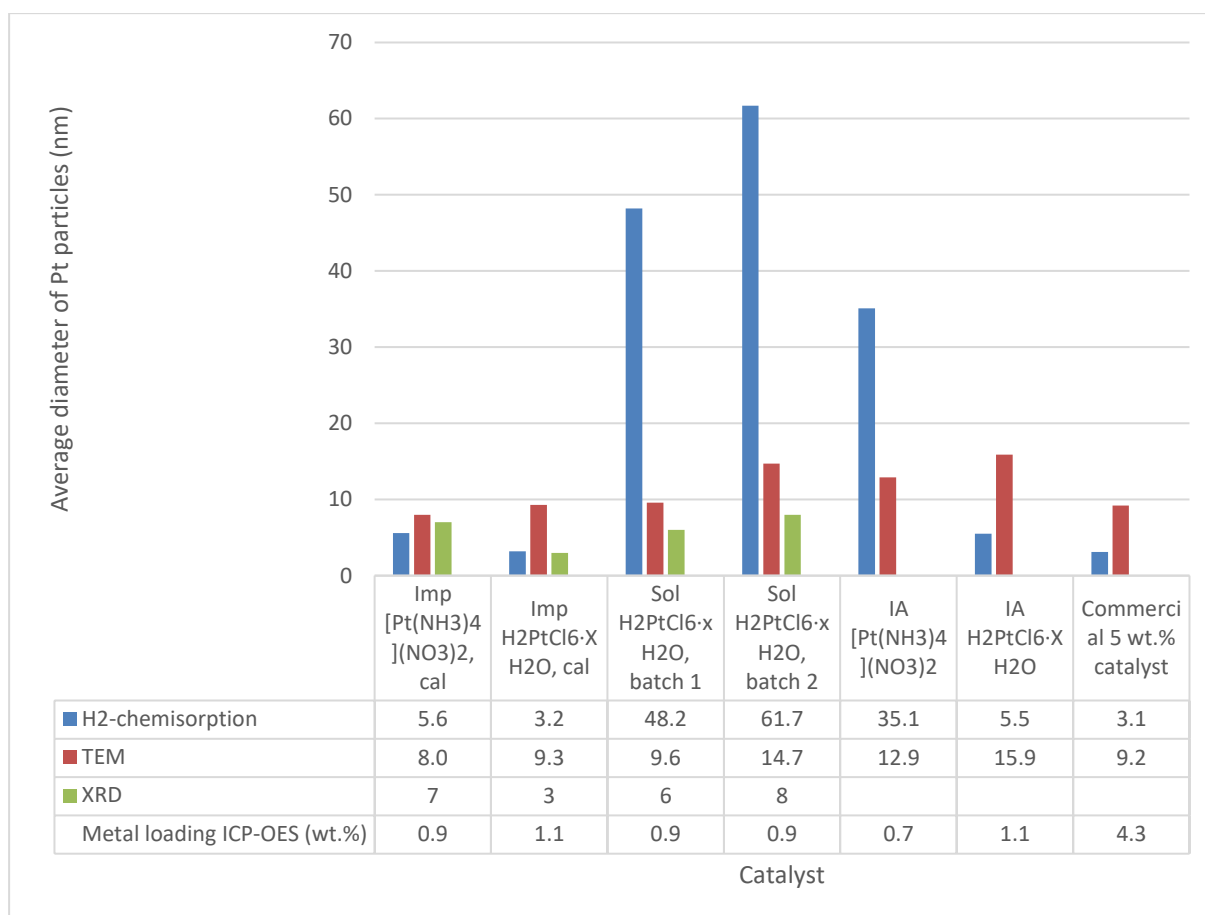
For the impregnations it was thought that the platinum loading could be enhanced by adjusting the pH of the precursor solution before adding it to the support. The support Norit SX ULTRA activated carbon has a point of zero charge at pH 8.1 [36]. Both precursor solutions are acidic (the stock solution of $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ had a pH of 1.02 and the $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ solution a pH of 3.88), meaning that the impregnation took place in an acidic environment and the support had an overall positive charge. For the $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor this was desired, since the ion that interacts with the support has a negative charge (PtCl_6^{2-}). The $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ precursor on the other hand gives a positive Pt^{2+} ion, which can be repelled by the also positively charged support.

In the third impregnation batch the pH of the $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ solution was adjusted to 9.23 with diluted 25% ammonia solution. This did not result in a higher platinum loading for this precursor (see Appendix IV). However, the loading of the with $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor impregnated catalysts from this batch was also lower than the batches before. Since this impregnation batch deviated from the two made previously, it is difficult to say whether the pH-adjustment would have resulted in a higher loading for the $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ precursor. However, for the other two techniques the pH was taken into account for both precursors and it still resulted in lower Pt loading for the with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ precursor prepared catalysts.

To test the reliability of ICP-OES, the precursor $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ used during the preparation of the catalysts was measured as well. The values found with ICP-OES correspond with the expected platinum content of the precursor. Also two old samples were measured again in a second measurement, to see if there were significant differences. This turned out not to be the case. Therefore, it is concluded that this technique is precise enough to give insight on the platinum lost due to leaching during the reactions (see Section 3.1.3).

3.1.1.3 Summary of characterization

There were 4 techniques used to characterize the differently prepared catalysts and 3 parameters obtained: average particle diameter size (measured with TEM, chemisorption and XRD), metal dispersion (calculated with TEM and chemisorption) and metal loading (measured with ICP-OES). Three different techniques were used to measure the particle size because this gives a better idea about the actual size of the platinum particles. The comparison of the particle size measured with different methods is given in Graph 7.



Graph 7. Comparison of the average diameter of the platinum particles calculated with TEM data, chemisorption and XRD. Imp=impregnated, Sol= sol immobilisation, IA=ion adsorption.

When looking at the impregnated catalysts, the catalyst prepared with H₂PtCl₆·xH₂O precursor seems to give smaller particles and a higher metal loading. However, the differences are not very big and the TEM values are almost identical. For impregnation the most suited precursor would be H₂PtCl₆·xH₂O, based on this data.

As was discussed earlier, the chemisorption results for the with sol immobilisation prepared catalysts are not very reliable, since probably something (either PVA or substrates from the oxidation) remained attached to the Pt particles, disturbing the H₂ uptake. These attached molecules do not interfere with the other two characterization techniques.

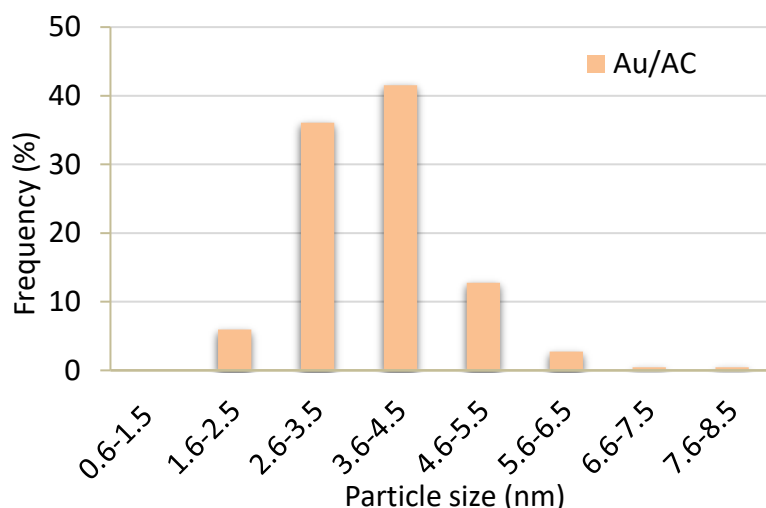
A significant difference is observed between the particle size of the sol immobilisation catalysts measured with TEM, while the XRD results state that they have almost the same average particle size. This is probably because the XRD is unable to measure particles under the 3 nm. When looking at Graph 2, a larger amount of particles under the 3 nm is observed for the first batch, producing a lower average for the TEM results of batch 1.

The chemisorption data suggests that the with ion adsorption and [Pt(NH₃)₄](NO₃)₂ precursor prepared catalyst has a much higher average particle size than its counterpart with H₂PtCl₆·xH₂O precursor. This is in complete discordance with TEM data, where it was visible at the particle size distribution graphs (Graph 3) that the ion adsorption Pt/AC with H₂PtCl₆·xH₂O precursor had almost only particles above the 10 nm. An explanation could be that only a very small and unrepresentative fraction of the two catalysts was observed during the TEM analysis.

There does not seem to be a connexion between the platinum loading of the catalyst and the average particle size or the dispersion of the platinum particles. All three techniques suggest that impregnation is the best technique to obtain a catalyst with small average particle size.

3.1.2 Finding the Pt/AC catalyst most similar to the Au/AC catalyst from previous work

The gold catalyst on activated carbon prepared with sol immobilisation in previous work had a metal loading of 0.9-1.0 wt.% and an average volume-surface diameter size of platinum particles d_{vs} (calculated from TEM data) of 4.3 nm. The particle size distribution is shown in Graph 8.



Graph 8. Particle size distribution of Au/AC made in previous work [15].

When comparing the average volume-surface diameter size of platinum particles d_{vs} , none of the prepared Pt/AC meets the requirements, as they all have an average above the 8.0 nm. When looking at the particle size distribution, the impregnated with $H_2PtCl_6 \cdot xH_2O$ precursor catalysts comes very close (see Graph 8 and Graph 1). However, its d_{vs} is 9.3 nm, more than twice as much as the gold catalyst. As for the metal loading, only the with $[Pt(NH_3)_4](NO_3)_2$ precursor sol immobilisation (0.1 wt.%) and ion adsorption (0.7 wt.%) do not come close to the loading of the Au/AC (see Graph 6). When looking at TEM pictures, the sol immobilisation Pt/AC catalysts do look the most like the Au/AC (see Appendix I). However, the Pt/AC catalysts made with sol immobilisation do have some big platinum particles, while these do not occur with the Au/AC (or at least they were not seen with TEM).

From the Pt/AC made during this research, it would have been expected that catalysts prepared by sol immobilisation are the most similar to the Au/AC, since the preparation method is practically the same. However, it is safe to say that none of the catalysts made is physically similar to the Au/AC made in previous work.

3.1.3 Oxidation performance

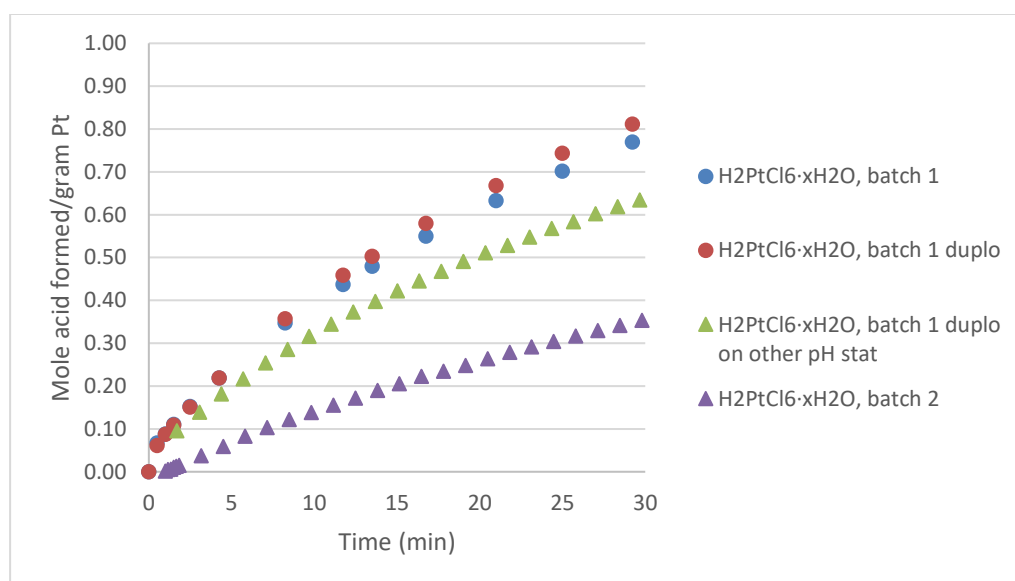
The heterogeneous oxidation of glucose was used as model reaction to look at the performances of the differently prepared catalysts. All reactions were conducted under the same conditions, as specified in Section 2.3. The catalysts prepared by sol immobilisation and $[Pt(NH_3)_4](NO_3)_2$ precursor were not tested because of the low Pt loading measured with ICP-OES (see Section 3.1.1.2)

Base addition

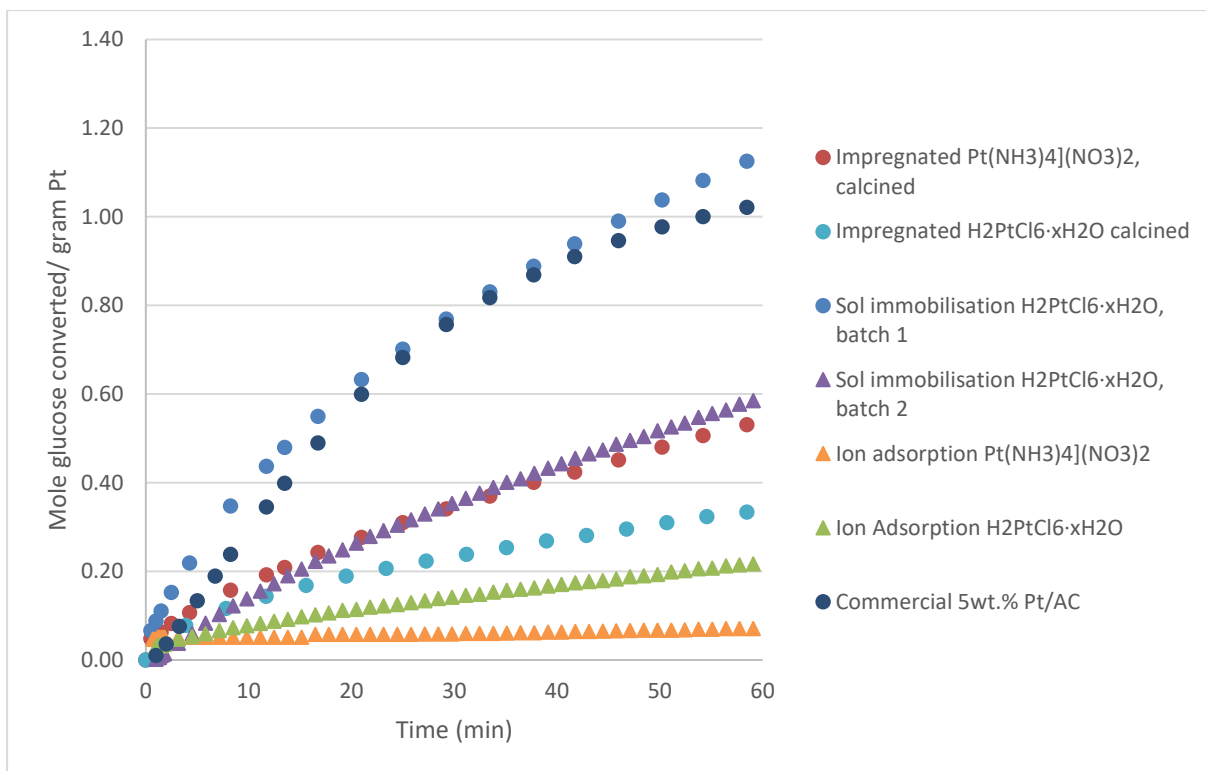
It is assumed that per mole base added to the reaction mixture by the pH-stats to maintain the pH at 9.0, a mole acid is formed. Following this, the formation of acid products can be calculated. In case of 100% selectivity, this corresponds to the moles gluconic acid formed. In Graph 10 the acid production

per gram platinum is shown for the selected catalysts in the first hour of the reaction. The catalytic activity of all made catalysts is shown in Appendix V.

As was said in Section 2.3, two different pH-stats were used to maintain the pH at 9.0. In order to check whether the base added by the second pH-stat corresponded with the first pH-stat, two duplo experiments were conducted. A slower base addition was observed with the second pH-stat, the reason could be a malfunctioning electrode. Since it is not known which pH-stat worked properly, it is risky to make conclusion from this information. However, it gives an indication of the course of the reaction. In Graph 9 a comparison between the two pH-stats is shown. In the graphs the measuring points of pH-stat 1 (Ω Metrohm 800 Dosino) are given with dots and the measuring points of pH-stat 2 (Ω Metrohm 877 Titrino plus) are given with triangles.



Graph 9. Comparison between the two different pH-stats. The sol immobilisation catalysts were used as reference. The dotted lines show base addition from pH-stat 1, the triangle lines from pH-stat 2.



Graph 10. Catalytic activity of the different platinum catalysts during the first 60 min of glucose oxidation. The dotted lines show base addition from pH-stat 1, the triangle lines from pH-stat 2.

The first sol immobilisation batch catalyst has a similar activity to the commercial catalyst and even seems to continue the reaction where the commercial catalysts' activity starts to decrease. Both of the sol immobilisation batches have the greatest activity from the made catalysts, on both pH-stats. The impregnated with $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ catalyst seems to have a similar activity to the second sol immobilisation batch catalyst. However, since the data are from two different pH-stats it is not possible to make a fair comparison.

The impregnated with $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ catalyst has a higher activity than the with $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor prepared catalyst. By the ion adsorption catalysts a similar difference is observed in activity, but now the catalyst prepared with $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor has the higher activity; the catalyst prepared with $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ precursor barely had any activity at all. Since a comparison between the two precursors cannot be made for the sol immobilisation catalysts, no conclusion can be drawn about which precursor leads to the catalyst with the highest activity.

HPLC

With the data obtained from the HPLC analysis, the amount of glucose and gluconic acid per sample could be calculated. With these values different results were obtained, which are displayed in Table 7. Separate graphs of the data of each catalyst can be found in Appendix V.

Table 7. Oxidation performance of Pt/AC prepared with different techniques based on HPLC data

	Incipient wetness impregnation, calcined		Sol immobilisation		Ion adsorption		Commercial 5 wt.% catalyst
Precursor	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O	H ₂ PtCl ₆ ·xH ₂ O, batch 1	H ₂ PtCl ₆ ·xH ₂ O, batch 2	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O	
Conversion after 60 min	14%	11%	17%	13%	7%	9%	100%
Time to reach 10% conversion (min)	22.2	43.5	8.0	34.4	91.6	65.2	Less than 5 minutes
Specific reaction rate after 60 min (mole/g metal*min)	1.04E-02	5.26E-03	1.05E-02	9.90E-03	6.64E-03	6.17E-03	2.52E-02
Selectivity to gluconic acid at 10% conversion	89%	100%	98%	96%	8%	69%	100%

The highest specific reaction rates are observed with the first sol immobilisation H₂PtCl₆·xH₂O precursor batch and the Pt(NH₃)₄](NO₃)₂ impregnated catalyst. However, the sol immobilisation catalyst reaches 10% conversion faster than the impregnated catalyst. It has been shown that the use of H₂PtCl₆·xH₂O as a precursor can cause sintering of the Pt atoms due to the presence of chlorine in the catalyst [44]. This would explain why after 60 minutes the conversions reached by both catalyst are in the same range. However, this is not visible when looking at Graph 10.

The outcomes of the HPLC data for the two impregnated catalysts are in tune with the base addition results. The same applies to the ion adsorption catalysts. The only remarkable thing is that the specific reaction rate of the [Pt(NH₃)₄](NO₃)₂ ion adsorption catalyst is higher than that of the H₂PtCl₆·xH₂O catalyst, while its conversion after 60 minutes is lower. It is hard to say if the two different sol immobilisation batches behave as expected on the base addition data, since the pH was monitored on two different pH-stats.

There is a significant difference in performance between the sol immobilisation batches when looking at the HPLC data (Table 7). The specific reaction rate of the first batch is higher, as is the conversion reached after 60 minutes. When it is taken into account that the first sol immobilisation batch had a smaller average particle size than the second batch, this outcome is predictable. However, not all catalytic performances follow the expectations based on average particle size (see Section 3.1.1.1).

The selectivity of the catalyst prepared by ion adsorption with [Pt(NH₃)₄](NO₃)₂ precursor was calculated at 8%. However, this does not seem very realistic. This value is probably the result of a very low conversion, difficult for the HPLC to detect. Something remarkable from the data shown in Table 7 is that the selectivity to gluconic acid seems to be higher for the catalysts prepared with H₂PtCl₆·xH₂O precursor than for the catalysts prepared with Pt(NH₃)₄](NO₃)₂ precursor.

Leaching

After each oxidation the catalyst used was filtered and dried in the oven at 60°C. The platinum loading of these spent catalysts was measured with ICP-OES, in order to determine whether leaching is an important problem during the reaction. The results are shown in Table 8.

