



Selective reduction of nitrobenzene to aniline over electrocatalysts based on nitrogen-doped carbons containing non-noble metals

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ABSTRACT

Non-noble metals (Fe, Co or Cu) supported on N-doped carbons were investigated for the first time as electrocatalysts for the reduction of nitrobenzene to aniline in a half-cell setup. The electrocatalysts were prepared by pyrolysis of composites of activated carbon (AC) and polyaniline (PANI) with incorporated metal sites. The electrocatalyst performance was strongly influenced by the nature of the metal and by the synthesis method. For the latter, a different optimum was identified for each metal. The Cu-based electrocatalyst synthesised with a low amount of PANI and Cu relative to AC, was identified as the best electrocatalyst based on its onset potential, kinetic current density and selectivity to aniline. Most importantly, unprecedented selectivity to aniline was obtained (82%, as determined by chronoamperometry) with this electrocatalyst in a half-cell setup. This makes it a promising candidate for the electrochemical cogeneration of the industrially valuable aniline and electricity in a proton-exchange membrane fuel cell.

1. Introduction

Aniline is an important industrial chemical product [1], which is largely employed as reagent for the synthesis of polyurethane [2]. In 2010, the world aniline production was ca. $2.3 \cdot 10^6$ tons, of which 2/3 was utilised in the production of polyurethane [3]. Currently, aniline is mainly produced through the hydrogenation of nitrobenzene with Raney nickel or other nickel alloys as catalyst [1,4,5]. In order to achieve sufficiently high conversion and selectivity towards aniline (currently between 80 and 90%, with azobenzene and azoxybenzene as the main side-products), the reaction is performed at 35–125 °C, at high H_2 pressure (≥ 0.6 MPa) and with long reaction times [1,2,4,5]. Furthermore, since this hydrogenation reaction is exergonic ($\Delta_r G^\circ < 0$), a high amount of heat is typically lost in the process. In general, safe heat removal can be challenging and might lead to reactor hot spots, lowering the reaction yields [6,7].

An attractive, green alternative to this process could be provided by an electrochemical approach, where aniline is produced at room temperature in a fuel cell and the chemical energy liberated by the reaction is converted into electricity. In this way, the synthesis of a valuable

product like aniline can be coupled with electricity generation, giving rise to a more sustainable and more energy-efficient process [8,9]. Moreover, the electrochemical aniline production would offer the possibility to control the reaction rate and the selectivity by tuning the electrical potential [10]. For this route to become competitive with the current industrial production, research should be dedicated to the development of an active, selective, stable and affordable electrocatalyst, which is the focus of this work, of an efficient and cost-effective membrane, and to the assembly of these components into a fuel cell [11,12].

The possibility to reduce nitrobenzene electrochemically was first investigated by Haber et al. and has been further developed since then [7–9,13]. The electrochemical cell typically consists of an anodic and a cathodic compartment, which are separated by a proton exchange membrane (PEM). At the anode, protons and free electrons are generated from the oxidation of hydrogen. Both flow to the cathodic compartment, the electrons through an external circuit and the protons through the PEM. Once they reach the cathode, they are involved in the reduction of nitrobenzene. The overall reactions are:

Anode:

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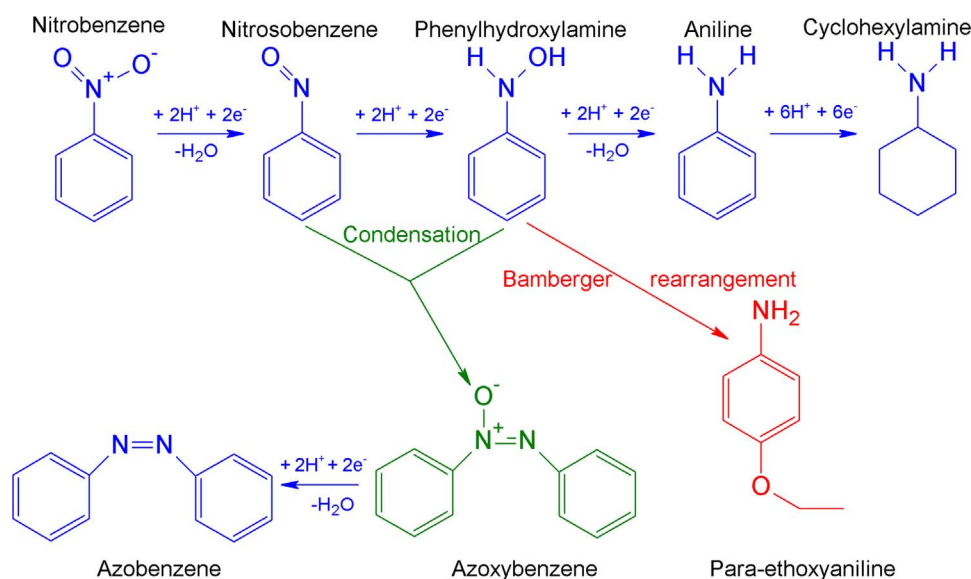
E-mail address: p.p.pescarmona@rug.nl (P.P. Pescarmona).

