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Stability study of silver nanoparticles towards the halide electroreduction

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ABSTRACT

The field of electrosynthesis has undergone a tremendous advancement in the past few decades by implementation of a catalyst at the nanoscale level. While significant knowledge on factors that influence the activity of specific reactions such as carbon-halogen (CX) bond activation has been gained, many questions regarding the stability and degradation of nanoparticles still remain unsolved. Through the combination of a three-folded advanced characterization approach that combines electrochemical, analytical and microscopic results we are for the first time able to map the degradation of nanoparticles for CX bond activation reaction. This methodology is exemplified on the stability study of the most active nanoparticles towards CX bond activation, namely Ag nanoparticles. Results indicate that under electrochemical operation conditions Ag nanoparticles degradation occurs via two mechanisms: (i) agglomeration/coalescence and (ii) electrochemical dissolution of nanoparticles in the electrolyte. Identification of these degradation mechanisms is a first step in the understanding and subsequently controlling the synthesis of active and sustainable catalyst towards industrial applications.

1. Introduction

In the past decade organic electrosynthesis has manifested itself as one of the methodologies that can fulfill several important criteria that are needed if society is to develop environmentally compatible industry [1]. Organic electrosynthesis processes are characterized with a high chemo selectivity, good functional group tolerance and relatively mild operation conditions [2–4]. Furthermore, the ease with which many electrochemical reactions can be scaled up, as well as the intrinsic “greenness” of the reactions (the electron being an affordable, clean and energy efficient reagent) make these processes attractive for industrial applications [4]. Since electrochemistry offers a selective addition and/or removal of electrons from organic molecules, it is an ideal tool to activate functional groups [2,5]. To ensure that a specific functional group is converted and the overpotential (e.g., activation energy) of the reaction is reduced an electrocatalyst is often used [6,7]. One of the most important features of electrocatalysis arises from the different electrode kinetics using various materials and crystallographic orientations of the electrode surface [8,9]. The choice of an appropriate electrode material and morphology is thus crucial to boost the catalytic activity.

The reductive cleavage of organic halides (RX) is a reaction where an electrocatalyst plays an effective role [10–13]. The electrocatalytic reduction of RX compounds proceeds through an attenuated radical intermediates involving R, X and M [14–16]. It has been shown that the molecular structure (R) [10], the nature of the halogen atom (X) [17], cathode material [12,18,19], (Me) and surface morphology [20,21] of the electrode play an important role in the electrocatalytic process. Research indicates that metals such as Ag, Au, Cu, Pd, Pb, Ni and Hg possess beneficial catalytic properties towards the halide reduction [10], [17]. Efforts to further improve the activity of the electrocatalyst towards RX bond activation have been directed towards shifting from bulk electrodes to nanoparticles and via introduction of a second or third metal [11,18]. While significant knowledge on factors that influence the activity of CX bond activation is obtained, many questions regarding the stability and degradation of nanoparticles still remain unsolved.

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Nanoparticles need to preserve their activity in time and remain stable during electrochemical operation conditions. When nanoparticles degrade, this is typically macroscopically reflected by a loss of EASA, which results in efficiency loss. In aqueous media, a multitude of studies has been carried out to investigate the degradation behaviour of the electrocatalyst [22,23]. One of the predominant stability issues is the growth of particles, which is accompanied by a decrease in EASA [24]. Identified degradation mechanisms are agglomeration/coalescence/coarsening [25], Oswald Ripening [26,27], dissolution and reshaping [28]. However, accurate knowledge of the degradation mechanism of nanoparticles in organic media for specific reactions such as C-X bond activation is still absent. This is a serious limitation for better electrocatalysts in applications since an understanding of the degradation processes is crucial in developing sustainable active electrocatalysts.

The aim of this study will be to investigate the stability of metallic electrocatalytic nanoparticles towards CX-bond activation. The stability study will be exemplified on Ag nanoparticles that are known for their excellent electrocatalytic activity towards the CX reduction. In supplementary information (Tables S1–S2), we additionally show the stability of other nanoparticles such as Ni, Cu, Pb and Pd, which show similar degradation processes as Ag. The stability of the nanoparticles is investigated with different benzyl halides having bromine, chlorine and iodine atom for an in-depth study of the role of the halogen atom in the degradation. The degradation mechanism is simulated with an accelerated-aging protocol at low-temperature conditions. During this protocol voltage cycling is repeated between the potential window where CX bond activation takes place, −2 V and 0 V, at the rate of 1 cycle every few seconds. Repetitions of up until 15.000 cycles allow for appropriate distinction between the different electrocatalysts durability.

