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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.

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 (Table 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 al. [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<sub>3</sub> (Sigma Aldrich, >99%). Before each deposition, the electrolyte was deaerated with N<sub>2</sub> 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 1mM 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  $83\Omega$ ) 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 3-15 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 Figure 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 (Figure 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. 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

Figure 1 presents repetitive voltammograms of Ag nanoparticles for the reduction reaction of respectively (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  $50\text{ mVs}^{-1}$  without rotation. After the cycle at slow scan rate, the speed of the scan rate is

increased until  $1\text{Vs}^{-1}$  to ensure a time feasible experiment. In the supplementary information (Table S5), we additionally show that the number of cycles is the cause of the degradation of the nanoparticles and not the scan rate. The Ag nanoparticles are repeatedly scanned in an organic electrolyte solution of ACN to cathodically cleave the CX bond. Although ACN is used as a solvent similar results can be obtained in MeOH and DMSO as solvents (Supplementary Information, Table S3). The CV measurements show for the first scan a distinct cathodic peak (Figure 1, see arrows) at  $-0.95\text{ V}$  (C-Br, Figure 1A),  $-1.76\text{ V}$  (C-Cl Figure 1B) and  $-0.62\text{ V}$  (C-I, Figure 1C). These reduction potentials are in complete accordance with literature [35].

The curves for the cycled electrodes almost coincide with each other in respect with the reduction peak potential (Figure 1 and Table 1). In Figure 1A a small splitting of the peak can be notice. Authors speculate that this feature is caused by the presence of different morphologies or crystal facets structures. The change of the reduction peak potential is plotted in Table 1 exhibits a steady-state potential. Since the overpotential contributes to the activation energy due to the rate of the electron transfer process at the electrode surface or processes that precede/follow it, this indicates that the intrinsic catalytic activity of the nanoparticles remains unaltered for all investigated C-X bond ruptures (Figure 1- Table 1). In the present case, an excess of electrocatalytic material is present in comparison with the concentration of reactant whereby small changes in electrocatalytic properties might not be visible. Therefore the concentration of one benzyl halide (benzyl bromide) is increased until  $0.1\text{ M}$  (Table S4). By increasing the concentration from  $1\text{ mM}$  to  $0.1\text{ M}$  the reduction peak potential shifted towards more cathodic values with ca.  $150\text{ mV}$  (Table S4). This higher flux of electrochemically active species towards the electrode surface is caused by the increased concentration gradient between bulk and surface, where the species get consumed. This enhanced diffusion (e.g., a higher concentration of reactants at the surface) ensures that the mass diffusion-controlled region is reached at a lower potential. The onset potential does not change for all measured concentrations. More importantly, the reduction peak potential does not shift, for the same concentration, with the ongoing cycles indicating that the stable electrochemical activity is not due to an excess of Ag nanoparticles (as discussed in the previous sentences), but most likely due to the decreased coverage of Ag nanoparticles on the CR electrode.



However when the current density is evaluated different results are obtained. The current densities at peak potentials shown in Figure 1 and Table 1 are calculated vs. the geometric surface area. This is done to take into account possible changes in electrochemical active surface area. With an increasing number of cycles the current density drops for all carbon-halogen bond cleavages until a value of less than half of the initial current density (Table 1). An identical decrease can be observed when the charge of the reduction peak is evaluated as a function of the number of degradation cycles (not shown). The authors speculate that this drop in current density can be caused by two phenomena. (i) A poisoning or passivating where the nanoparticles not get altered or (ii) the opposite where the change is purely structural. The former is caused by the reaction when the carbon-halogen bond is ruptured halide anions are formed, which are stabilized in non-aqueous solutions. The presence of specific adsorbed anions can significantly influence the EASA by formation of a high-density ordered phase that can compete in adsorption with the other species (poisoning). Additionally the halide ion is one of the three species involved in the three-centered intermediate of the process, promoting direct formation of the final reaction product in a concerted mechanism, with respect to a stepwise mechanism including a stable radical anion intermediate. However, research has shown the rate of the concerted mechanism is slow down by the presence of the halide ions giving rise to less conversion of the reactant [8]. Structural changes can be observed when the dissociative electron transfer theory developed by Savéant [32-33] is taken in to account. In this theory, it is suggested that a bond is required in order to transfer charge from the electrocatalytic nanoparticle to the organic halide. During the electron transfer itself all positions of the atoms and the atoms themselves are frozen, obeying the Franck-Condon principle [37], [38] but after the electron transfer during the desorption small Ag atoms can still be detached depending on the strength of the sorption bond [34-35]. This desorption process can lead to loss of Ag atoms from the nanoparticles or even complete small silver nanoparticles in the solution. This is consequently observed as a decrease in weight % of electrocatalyst and EASA. In Table 1 it can be seen that although the decrease in current density occurs for all investigated CX bonds, it is not identical. For C-Br and C-Cl, the current density drops until ca 50 % of its initial value while for C-I a drop of 70 % is measured. This feature can be explained by taking into account the bond energy between the Ag

