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B. Vanrenterghem[1*], A. Papaderakis[2], S. Sotiropoulos[2], D.Tsiplakides[3], S.Balomenou[3], S. Bals[4], T. Breugelmans[1]

[1] University of Antwerp, Research Group Advanced Reactor Technology, Salesianenlaan 90, 2660 Hoboken, Belgium

[2] Department of chemistry, Aristotle University of Thessaloniki, Thessaloniki 54124,

[3] Chemical Process Engineering Research Institute, The Center for Research and Technology Hellas, 570 01, Thermi, Thessaloniki, Greece

[4] University of Antwerp, Research Group Electron Microscopy for Material Science, Groenenborgerlaan 171, 2020 Antwerp, Belgium

[*] Corresponding author bart.vanrenterghem@uantwerpen.be, tom.breugelmans@uantwerpen.be

ABSTRACT

A two-step procedure was applied to prepare bimetallic Ag-Ni glassy carbon supported catalysts (Ag-Ni/GC). First Ni layers were prepared by means of electrodeposition in an aqueous deaerated nickel chloride + nickel sulfamate + boric acid solution. Second, the partial replacement of Ni layers by Ag was achieved upon immersion of the latter in solutions containing silver nitrate. Three different pretreatment protocols were used after preparation of the Ag/Ni deposits; as prepared, cathodised in alkali and scanned in acid. After the pretreatment the surface was characterised by means of spectroscopy techniques (scanning electron microscopy and energy dispersive x-ray) and electrochemically in an alkali NaOH solution through cyclic voltammetry (CV). Afterwards the modified electrodes were tested for the reduction of benzylbromide in acetonitrile solutions by using CV and were found to show improved activity compared to bulk Ag electrode. The highest activity towards benzylbromide reduction was observed for pre-cathodised Ag-Ni electrodes. A final stage of the research focuses on the development of a practical Ag/Ni foam catalyst for the reduction of benzylbromide. Due to the high electrochemical active surface area of Ag/Ni foam, a higher conversion of benzyl bromide was obtained in comparison with bulk Ag.

Keywords: benzylbromide reduction; silver catalysts; galvanic replacement, bimetallic catalyst

1. Introduction

The electrochemical activation of the carbon-halogen (C-X) bond has been the object of numerous studies [1]–[4]. The substantial interest for C-X bond activation is caused by numerous applications in organic synthesis [5], abatement of environmental pollution [6] and understanding of the dissociative electron transfer mechanism [7]. During recent years a large number of efficient homogeneous catalysts such as Ni-complexes have been reported but only a few metal electrodes (including Ag, Au, Cu, Pd, Ni and Hg) are known to have catalytic properties towards the halide reduction [1]. Among them, Ag has attracted the most attention due to its good catalytic properties which are applicable to a wide variety of halide reductions [8]–[11].

The use of Ag planar electrodes for C-X bond activation induces a shift in the reduction potential of ca. 500mV compared to inert bare glassy carbon electrodes [10]. Despite this shift, the reduction potential of C-X activation remains strongly negative (-1.05V vs. Ag/AgCl for C-Br). The large overpotential and high capital cost of bulk silver make this process inadequate for use in industrial production processes. A further reduction of the overpotential requires an improvement of the catalytic activity. A possible way to boost the catalytic activity is by changing from bulk electrodes to multi-metallic catalysts [10], [12]. These catalyst show altered catalytic properties due to favourable metal-metal interactions. The origins of a beneficial catalytic effect can be grouped in four categories: (1) ligand effect modifications of electronic properties; (2) lattice changes due to different sizes of system components, resulting in electronic modifications; (3) the second metal disrupting the continuity of the lattice of the first metal and hence its interaction with adsorbed intermediates ("third body effect"); (4) the synergistic effect in bifunctional systems whereby each metal plays a different role in the reaction mechanism (e.g. reaction of initial reactant, poison removal etc.) [13]. Multimetallic catalyst can be formed by impregnation

of a high surface area substrate with metal ions followed by chemical reduction in a solution of appropriate reducing agents. The high toxicity of the reducing agents ($SnC_{12}H_{28}$, $NaBH_4$, N_2H_4) have triggered the search for other alternative synthesis methods. An environmental friendly alternative for the preparation of multimetallic catalysts is galvanic replacement or transmetallation.