Table 8. ICP-OES results from catalysts before and after the oxidation, used to measure the amount of platinum that leaches from the catalysts.

	Incipient wetness impregnation, calcined		Sol immobilisation		Ion adsorption		5 wt.% Pt/AC commercial catalyst
Precursor	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O	H ₂ PtCl ₆ ·xH ₂ O, batch 1	H ₂ PtCl ₆ ·xH ₂ O, batch 2	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O	
Reaction stopped after...	44 h	65 h	20 h	2.5 h	1 h	3 h	2 h
Loading before oxidation	0.9%	1.1%	0.9%	0.9%	0.7%	1.1%	4.3%
Loading after oxidation	0.8%	0.7%	0.7%	0.7%	0.5%	.8%	Not measured
Platinum lost due to leaching	0.1%	0.4%	0.2%	0.2%	.2%	0.3%	Not measured
Percentage of platinum lost due to leaching	14.6%	34.5%	21.2%	24.7%	24.6%	26.7%	Not measured

The duration of the oxidations varied strongly for each catalyst. The most stable catalysts seems to be the impregnated and calcined with [Pt(NH₃)₄](NO₃)₂ precursor, which after 44 hours of reaction lost 14.6% of its platinum content. This in contrast to its impregnated counterpart, which lost almost 2 times as much platinum in a comparable range of time. For the sol immobilisation it doesn't seem to matter whether the reaction takes 2.5 or 20 hours, the leaching is very similar. The ion adsorption catalysts have a slightly higher leaching than the sol immobilisation catalysts, but since the reactions were stopped earlier it is not possible to say if this would have increased with time.

In general it is safe to say that significant leaching of platinum does occur under the oxidation conditions. Leaching of platinum is a common problem, but not in these amounts. Values of 0.8 to 1.5% of the platinum content loss were encountered when used for the oxidation of alcohols [45, 46]. Why such high leaching values were found with these catalysts is not known.

TOF calculation

The turnover frequency was calculated according to Equation 10 of Section 2.4. Results of these calculations are shown in Table 9. Only the TOF values based on the TEM results are shown, since the chemisorption data for the sol immobilisation catalysts are dubious. For TOF values calculated with chemisorption data see Appendix V.

Table 9. Turnover frequencies (TOFs) of the catalysts prepared based on TEM data. The TOF is defined as mole substrate converted per mole surface metal * time (s⁻¹).

	Incipient wetness impregnation, calcined		Sol immobilisation		Ion adsorption		5 wt.% Pt/AC commercial catalyst
Precursor	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O	H ₂ PtCl ₆ ·xH ₂ O, batch 1	H ₂ PtCl ₆ ·xH ₂ O, batch 2	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O	
TOF at 10% conversion with TEM data (s ⁻¹)	0.46	0.29	0.73	0.52	0.31	0.35	0.83

When looking at the TOFs calculated with TEM data all the values are in the same range. The sol immobilisation catalyst of the first batch has the highest value, which comes close to the TOF value of the commercial catalyst. The TOF from the second sol immobilisation batch is somewhat lower and comparable to the TOF from the impregnated with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ catalyst. The 3 remaining catalysts have slightly lower and similar TOF values.

Something remarkable is the fact that the size of the platinum particles does not seem to have a big impact on the TOF of the ion adsorption catalysts. Around 92% of the particles from the catalyst prepared with ion adsorption and $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ are above the 10 nm, and it has an even higher TOF than its counterpart with 85% of its particles around the 2-3 nm (see Section 3.1.1.1). It does seem to influence the sol immobilisation catalysts, where a clear difference in TOF can be linked to the higher amount of particles above the 10 nm found in the second batch.

Influence of calcination

During the preparation of the catalysts, some batches of the impregnated and ion adsorption catalysts were calcined. The influence of this step was investigated. A comparison is made on average particle size, metal loading and oxidation performance, visible in Table 10. Since chemisorption was the only technique used to measure all made catalysts, it is the only value shown for the average particle size.

In the case of the catalysts made by impregnation with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ precursor, calcination seems to increase the metal loading. This means that the NH_3 and NO_3 groups are successfully removed during this step. This also reflects in the oxidation performance; the calcined catalyst has a higher activity than the non-calcined catalyst.

The non-calcined and calcined catalysts impregnated with $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ have the same metal loading. This is expected, since elimination of chlorides by calcination is not that easy to achieve. The oxidation performance of the two catalysts is also virtually the same.

As for the ion adsorption catalysts, it immediately stands out that both of the catalysts prepared with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ precursor have a very large average particle size. Both do have a low metal loading; it is possible that the amount of catalyst put into the chemisorption apparatus was not enough to make a significant measurement.

No major differences are observed in the metal loading for the calcined and non-calcined ion adsorption catalysts, meaning that there are probably no groups removed from the support during calcination. Considering this, one would expect no influence of the calcination step at all. However, a decrease in oxidation performance is observed by the calcined catalysts prepared with ion adsorption. It could be that, since there were no groups available to eliminate during the calcination step, the heat treatment caused sintering of the platinum particles. The average particle size of the calcined catalyst prepared by ion adsorption with $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ is higher than the non-calcined version of this catalyst, reinforcing this statement. However, this trend is not visible by the catalysts prepared by ion adsorption with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ precursor. Nevertheless, as stated earlier, it is possible that the values found for the average particle size are not very reliable because of the low loading of the catalysts.

Summarizing, calcination seems to be beneficial for the preparation of an impregnated catalyst with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ precursor. There seems to be no influence when calcining an impregnated catalyst prepared with $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor. Calcination has prejudicial effects on ion adsorption catalysts.

Table 10. Comparison between calcined and non-calcined catalysts. The batches used for comparison in the Results and Discussion section are shown in orange. The data related to each other is shown in the same colour.

	Incipient wetness impregnation		Incipient wetness impregnation, calcined		Ion adsorption		Ion adsorption, calcined	
Precursor	$[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$	$\text{H}_2\text{PtCl}_6 \cdot x \text{H}_2\text{O}$	$[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$	$\text{H}_2\text{PtCl}_6 \cdot x \text{H}_2\text{O}$	$[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$	$\text{H}_2\text{PtCl}_6 \cdot x \text{H}_2\text{O}$	$[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$	$\text{H}_2\text{PtCl}_6 \cdot x \text{H}_2\text{O}$
Reduction temperature	300°C				200°C			
Average diameter (hemisphere) of Pt particles (nm) H_2 chemisorption	3.0	5.6	5.6	3.2	35.1	5.5	25.4	7.2
Expected theoretical loading (wt.%)	0.9	1.0	1.0	1.1	1.1	1.2	1.1	1.2
Loading measured with ICP-OES (wt.%)	0.7	1.0	0.9	1.1	0.7	1.1	0.7	1.0
Conversion after 60 min	8%	11%	14%	11%	7%	9%	5%	-
Specific reaction rate after 60 min (mole/g metal*min)	4.01E-03	4.77E-03	1.04E-02	5.26E-03	6.64E-03	6.17E-03	1.61E-03	-
Time to reach 10% conversion (min)	112.3	43.6	22.2	43.5	91.56	65.23	154.0	85.6
Amount of substrate converted at 10% conversion (moles)	5.49E-04	4.28E-04	7.09E-04	3.44E-04	8.46E-04	6.82E-04	4.72E-04	7.24E-04
Selectivity to gluconic acid at 10% conversion	94%	100%	100%	100%	8%	54%	34%	20%

3.1.4 Selection of suitable catalyst for the oxidation of starch

All relevant data obtained from the characterization techniques and the oxidation performances is shown in Table 11. To facilitate the comparison between the different preparation techniques, the results from batch 1 and 2 of the sol immobilisation catalysts were averaged. It was chosen to show only the average particle size and not the dispersion, since these values are linked to one another. Moreover, there is no equation available to calculate the dispersion based on average particle size measured with XRD.

The desired catalyst has:

- A low average particle size with a narrow particle distribution
- Metal loading close to the theoretical loading
- High turnover frequency
- Little or no platinum leaching

Table 11. Summary of the characterization of the platinum catalysts. The data related to each other is shown in the same colour.

	Incipient wetness impregnation, calcined		Sol immobilisation	Ion adsorption	
Precursor	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O	H ₂ PtCl ₆ ·xH ₂ O batch 1 and 2, averaged	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O
Average volume-surface diameter of platinum particles (nm) TEM	8.0	9.3	12.2	12.9	15.9
Average diameter (hemisphere) of Pt particles (nm) chemisorption	5.6	3.2	55.0	35.1	5.5
Average diameter of Pt particles (nm)	7	3	7	-	-
Expected Pt loading ICP-OES (wt.%)	1.0	1.1	1.1	1.1	1.2
Pt loading ICP-OES (wt.%)	0.9	1.1	0.9	0.7	1.1
Specific reaction rate after 60 min (mole/g metal*min)	1.04E-02	5.26E-03	1.02E-02	6.64E-03	6.17E-03
Time to reach 10% conversion (min)	22.2	43.5	21.2	91.6	65.2
TOF at 10% conversion with TEM data (s ⁻¹)	0.46	0.29	0.63	0.31	0.35
Selectivity to gluconic acid at 10% conversion	89%	100%	97%	8%	69%
Percentage of platinum lost due to leaching	14.6%	34.5%	23.0%	24.6%	26.7%

In Table 11 the catalyst that meets (or is the closest to) the requirement mentioned above is marked in green. Immediately, when not taking into consideration the chemisorption data because of its dubious reliability, three catalysts stand out: both the impregnated catalysts and the sol immobilisation catalyst. However, when looking at catalytic performance, the catalyst impregnated with [Pt(NH₃)₄](NO₃)₂ precursor has the highest activity and is therefore compared with the sol immobilisation catalyst.

The impregnated catalyst has a smaller average particle size than the sol immobilisation catalyst according to the TEM data. However, it is important to recall the distribution of the particle size of these two catalysts (see Section 3.1.1.1). The impregnated catalyst had a broad range of different sizes,

whereas the sol immobilisation had a bimodal distribution, with particles around the 2 nm and particles above the 10 nm. It is expected that smaller particles will contribute more to the enhancement of the catalysts' activity.

Since the chemisorption data for the sol immobilisation catalysts is unreliable, it will not be discussed. The platinum loading and the specific reaction rate of the impregnated and sol immobilisation catalyst are practically the same. The sol immobilisation catalyst reaches 10% conversion earlier than its impregnated counterpart and has a higher TOF value, but it leaches more platinum. When considering starch oxidation, the impregnated catalyst is the better candidate.

Because of the better performance of the sol immobilisation catalyst and the assumption that its small particles have a high influence on this performance, this catalyst was chosen to continue this research.

3.2 Stage 2: Further oxidations with sol immobilisation

$\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ catalyst

During this stage, the catalyst prepared with sol immobilisation and $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor was used to oxidise maltose, maltotriose and methyl α -D-glucopyranoside. It is important to inform the reader that for these oxidations the second batch of the sol immobilisation catalyst was used, as the first one was spent. The influence of the molecular weight of the substrate and a comparison with the performance of the Au/AC catalyst made in previous work was investigated.

3.2.1 Influence of molecular weight of the substrate on the performance of Pt/AC

The reaction conditions for the oxidation of maltose and maltotriose were the same as for glucose oxidation. The base addition for glucose, maltose and maltotriose oxidation is shown in Graph 11. For the comparison of the Pt/AC catalysts with the Au/AC catalysts when oxidising these three substrates, only the base addition during the reaction was taken into consideration. Since the pH of the three reactions was held constant with the same device, the results are comparable. Furthermore, it is impossible to measure the conversion with HPLC, as the substrates and products of the three substrates have very similar retention times. It is only possible to make a distinction between the substrate and product peaks if standards of both are available. This is the case for glucose and gluconic acid, but not for the products of maltose and maltotriose. Nonetheless, HPLC chromatograms of the oxidation of maltose and maltotriose are available in Appendix V.

In order to determine whether the products formed were indeed the oxidised versions of maltose and maltotriose, mass spectroscopy of the samples were conducted. The expected masses of 358 m/z for maltobionic acid and 520 m/z for maltotronic acid confirmed their presence. The mass spectra are shown in the Appendix. Below the structures of the substrates and products are shown in Figure 4 and Figure 5.

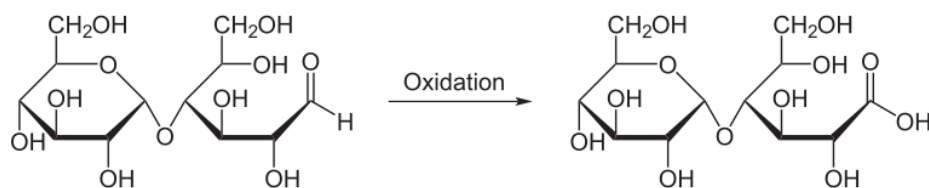


Figure 4. Oxidation of maltose to maltobionic acid

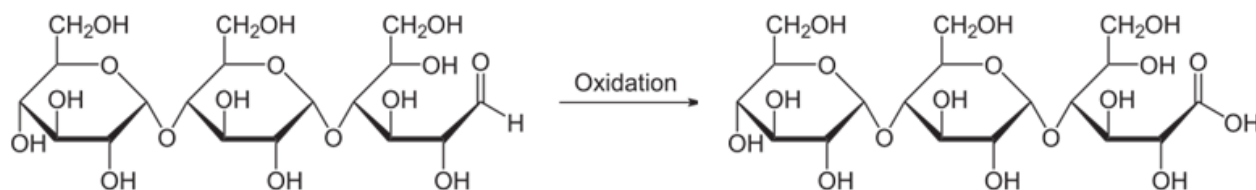
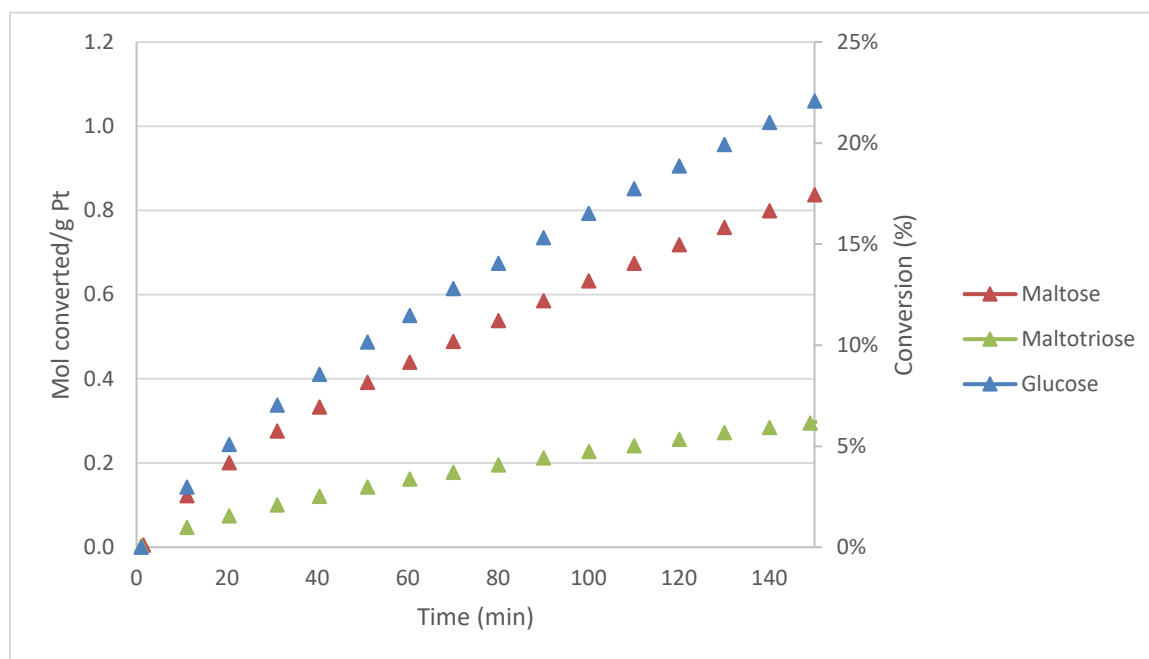


Figure 5. Oxidation of maltotriose to maltotrionic acid

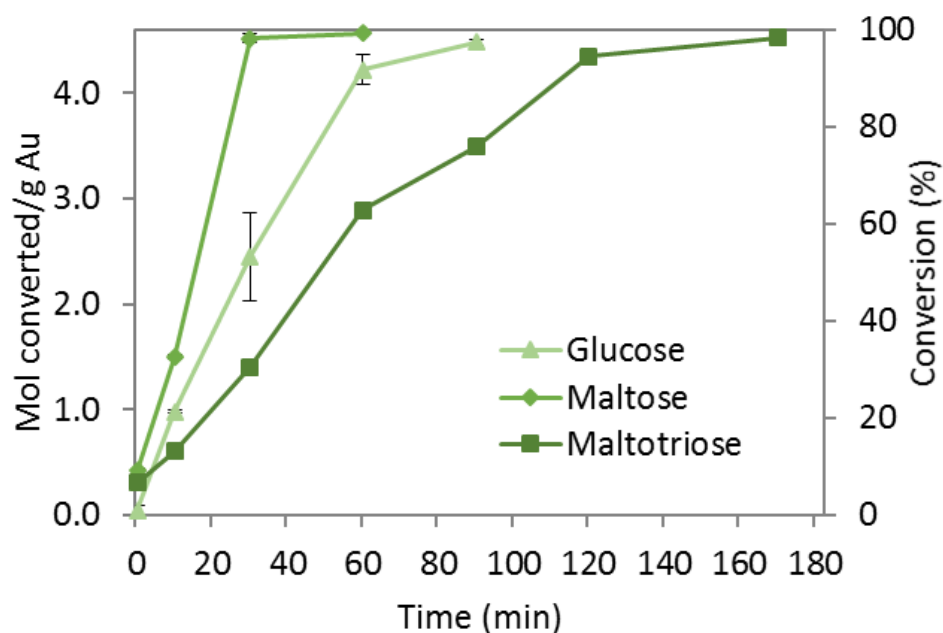


Graph 11. Catalytic activity of Pt/AC when oxidising glucose, maltose and maltotriose. The triangle lines show the data from pH-stat 2.

As discussed in the Research objectives (Section 1.3), lower catalytic activity is expected with increasing molecular weight. A larger substrate with a larger amount of functional groups could interact more strongly with the support than a smaller substrate. This can hinder the catalytic activity when the interaction gets too strong, and the catalyst gets saturated, keeping other substrates from interacting with it. This trend of decreasing activity with increasing molecular weight is observed in Graph 11.

3.2.2 Performance of Pt/AC against Au/AC

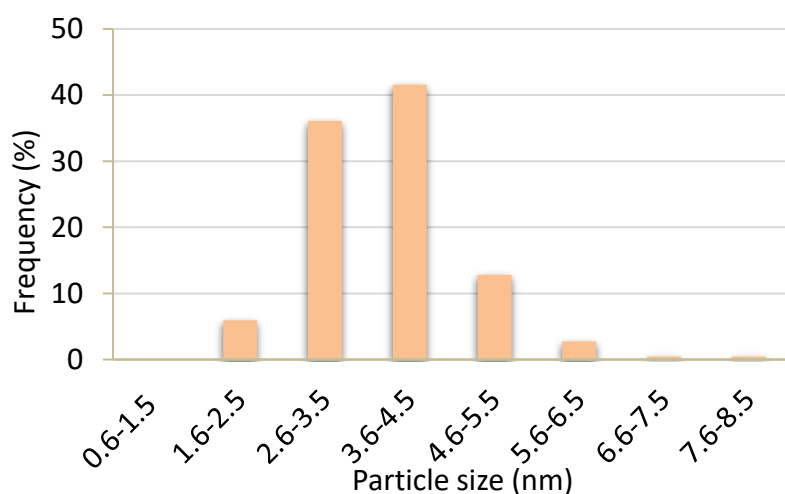
The catalytic activity of Au/AC and Pt/AC are given in Graph 12 and Graph 11 respectively. Also the conversion of the substrates is given on the second axis.