nanoparticle and the halide ion. The bond dissociation energy between Ag and Br/Cl is approximately 280 kJ/mol while Ag-I has a lower bond energy of 234 kJ/mol [40]. This value confirms our previous suggestion as the current density for C-Br and C-Cl drops more in comparisons with C-I (Table 1) where a weaker bond with the Ag nanoparticles is formed.

*Figure 1: CV measurements of Ag nanoparticles in ACN + 0.1M TBAP for the cathodic cleavage of (A) benzyl bromide (B) benzyl chloride and (C) benzyl iodide performed at 50 mVs<sup>-1</sup>.*

*Table 1: Voltammetric data of the CV measurements of Figure 1 for the cathodic cleavage of Benzyl Bromide, Benzyl Chloride and Benzyl Iodide.*

To confirm our findings of the CV measurements additional LSV-RDE measurements are done. We want to acknowledge that the principles of LSV-RDE are only accountable for planar electrode surface and not nanoparticle decorated surfaces. MeOH is chosen as a solvent because the velocity profile is easier to control in comparisons with ACN [14–16]. Therefore our results will only be used to evaluate trends and not exact values. These measurements, shown in Figure 2 are recorded after respectfully 0, 5000, 10000 and 15000 cycles and taken at a constant rotation rate of 600 RPM. When evaluating the LSV-RDE results at several lifetime cycles again, some clear remarks can be made. The onset potential (indicated with the black arrow in Figure 2) stays constant. Much like the onset potentials measured in Figure 1 that occur at more slightly higher potentials due to the faster voltage scan rate. The electrochemical activity of the nanoparticles with respect to the potential stays unaltered. Similar to the previous results shown in Figure 1 the current density exhibits a decay as more cycles are performed. For benzyl bromide and benzyl chloride, a drop of ca. 50 % is measured while benzyl iodide features a drop of 73 %. These values are almost identical to the drop in current density measured during the CV measurement confirming our previous findings.

*Figure 2: LSV-RDE voltammograms of Ag nanoparticles recorded at 600 RPM and 1 mVs<sup>-1</sup> in MeOH +0.1 M TBAP for the reductive cleavage of benzyl halide 1 mM. (A) Benzyl Bromide, (B) benzyl Chloride and (C) benzyl iodide.*

In the kinetic and mixed region, a decrease in current density can be expected by the loss in EASA. However, in the mass diffusion-controlled region, the variation of the current is usually not affected if reaction mechanism stays the same. Two main reasons can be cited to explain this change; (i) Strong sorption/poisoning at both the nanoparticles and carbon rod. As previously suggested, the formation of a high-density ordered phase (which can compete in adsorption with benzyl halide reactants). (ii) Major decrease of the EASA below the geometric surface area of the carbon support electrode can also affect the mass diffusion-controlled current density. In addition, the formation of clusters or nanoparticles with small pores can also provoke mass transport limitation and a disruption of the Levich layer during the LSV-measurements. Although CV and LSV give a good representation of the experimental electrochemical degradation, microscopic and analytical characterization is needed to fully distinguish between the two options and thus understand the electrochemical degradation processes.