Galvanic replacement consists of the spontaneous replacement of surface layers of a metal (M) by a more noble metal (M_{noble}) upon immersion of the former in a solution containing ions of the latter:

$$M_{noble}^{n+} + n/m\ M \rightarrow M_{noble} + n/m\ M^{m+} \qquad (1)$$

with the driving force being the difference in the metals' standard potentials ($E^0_{Mnoble} - E^0_M > 0$). The method has been introduced as an alternative route for the production of inexpensive (due to the presence of small quantities of the noble metal on the surface of the catalyst) and more efficient (due to metal-metal interactions) electrocatalysts for fuel cell related reactions [14]–[17].

Despite a large number of papers for silver coatings on other metals (for decorative, anticorrosion, antimicrobial, electronic and optical applications [18], [19]) there is little work on deposition of Ag by galvanic replacement. Ag nanostructures have been prepared on Al templates or on AlCu alloys [20] and Ag dentrites with superhydrophobic properties have been prepared on stainless steel substrates [21]. There is a single paper where Ag-Cu particles prepared by galvanic replacement have been tested in benzylchloride reduction [10] (which is often considered as a model molecule to study the halide reduction) but no study has been reported for the reduction of benzylbromide on similarly prepared Ag-Ni systems.

Following our recent findings that Ag nanoparticles electrodeposited on a Ni substrate show improved catalytic activity for benzylbromide reduction [22], a more elaborated study is needed to investigate whether this is due to particle size and shape or/and Ag-Ni substrate interactions. The preparation of a continuous Ag deposit on the surface of Ni substrates by galvanic replacement should provide a system where only the overlayer-substrate interactions may prevail.

The aim of this work is the preparation of Ag layers by galvanic replacement on Ni substrates to study the effect of metal-metal interactions on benzyl bromide reduction. In addition, the use of a practical catalyst in the form of Ag/Ni-foam for the reaction is investigated. Towards these directions our specific objectives have been: *i.* The formation and microscopic/spectroscopic characterisation of Ag deposits on Ni electrodeposited on glassy carbon substrates and of Ag deposits formed on Ni foams; *ii.* The electrochemical characterisation of the Ag-Ni electrodes by means of surface electrochemistry in alkali and *iii.* Comparison of the catalytic activity of the Ag-Ni electrodes with that of bulk Ag for benzylbromide reduction under different electrochemical pretreatment conditions; as prepared, cathodised in alkali, scanned in acid.

2. Experimental

2.1 *Preparation of Ag deposits on Ni electrodeposits and Ni foams*

Ni layers were electrodeposited on a glassy carbon (GC) substrate (denoted as Ni/GC). Before each deposition the GC substrate (0.0725 cm²) was intensively polished with emery paper (grain size 1000μm) and alumina suspension (0.3 μm, Buehler) followed by ultrasonic rinsing in double distilled water. The GC substrate was ancillary cleaned with a precondition step by applying a more positive potential *(-0.2 V vs Ag/AgCl)* to avoid

spontaneous deposition of metals on the support material. Electrodeposition of Ni-layer was carried out from 0.01 M $Ni(SO_3NH_2)_2$ (Fluka, $\geq$ 99.0%) + 0.227 mM $NiCl_2$ (Merck, $\geq$ 97.0%) + 0.025 M H_3BO_3 ($\geq$ 99.0%) deaerated solutions at -1.10 V vs. Ag/AgCl (3 M KCl) in the kinetic control region. The charge density passed was 375 mC cm^{-2}, resulting in a Ni film of 129 nm (assuming a smooth deposit and using the bulk density of Ni) [23]. Specimens of Ni foams (Goodfellow, LC210248LC, 43 pores/cm, 96.5 % porosity, 1.6 mm thick) were used as received without further purification steps and the usage of a support material. The electrode specimen dimensions were 1 cm x 1 cm x 0.16 cm, resulting in an estimated 6.4 cm^2 total geometric area (based on the BET area results of Langlois et all for similar Ni foams [24]).

The as-prepared Ni/GC and Ni foam were subsequently immersed in a deaerated 1 mM (Ni/GC deposit) and 10 mM (Ni foam) $AgNO_3$ (BDH, $\geq$ 99.0%) + 10^{-3} M $HClO_4$ (pH of ca. 3) solution for 15 min so that spontaneous replacement by Ag could take place. Electroless deposition of Ag with concurrent galvanic (partial) replacement of Ni is expected to occur:

$$Ni + 2Ag^+ \rightarrow 2\,Ag\, + Ni^{2+} \qquad (2)$$
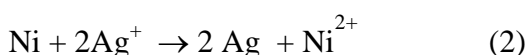
as expected from the positive sign of the $E^0_{Ag^+/Ag} - E^0_{Ni^{2+}/Ni}$ standard potential difference [13].