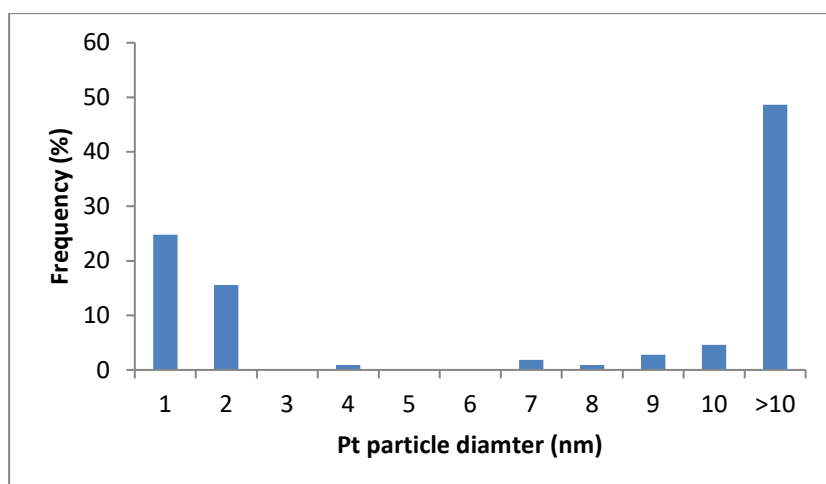
Graph 12. Catalytic activity of Au/AC when oxidising glucose, maltose and maltotriose. [15]

There is a significant difference in catalytic activity between the Au/AC made in previous work and the with sol immobilisation and $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor prepared Pt/AC. The gold catalyst is able to fully oxidise the three substrates after 60 min, 100 min and 170 min for maltose, glucose and maltotriose respectively. The platinum catalyst reaches 22%, 16% and 6% conversion for glucose, maltose and maltotriose after 150 min of oxidation.

The preparation method is practically the same, based on the same protocol [39]. The metal loading is similar for both catalysts (0.9-1.0% for the Au/AC against .9% for the Pt/AC), so this cannot be the reason of the difference in performance. The average particle size of the two catalysts is very different: the Au/AC has an average particle size of 3.4 nm whereas the Pt/AC 14.7 nm. This means that the metal dispersion of the gold catalyst is higher than that of the platinum catalyst and a higher activity of the former is to be expected. The distribution of the particle size was also very different for the two catalysts. Half of the particles from the Pt/AC are above the 10 nm, whereas the particles of the Au/AC oscillate between the 2-6 nm (see Graph 13 and Graph 14). This could be the reason of the so different performances.



Graph 13. Particle size distribution of Au/AC made in previous work, based on TEM images [15].

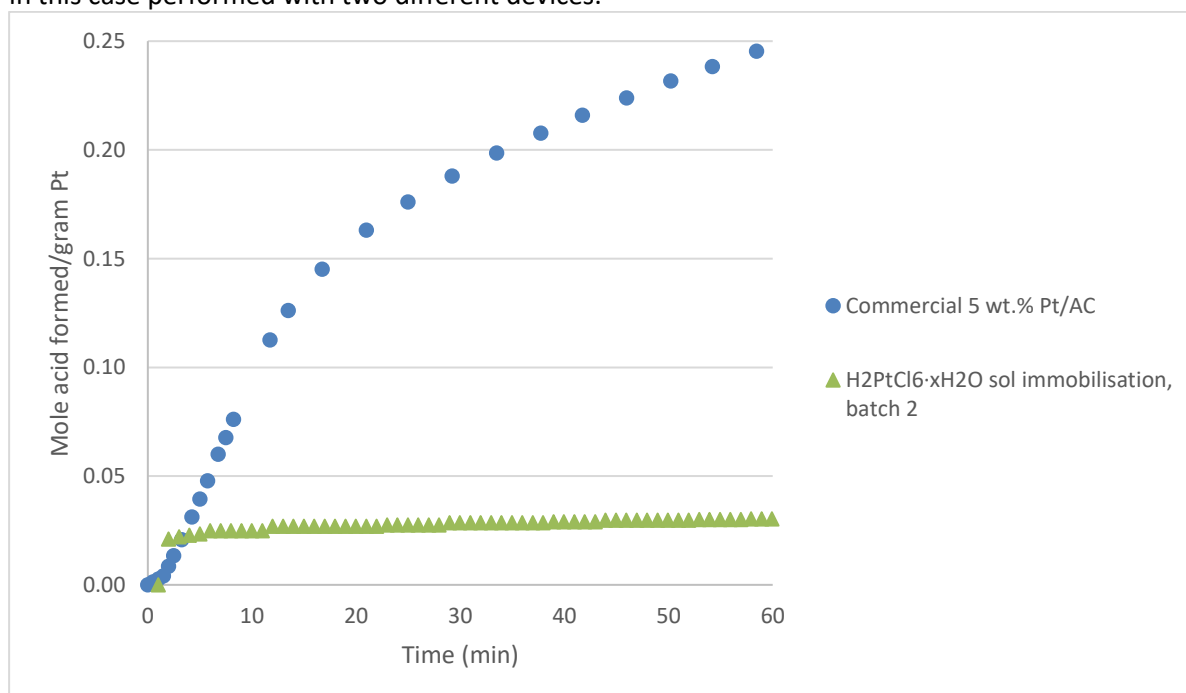


Graph 14. Particle size distribution of sol immobilisation with $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor prepared Pt/AC, batch 2. Data based on TEM images.

The Au/AC showed a strange phenomenon, where the activity of the maltose oxidation was higher than the activity of the glucose oxidation (see Graph 12). In previous work two gold catalysts were made, one supported on AC and the other supported on CNF. The Au/CNF did not show this phenomenon, so it was the question if it would happen for the Pt/AC as well, as the same activated carbon was used for the preparation of this catalyst. This is not the case. As stated above, with increasing molecular weight of the substrate a decrease in catalytic activity is observed for the Pt/AC.

3.2.3 Oxidation of methyl α -D-glucopyranoside

As was discussed in the Introduction, the reason for the selection of a platinum catalyst instead of a gold catalyst was the ability of platinum to oxidise primary and secondary alcohols, which is of importance when the catalyst is used to oxidise starch. In order to test this, methyl α -D-glucopyranoside, a sugar without reducing end was oxidised with the commercial 5 wt.% Pt/AC catalyst and with the chosen Pt/AC catalyst. The base addition is shown in Graph 15. The addition of base was in this case performed with two different devices.



Graph 15. Catalytic activity during the first 60 min of methyl α -D-glucopyranoside oxidation. The dotted lines show base addition from pH-stat 1, the triangle lines from pH-stat 2.

At the time the oxidation with the commercial catalyst was performed, there was no standard available of the oxidised product of methyl α -D-glucopyranoside. When the oxidation took place with the catalyst prepared with sol immobilisation and $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor, a standard was also injected into the HPLC. However, the activity was so low that no significant product was measured. Therefore, those results are not shown and only the base addition is used as comparison. A HPLC chromatogram of the reaction is shown in Appendix V.

Since no standard was available at the time of the oxidation with the commercial catalyst, mass spectroscopy was used to determine whether the expected product was formed. The expected mass of 210 m/z was found, confirming the presence of oxidised methyl α -D-glucopyranoside. The mass spectrum can be found in Appendix VI. The structure of the substrate and product are shown in Figure 6.

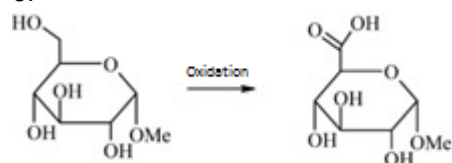


Figure 6. Oxidation of methyl α -D-glucopyranoside to α -methyl glucuronic acid).

When looking at the base addition curve of the commercial catalyst in Graph 15 we see a clear increase, and therefore formation of acidic (oxidised) products. A conversion of 24% was measured after one hour of reaction. This means that platinum is indeed capable of oxidising non-reducing ends, as was found in literature. However, the chosen Pt/AC catalyst showed practically no conversion of methyl α -D-glucopyranoside. A reason for this could be the nearly 100% selectivity to gluconic acid of this catalyst (see Section 3.1.3), meaning that this platinum catalyst only oxidises the reducing ends. This makes this catalysts unfit to work further with for the oxidation of starch.

4 Conclusions

During this research, several Pt/AC catalyst were made using two platinum precursors ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ and $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$), and three different preparation methods: incipient wetness impregnation, sol immobilisation and ion adsorption. The objective was to find a suitable platinum catalyst for the oxidation of starch, as gold was proven unfit in previous research. In order to assess which one of the 14 prepared Pt/AC catalysts was appropriate, the catalysts were characterized using TEM, chemisorption, XRD and ICP-OES. The oxidation of glucose was used as a model reaction. Based on the outcomes of the characterization and the catalytic activity observed by the oxidation of glucose, one catalyst was to be chosen to oxidise bigger substrates, as a model for starch oxidation.

When looking at the characterization results only, the impregnated catalysts stood out, regardless of the precursor used. Even though the outcomes of the TEM and chemisorption measurements were not in complete concordance, both techniques pointed out that impregnating was the best technique to obtain a high metal dispersion and a small average particle diameter. As for the metal loading, the values determined with ICP-OES suggest that when using $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ as a precursor, a higher platinum loading can be obtained than with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$, regardless of the technique used.

These characterization results, in combination with the performances of the catalysts during the oxidation of glucose left two main candidates to work further with. The Pt/AC prepared with sol immobilisation and $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor had a TOF of 0.63 s^{-1} . TEM analyses showed abundant platinum particles with a diameter of 2 nm, although the average diameter of the particles was 12.2 nm. Its selectivity from glucose to gluconic acid is 97%. The Pt/AC impregnated with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ precursor had a TOF of 0.46 s^{-1} and had the smallest average diameter size measured with TEM (8.0 nm). The selectivity of this catalyst from glucose to gluconic acid was 89%. Based on the higher TOF and the abundant presence of 2 nm diameter platinum particles, the Pt/AC catalyst prepared with sol immobilisation and $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor was chosen to continue further oxidations with.

The influence of increasing molecular weight of the substrate on the activity of the catalyst was tested on this catalyst. A decrease in activity was observed with increasing substrate size, confirming the expectations. However, the activity measured with the Pt/AC catalyst was significantly lower than the activity measured with Au/AC in previous work. Where conversions of 22%, 16% and 6% were measured for glucose, maltose and maltotriose oxidation on Pt/AC after 150 min, all three substrates were fully converted in the same time on Au/AC. The selectivity towards maltobionic acid and maltotronic acid of the platinum catalyst could not be determined, as there were no standards of these products available. However, no other products could be seen on the HPLC chromatograms of these reactions.

The final test was the oxidation of methyl α -D-glucopyranoside, a glucose analogue without a reducing end. There was no conversion noticeable on the chosen Pt/AC, as was the case with the gold catalyst made in previous work. This is no surprise, considering the 96% selectivity to gluconic acid that was measured when oxidising glucose, indicating only oxidation at the reducing ends. This important property was not considered when selecting the catalyst. This leads to the supposition that an incorrect choice was made.

The oxidation of methyl α -D-glucopyranoside was also conducted on a commercial 5 wt.% Pt/AC, where a conversion of 24% was measured after one hour. This proves that platinum is capable of oxidising non-reducing ends and reinforces the thought that a catalyst with a lower selectivity for gluconic acid is required for the oxidation of starch.

5 Recommendations

As was discussed in the Conclusions, a different Pt/AC catalyst for the oxidation of starch must be selected. This time, it is important to take the selectivity of the catalyst into account. The catalyst prepared by impregnation with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ has a high TOF and also a selectivity from glucose to gluconic acid of 89%. Also both ion adsorption catalysts had a low selectivity, 8% for the $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ precursor and 69% for the $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor. However, the selectivity of the catalyst prepared by ion adsorption with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ precursor is dubious, since its activity was very low. Therefore, the most interesting candidates to investigate would be the $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ precursor impregnation catalyst and the $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor ion adsorption catalyst.

It might be interesting to go to a 5 wt.% platinum loading, since the 1 wt.% platinum catalysts made during this research showed a low activity when compared to the 1 wt.% gold catalysts. In this way, a more efficient activity measuring can take place.

The optimal reduction temperature should be investigated further. Two different reduction temperatures were used, but this was not based on a TPR measurement.

Because of the high values for the average particle size found when conducting chemisorption on the sol immobilisation catalysts, several measures were taken in order to get realistic results. The deviation of this results was attributed to something (either PVA or substrates from the oxidation) remaining attached to the Pt particles, disturbing the H_2 uptake. To investigate whether the substrate really remains attached to the catalyst after oxidation, other spent catalysts should be tested as well.

High platinum leaching values were found based on ICP-OES data. Too high, according to literature. In order to test whether it is a consequence of the reaction conditions, leaching of the spent commercial catalyst should be measured as well. It might also be interesting to consider other techniques to determine platinum leaching, such as elemental analysis of the reaction filtrate.

The accuracy of the measurements of the oxidised products of maltose, maltotriose and methyl α -D-glucopyranoside can be increased by injecting standards of these compounds into the HPLC. It was also discovered that maltobionic acid and maltotronic acid are better visible when measured at UV at 280 nm instead of 210 nm.

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Appendix

Table 12. Summary of the preparation conditions of the Pt/AC catalysts.

[Pt(NH ₃) ₄](NO ₃) ₂ and H ₂ PtCl ₆ ·xH ₂ O precursors used with all techniques							
Technique	Impregnation			Sol immobilisation		Ion adsorption	
Batch	1	2	3	1	2	1	
Calcination step	No	Yes	No	Not applicable	Not applicable	Yes	No
Reduction temperature	300°C	300°C	200°C	Not applicable	Not applicable	200°C	200°C

I. TEM

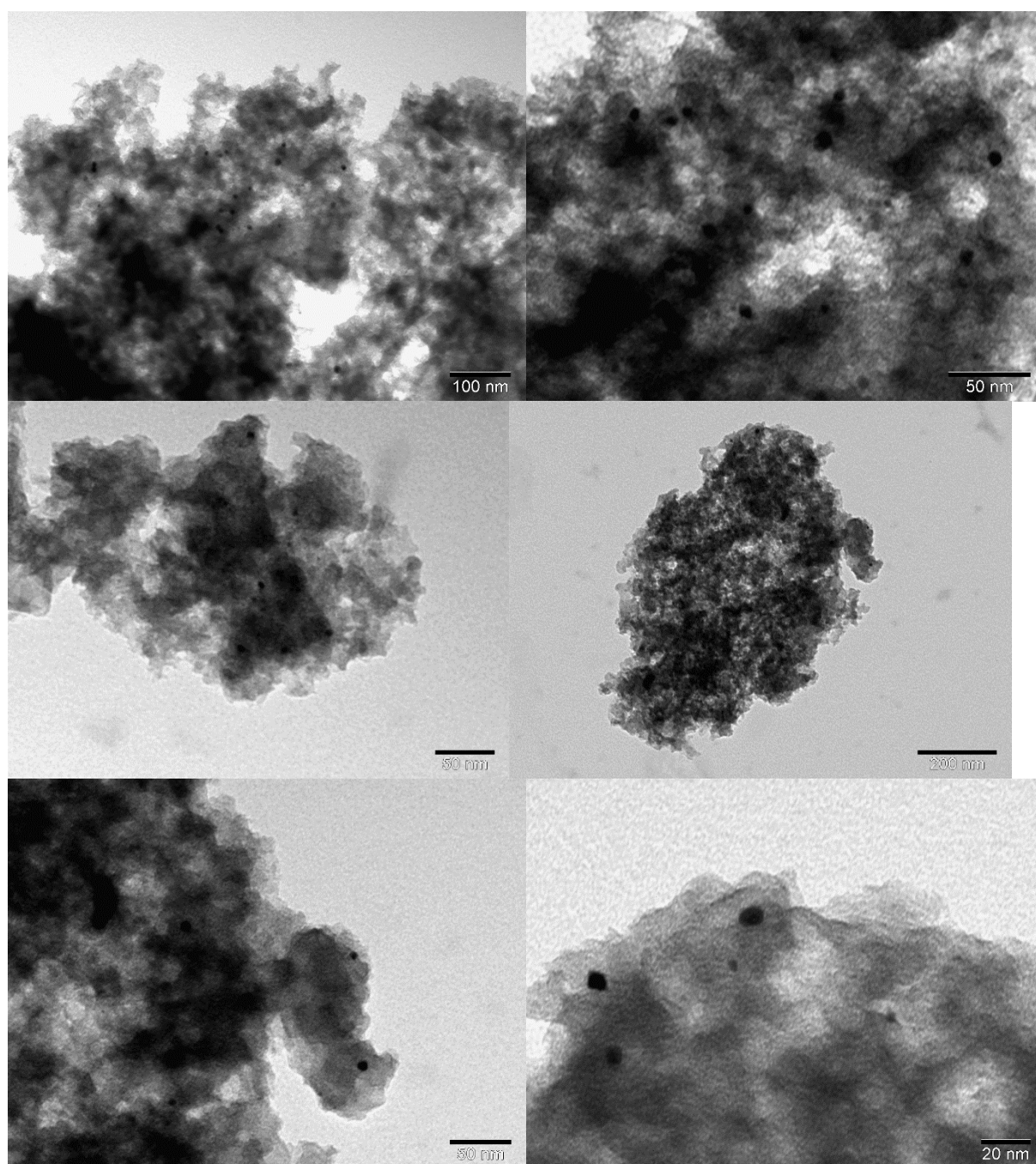


Figure 7. TEM photos of Pt/AC catalyst prepared by impregnation with [Pt(NH₃)₄](NO₃)₂ precursor, calcined

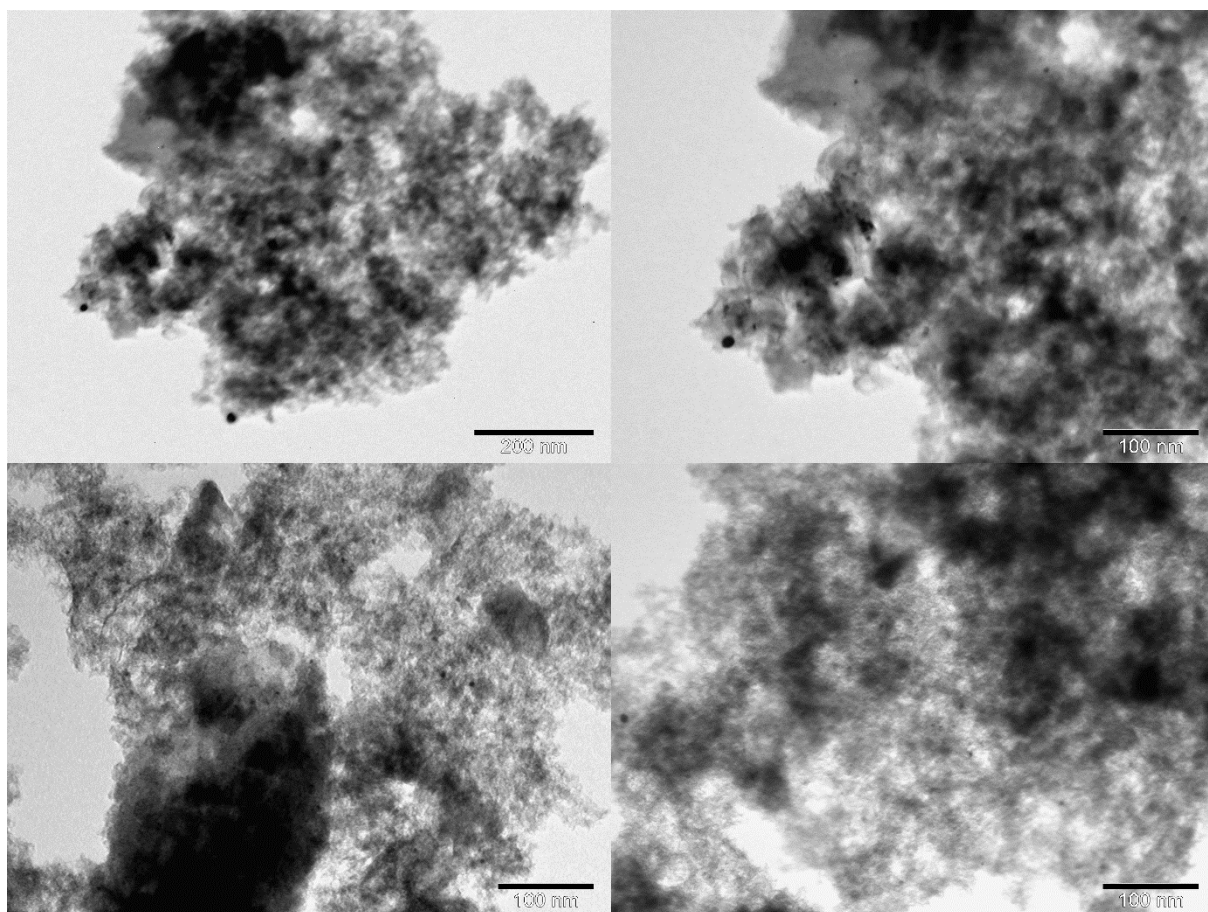


Figure 8. TEM photos of Pt/AC catalyst prepared by impregnation with $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor, calcined

