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Electrochemical activation of carbon–halogen bonds: Electrocatalysis at silver/copper nanoparticles

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ABSTRACT

Cu nanoparticles (NPs) of average dimension of 20–30 nm were deposited following a double step potential deposition on glassy carbon (GC). Cu NPs morphology, shape, dimension and distribution were investigated by scanning electron microscopy (SEM). According to SEM the electrochemical deposition of Cu produces two different type of NPs (spherical and polyhedral), which result randomly distributed all over the GC support. In a second step, Ag was deposited over Cu NPs by displacement deposition giving a Cu nanostructured electrode decorated with very small Ag NPs (hereafter Ag/Cu). The electrodes were fully characterized by X-ray photoemission spectroscopy and energy dispersive X-ray spectroscopy, which provided the surface and bulk chemical composition of the electrodes.

The reductive cleavage of a series of organic chlorides, including chloroaromatics, benzyl chlorides, trichloroethylene and polychloromethanes, was investigated both at Cu and Ag/Cu NPs in DMF + 0.1 M $(C_2H_5)_4NBF_4$. Cu and Ag/Cu NPs electrodes have shown remarkable electrocatalytic reduction properties for the halides following concerted dissociative electron transfer. The peak potentials recorded at Cu and Ag/Cu NPs electrodes at $v = 0.2\ \mathrm{V\,s^{-1}}$ are positively shifted by 0.3–0.5 V with respect to the reduction potentials measured at a non-catalytic electrode such as GC and in some cases the catalytic effect is even better than bulk Ag and Cu.

1. Introduction

Halogenated organic compounds represent one of the most important class of molecules employed in organic synthesis both as reagents and solvents. This is particularly true in the case of organic chlorides, since they are easily affordable and on hand. The efficient formation of carbon-carbon bonds is the most challenging aspect of the organic synthesis and innumerable examples can be found in the literature or in text books as well, where organic chloride or bromides are employed in coupling [1,2], carboxylation [3,4] cyclization [5] and polymerization reactions [6,7]. These are just few examples for emphasizing the huge quantity of chemicals that every passing minutes are processed for affording useful drugs, material or products for the everyday life. The other side of the coin is that a variegated range of waste with stable chemical properties and toxicity is produced. In fact, organic chlorides cannot undergo an easy and fast natural degradation and this put some concern on their disposal and treatment. The degradation or conversion of organic chlorides is usually based on the reductive hydrodehalogenation reaction. However, because of the relatively high dissociation energy of C—Cl bond, catalysts are needed: the hydrodehalogenation process is usually mediated by a transition-metal catalyst, such as Pd or Fe under hydrogen pressure [8,9] or by microbial methods [10,11]. Besides to chemical or biological methods, the electrochemical approach is becoming a valid alternative. In fact, electrocatalysis can be successfully employed either in organic electrosynthesis [12,13] or in degradation or conversion of halogenated pollutants to less harmful and possibly more valuable compounds [14,15]. This has boosted over the last decade the research of electrode materials active toward the C—X bond breaking, and, so far, Ag [16–19], Cu [20–22] and Pd [23,24], and some of their combinatorial alloys [25,26] were found to possess interesting electrocatalytic properties. However, despite nano-catalysts have emerged as a sustainable and competitive alternative in recent years, there are very few examples in the literature reporting the employments of NPs decorated electrodes

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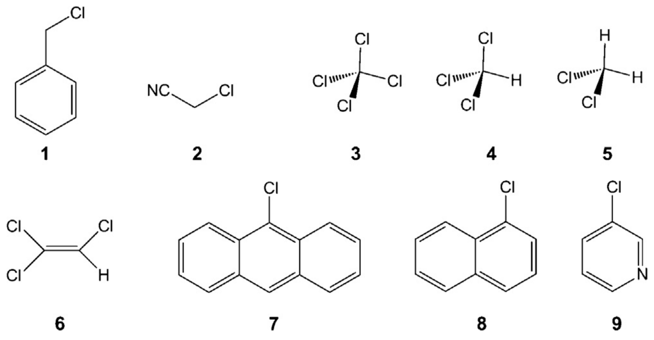

Scheme 1.

in the field of C—X bond activation and the most of them are based on Ag NPs [16,23,27–30]. Actually, a fine dispersion of the metal NPs and/or the modulation of their electronic properties by interaction with support chemical or morphological defects may increase the catalytic activity and selectivity [23]. Furthermore, because of the high surface-to-volume ratio it is possible to obtain high current density despite a low loading of active phase, thus enhancing the efficiency while decreasing the reaction time and the process costs.