2.2   *Microscopic (SEM) and spectroscopic (EDS) characterisation of the catalysts*

Microscopical analysis was carried out using a FEI Quanta field emission gun 250 scanning electron microscope (SEM) in combination with energy dispersive X-ray spectroscopy (EDS) equipped with an octane silicon detector. Before each measurement the electrodes were rinsed in acetonitrile (Sigma Aldrich, HPLC grade) and dried to air overnight. All measurements were conducted at acceleration voltage between 10-20 keV.

SXM 192.1 was used as data processing software to extract the composition, particle diameter and density from thresholded SEM images.

2.3   Electrochemical characterisation of coatings and catalytic activity

Voltammetric experiments were carried out with an Autolab PGSTAT 302N system using a Pt wire counter electrode and a Ag/AgCl (3M KCl) reference electrode. A standard three-compartment cell was used with the counter and reference electrode chambers separated from the working electrode chamber by a glass frit or an electrolyte bridge in connection with a lugin capillary respectively.

After the transmetallation step, electrochemical experiments designed for pretreatment and surface mapping of the Ni-Ag deposits were carried out. The electrolyte solution for surface electrochemistry mapping experiments consisted of an aqueous deaerated 0.1 M NaOH solution. The experiments were conducted at a scan rate of 50 mV s^{-1} for the Ni/GC and 10 mV s^{-1} for the Ni foam transmetallated substrates. The potential range was chosen between -0.2 V and 0.75 V vs. Ag/AgCl. The electrodes were scanned repeatedly (10 cycles) until a steady state CV was obtained.

Three different electrochemical pretreatment protocols, after the synthesis of Ni-Ag deposits, were tested to investigate their influence on the catalytic activity for the benzyl bromide reduction reaction. This approach resulted in three-types of electrodes: as prepared, cathodised in alkali and scanned in acid. The first protocol (as prepared) is of obvious practical significance; the second (cathodised in alkali) ensures that both metals are in their reduced-metallic form and that no Ag or Ni thick surface oxides are present (it was realized by keeping the potential at -0.60 V vs. Ag/AgCl in a 0.1 M NaOH solution); the third protocol (scanned in acid) was used to anodically dissolve parts of the precursor

Ni layer that had not been covered by a protective Ag shell (it was realized by repetitive potential scanning at 50 mV s^{-1} between -0.60 V and -0.10 V vs. Ag/AgCl in a deaerated 0.1 M H$_2$SO$_4$ solution, until the anodic current due to Ni dissolution decreased to zero).

The electrocatalytic activity of the Ag-Ni deposits and Ag-Ni foams for the halide reduction of benzylbromide was tested in an electrolyte solution of acetonitrile (Sigma Aldrich, HPLC grade) + 0.1 M tetrabutylammonium perchlorate (Bu$_4$NClO$_4$) (Sigma Aldrich) + 10^{-3} M benzylbromide (reagent grade, 98%, Sigma Aldrich) by means of CV until a steady state voltammogram was obtained. The reference and counter electrodes as well as the electrochemical cell were identical as used in the experiments described before.

2.4   Bulk electrolysis experiments

All bulk electrolysis experiments were performed in batch under potential control in an unstirred solution. The potential was set on -1.05 V vs. Ag/AgCl i.e. the reduction peak of benzylbromide on bulk Ag. The electrochemical set-up for the measurements was identical to the one used for the determination of the catalytic activity. Product identification and distribution was carried out using a 210-MS Ion Trap Mass spectrometer and a Thermo Trace 1300 GC-FID.

3.   Results and Discussion

3.1   Microscopic (SEM) and spectroscopic (EDS) characterisation of Ag deposits on Ni layers electrodeposited on glassy carbon electrodes and Ni foams

Figure 1 shows SEM micrographs (at two different magnifications) for an as prepared Ag-Ni/GC sample. EDS analysis (not shown) of the entire area depicted in Figure 1 gave a 6.99% w/w Ag and 65.10% w/w Ni composition of the coating (corresponding to a ca. 1÷17 Ag÷Ni atom ratio). With the exception of some uncovered GC areas (black areas, as confirmed by EDS spot analysis) a continuous deposit can be seen, decorated by Ag

particles (white spots, analysed by EDS) with a diameter smaller than 500 nm. It should be stressed that Ag was also detected on all other locations (grey areas), indicating that the formation of a Ag overlayer extended over most of the precursor Ni deposit.

