

# Electrochemical reduction of benzaldehyde at platinum single crystal surfaces

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## 1. Introduction

Nowadays, catalytic technologies are the object of a great interest for industrial, business and ecological sectors all over the world. It is known that nowadays considerable amount of the heterogeneous catalysis processes include hydrogen, which is mostly produced by steam reforming of various organic compounds e.g. methanol and natural gas. As this process produces incredible amounts of CO<sub>2</sub> in contrast to steam reforming, reduction of CO<sub>2</sub>-emissions from the chemical sector require the CO<sub>2</sub> neutral production of hydrogen. This can be achieved by the electrochemical production of hydrogen when the used electricity stems from zero-emission technologies. Hence, heterogeneous hydrogenation would require a hydrogenation plants and an electrolysor. However, it can be more cost effective if the hydrogenation of organic compounds will occur due to electrolysis. In that case there is no more need in hydrogenation plant. This idea motivates scientists to study the mechanisms of electrocatalytic hydrogenation of organic compounds.

In order to study the process of benzaldehyde reduction at platinum single crystal surfaces cyclic voltammetry (CV) experiments were carried out. There were different types of single crystal electrodes used during experiments: Pt(111), Pt(110) and Pt(100).

There were already several papers where reduction of acetaldehyde, acetone and acetophenone were studied [1,2,3,4,5,6,7]. Basically, their aim was to study the reduction process of organic compounds at different single crystal electrodes in acidic media and by doing so they could suggest their mechanisms for reduction processes. From these papers the trend of C–C bond stability acetaldehyde < acetone <

acetophenone was acquired. It is interesting to know, where is benzaldehyde placed in this stability trend.

The comparison of the CVs in blank electrolyte and the electrolyte with benzaldehyde showed, that the presence of benzaldehyde suppresses the features of all the single crystals. What exactly is happening is hard to say, however it was suggested that there might be a poisoning reaction occurring at single crystal surfaces. This can be caused by CO adsorbing at the surface, as well as the phenyl ring from benzaldehyde or the products of its reduction or oxidation. All processes occur due to the cleavage of C–C bond in benzaldehyde.

The aim of the experiments is to define whether any processes occurring at the platinum surfaces of electrodes in acidic media in presence of benzaldehyde.

## **2. Experimental**

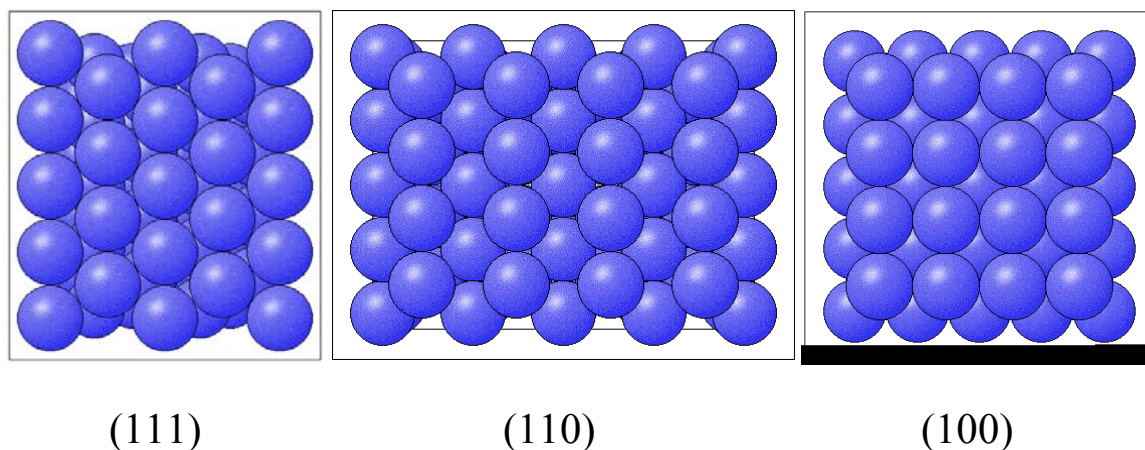
The blank electrolyte was 0.1 M H<sub>2</sub>SO<sub>4</sub>, prepared from MiliQ-water and H<sub>2</sub>SO<sub>4</sub> (suprapure, Merck). Experiments on benzaldehyde reduction were performed with the blank electrolyte containing 20 mM of benzaldehyde. Benzaldehyde (99.5%, Sigma-Aldrich) was used. As it is important to keep the electrolyte cell free from oxygen to prevent unwanted reactions, all solutions were freed from oxygen by purging with argon (6.0, Linde).