In this paper we have investigated the electrochemical deposition of Cu and mixed Ag/Cu NPs on glassy carbon (GC). GC has been chosen as electrode support since among various forms of carbon, it is an optimal material for a basic investigation of the catalytic activity of the loaded catalyst, minimizing the possible morphological and/or chemical effects of the support. In fact, GC is generally considered an inert material with respect to halogen reduction [31], it possesses very low electrical resistivity and it is non-porous and impermeable to gases [32]. Furthermore, it can be easily polished and managed allowing a good reproducibility among different experiments. Copper NPs have been chosen as an electroactive phase alternative to Ag NPs in the reduction of organic halides. Actually, Cu electrodes have been found to possess good electrocatalytic properties for the reduction of alkyl bromides, iodides and chlorides [33,34,24,22] but there is no report in the literature confirming such activity also for Cu NPs. Furthermore, Cu has the advantages of excellent electrical conductivity (only 6% less than that of Ag) and much lower price. On the other hand, Cu NPs oxidizes rapidly under ambient conditions and this can put a severe limit to their practical application. A viable strategy to overcome the problem is the introduction of a second metal, which can improve the oxidation resistance. In this sense, Cu NPs with Ag coating appear a promising material to be employed in electrocatalysis [35,36], and by limiting the more expensive and reactive metal Ag to the surface of the NPs a substantial saving is possible. Ag/Cu NPs were prepared via a cheap and convenient method: Cu NPs are preliminary deposited on GC and then plated with Ag by a displacement reaction with a silver salt. Therefore the aim of this study is to understand whether the electrocatalytic activities of these nanostructured electrodes can approach or even outclass those of the relative bulk materials. The Cu and Ag/Cu nanostructured electrodes were fully characterized by X-ray photoemission spectroscopy (XPS), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), while the electrochemical reactivity was tested toward the reduction of a series of different organic chlorides, including benzyl chloride, which so far is considered as a benchmark molecule for investigating the carbon-halogen bond activation (Scheme 1). The other selected compounds allow examination of the effect of molecular structure on the electrocatalytic properties.

2. Experimental

2.1. Chemicals

Dimethylformamide (DMF) (Prolabo ≥ 99.8) was kept over anhydrous Na_2CO_3 for several days and stirred from time to time. It was then fractionally distilled twice under reduced pressure and stored in a dark bottle under argon. Tetraethylammoniumtetrafluoroborate ($TEABF_4$, Fluka, 98%) was recrystallized twice from absolute EtOH and dried in a vacuum oven at 70 °C. The deionized water used for the experiments was previously bi-distilled in the presence of $KMnO_4$. All other reagents were commercially available with good purity and were used without further purification.

2.2. Instrumentation

The morphological characterization of Cu and Ag/Cu nanoparticles deposited onto GC was performed by field emission scanning electron microscopy (Zeiss Supra 35 VP).

The XPS characterization of the samples was performed in an UHV chamber (base pressure $<5 \times 10^{-9}$ mbar), equipped with a double anode X-ray source (Omicron), a hemispherical electron analyzer (VG Scienta). All the XPS measurements were performed at room temperature, using non-monochromatized Mg-Kα radiation ($h\nu = 1253.6$ eV) and a pass energy of 50 eV and 20 eV for the survey and high-resolution spectra, respectively. The calibration of the binding energy (BE) scale was carried out using Au 4f as reference (BE = 84 eV).

Electrochemical experiments were performed at 25 °C by using an Autolab PGSTAT100 N potentiostat/galvanostat. The electrocatalytic activity of the nanostructured surfaces for organic chloride reduction was investigated using cyclic voltammetry (CV) and were carried out in a three-electrode cell system with a GC, either modified or unmodified, or Ag and Cu disc as working electrode. The working electrodes for cyclic voltammetry were embedded in glass or Peek and were built from a 3 mm diameter GC rod (Tokai GC-20) or from a 2 mm diameter Ag or Cu wire (Alfa Aesar, 99.999%) and were polished to a mirror finish with silicon carbide papers of decreasing grain size (Struers, grit: 800, 2400, 4000) followed by diamond paste (3-, 1-, 0.25-μm particle size). They were then cleaned in ethanol in an ultrasonic bath for about 5 min. Prior to each experiment the electrode surfaces were refreshed by polishing with a 0.25 μm diamond paste, followed by ultrasonic rinsing [37]. The counter and reference electrodes were a Pt wire and Ag|AgI|Bu_4NI 0.1 M in DMF, respectively. All potentials are reported versus the saturated calomel electrode (SCE). This has been achieved by calibrating the Ag|AgI|I^- reference system at the end of each experiment against the ferricenium/ferrocene couple ($E_{Fc^+/Fc} = 0.476$ V vs. SCE in DMF) and converting the potentials to the SCE scale [38].

The Cu and Ag/Cu NPs were freshly prepared on GC, before recording each set of cyclic voltammetries, by electrodeposition of Cu on an exposed area of 3 mm diameter GC disc. The electrochemical deposition of Cu NPs was carried out in a three-electrode cell system containing 5 mM $CuSO_4$ + 0.1 M $LiClO_4$ in H_2O. GC was set as working electrode, while the counter electrode and the reference electrode were a Pt wire and a Hg|Hg_2SO_4|K_2SO_4 saturated electrode, respectively. The reference electrode was separated by the working electrode compartment, through a salt bridge which avoided any contamination of the working electrode. The conversion of the potential measured versus Hg|Hg_2SO_4|SO_4^{2-} to the SCE scale is obtained adding +0.373 V to the measured value. All experiments were carried out at 25 °C.

Underpotential deposition measurements on bulk and modified electrodes were carried out by CV in an oxygen free water solution