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The electrocatalytic behaviour of Pt and Cu nanoparticles supported on carbon nanotubes for the nitrobenzene reduction in ethanol

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ABSTRACT

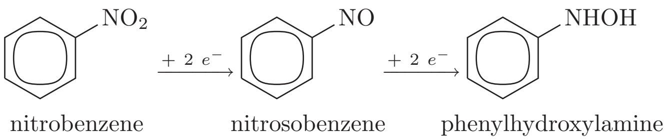
In view of investigating the possibility of cogeneration of chemicals and electricity in a fuel cell type reactor, a suitable electrocatalyst and optimal reaction conditions have to be found. The nitrobenzene reduction was taken as the case study reaction for this investigation. In literature no suitable electrocatalyst has been found for this reaction. Pt and Cu nanoparticles, supported by multiple wall carbon nanotubes, were taken as electrocatalysts and ethanolic and acidic ethanolic environments were studied as possible reaction media. The Cu nanoparticle catalyst displayed superior electrocatalytic behaviour since less overpotential is needed for the nitrobenzene reduction in both ethanolic and acidic ethanolic environment. The acidic ethanolic conditions were superior to the ethanolic conditions as less overpotential was required for the nitrobenzene reduction reaction and a higher conversion of nitrobenzene is obtained. In acidic ethanolic environment, a four-electron reduction is taking place, which was assigned to the reduction of nitrobenzene into phenylhydroxylamine. This compound is re-oxidised into nitrosobenzene when the solution comes into contact with oxygen, and the formed nitrosobenzene selectively reacts with another phenylhydroxylamine molecule, yielding azoxybenzene. The latter is an important compound in organic synthesis.

1. Introduction

In the chemical industry, many processes rely on oxidation and reduction reactions for the production of various chemicals. As these processes are typically heavily exothermic, this leads to a high amount of waste heat, which cannot be fully recuperated. The energy efficiency of these processes is thus often low. Moreover, the selectivity of the reactions that take place in these processes is usually rather low. Apart from leading to loss of raw material, this implies that extra purification steps, that introduce additional costs, are necessary.

The difficulties described above could be overcome by electrochemical production of these chemicals in a fuel-cell type reactor. Such reactor would offer unique opportunities both for energy saving (by cogeneration of electricity) and for selectivity (by using the optimal electrocatalyst). In this work, the hydrogenation of nitrobenzene is selected as a case study reaction, as its feasibility for cogeneration was proven by Yuan et al. [1] and it has a vast range of useful end-products, including aniline, p-aminophenol, azoxybenzene and cyclohexylamine.

The reaction mechanism of the electrochemical reduction of nitrobenzene has been studied extensively in the last decades [2–11]. It is generally understood that the reduction of nitrobenzene occurs in two steps; in the first step, four electrons are exchanged: nitrobenzene is reduced to phenylhydroxylamine through the intermediate of nitrosobenzene (Eq. (1)).



(1)

Although the reaction mechanisms differ, the formation of phenylhydroxylamine can occur in acidic [6], neutral and alkaline conditions [8]. After the formation of phenylhydroxylamine, in

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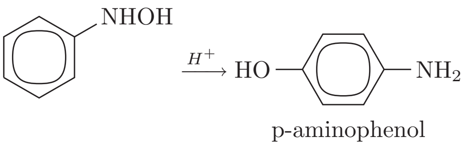
acidic environment, two pathways are possible, namely the chemical rearrangement of phenylhydroxylamine to p-aminophenol, and the electrochemical exchange of two more electrons, producing aniline. In neutral and alkaline environment p-aminophenol is not formed.



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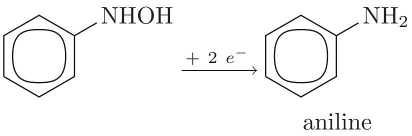
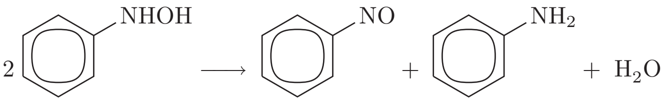


(3)

The cathode material on which the reduction of nitrobenzene takes place is expected to have a strong influence on the rate of the different reactions that can occur. For instance, Kokkinidis et al. [6] found that Pb electrode materials and Pb adsorbates on Ag completely suppress the formation of aniline. Cyr et al. [9] showed that Cu electrodes can promote the reduction of phenylhydroxylamine to aniline, regardless the pH of the supporting electrolyte.

Besides the obvious effect of the acidity of the supporting electrolyte, the electrolyte has another strong influence on the reactions taking place. This was illustrated by Pintauro et al. [12]. They found that in tetraethylammonium p-toluenesulphate, an aprotic solvent, nitrobenzene could be reduced as far as to cyclohexylamine, whereas in protic solvents aniline could not be reduced further.