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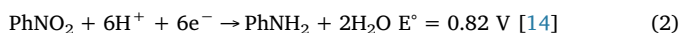
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Scheme 1. Reaction scheme of the reduction of nitrobenzene.



Cathode:



However, the full reaction scheme is more complex and can involve both electrochemical and chemical steps [7–9,15]. It is generally accepted that the reduction of nitrobenzene to aniline consists of two main steps: first, nitrobenzene is reduced to phenylhydroxylamine (PHA) through a 4-electron exchange, with nitrosobenzene (NSB) as an intermediate. Then, a 2-electron reduction step converts PHA to aniline (Scheme 1) [16,17]. Nitrosobenzene is generally not detected since it is rapidly converted to PHA via a second 2-electron reduction [17]. PHA is a very unstable compound and, besides being reduced to give aniline, it can also react further through three competitive chemical reactions, leading to the formation of side-products as azoxybenzene, azobenzene and para-ethoxyaniline (Scheme 1). These competitive reactions have already been discussed in detail elsewhere [7–9,18–20]. If aniline is obtained through the electrochemical reduction of nitrobenzene, care should be taken to avoid further reduction to cyclohexylamine. The formation of this side-product has been reported to take place on carbon-supported platinum (Pt/C) electrocatalysts in a fuel cell [21].

The outcome of the nitrobenzene reduction is strongly influenced by the employed electrocatalyst [7,16,17,19,22–26] and by the reaction conditions, such as the electrode potential [17,19,24] and the pH of the electrolyte solution [16,23,24,27]. It has already been demonstrated that the selectivity towards aniline can be increased by applying more negative electrode potentials. However, an optimal potential exists since the possibility to further reduce aniline towards cyclohexylamine becomes more likely at increasingly negative potentials. Furthermore, at these potentials the Faradaic efficiency towards the reduction of nitrobenzene is decreased by a competing reaction, i.e. the hydrogen evolution [17,24]. The effect of the pH was investigated previously and it was determined that nitrosobenzene is detected in alkaline environments, suggesting slower reaction kinetics [27] and that the 2-electron reduction step to form PHA is strongly hindered in alkaline environment compared to acidic or neutral environments [7,24]. In this work, the electrochemical reduction of nitrobenzene was investigated in acidic (HClO_4) ethanolic environment, in a half-cell setup by means of linear sweep voltammetry (LSV) and chronoamperometry.

The nature of the electrocatalyst used at the cathode has a crucial impact on the nitrobenzene reduction rate and at the same time on the selectivity of the reaction. Therefore, the development of efficient and

cost-effective electrocatalysts is of utmost importance for enabling the practical application of the electrochemical route to produce aniline with cogeneration of electricity. Commonly used cathode electrocatalysts for this specific reaction are noble metals like Pt, Pd, or Au supported on activated carbon or carbon nanotubes [7,9,21,25]. Even if these materials offer a good activity and stability, their high cost is a drawback, which limits commercialisation [7,17,24]. Non-noble metals such as Cu or Fe have been identified as less expensive alternatives to the noble metals but in an electrochemical approach they do not reach sufficiently high selectivities to aniline [7,24,26]. Recently, it was demonstrated that the presence of a metal is not strictly necessary as N-doped diamond [24] was shown to be an efficient electrocatalyst for the production of aniline from nitrobenzene. A drawback of N-doped diamond is that it is synthesised through chemical vapour deposition, which requires severe conditions and implies a high production cost [12]. In order to make the electrochemical cogeneration approach economically viable, more research is necessary to further enhance the selectivity to the target product, aniline, and this in combination with a reduction of the electrocatalyst manufacturing costs.

In this work, non-noble metals (Fe, Co or Cu) supported on N-doped carbons were investigated for the first time as electrocatalysts for the cogeneration of aniline and electricity. Iron, cobalt and copper were chosen as metal species in the electrocatalysts because they are affordable and abundant and they have several accessible oxidation states, which can be beneficial to promote the reduction reaction. Previous work by our group already investigated the use of supported copper nanoparticles as electrocatalysts for the nitrobenzene reduction reaction [7–9]. However, since the selectivity was still low, further improvements were required. Therefore, in this work it is proposed to replace the multi-walled carbon nanotubes as a support by N-doped carbons. The nitrogen doping is expected to enhance the electrocatalytic performance by generating extra active sites for the nitrobenzene reduction (N-doping generates partially positively charged carbon atoms, which might act as active sites) [12] and by improving the interaction between metal and support (possibly enhancing electron exchange). Inspired by our previous observations that Cu outperformed Pt as a consequence of its more electropositive behaviour, iron and cobalt, which are both more electropositive than copper, were chosen as alternative metals in an attempt to further enhance the reduction performance [7]. Our design of catalysts also shows a relationship to recent developments in the chemical reduction of nitrobenzene over heterogeneous catalysts, in which N-doped carbons with different morphologies were employed as support for noble and non-noble

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