All potentials were measured versus a reversible hydrogen electrode (RHE) in contact with the blank electrolyte containing 0.1 M H<sub>2</sub>SO<sub>4</sub>. A platinum wire was used as a counter electrode. Prior to use the counter electrode it was rinsed with MiliQ water followed by annealing.

Cyclic voltammograms were recorded on Iviumstat (Ivium Technologies) and Bio-Logic VSP-300 (Science Instruments).

There are many different types of single crystals with different atomic orientation. This research was conducted with the use of Pt(111), Pt(110) and Pt(100) single crystal surfaces. Fig. 1 represents the atomic arrangements mentioned above types of single crystal atomic arrangements. Thus, (111) surface has typical hexagonal arrangement of atoms, (100) has square arrangement and (110) has rectangular arrangement of atoms.

In order to achieve a single crystalline surface, the electrode was prepared by the Clavier method [8]. After flame annealing the crystal was cooled in an atmosphere of 80% argon and 20% hydrogen. After a cooling period of 20-30 s the crystal was dipped in water, saturated with the above-mentioned gas mixture, and transferred to the electrochemical cell.



**Fig. 1.** View from the top at the atomic arrangement of (111), (110) and (100) surfaces

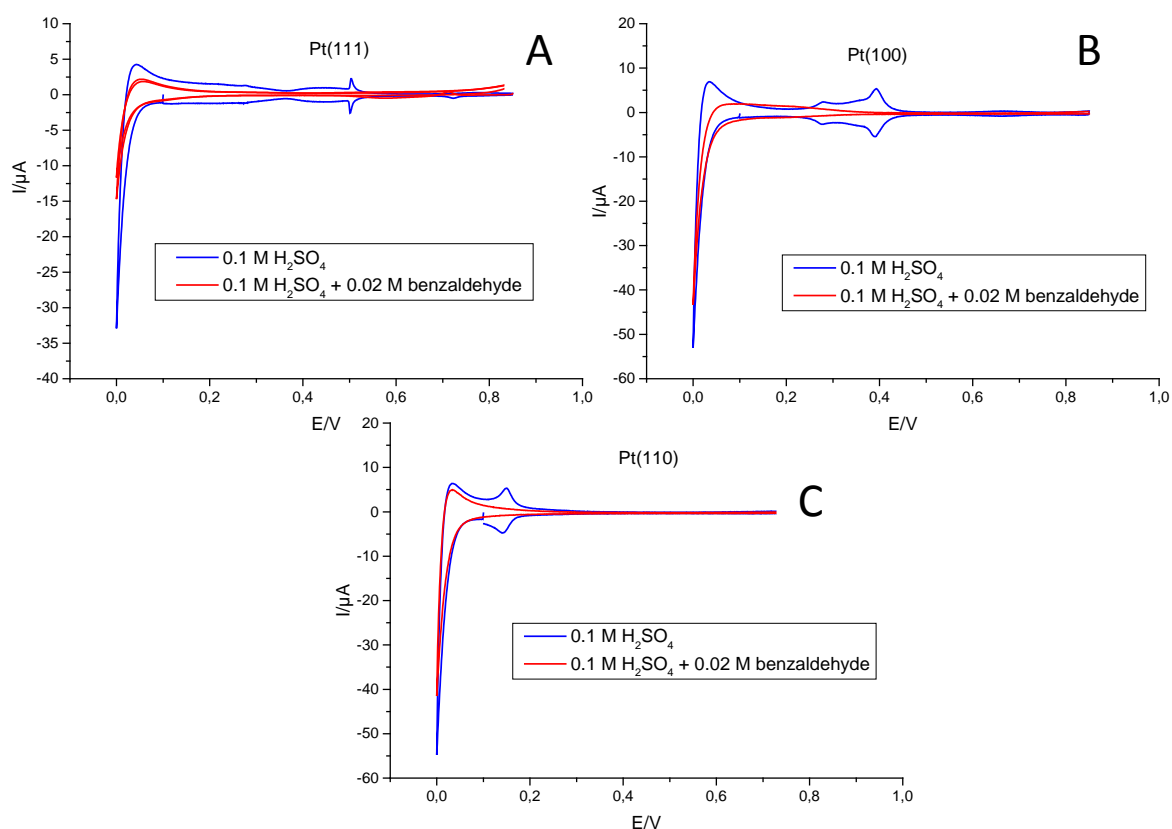
Cyclic voltammetry experiments were conducted with bead type single crystals. The glassware used in experiments was kept in permanganate solution for at least 8 hours. Before using glassware, it was cleaned with solution of sulfuric acid (95-97%, ACS reagent) and hydrogen peroxide (35%, Merck) and must be boiled in MiliQ water for at least 3 times. Used sulfuric acid and hydrogen peroxide solution were neutralized before pouring it out into a sink. In order to do this sodium bicarbonate powder (100%, VWR Chemicals) was used.