The stability of the intermediates has to be considered as well. Grosková et al. [13] determined that phenylhydroxylamine can easily disproportionate to aniline and nitrosobenzene (Eq. (4)) in the presence of clay catalysts. Because nitrosobenzene can react with an extra phenylhydroxylamine towards azoxybenzene (Eq. (5)), an equal amount of azoxybenzene and aniline is found in the solution. Because of this distribution of end-products, the disproportionation of phenylhydroxylamine is not selective, making it undesirable in the fuel cell-type reactor.



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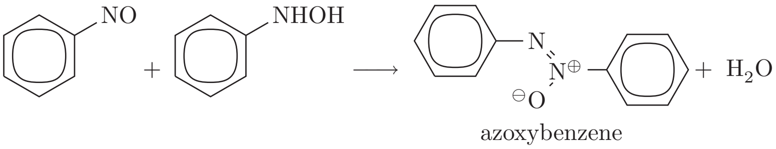

(5)

All the described reaction mechanisms were derived from studies on bulk electrodes. For a cogeneration fuel cell-type reactor, a suitable electrocatalyst is needed, with high surface area and decreased costs compared to bulk electrodes. No previous studies have been found on finding suitable metal nanoparticle electrocatalysts for the nitrobenzene reduction. Therefore, the innovative goal of this study is to find a suitable electrocatalyst and optimal reaction conditions for the reduction to take place. The products that are formed during the reduction are also investigated. Pt and Cu nanoparticles, supported by multiple wall carbon nanotubes (MWCNT), are considered as electrocatalysts. Reaction conditions were set to favour aniline. Because aniline is only slightly soluble in water but highly soluble in ethanol, ethanolic and acidic ethanolic solutions where considered as supporting electrolyte. As the anodic reaction in a fuel cell for cogeneration will consist of hydrogen oxidation, alkaline solutions are not considered for the supporting electrolyte, even though they have been reported as good electrolytes for the production of aniline in half-cell setups [7].

2. Experimental

The electrocatalysts used in this study are part of a group of catalysts specifically developed for the nitrobenzene reduction. The two electrocatalysts present in this study are Pt/MWCNT and Cu/MWCNT-H_2. They have been selected to investigate the effect of reaction conditions. Pt/MWCNT was prepared following a modification of a previously reported method [14,15]. $H_2PtCl_6.6H_2O$ was reduced by ethylene glycol and sodium acetate as stabiliser. The preparation of the Cu/MWCNT-H_2 catalyst consisted of the reduction of $Cu(NO_3)_2$ by H_2. The support of both catalysts consists of commercially available multiwalled carbon nanotubes (Nanocyl, 90%) with an average diameter of 9 nm and lengths of 20–50 nm. Further information about the different catalysts can be found in Sheng et al. [16]

All electrochemical measurements were carried out using an Autolab 302N potentiostat or a BioLogic VMP3 multichannel potentiostat. Analysis of the formed products after chronoamperometry was performed using HPLC (Shimadzu equipped with a Prevail C18 column, particle size 5 μm, 250 mm × 4.6 mm I.D. and UV–vis detector SPD 10 Avp).

Porous rotating disc electrodes were used for all electrochemical measurements. For the preparation of the electrodes, 8.0 mg of electrocatalyst was dispersed in a 1m% solution of polystyrene in toluene. Five microliters of this dispersion was then added in the form of a drop on a glassy carbon electrode, after which the toluene was evaporated during 20 min at 50° C. The glassy carbon electrode consisted of a 6.0 mm diameter glassy carbon rod encased in a 18.0 mm diameter PTFE sheet. The electrolyte used in the measurements consisted of either 0.2M $LiClO_4$ (Sigma–Aldrich, 98.0%) or 0.3M $HClO_4$ (VWR, Analar Normapur, 70%) in absolute ethanol (VWR, Analar Normapur, 99.9%). Nitrogen gas was bubbled through the electrolyte to remove oxygen. The temperature of the electrolyte was set to 25°C using a thermostatic bath. A Pt grid was used as counter electrode, while the reference electrode was a Ag/AgCl (sat. LiCl) electrode (Autolab). The exact potential of the reference electrode was measured by a cyclic voltammetry measurement of the ferrocene/ferrocenium (Fc/Fc^+) reference couple ($E^0_{Fc/Fc^+} = -0.64\,V$). All potentials in this paper are referred to this redox couple.

The electrolyte resistance was calculated using the method described in [17] using conductivity measurements, and the calculation was confirmed by the impedance found in EIS measurements (ranging from 100 mHz to 200 kHz) at the high frequency range. An electrolyte resistance of $190\,\omega$ and $96\,\omega$ was found for the 0.2 M $LiClO_4$ and the 0.3 M $HClO_4$ solutions in ethanol respectively.

The linear sweep voltammetry (LSV) measurements consisted of two steps; first the electrode ‘blank’ was measured three times