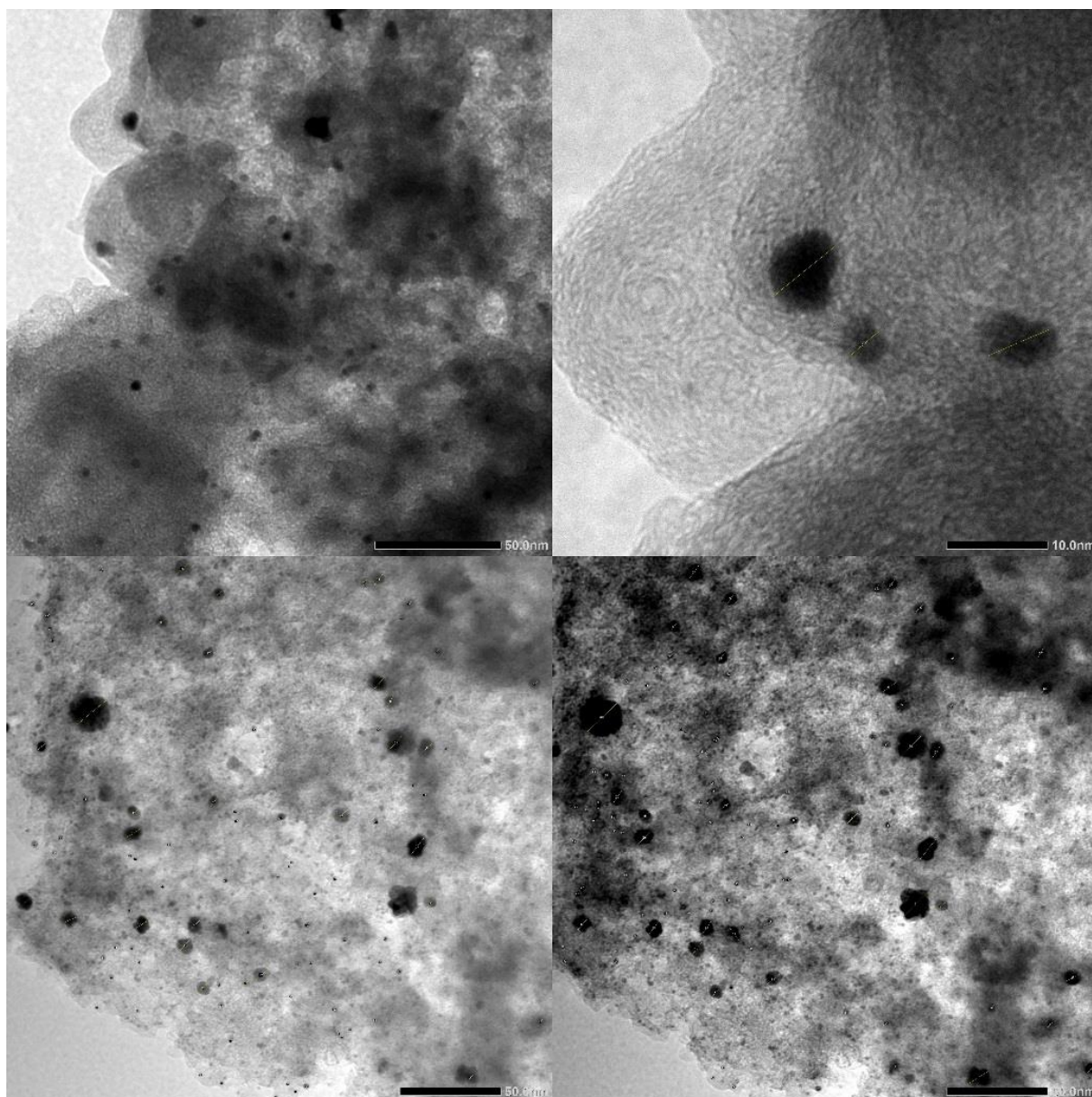


Figure 9. TEM photos of Pt/AC catalyst prepared by sol immobilisation with $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, batch 1

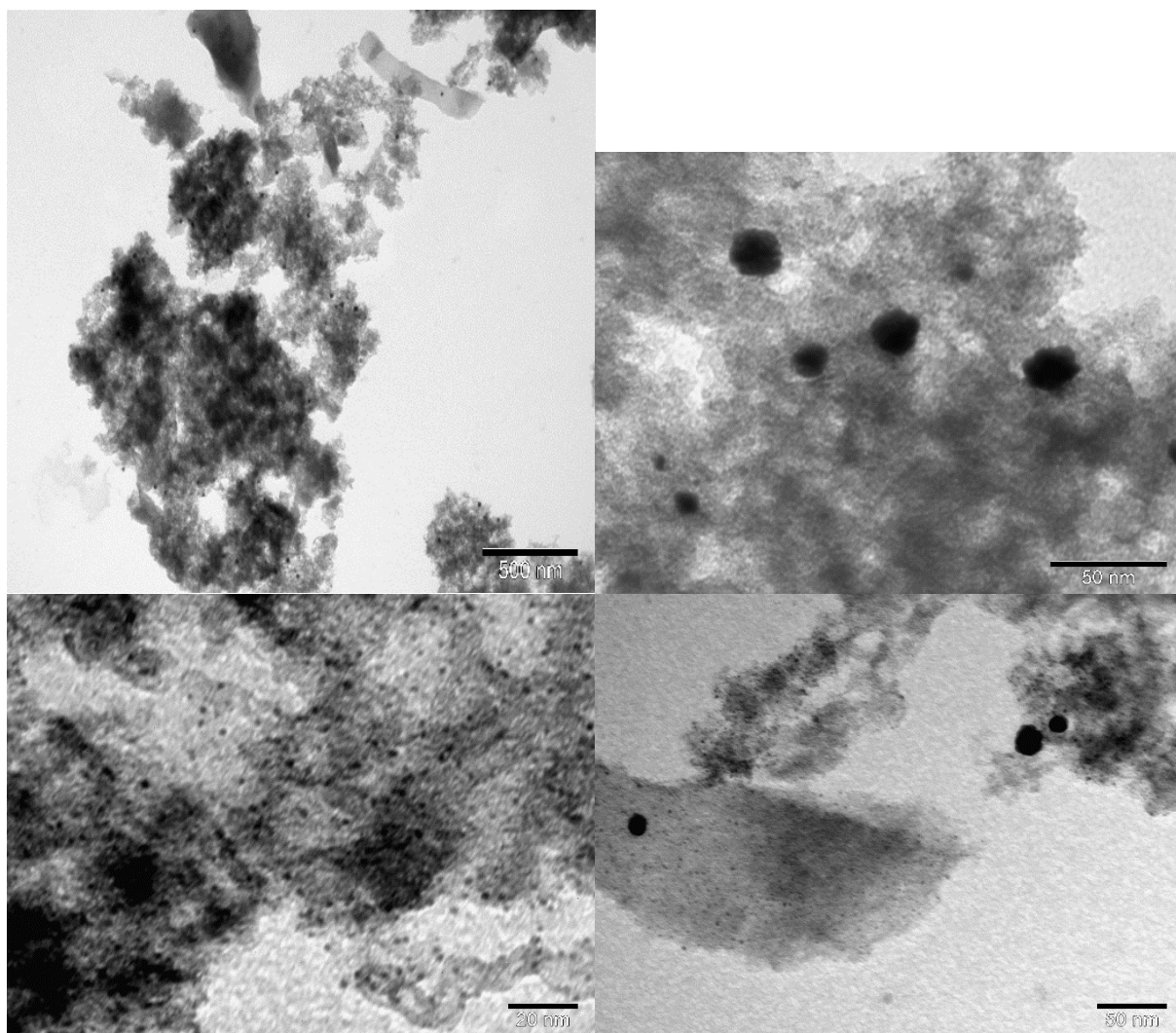


Figure 10. TEM photos of Pt/AC catalyst prepared by sol immobilisation with $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, batch 2

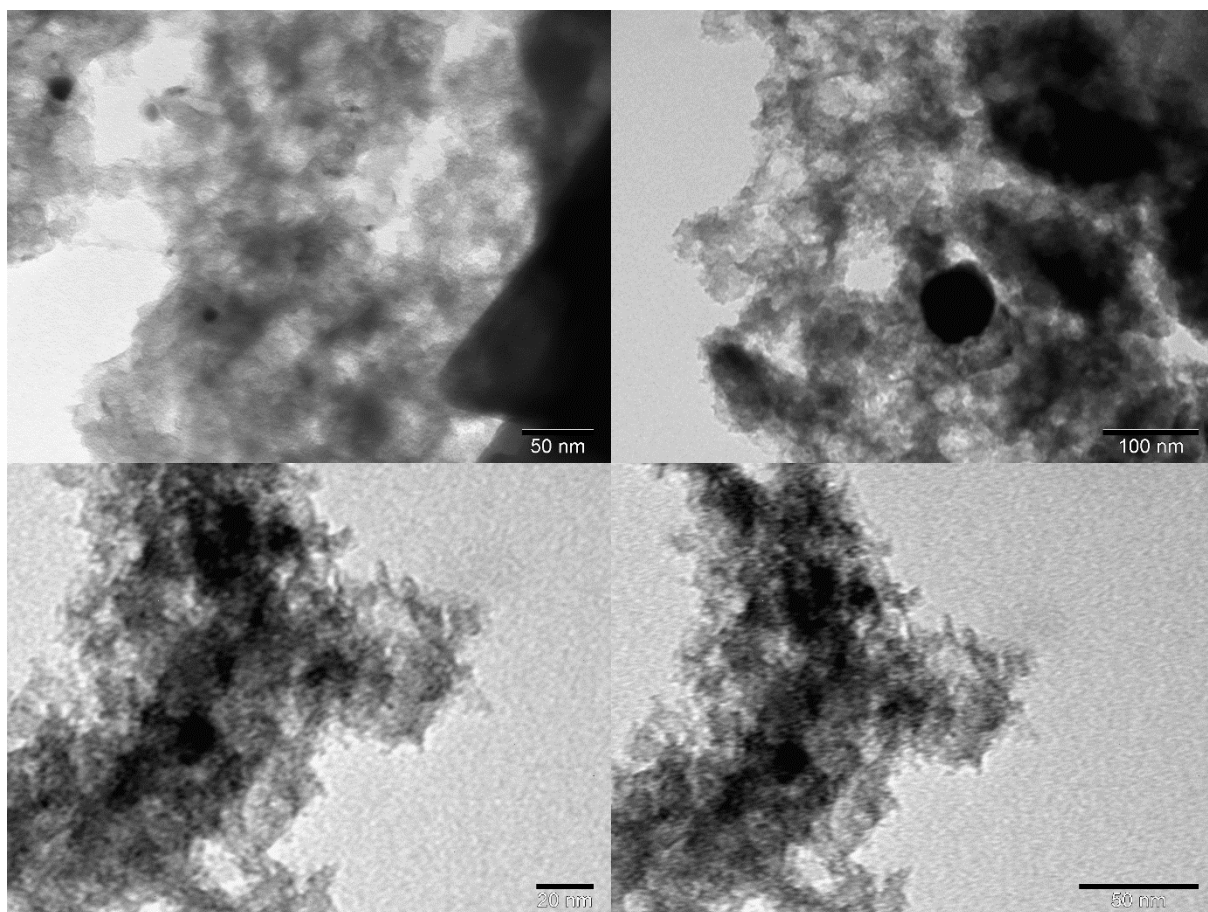


Figure 11. TEM photos of Pt/AC catalyst prepared by ion adsorption with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ precursor

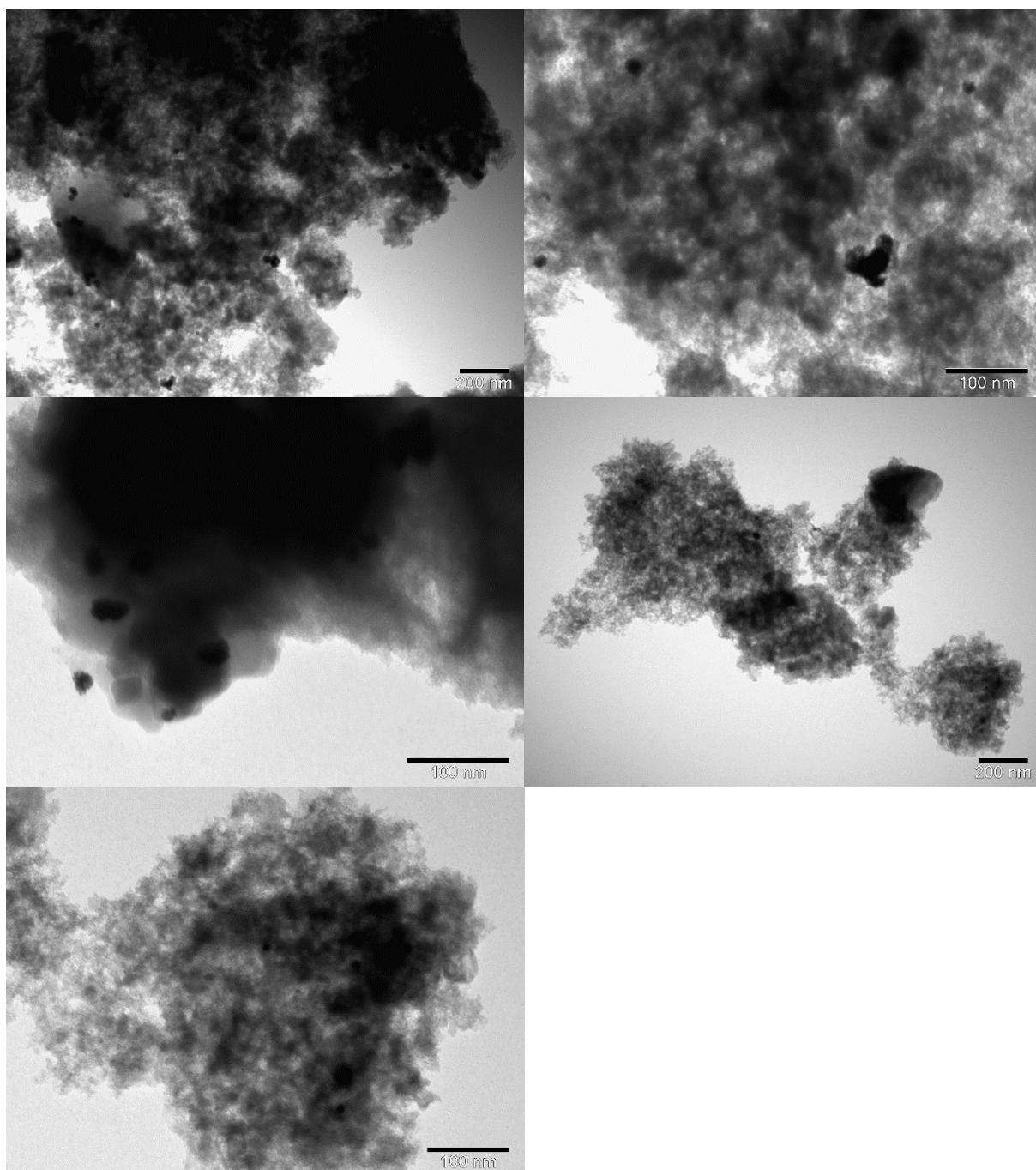


Figure 12. TEM photos of Pt/AC catalyst prepared by ion adsorption with $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor

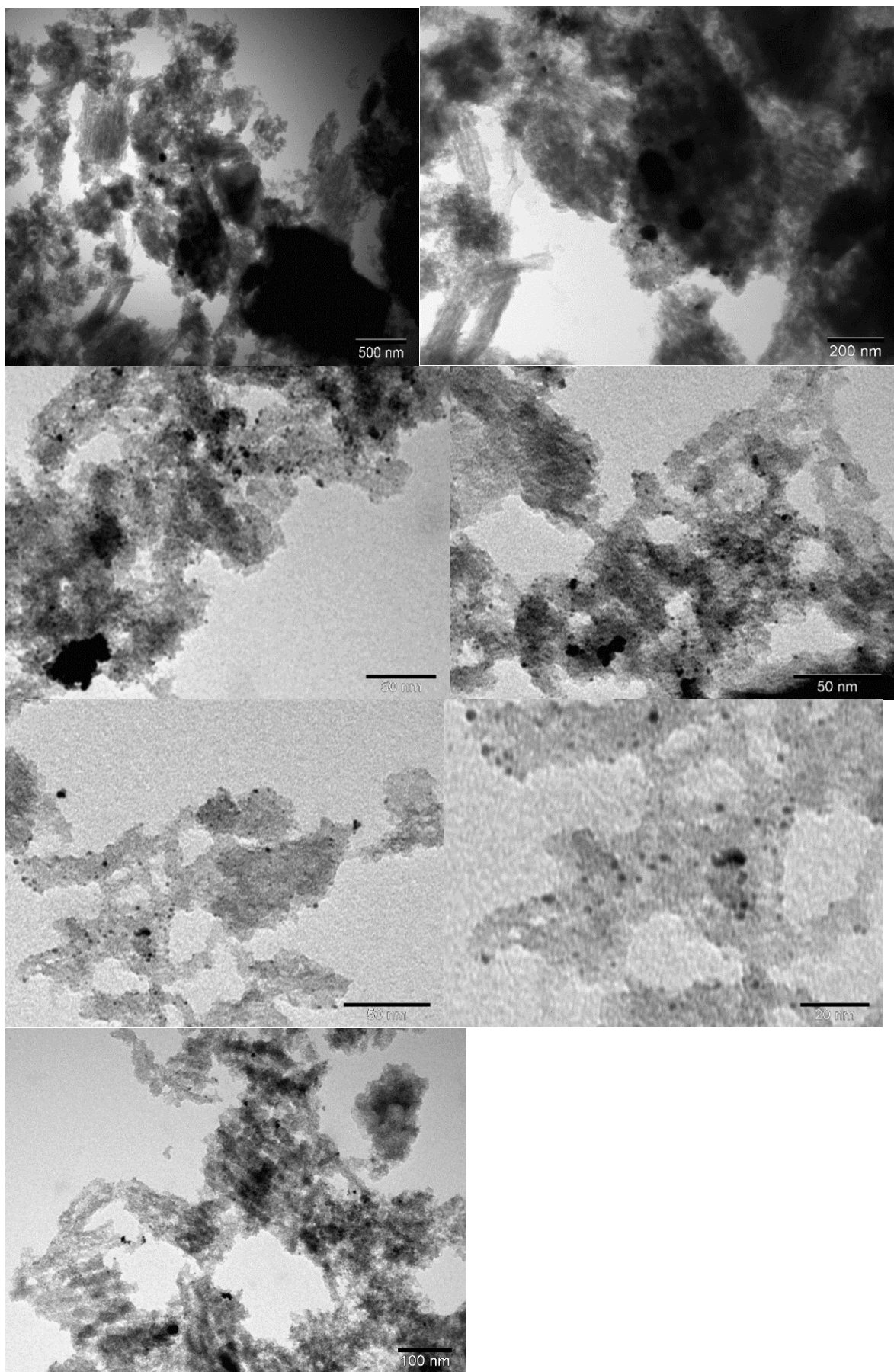


Figure 13. TEM photos of commercial 5.wt% Pt/AC catalyst

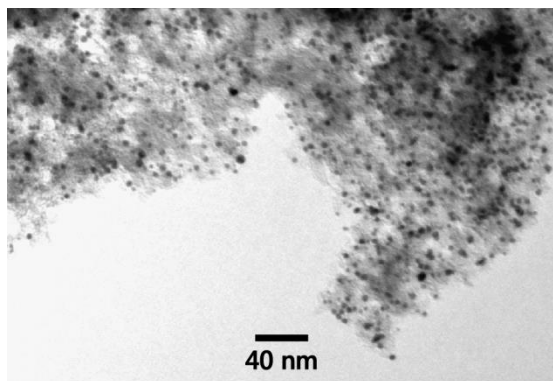


Figure 14. TEM photo of Au/AC catalyst made in previous work

II. Chemisorption

Table 13. Average diameter (hemisphere) of Pt particles of impregnated Pt/AC catalysts in nm. Comparison between H₂ and CO pulse chemisorption outcomes. The batches in orange are shown in chapter Results and discussion.

