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Electrocatalytic oxidation of glucose and starch over Pt based catalysts

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PURPOSE OF THE ABSTRACT

Introduction

With the transition towards the use of renewable feedstocks and renewable energy the use of bio-based molecules as feedstock and electrocatalytic conversions gain in interest. Our target is to electrocatalytically convert starch to oxidized starch, which forms a replacement for the currently used fossil based poly-acrylates. To develop efficient electrocatalysts for the oxidation process fundamental insights in catalyst property-performance relationships are essential. Since starch is a complex molecule we aim at getting these insights by using gradually more complex feedstocks, going from monomers to oligomers to polymers (e.g. from glucose to cellobiose to starch).

In earlier work we showed that the presence of surface oxygen groups on carbon nanofiber supported catalysts can have a significant influence on the performance of the catalyst. For example for the hydrogenation of cinnamaldehyde over Pt on carbon nanofibers (Pt/CNF) it was shown that the activity increased by decreasing the number of oxygen groups on the CNF support1. Later we showed that the presence of oxygen groups is beneficial for the decarboxylation of lipid based feedstocks towards alkanes and alkenes2. In both cases the modified adsorption of the reactants and products influenced by the oxygen groups i.e. polarity of the support could explain the observed catalytic performance. Here we will show that for the electrocatalytic oxidation of glucose over Pt/CNF, carboxylic acid groups on the carbon support have a negative influence on the catalytic activity, while hydroxyl groups have a positive influence. We will also show preliminary results on the electrocatalytic oxidation of starch over polycrystalline Pt catalysts.

Materials and Methods

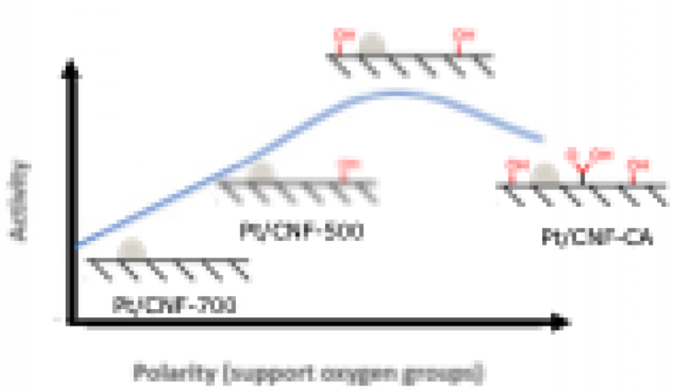
CNF supports were synthesized by chemical vapor deposition using CO/H2 and a Ni/SiO2 growth catalyst. After synthesis the mixture was treated in sequential steps with 1M NaOH and 68% HNO3 to remove the growth catalyst and to introduce carboxylic acid and hydroxyl groups on the support (CNF-CA).1 Incipient wetness impregnation of Pt ammonium nitrate on CNF-CA followed by calcination was used to make the catalyst (5.0 wt.% Pt/CNF-CA). Pt/CNF-CA was heat treated at 300, 500 and 700 ?C to gradually remove the support oxygen groups (samples are denoted as Pt/CNFx with x the treatment temperature).1 The prepared electrocatalysts were drop-casted on a glassy carbon electrode to evaluate their performance for glucose oxidation by linear sweep voltammetry (LSV) and chronoamperometry (CA). The properties of the electrocatalysts were thoroughly analyzed by N2-physisorption, TEM, CO-stripping, TPD-MS, TGA, XPS, CV and titration.

Results and Discussion

Figure 1 shows a summary of the linear sweep voltammetry of glucose over Pt/CNF with different amounts of oxygen groups on the CNF surface (amounts of oxygen groups determined by TGA and XPS). Clearly a maximum exists in the activity as function of the number and type of oxygen groups. We explain this by an optimal concentration of glucose on the surface of the catalysts with the highest amount of OH groups (Pt/CNF-300) but without carboxylic acid groups (Pt/CNF-CA). We hypothesize that the type and presence or absence of support oxygen groups can either improve: 1) the electron charge transfer to the catalyst or 2) the hydrophilic interaction of the reactant with the support in close proximity to the catalyst surface (electronic effects were not apparent from XPS).

In a next step we attempted electrocatalytic starch oxidation over polycrystalline Pt. Figure 2 shows a typical cyclic voltammogram for that reaction. The two oxidation peaks at 0.75 and 1.1V indicate the oxidation of starch molecules over metallic Pt and PtO2 respectively. Therefore we conclude that it is possible to oxidize large biobased molecules such as starch in an electrochemical cell. The use of 3D Pt/CNF electrodes for starch oxidation are currently under investigation.

FIGURES



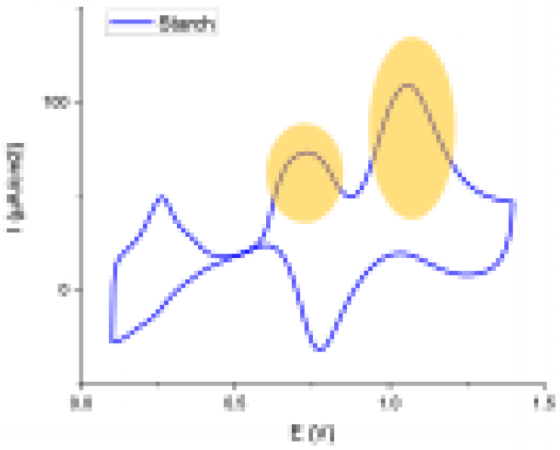


FIGURE 1

Figure 1

Figure 1: influence of support polarity on the electocatalytic oxidation of glucose over Pt/CNF. Linear sweep voltammetry of 0.1M glucose at pH1 after subtraction of the supporting electrolyte contribution.

FIGURE 2

Figure 2

Figure 2: Cyclic voltammetry of starch (0.1M, pH=13) over polycrystalline Pt. In the forward scan the desorption of hydrogen (0.25V), starch oxidation over metallic Pt and PtO2 (0.75 and 1.1.V, highlighted in yellow) and in the backward scan Pt reduction

KEYWORDS

Starch oxidation | electrocatalysis | support effect | glucose oxidation

BIBLIOGRAPHY