### 3.2 Microscopic investigation

The electrochemical behavior changes when the metallic nanoparticles are subjected to electrochemical operation conditions. Unfortunately, the direct insight into the processes occurring at the nanoscale microscopic level is relatively poor. Therefore an IL-SEM technique is used. Carbon rod's specific surface morphology helps to track the same spot for several lifetime cycles. This would be more difficult on a polished planar Glassy carbon electrode. As-electrodeposited nanoparticles are spherically shaped and homogeneously dispersed through the electrode surface. Close inspection of the SEM images reveals a dual size dispersion of as-prepared Ag nanoparticles at 0 cycles (Supplementary information, Figure S2). Larger particles have a mean size of 143 nm and are significantly larger compared to the smaller particles with an average particle size of 51 nm, whose number decreases. The total count of larger circular particles is 501 particles per  $100 \mu\text{m}^2$  (calculated from Figure 3) with an overall particle size of 125 nm (0 cycles).

Upon potential cycling nanoparticle exhibit morphology change. With an increasing amount of cycles, individual nanoparticles start to move and come together (agglomerate or coalesce) to form large clusters. Although only minor visual changes can be observed between 0 and 5000 cycles and the overall average particle size stays approximately constant at 131 nm (5000 cycles), no dual size dispersion is observed (Supplementary information Figure S3). This suggests that smaller nanoparticles of 51 nm (0 cycles), which

are more mobile, aggregate to form larger particles ( ca. 131 nm ). This finding is also confirmed by the lower overall amount of particles, 408 particles per 100  $\mu\text{m}^2$ , on top of the electrode surface.

Between 0 and 15 000 cycle, the average particle size increases from 143 nm until 604 nm (calculated from Figure 3) while the number of particles decreased from 501 particles per 100  $\mu\text{m}^2$  until 45 particles per 100  $\mu\text{m}^2$  (calculated from Figure 3). The formation of clusters under electrochemical operation conditions can be due to Ostwald ripening or agglomeration. Particles growth is always thermodynamically favorable phenomena with the driving forces being the minimization of the clusters' Gibbs free energy.

*Figure 3: IL SEM image of Ag nanoparticles for C-Br at 0, 5000, 10000 and 15000 cycles*

Close inspection of the IL-SEM figures (Figure 3) reveals two unique features: (i) particles clearly move from their primary position, and (ii) the degraded samples (10 000 and 15 000 cycles) contains typical irregular and even anisotropic nanoparticle morphologies produced by consumption of primary small nanocrystals as building blocks. The IL-SEM images of Figure 3 show unambiguous conformation on particle movement. This indicates that no particle growth via Ostwald ripening occurs since it predicts only stagnant nanoparticles. Consequently, the predominant mechanism for particle growth is agglomeration.

Two other possibly occurring degradation mechanisms are reshaping and carbon support corrosion. The first mechanism can be excluded since, like Ostwald ripening and particle growth, it predicts no particle movement. Corrosion of the support could, therefore, be the reason for the particle movement, however it is highly unlikely at this potentials. Further discussion can be found in the next section.

For the electrochemical cleavage of C-Cl and C-I identical degradation occurs. In Figure 4 and 5 it can be seen that the Ag nanoparticles undergo degradation caused by coalescence resulting in an altered particle size of 140 nm until 548 nm for C-Cl and 109 nm until 434 nm for C-I. For other investigated nanoparticles (Cu, Ni, Pb and Pd) a similar mechanism is observed but slightly slower (not-shown).

Figure 4: SEM images of Ag nanoparticles for C-Cl. Left-(0 cycles), right (15 000 cycles)

Figure 5: SEM images of Ag nanoparticles for C-I. Left (0 cycles), right (15 000 cycles).