Impregnated catalysts	Batch 1		Batch 2, calcined		Batch 3	
Precursor	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O
H ₂ chemisorption	3.0	5.6	5.6	3.2	35.1	6.6
CO chemisorption	6.0	Not measured	Not measured	5.9	70.8	18.8

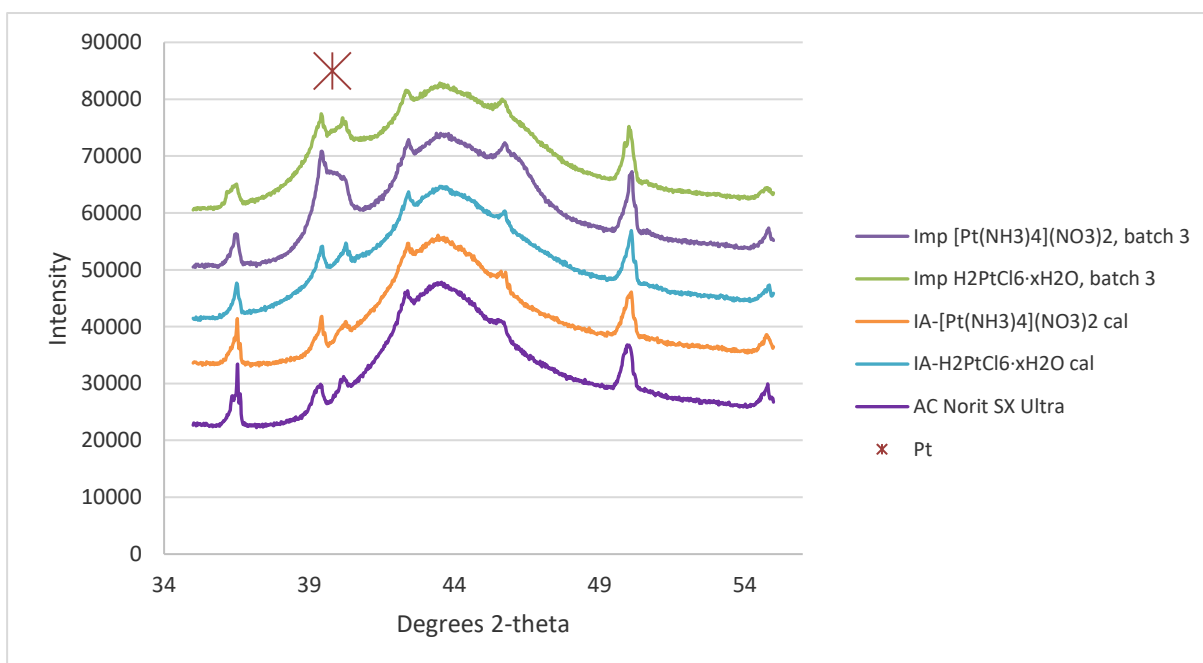
Table 14. Average diameter (hemisphere) of Pt particles of sol immobilisation Pt/AC catalysts in nm. Comparison between H₂ and CO pulse chemisorption outcomes. The batches in orange are shown in chapter Results and discussion.

	Sol immobilisation. Batch 1		Sol immobilisation. Batch 2		
Precursor	H ₂ PtCl ₆ ·xH ₂ O	H ₂ PtCl ₆ ·xH ₂ O after oxidation	H ₂ PtCl ₆ ·xH ₂ O	H ₂ PtCl ₆ ·xH ₂ O after oxidation	H ₂ PtCl ₆ ·xH ₂ O washed after oxidation
H ₂ chemisorption	48.2	No uptake	61.7	49.2	49.0
CO chemisorption	Not measured	Not measured	31.2	Not measured	Not measured

Table 15. Average diameter (hemisphere) of Pt particles of ion adsorption and commercial Pt/AC catalysts in nm. Comparison between H₂ and CO pulse chemisorption outcomes. The batches in orange are shown in chapter Results and discussion.

	Ion adsorption		Ion adsorption calcined		Commercial 5 wt.% catalyst
Precursor	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O	
H ₂ chemisorption	35.1	5.5	25.4	7.2	3.1
CO chemisorption	23.2	Not measured	Not measured	Not measured	25.5

III. XRD



Graph 16. XRD diffractograms of different Pt/AC catalysts not shown in Section 3.1.1.1. The red star indicates the platinum peak.

IV. ICP-OES

Table 16. Expected loading and loading measured with ICP-OES of impregnated Pt/AC catalysts. The batches in orange are shown in chapter Results and discussion.

Impregnated catalysts	Batch 1		Batch 2, calcined		Batch 3	
Precursor	$[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$	$\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$	$[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$	$\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$	$[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$	$\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$
Expected theoretical loading (wt.%)	0.86	1.02	1.00	1.08	1.01	1.08
Loading measured with ICP-OES (wt.%)	0.68	0.95	0.89	1.13	0.78	0.87

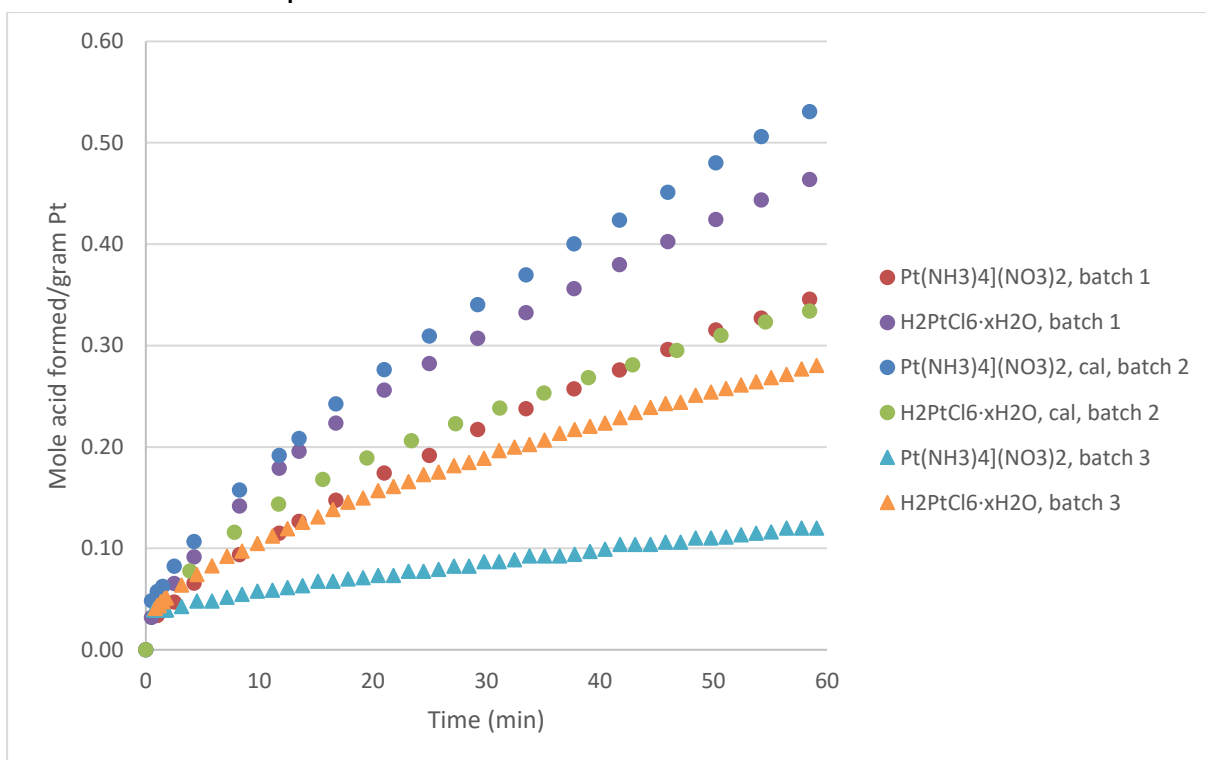
Table 17. Expected loading and loading measured with ICP-OES of sol immobilisation Pt/AC catalysts. The batches in orange are shown in chapter Results and discussion.

	Sol immobilisation. Batch 1		Sol immobilisation. Batch 2
Precursor	$[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$	$\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$	$\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$
Expected theoretical loading (wt.%)	1.05	1.06	1.15
Loading measured with ICP-OES (wt.%)	0.09	0.85	0.89

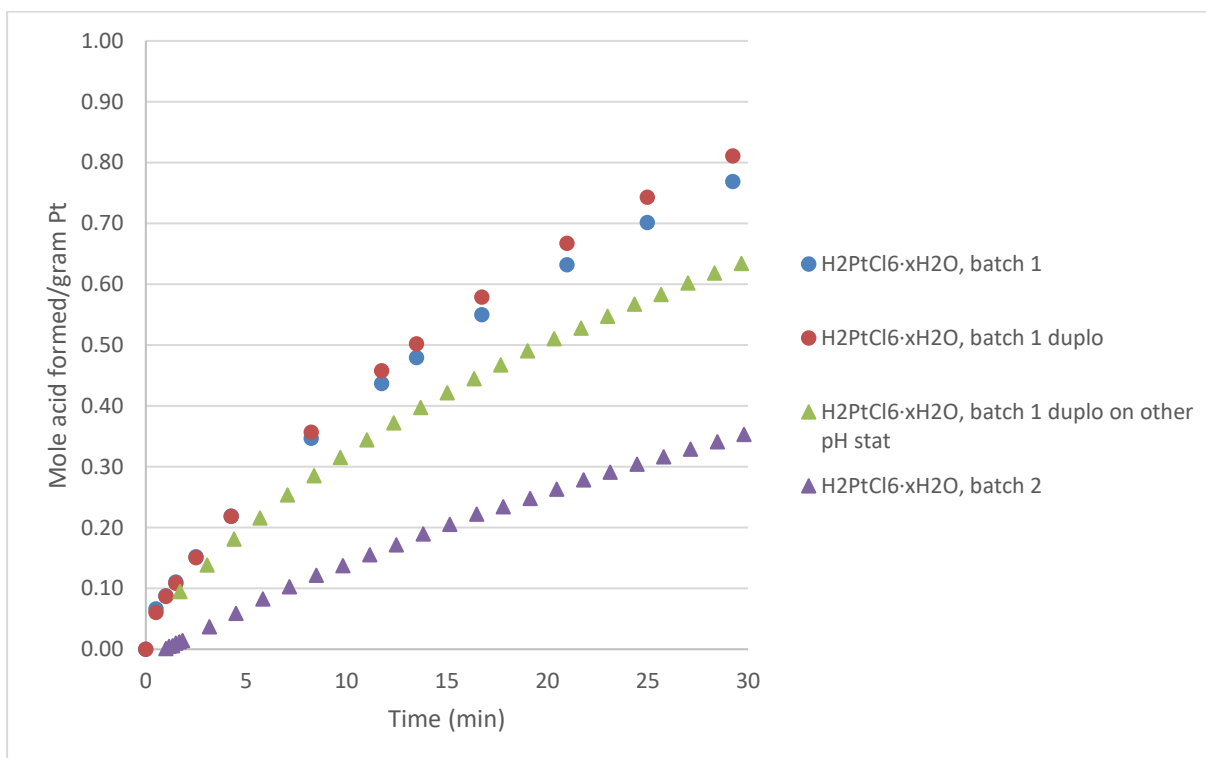
Table 18. Expected loading and measured loading with ICP-OES of ion adsorption and commercial Pt/AC catalysts. The batches in orange are shown in chapter Results and discussion.

	Ion adsorption		Ion adsorption calcined		Commercial 5wt.% catalyst
Precursor	$[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$	$\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$	$[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$	$\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$	
Expected theoretical loading (wt.%)	1.05	1.18	1.05	1.18	5.00
Loading measured with ICP-OES (wt.%)	0.65	1.05	0.68	1.04	4.32

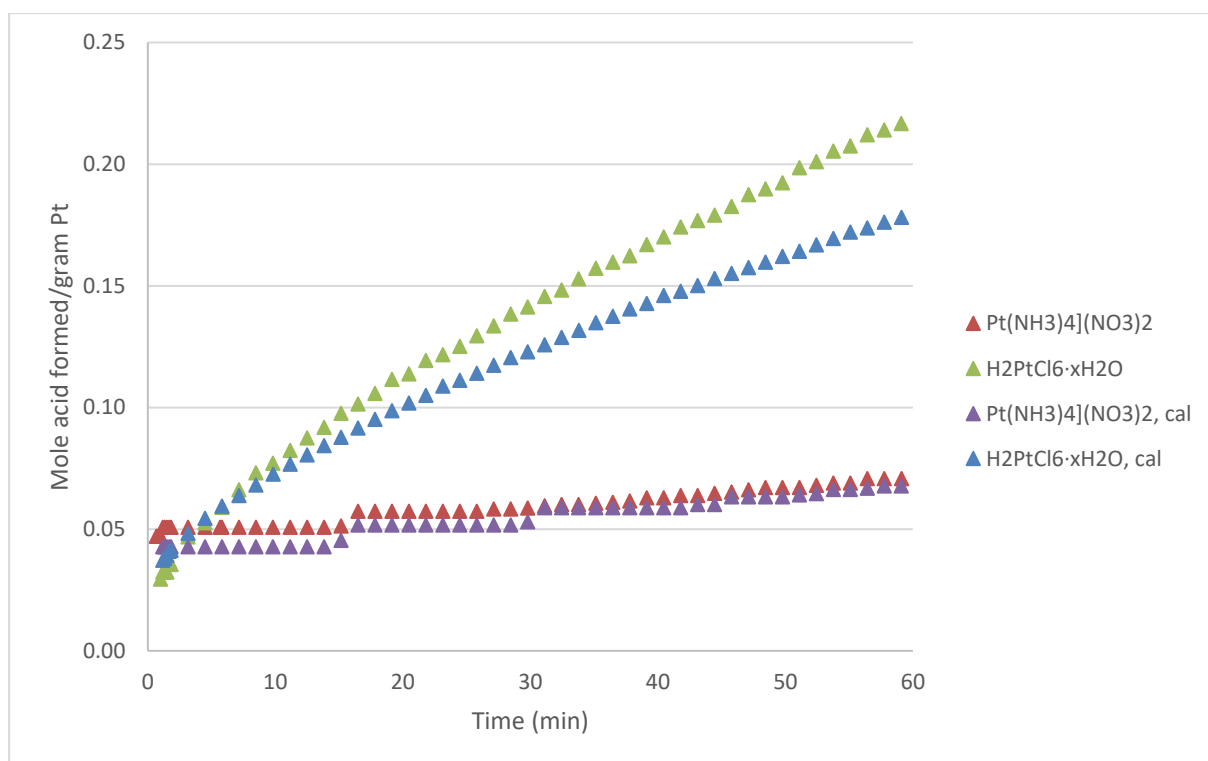
V. Oxidation performance



Graph 17. Catalytic activity of the Pt/AC catalysts prepared by impregnation during the first 60 min of glucose oxidation. The dotted lines show base addition from pH-stat 1, the triangle lines from pH-stat 2.



Graph 18. Catalytic activity of the Pt/AC catalysts prepared by sol immobilisation during the first 60 min of glucose oxidation. The dotted lines show base addition from pH-stat 1, the triangle lines from pH-stat 2.



Graph 19. Catalytic activity of the Pt/AC prepared by ion adsorption during the first 60 min of glucose oxidation. The dotted lines show base addition from pH-stat 1, the triangle lines from pH-stat 2.

Table 19. Oxidation performance of impregnated Pt/AC catalysts. The batches in orange are shown in chapter Results and discussion.

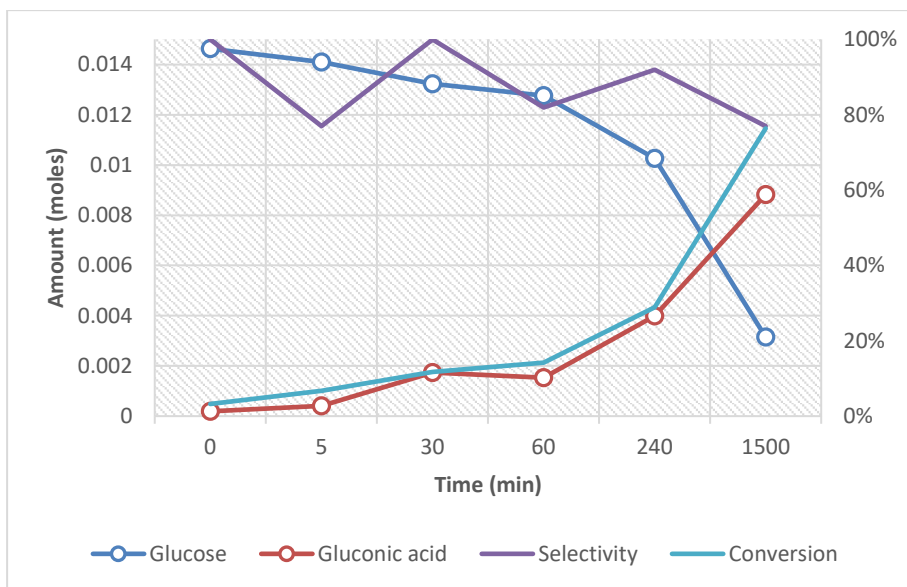
Impregnated catalysts	Batch 1		Batch 2, calcined		Batch 3	
Precursor	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O	[Pt(NH ₃) ₄](NO ₃) ₂	H ₂ PtCl ₆ ·xH ₂ O
Conversion after 60 min	8%	11%	14%	11%	4%	8%
Time to reach 10% conversion (min)	112.3	43.6	22.2	43.5	184.8	123
Amount of substrate converted at 10% conversion (moles)	5.49E-04	4.28E-04	7.09E-04	3.44E-04	5.74E-04	6.25E-04
Specific reaction rate after 60 min (mole/g metal*min)	4.01E-03	4.77E-03	1.04E-02	5.26E-03	1.86E-03	5.37E-03
Selectivity to gluconic acid at 10% conversion	94%	100%	100%	100%	100%	87%

Table 20. Oxidation performance of sol immobilisation Pt/AC catalysts. The batches in orange are shown in chapter Results and discussion.

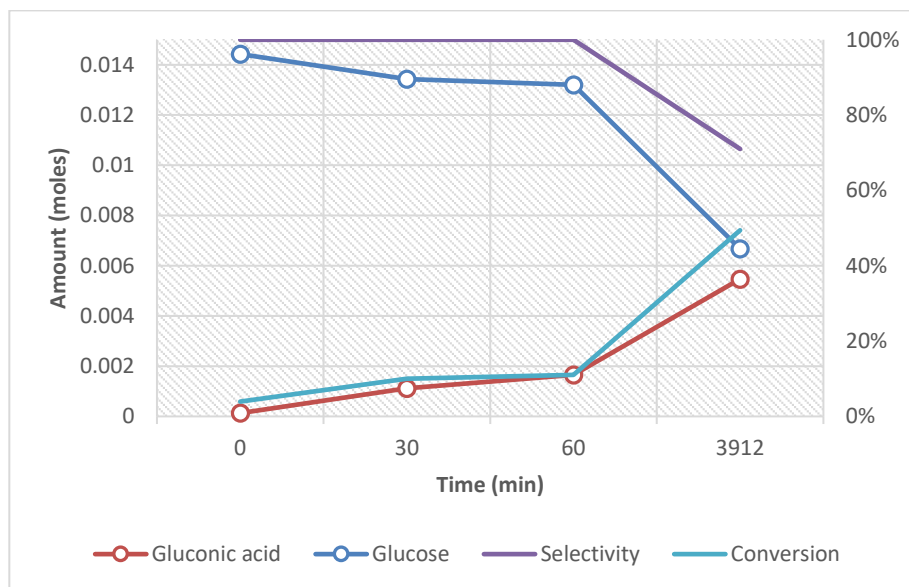
	Sol immobilisation. Batch 1			Sol immobilisation. Batch 2
Precursor	$\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$	$\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ (Duplo)	$\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ (Duplo on second pH-stat)	$\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$
Conversion after 60 min	17%	16%	18%	13%
Time to reach 10% conversion (min)	8	24.5	29.3	34.4
Amount of substrate converted at 10% conversion (moles)	4.72E-04	5.35E-04	2.93E-04	6.37E-04
Specific reaction rate after 60 min (mole/g metal*min)	1.05E-02	1.18E-02	1.55E-02	9.90E-03
Selectivity at 10% conversion	98%	98%	93%	96%

Table 21. Oxidation performance of ion adsorption Pt/AC catalysts. The batches in orange are shown in chapter Results and discussion.