Since CX bond activation involves the use of organic solvents (e.g. Methanol, Acetonitrile), presents of halogens (which are known for catalyst poisoning) and negative electrode potentials (until ca −2 V vs. Ag/AgCl) a basic electrochemical approach with cycling, pulsing and the use of rotating disk experiments (RDE) is not adequate for an in-depth degradation study. For this reason, we propose a threefold advanced characterization strategy that covers (i) the electrochemical, (ii) analytical and (iii) the microscopic aspects of this study. The electrochemical investigation is conducted using Cyclic Voltammetry (CV) and Linear Sweep Voltammetry in combination with rotating disk electrodes (LSV-RDE) as primary investigation techniques. For the analytical determination of dissolved/detached nanoparticles, we propose a completely new approach by coupling an electrochemical flow cell with atomic absorbance spectrometry (AAS). Similar to the electrochemical flow cell coupled to inductively coupled plasma mass spectrometry used to study stability of noble metal nanoparticles [29–32]. We show that by on-line dilution of the solvent stream it is possible to determine the removed metal content. Finally, the microscopic study is carried out using an Identical Location Scanning Electron Microscopy approach (IL-SEM). This method allows, as the name suggests, the observations of the same site (and thus the same nanoparticles) before and after electrochemical treatment (polarization) and was previously described by Hodnik et all [28–30].

2. Materials and methods

2.1. Catalyst preparation

Nanoparticles were electrodeposited on a carbon rod or glassy carbon electrode (denoted as respectfully GC). Before each deposition, the GC was intensively polished to prior extend by ultrasonic rinsing in isopropanol and ultra-pure water (18.2 MΩ.cm). Electrodeposition occurred in an electrolyte solution of methanol (MeOH) (J.T. Baker, HPLC gradient) containing tetrabutylammonium perchlorate (TBAP, Sigma Aldrich, 99%) and 1 mM $AgNO_3$ (Sigma Aldrich, >99%). Before each deposition, the electrolyte was deaerated with N_2 to prevent oxide formation. For a complete description of the electrodeposition procedure, the authors refer to their previous work [21]. Electrodeposition and all electrochemical measurements (CV- LSV/RDE) were carried out with an Autolab PGSTAT 302F in a classical three electrode electrochemical cell with a GC working electrode, Pt counter electrode and Ag/AgCl reference electrode. The reference electrode was separated from the working electrode through a salt bridge, limiting chloride or water contamination in the measurement medium. Unless stated otherwise all mentioned potentials were reported vs. Ag/AgCl. The electrochemical stability measurements were performed in an organic electrolyte solution of Acetonitrile (ACN Sigma Aldrich, HPLC grade), 0.1 M TBAP and 1 mM of the investigated halide (Benzyl bromide, Sigma Aldrich 95%; Benzyl Chloride, Sigma Aldrich 95% or Benzyl Iodide, Sigma Aldrich 97%). In supplementary (Table S3) we additionally investigate the degradation in other solvents; MeOH (J.T. Baker, HPLC gradient) and dimethylsulfoxide (Biosolve, HPLC gradient). Before all measurements the ohmic drop of the electrochemical system was measured (average 83Ω) with electrochemical impedance spectroscopy and compensated until 60% of this value. Higher compensation percentages gave rise to oscillation and noise and were therefore omitted.

2.2. Microscopic characterization

CR/GC rods with Ag nanoparticles were characterized with a field-emission SEM (Supra 35 VP Carl Zeiss and Quanta FEG 250). Before each SEM measurement the electrodes were dried to air overnight while imaging took place at acceleration voltages of between 3 and 15 kV. ImageJ SXM 192.1 was used to extract the average particle diameter from thresholded SEM images.

2.3. Analytical characterization

To investigate the loss of electrochemically active material during operation conditions Atomic Absorption Spectroscopy (AAS) or Inductively coupled mass spectrometry (ICP-MS) was coupled with an electrochemical flow cell (shown in Supplementary Information Fig. S1). This on-line approach enables the determination of the dissolution profile under electrochemical operation conditions. An overview of the set-up can be consulted in the supplementary information (Fig. S1). For the flow cell, a continuous flow of 0.1 mL/min was set. To ensure stable operating conditions of the furnace, the electrochemical flow stream was diluted one half with milli-Q water. Standards for the calibration curve were prepared in-house by dilution of certified, traceable, single-element standards (Merck Certipur). For detection of the samples an iCE AAS Atomic Absorption Spectrometer with furnace atomizer and D_2 background correction was used.

3. Results and discussion

3.1. Electrochemical

Fig. 1 presents repetitive voltammograms of Ag nanoparticles for the reduction reaction of respectfully (A) benzyl bromide (B) benzyl chloride (C) benzyl iodide (C). To reflect the change of the CVs over the whole testing time, cycle number 0, 5000, 10000 and 15000 are shown. These cycles are recorded at a slow scanning rate of 50 mVs^{-1} without rotation. After the cycle at slow scan rate, the