### 3. Results and discussion

Fig. 2 compares CVs obtained in the blank electrolyte of 0.1 M  $\text{H}_2\text{SO}_4$  with those obtained in the electrolyte of 0.1 M  $\text{H}_2\text{SO}_4$  and 0.02 M of benzaldehyde. In the CV of Pt(111) obtained in the blank electrolyte adsorption/desorption at the Pt(111) terraces is observed in the potential range of 0.15 to 0.35 V. In the potential range of 0.0 to 0.15 V there is a current which corresponds to hydrogen evolution and it is present at all types of single crystals. The typical sulfate spike at Pt(111) is present at 0.5 V. In contrast, CV in the electrolyte with benzaldehyde shows that Pt(111) features were

suppressed, which means that during the experiment some species were adsorbed at the platinum surface. As these species can no longer be removed by cycling to 0.85 V, they block the surface and fewer amounts of products can be adsorbed in further cycles. The current in the potential region between 0.0 V and 0.15 V decreases with the addition of benzaldehyde to the blank solution. This feature indicates, that less hydrogen is evolved and if there is a benzaldehyde reduction, then less species are reduced. Hence, there is something being adsorbed at the Pt(111) surface in presence of benzaldehyde, that blocks the surface.

We do not observe an oxidation process in the first sweep starting from 0.85 V going in negative direction. This indicates that benzaldehyde does not oxidize or anything else present in the electrolyte as the oxidation process should already take place in the first sweep.