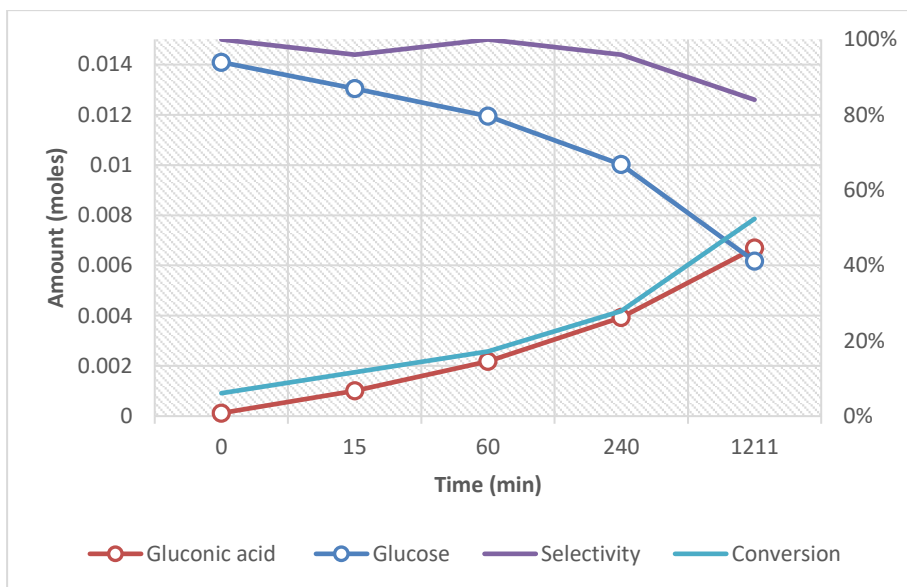
Oxidation performance	Ion adsorption		Ion adsorption calcined	
Precursor	$[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$	$\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$	$[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$	$\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$
Conversion after 60 min	7%	9%	5%	
Time to reach 10% conversion (min)	91.56	65.23	154	85.6
Amount of substrate converted at 10% conversion (moles)	8.46E-04	6.82E-04	4.72E-04	7.24E-04
Specific reaction rate after 60 min (mole/g metal*min)	6.64E-03	6.17E-03	1.61E-03	
Selectivity at 10% conversion	8%	54%	34%	20%



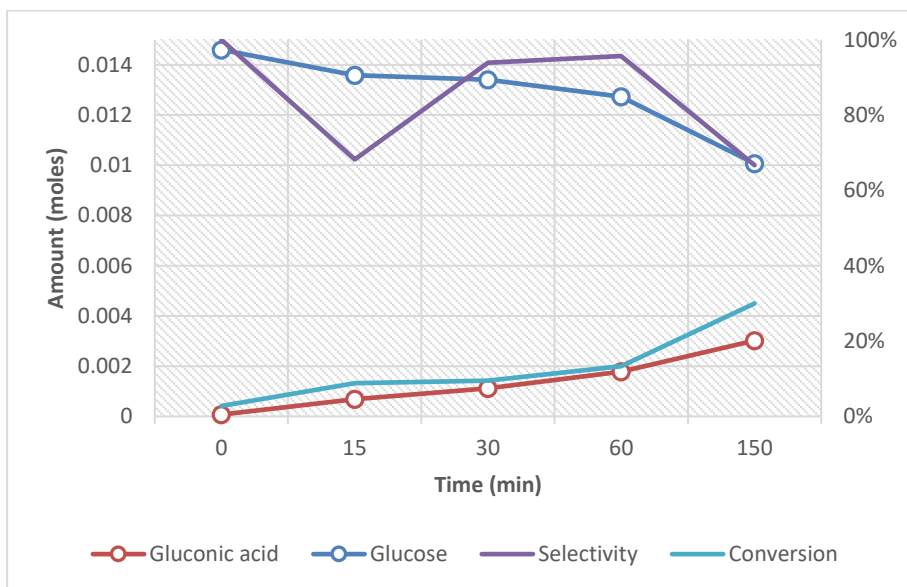
Graph 20. Reaction progress of Pt/AC catalyst prepared by impregnation with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ precursor, calcined, based on HPLC data.



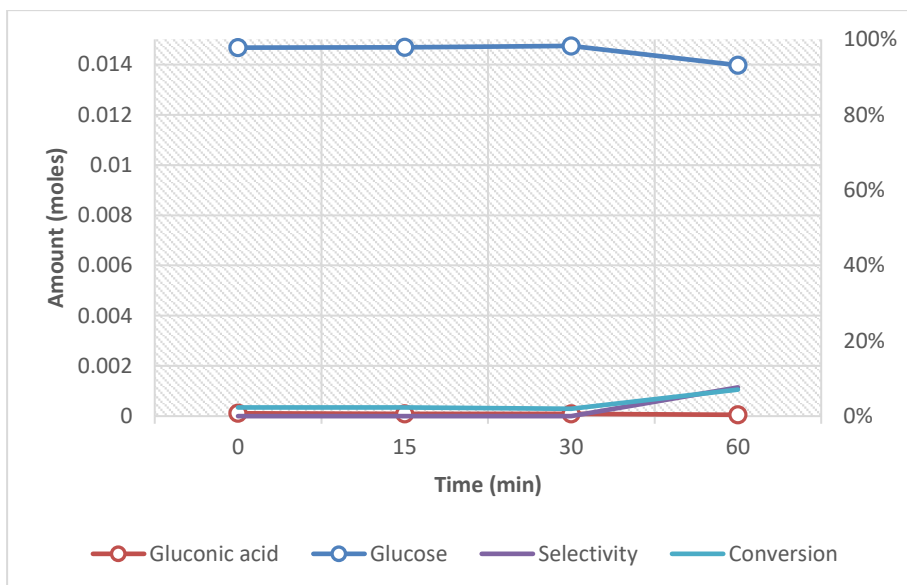
Graph 21. Reaction progress of Pt/AC catalyst prepared by impregnation with $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor, calcined, based on HPLC data.



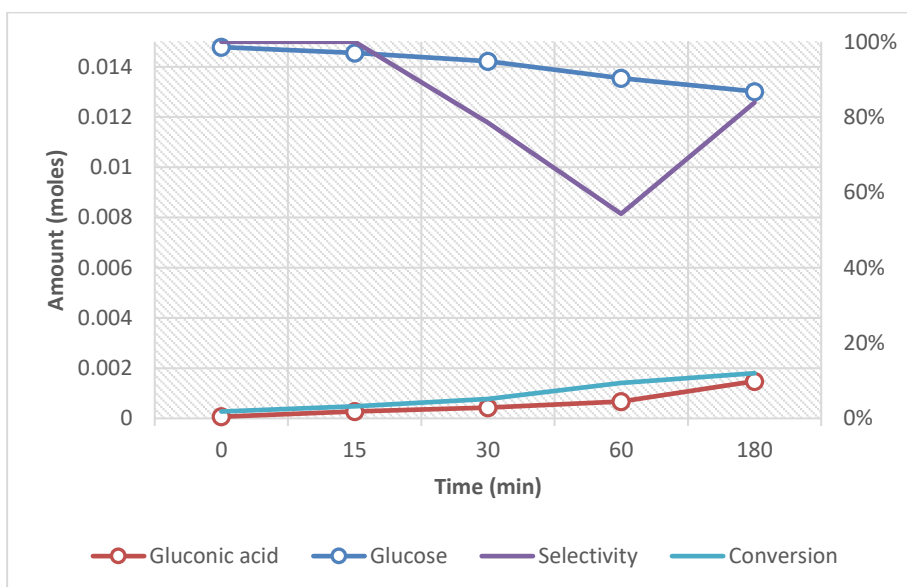
Graph 22. Reaction progress of Pt/AC catalyst prepared by sol immobilisation with $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor, batch 1, based on HPLC data.



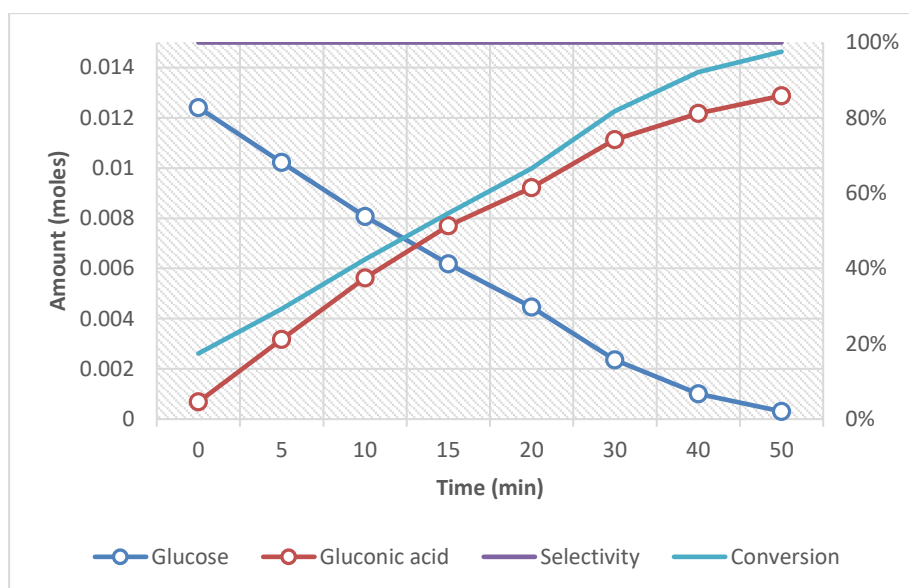
Graph 23. Reaction progress of Pt/AC catalyst prepared by sol immobilisation with $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor, batch 2, based on HPLC data.



Graph 24. Reaction progress of Pt/AC catalyst prepared by ion adsorption with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ precursor, based on HPLC data.



Graph 25. Reaction progress of Pt/AC catalyst prepared by ion adsorption with $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor, based on HPLC data.



Graph 26. Reaction progress of 5 wt.% commercial Pt/AC, based on HPLC data.

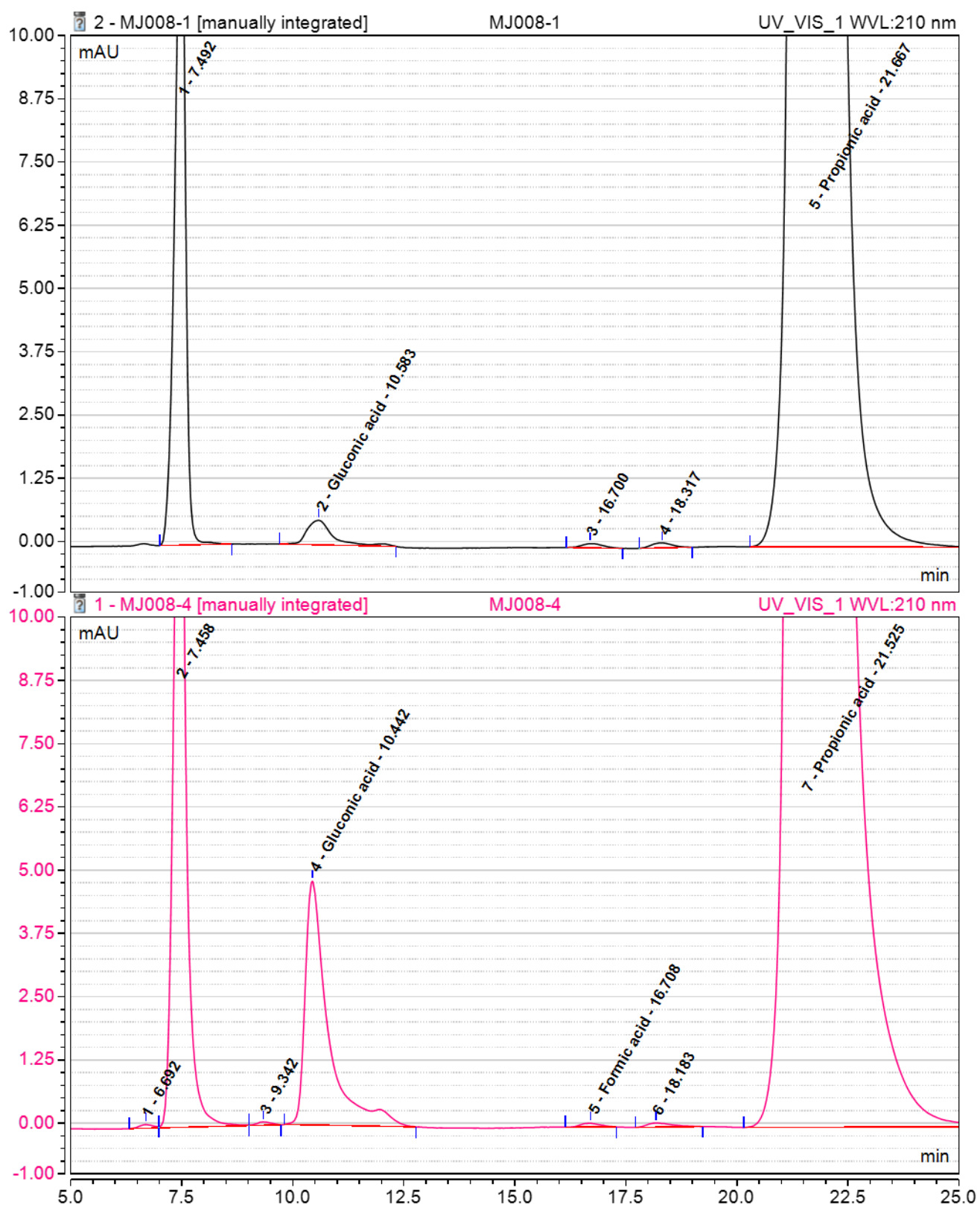


Figure 15. HPLC chromatogram of glucose oxidation on Pt/AC catalyst prepared by impregnation with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ precursor, calcined

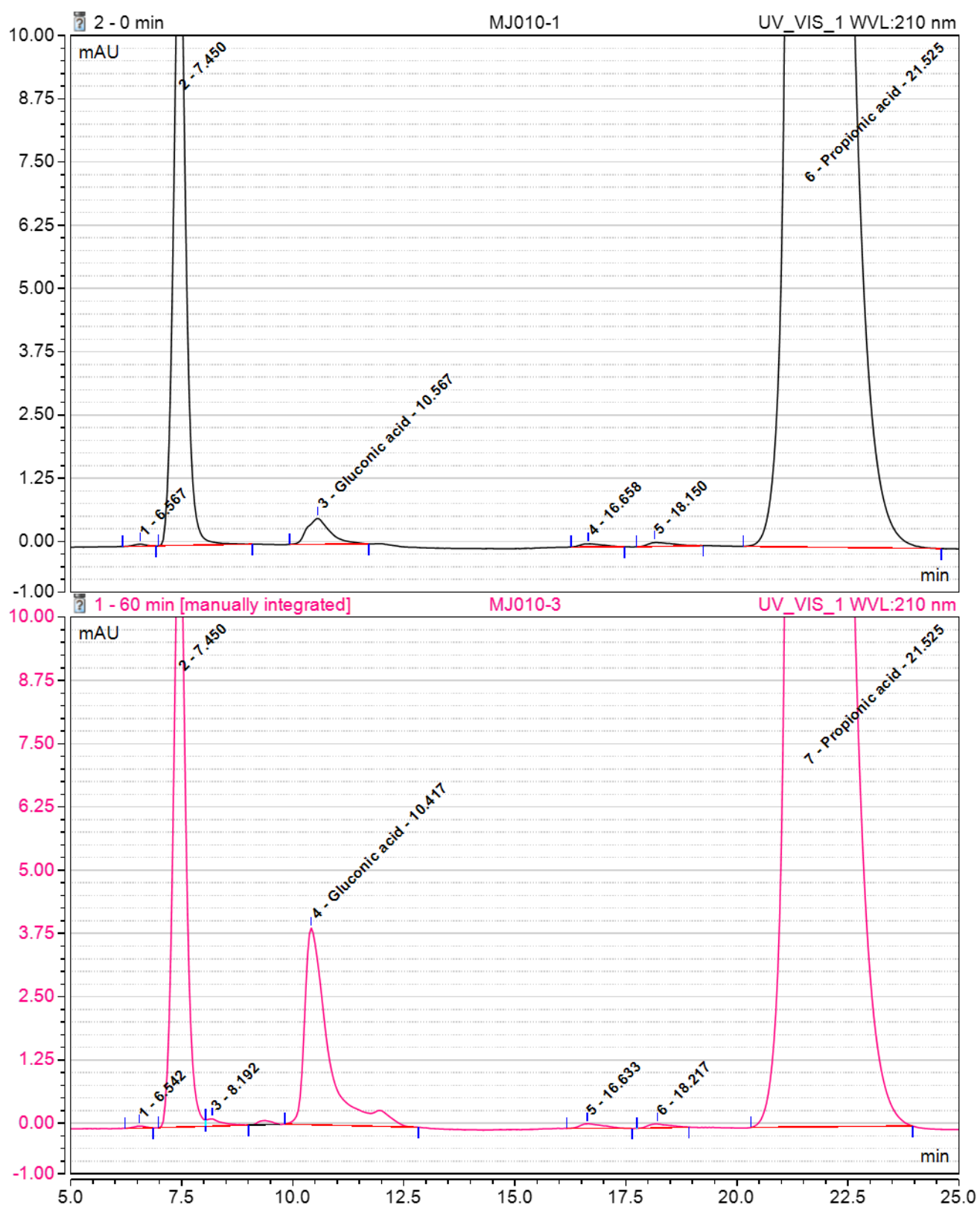


Figure 16. HPLC chromatogram of glucose oxidation on Pt/AC catalyst prepared by impregnation with $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor, calcined

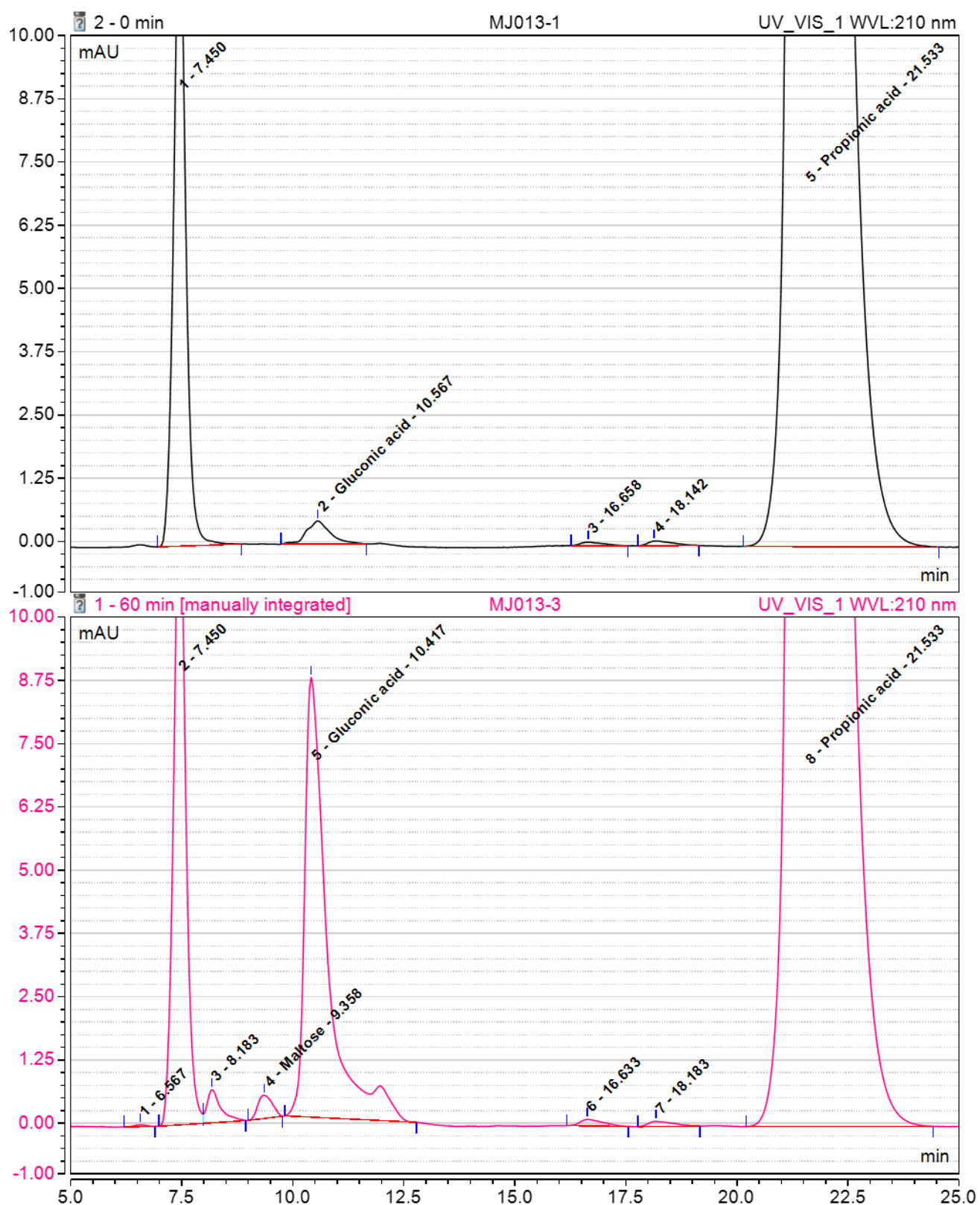


Figure 17. HPLC chromatogram of glucose oxidation on Pt/AC catalyst prepared by sol immobilisation with $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor, batch 1