### 3.3 Analytical

The concentration of the lost metal in the solution is investigated using an analytical electrochemical flow cell coupled with AAS/ICP-MS. This online approach is not only very precise but allows dynamic monitoring of metal dissolution during electrochemical operation conditions. The analysis is performed under **the** slow potentiodynamic regime, increasing the lower potential limit while the removed metal concentration is measured on-line. A schematically overview of the set-up can be consulted in the supplementary **information Figure S1**. **Figure 6** shows the results of the coupled measurements. The upper potential was limited till 0 V. This rather low upper potential limit was chosen in order to capture the degradation of Ag nanoparticles under cathodic operations conditions of the electrochemical system under investigation (e.g. benzyl halide reduction).

*Figure 6: Dissolution profiles of Ag nanoparticles in ACN + 0.1 M TBAP for the reductive cleavage of benzyl halide 1 mM. (A) Benzyl Bromide, (B) benzyl Chloride and (C) benzyl iodide*

When evaluating the results, two features can be observed. First, during each cycle a clear dissolution peak can be observed at -0.97 V (C-Br, Figure 6A), -1.23V (C-Cl Figure 6B) and -0.65 V (C-I, Fig 6C). The results are highly reproducible with a standard variation of less than 30 mV for the dissolution peak potential. The dissolution potential of the Ag nanoparticles is almost in complete accordance with the reduction peak potential where the C-X bond is reduced. This confirms our previous finding that the desorption of the halide of the nanoparticle surface gives rise to loss of Ag atoms and nanoparticles in the solution and dissolution occurs and thus **contributing** to an **overall** degradation. To additionally confirm this finding the potential was set on the reduction peak potential (Supplementary information, **Figure S4**). Results showed that there is a continuous outflow of Ag in the electrolyte. Secondly, during the complete electrochemical cycle, a (small) outflow of Ag is measured. This is the case for all investigated halides. The authors speculate that this phenomenon could be caused by particle surface migration when the particles move across the surface, which allows nanoparticles **agglomeration**. Out of these two remarks, we can conclude that **agglomeration**/coalescence as a secondary mechanism is caused by dissolution as **the** primary mode of degradation.

Although AAS offers an easy and stable method to track dissolution of nanoparticles, the sampling time is substantial. In order to get a more comprehensive insight into Ag dissolution under potentiodynamic conditions, the dissolution of Ag was monitored with coupled electrochemical and ICP-MS measurements shown in Figure 7 (C-Br). In contrast with the AAS measurements, two dissolution peaks are observed in the ongoing scan. Similar to AAS the dissolution of Ag starts at the onset of the reduction peak potential (-0.95 V for C-Br, black arrow in Figure 7). Authors speculate that the two dissolution peaks can be caused by a dual or broad particle size distribution as previously shown in the microscopic section.

The largest quantity of removed Ag (AAS measurement) was measured for the reductive cleavage of C-Br and C-Cl. For C-I an evident smaller amount of Ag is found. Confirming that a stronger bond dissociation of Br and Cl with the surface has as a consequence that more Ag is removed or even detached from the surface.

#### 4. Conclusion

In this work, we have performed an investigation of the electrochemical stability of Ag nanoparticles for the CX electroreduction via unique three folded advanced characterization approach that combines electrochemical, analytical and microscopic results. Electrochemical measurements show that Ag nanoparticles maintain their electrocatalytic intrinsic activity expressed as the reduction peak and onset potential. However, the current density clearly decreases for all investigated halides. Analytical and microscopic measurements have shown that this is caused by a decline in the electrochemical surface area or EASA. At the reduction peak potential of the carbon-halogen bond, a clear dissolution peak can be observed. Removal of metal is presumably caused by the interaction of the reaction intermediate with the metallic surface together with a continuous dissolution of metallic ions or detachment of small nanoparticles. SEM images show nanoparticles agglomeration/coalescence on the surface caused by particle surface migration. Leading to the conclusion that the main degradation mechanism for drop off monometallic nanoparticles effective surface area involved in the halide reduction is metal dissolution that triggers agglomeration/coalescence. Further studies are needed in order to better understand observed degradation mechanisms.

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