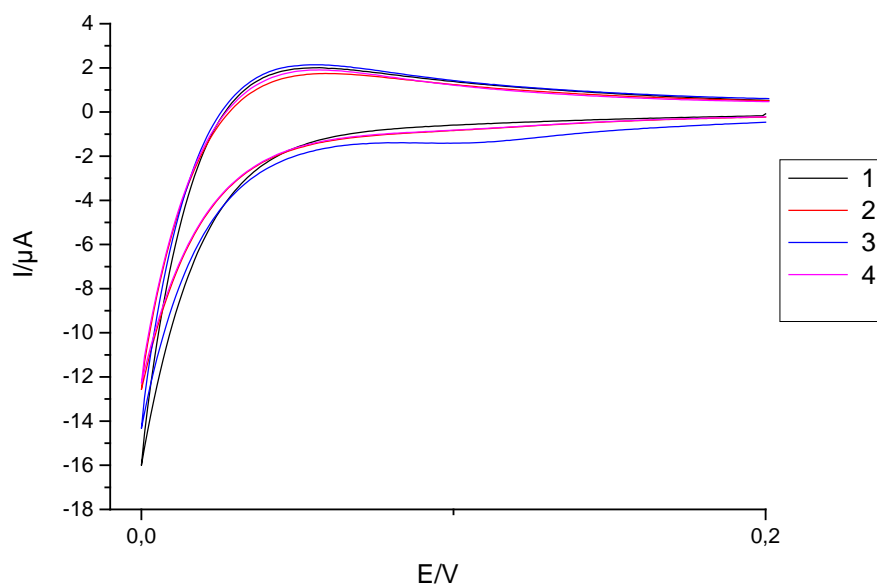
**Fig. 2.** CVs at different types of platinum single crystal electrodes in blank electrolyte (blue curves) and in solution containing 0.02 M benzaldehyde (red curves). CVs at Pt(111) (A), Pt (100) (B) and Pt(110) (C)

There is also a slight current increase at potentials starting from approximately 0.75 V at positive going sweep, which might indicate an oxidization process. Hence, there is something accumulating at the platinum surface during a cycle and at 0.75 V it starts to oxidize. This oxidation process might be the  $\text{CO}_{\text{ads}}$  being oxidized to  $\text{CO}_2$ , what usually happens at potentials starting from 0.5 V. There can also be some species related to the products of benzaldehyde reduction or oxidation, which adsorb at the platinum surface during a negative going sweep and they start to oxidize at higher potentials. These results are interesting because acetone does not suppress any Pt(111) features [5]. This means that acetone does not adsorb at the Pt(111) electrode and it appears to be inactive towards acetone reduction. In case of acetophenone Pt(111) features are suppressed due to reduction of acetophenone. Hence, there is strong acetophenone adsorption at the Pt(111) indicating considerable activity of the Pt(111) electrode for acetophenone reduction.

At the other types of the single crystal surfaces the situation does not change. The CV at Pt(100) in the blank electrolyte shows us a typical peak at 0.4 V indicating hydrogen adsorption at Pt(100) terraces. At Pt(100) the current corresponding to hydrogen evolution is observed between 0.0 V and 0.15V. With addition of benzaldehyde these processes are suppressed and the current, which corresponds to hydrogen evolution is reduced. The same situation is observed for Pt(110), where hydrogen adsorption takes place at the potential of 0.15 V. The addition of benzaldehyde to the blank electrolyte leads to the suppression of all reactions at any type of platinum surfaces. This is an indication of the adsorbate presence, which competes with the adsorption of hydrogen at the platinum surfaces. There is only one reduction region at potential range of 0.0 V to 0.15 V, where reduction of benzaldehyde can take place, or the hydrogen evolution occurs.

In order to see if the electrode can be reactivated specific experiment was conducted. This experiment was aimed to obtain a CV, which consists of 4 cycles in the solution with benzaldehyde at Pt(111). The first cycle is an ordinary cycle carried out without any changes. At the end of the second cycle the potential was stopped at 0.85 V for 3 minutes. Cycles number 3 and 4 were also obtained without any

changes. From the CV data shown at Fig. 3 the current between 0.0 V and 0.15 V is reduced in the second cycle compared to the first cycle. The deactivation of the electrode from the first to the second cycle indicates that an adsorbate accumulates at the surface of the Pt(111) electrode. On the other hand, reactivation of platinum crystal occurs in the third cycle, meaning that some adsorbate was oxidized, while staying at 0.85 V. It results in the increase of a current at the third cycle, meaning that less adsorbate was adsorbed at the third cycle in respect to the second cycle.