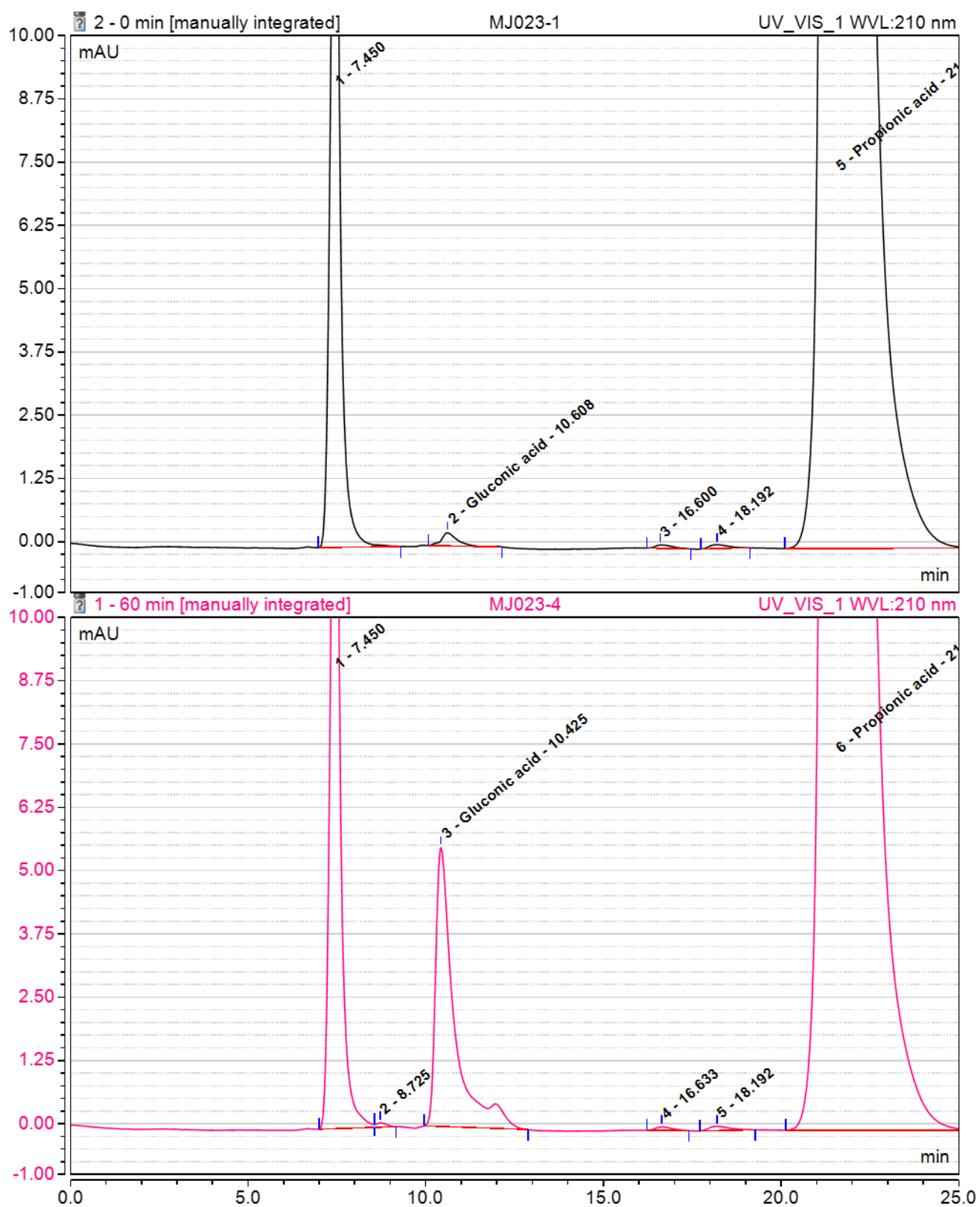


Figure 18. HPLC chromatogram of glucose oxidation on Pt/AC catalyst prepared by sol immobilisation with $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor, batch 2

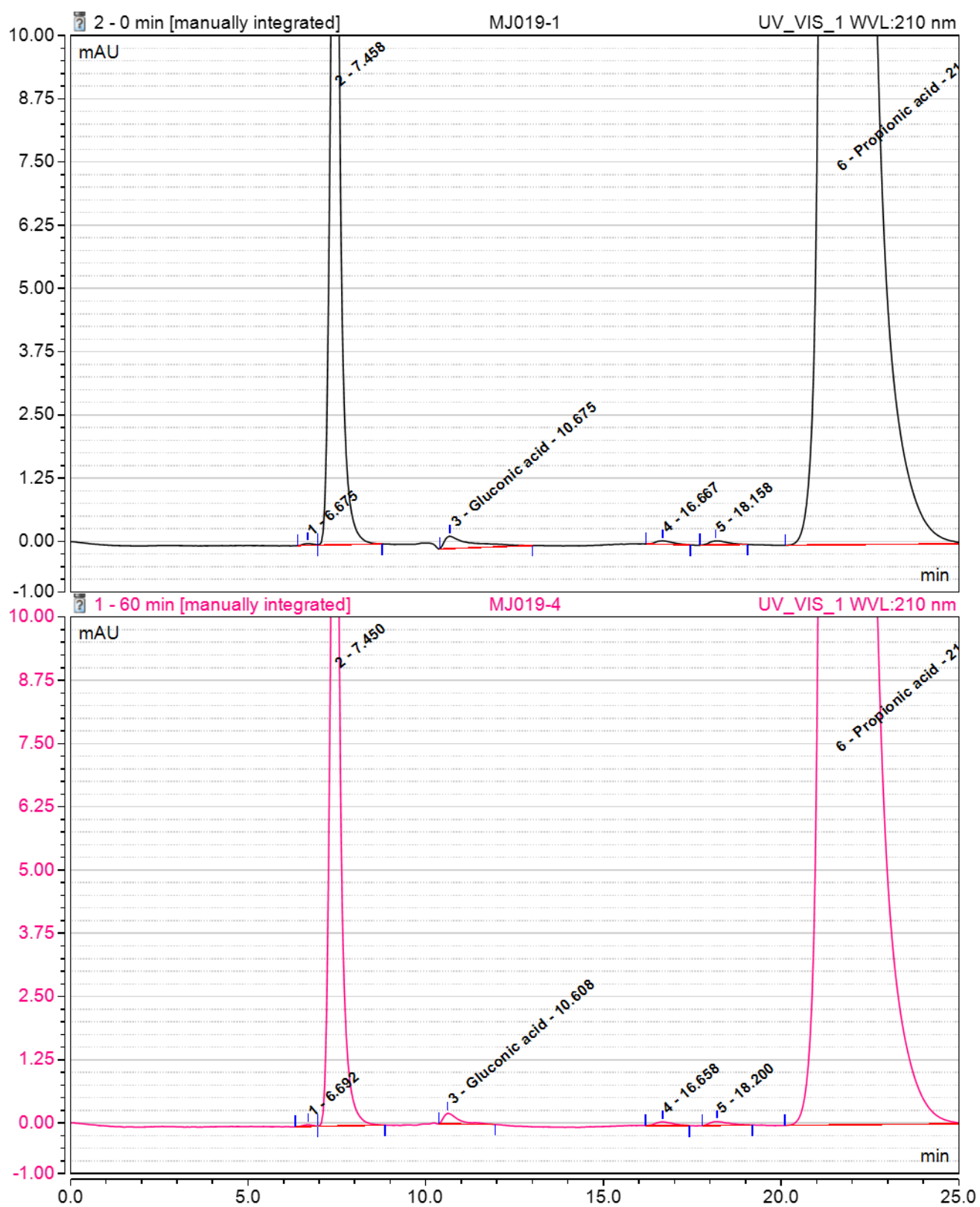


Figure 19. HPLC chromatogram of glucose oxidation on Pt/AC catalyst prepared by ion adsorption with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ precursor

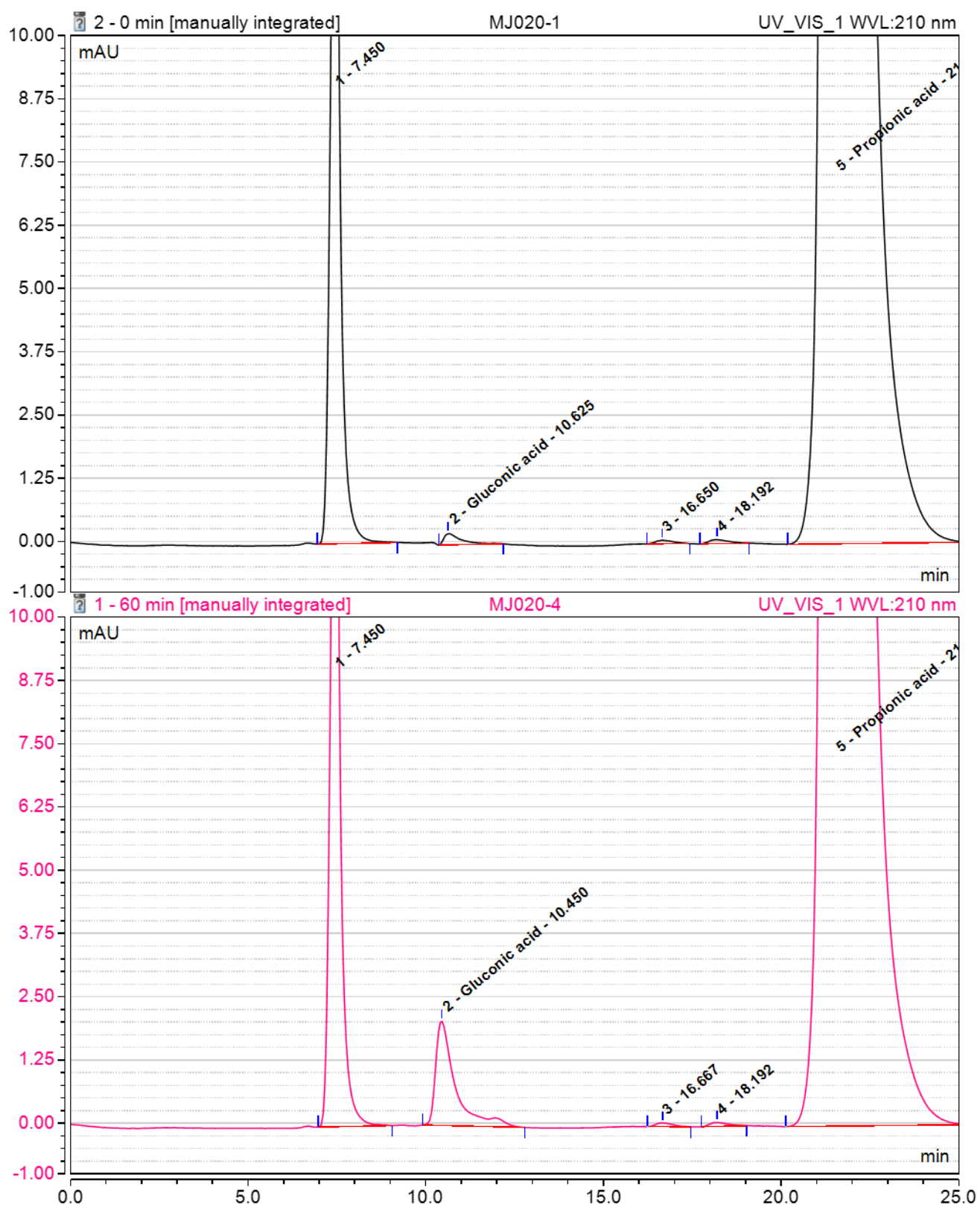


Figure 20. HPLC chromatogram of glucose oxidation on Pt/AC catalyst prepared by ion adsorption with $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ precursor

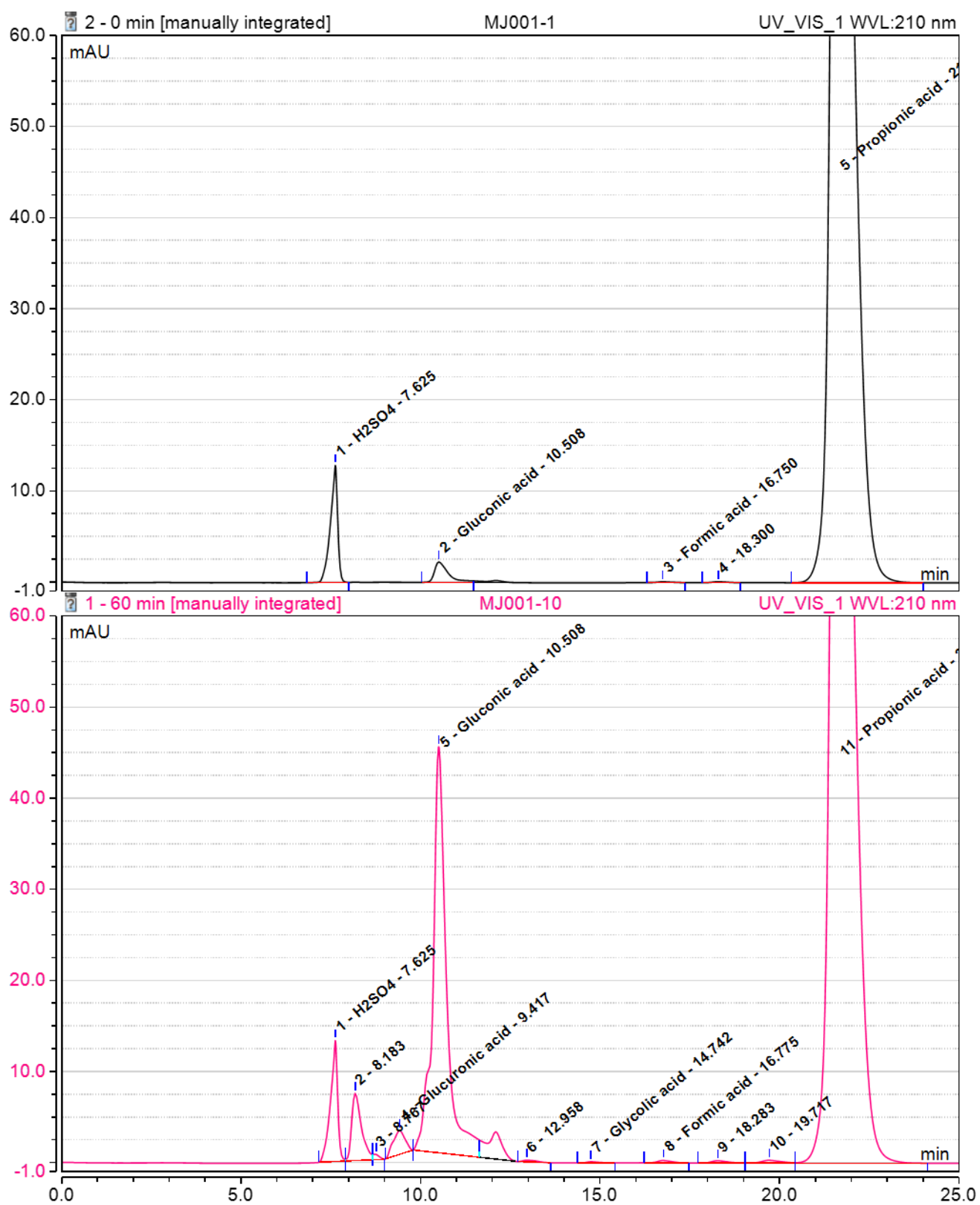


Figure 21. HPLC chromatogram of glucose oxidation on commercial 5 wt.% Pt/AC catalyst

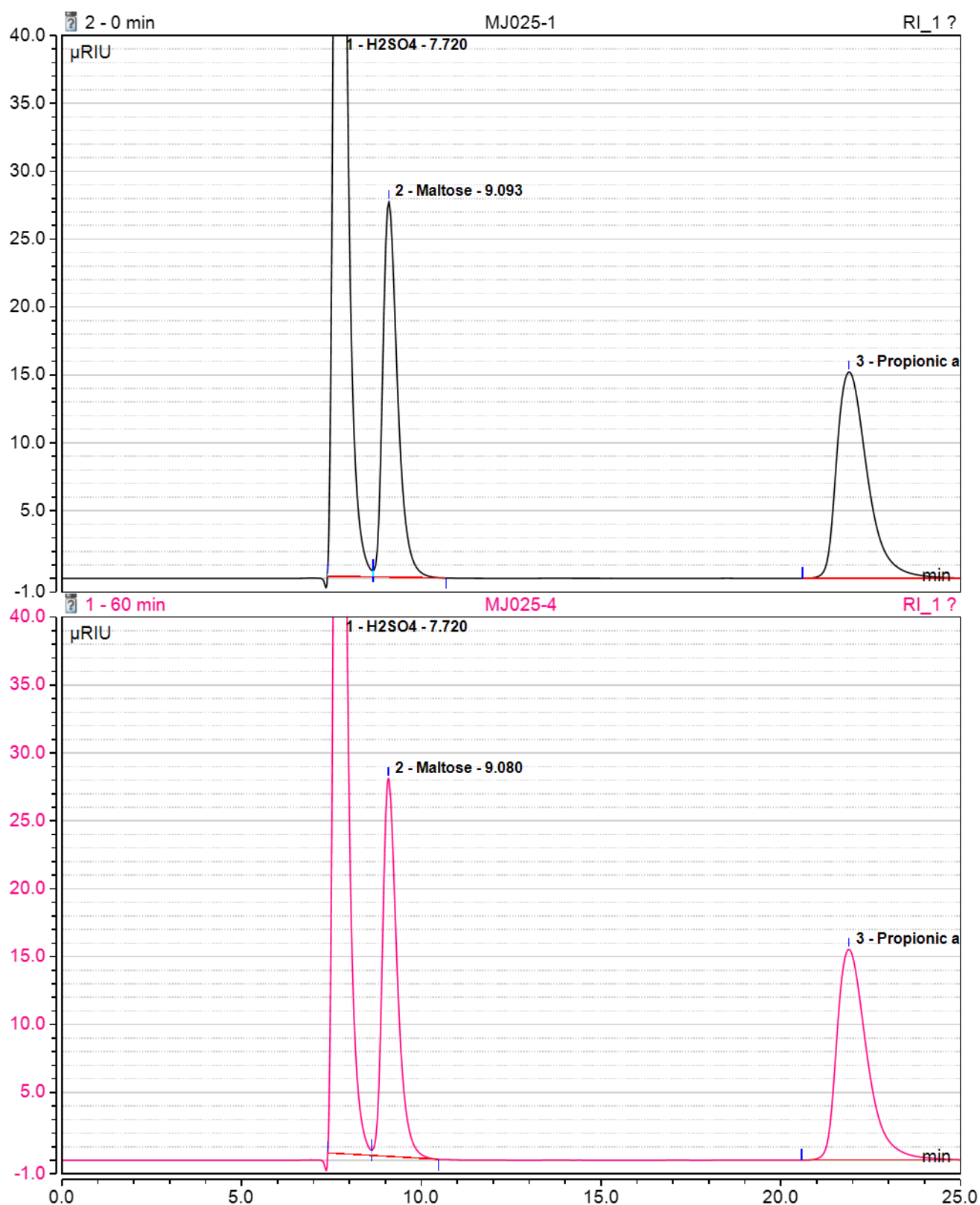


Figure 22. HPLC chromatogram of maltose oxidation on the selected Pt/AC catalyst. No difference is visible between 0 and 60 minutes because the substrate and product have very similar retention times. UV spectrum of this oxidation was taken at 210 nm, it was later proven that the product is more active at 280 nm.

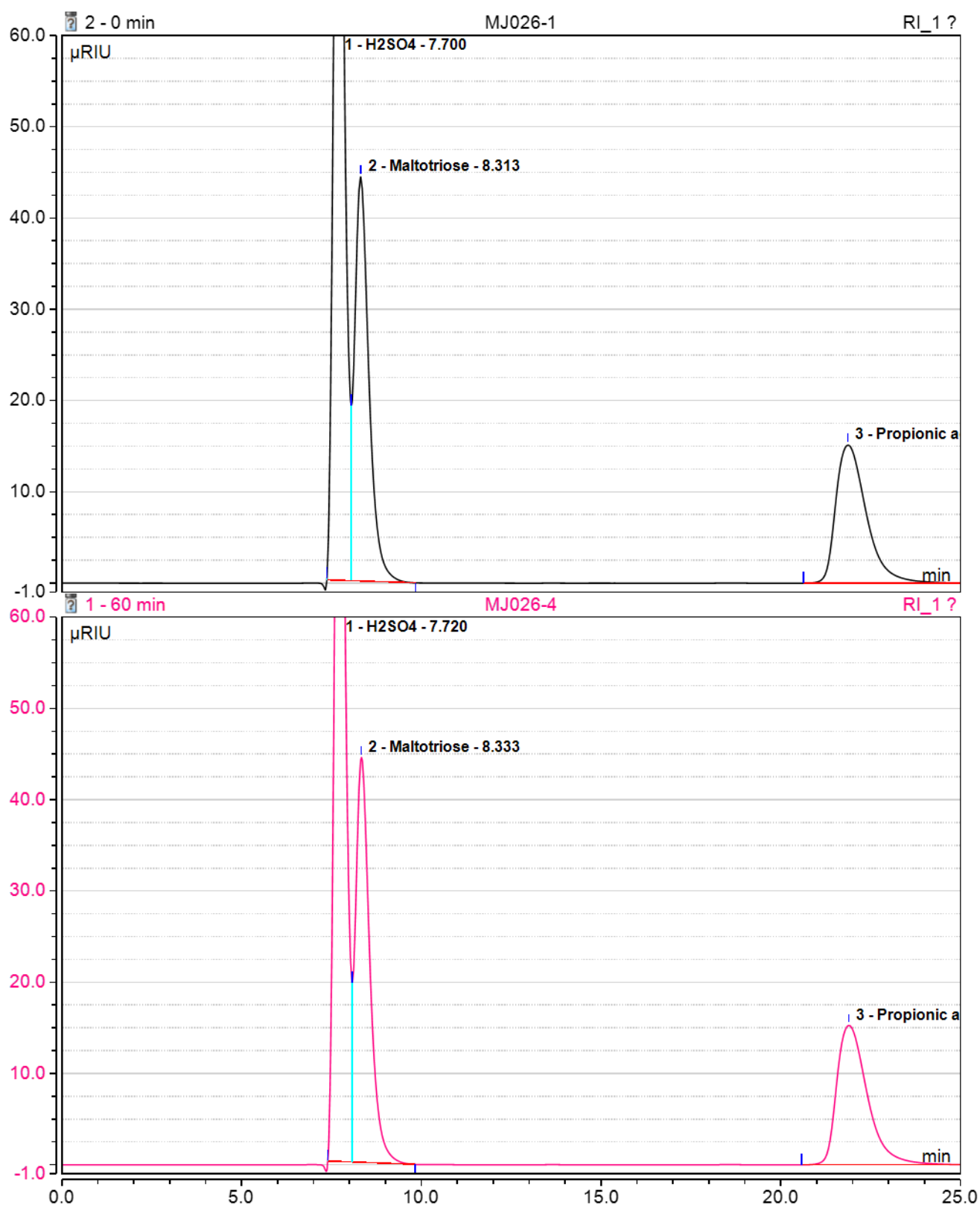


Figure 23. HPLC chromatogram of maltotriose oxidation on the selected Pt/AC catalyst. No difference is visible between 0 and 60 minutes because the substrate and product have very similar retention times. UV spectrum of this oxidation was taken at 210 nm, it was later proven that the product is more active at 280 nm.

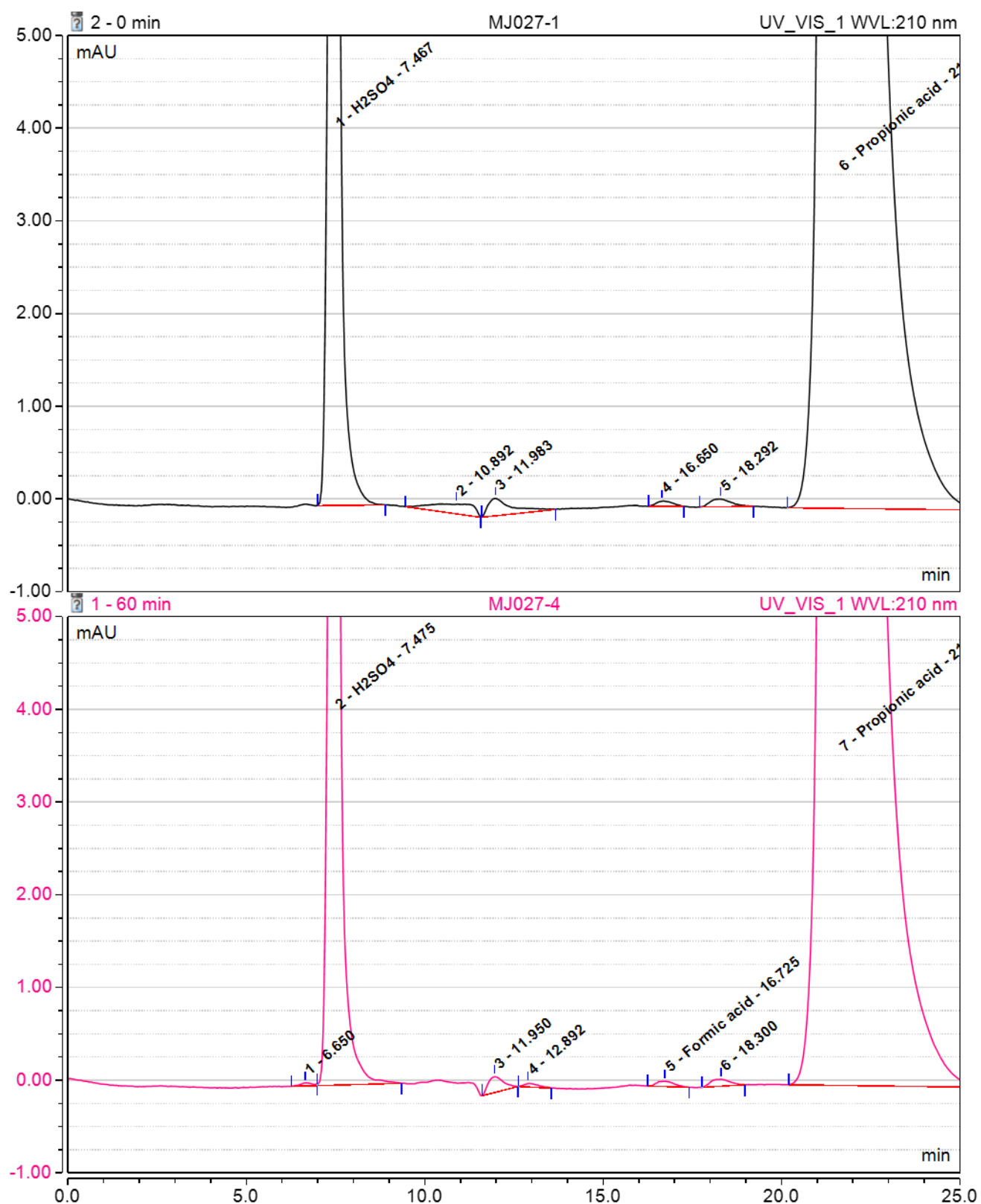


Figure 24. HPLC chromatogram of methyl α -D-glucopyranoside oxidation on the selected Pt/AC catalyst.

Table 22. Turnover frequencies (TOFs) of the differently prepared catalysts based on TEM and chemisorption data. The TOF is defined as mole substrate converted per mole surface metal * time (s^{-1}).

	Incipient wetness impregnation		Sol immobilisation		Ion adsorption		5 wt.% Pt/AC commercial catalyst
Precursor	$[Pt(NH_3)_4](NO_3)_2$	$H_2PtCl_6 \cdot xH_2O$	$H_2PtCl_6 \cdot xH_2O$, batch 1	$H_2PtCl_6 \cdot xH_2O$, batch 2	$[Pt(NH_3)_4](NO_3)_2$	$H_2PtCl_6 \cdot xH_2O$	
TOF at 10% conversion with TEM data (s^{-1})	.46	.29	.73	.52	.31	.35	.83
TOF at 10 % conversion with chemisorption data (s^{-1})	.26	.08	2.86	1.79	.68	.10	.22

VI. Mass spectra

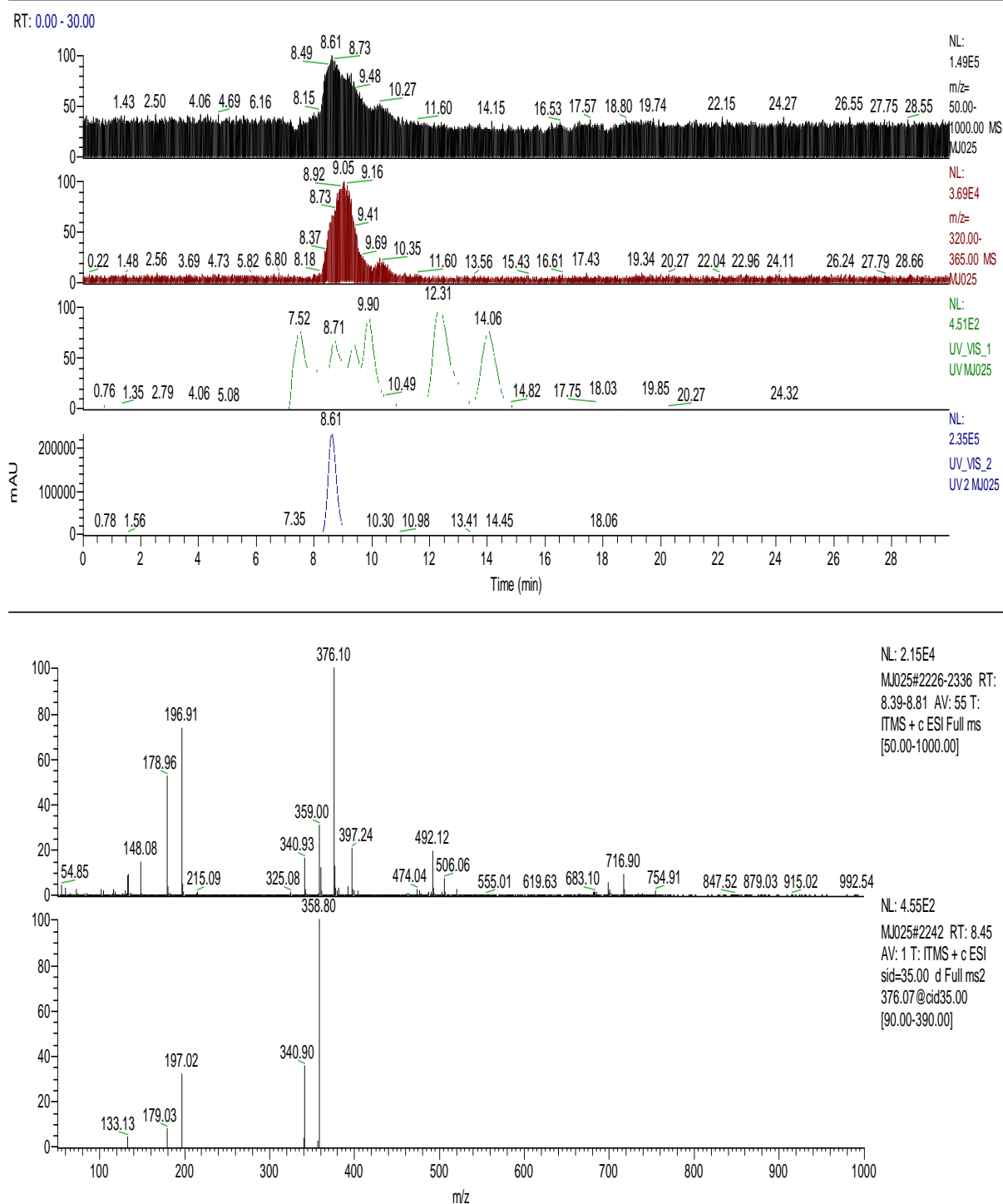


Figure 25. Mass spectrum of reaction mixture of maltose oxidation. Negative ionization was used. The first two graphs are the LC spectra, the last two graphs are UV spectra at 210 and 280 nm. Expected mass of maltose: 342 m/z, expected mass of product: 358 m/z. Maltose has a retention time of 8.9 min and is not visible with UV. Maltobionic acid has a retention time of 8.6 min and is visible at UV 280 nm (blue graph).

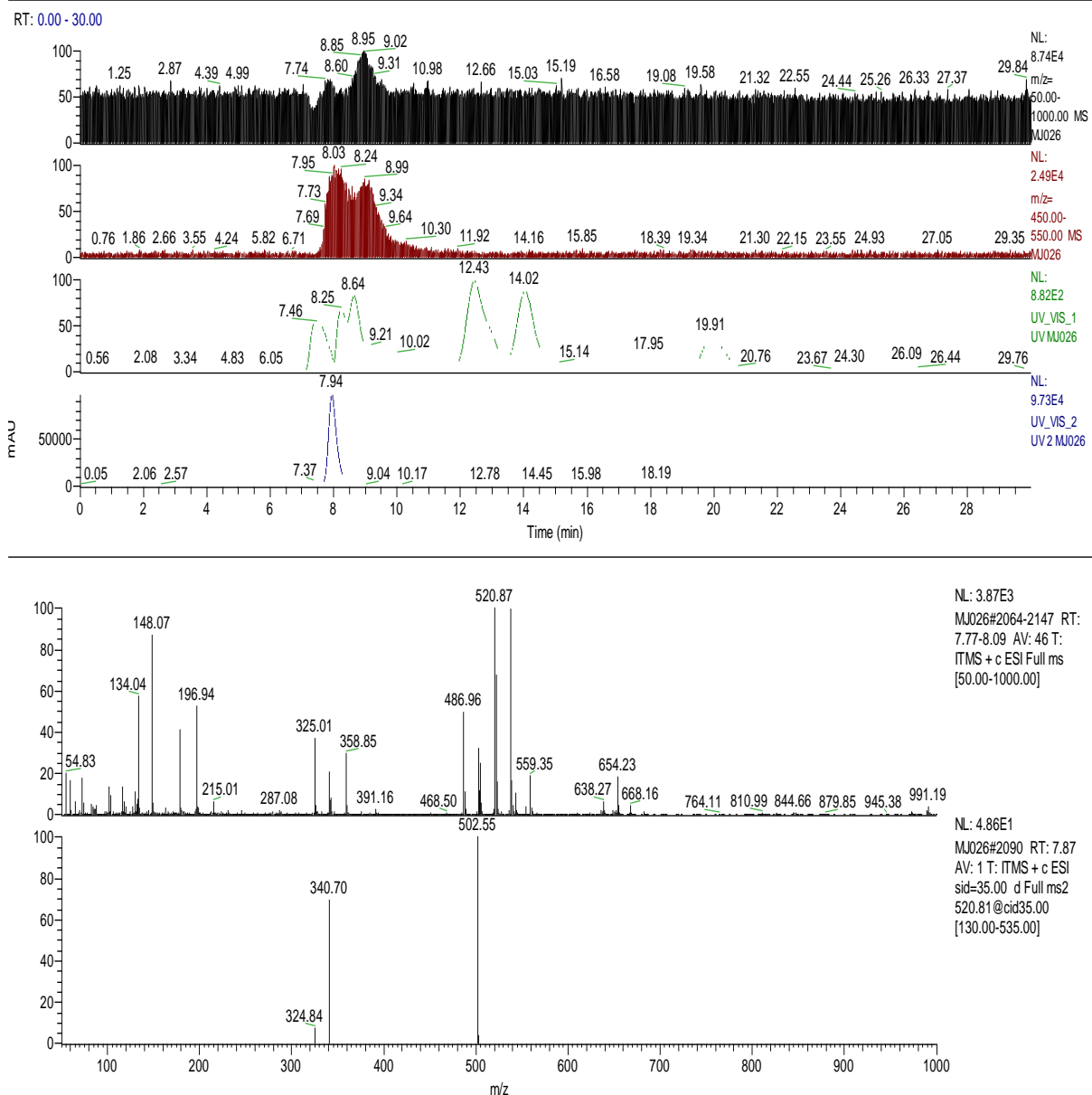


Figure 26. Mass spectrum of reaction mixture of maltotriose oxidation. Negative ionization was used. The first two graphs are the LC spectra, the last two graphs are UV spectra at 210 and 280 nm. Expected mass of maltotriose: 504 m/z, expected mass of product: 520 m/z. Maltotriose has a retention time of 8.1 min and is not visible with UV. Maltotriose has a retention time of 7.9 min and is visible at UV 280 nm (blue graph). There is also a peak visible at retention time 8.9 min, which could indicate the presence of maltose.

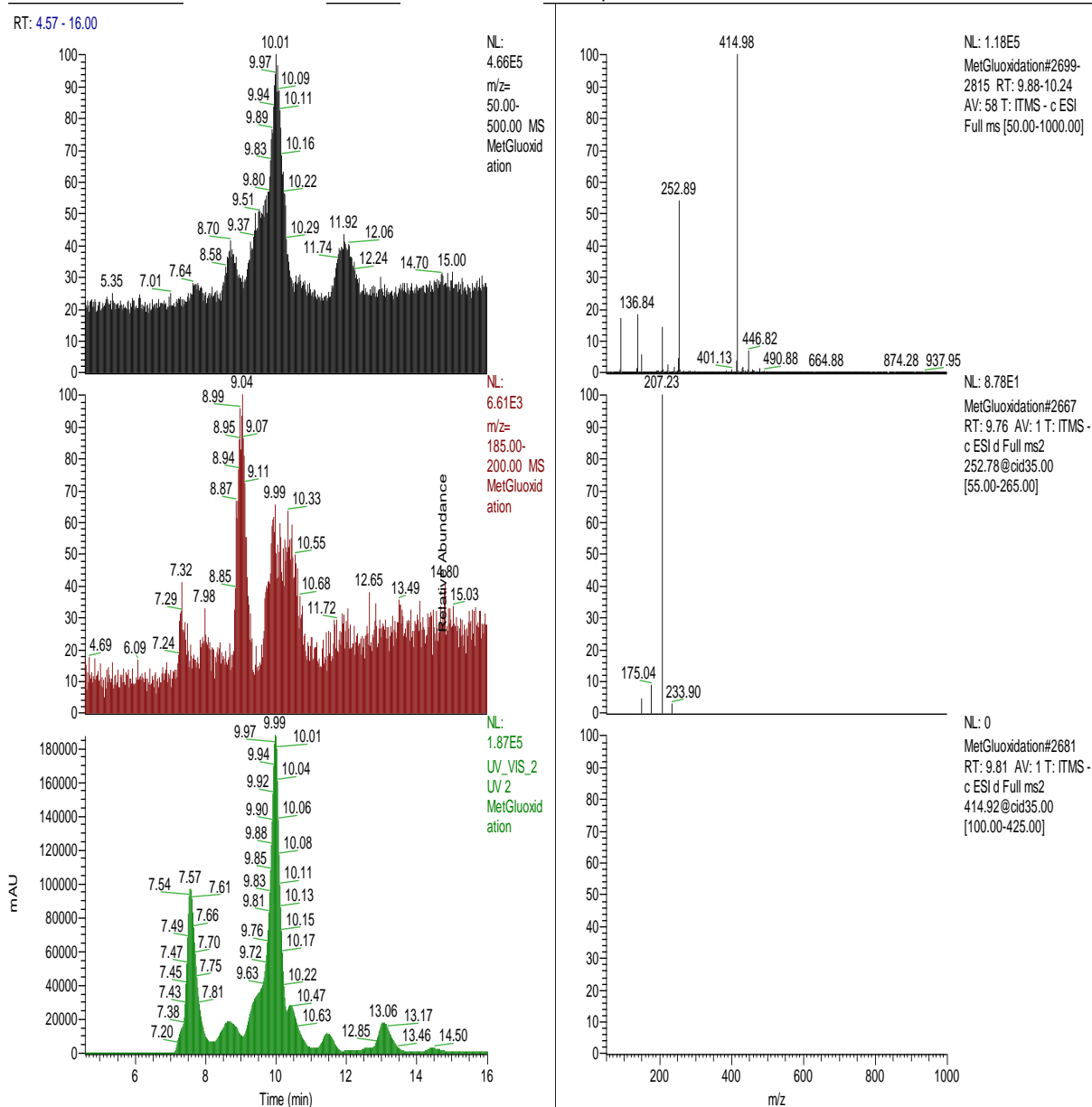


Figure 27. Mass spectrum of oxidised methyl α -D-glucopyranoside. Negative ionization was used. The first two graphs are the LC spectra, the last graph is a UV spectrum at 210 nm. Expected mass of methyl α -D-glucopyranoside: 194, expected mass of product: 210. Methyl α -D-glucopyranoside has a retention time of 11.9 and is not expected with UV. Two unknown products are visible at UV 210 nm (green graph). Retention time of product is 10.0, a second and unknown product was also measured at retention time 7.6.