**Fig. 3.** CV in the electrolyte containing 0.1 M  $\text{H}_2\text{SO}_4$  and 0.02 M benzaldehyde at Pt(111). Numbers are the sequence of the cycles

Hence, reactivation happened due to the oxidation process, that was taking place at the second cycle. However, reactivation is not complete, as the current between 0.0 V and 0.15 V in the first and the third cycles are different. That might indicate the presence of the species, which were not fully oxidized at 0.85 V for 3 minutes. Previously it was mentioned that adsorbed CO is oxidized around 0.5 V. If the adsorbate was only CO we would expect it to be removed at 0.85 V already. Hence, there is another fragment of benzaldehyde than CO accumulates at the Pt(111), which is more difficult to remove than the CO.

The results of this experiment show that adsorbate is being formed during the process at the platinum surface in solution containing benzaldehyde. The surface of

platinum single crystal can be reactivated if the potential remains at 0.85 V, but this reactivation is only partial. Some adsorbate remains at the surface of platinum electrode indicating poisoning reaction at Pt(111).

#### **4. Conclusions**

The data obtained from CVs indicate that a poisoning reaction leads to deactivation of the platinum single crystal surfaces. However, holding the potential at 0.85 V for extended periods of time reactivates the single crystal surface partially. Although, from the data obtained it is obvious that there is a poisoning reaction occurring at all types of single crystal surfaces these data are not enough to understand whether the poisoning reaction is adsorption of CO or the adsorption of species related to benzaldehyde or its products. We can only suggest in correspondence to literature, that  $\text{CO}_{\text{ads}}$  species are totally removed from the platinum single crystal surface at potentials higher than 0.5 V. If that is so then the poisoning reaction, which takes place at the platinum single crystals occurs due to the presence of benzaldehyde inside the cell with the electrolyte.

It is also hard to say if benzaldehyde reduction is taking place, so there is no clear evidence for the position of benzaldehyde in stability trend acetaldehyde < acetone < acetophenone. Hence further researches are required to answer this question, as well as to define whether benzaldehyde reduction is taking place at the platinum single crystal surfaces and if so, then which products are formed during the reduction.

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## References

- [1] De Hemptinne, X.; Schunck, K., Electrochemical reduction of acetone. Electrocatalytic activity of platinized platinum. *Transactions of the Faraday Society* **1969**, *65* (0), 591-597.
- [2] Bänsch, B.; Härtung, T.; Baltruschat, H.; Heitbaum, J., Reduction and oxidation of adsorbed acetone at platinum electrodes studied by DEMS. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1989**, *259* (1), 207-215.
- [3] Zinola, C. F.; Rodríguez, J. L.; Arévalo, M. C.; Pastor, E., A DEMS study of the electroreduction and oxidation of 3-buten-2-one and 2-butanone adsorbates on platinum in sulphuric solutions. *Journal of Electroanalytical Chemistry* **1998**, *454* (1), 161-172.
- [4] Bondue, C. J.; Koper, M. T. M., A mechanistic investigation on the electrochemical reduction of aliphatic ketones, SUBMITTED FOR PUBLICATION.
- [5] C. J. Bondue, F. Calle-Vallejo, M. C. Figueiredo, M. T. M. Koper, Structure-sensitive Selectivity of the Electrochemical Reduction of Aliphatic ketones at platinum Single Crystal Electrode, SUBMITTED FOR PUBLICATION.
- [6] Lai, S.; Koper, M., Lai, S. C. S. & Koper, M. T. M. Electro-oxidation of ethanol and acetaldehyde on platinum single-crystal electrodes. *Faraday Discuss.* **140**, 399-416. 2008, **140**, 399-416; discussion 417.
- [7] Lai, S. C. S.; Koper, M. T. M., The Influence of Surface Structure on Selectivity in the Ethanol Electro-oxidation Reaction on Platinum. *The Journal of Physical Chemistry Letters* **2010**, *1* (7), 1122-1125.
- [8] Clavilier, J.; Armand, D.; Sun, S. G.; Petit, M., Electrochemical adsorption behavior of platinum stepped surfaces in sulphuric acid solutions. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1986**, *205* (1), 267-277.