Fig.1   SEM images of as prepared Ag-Ni/GC deposits at different magnifications of 1000X (A) and

100000X (B)

Figure 2 presents the same type of electrode after cathodisation in alkali. Significant surface reorganisation is observed, whereby large patches of Ag-Ni deposits are seen (as large as 10-20 μm) over a continuous layer (similar to that of the as prepared sample). The lower coverage of Ag-Ni deposit on GC may be the result of a volume decrease as Ni oxides are reduced to metallic Ni upon cathodisation. EDS analysis (not shown) gave a 5.53% w/w Ag and 41.86% w/w Ni composition of the coating (corresponding to a ca. 1÷13 Ag÷Ni atom ratio).

Fig. 2   SEM images of cathodised Ag-Ni/GC deposits at different magnifications of 1000X

In Figure 3, a SEM micrograph corresponding to Ag-Ni/GC samples after scanning in acid is shown. Again, significant surface reorganization is observed, but the patches are now sparser and the underlayer seems rougher, as one would expect for partial Ni stripping from defective (not Ag-protected), uncovered areas. In this case EDS analysis gave a 4.09% w/w Ag and 8.84% w/w Ni composition (indicating an overall material loss with respect to the other two types of samples), corresponding to a ca. 1÷4 Ag÷Ni atom ratio (indicating enrichment in Ag due to higher Ni losses as a result of anodic dissolution at the positive limit of the potential scan range-see also below).

Fig. 3   SEM image of scanned in acid Ag-Ni/GC deposits at different magnifications of 1000X

Finally, Figure 4 presents micrographs of a Ag-coated Ni foam substrate (as prepared). Uniform coating of the substrate skeleton is seen in Figure 4(A) and, at the higher

magnification of Figure 4(B), the morphology of the deposit appears similar to that of the as prepared Ag-Ni/GC sample of Figure 1. EDS composition analysis gave 12.38% w/w Ag and 54.50% w/w Ni, corresponding to a ca. 1÷8 Ag÷Ni atom ratio.

Fig. 4   SEM images of as prepared Ag/Ni foams deposits at different magnifications of 1000X (A) and

100000X (B)

3.2   Electrochemical pretreatment of Ag-Ni/GC electrodes in acid and electrochemical

characterisation of Ag-Ni/GC and Ag-Ni foam electrodes in alkali

Figures 5(A)-(D) present repetitive cyclic voltammograms of as prepared Ni/GC (A), -Ag-Ni/GC (B-C) and -bulk Ag disc electrode (D) in 0.1 M $HClO_4$ solution. The Ag/Ni deposits are repeatedly scanned in an acid solution to anodically dissolve any exposed Ni. Figure 5A and 5D show at which potential Ni and Ag respectively dissolve in an acid solution. In Figure 5A a peak can be seen at ca. -0.050 V for Ni/GC caused by the anodic dissolution of Ni with a gradual decrease until the peak disappears when all exposed Ni is stripped of (after 15 scans respectively). The stripping peak for bulk Ag (Figure D) can be observed starting at ca. 0.30 V. When an Ag-Ni-GC deposits is scanned (Figure B) the clear feature of both the Ag- and Ni stripping peaks are present. To avoid any simultaneous Ni and Ag anodic dissolution and any Ni passivation, the third pre-treatment protocol (see Experimental) was modified to involve repetitive scanning up to the onset of Ni dissolution i.e. up to -0.10 V until the current decreased to near-zero levels (Figure 5(C)).

Fig. 5   Cyclic voltammograms of Ni/GC (A), Ag-Ni/GC (B-C) and of a bulk Ag disc electrode (D) at 50

mVs^{-1} in 0.1 M $HClO_4$

Whether used as prepared (first protocol), cathodised in alkali (second protocol) or scanned in acid (third protocol) (see Experimental) all electrodes, after tested for bezylbromide reduction, were subsequently subjected to potential scans in alkaline solutions for electrochemical surface characterisation and Ag electroactive area estimation. Figure 6(A)

presents the voltammetry of a bulk Ag electrode and of Ni layers electrodeposited on glassy carbon (Ni/GC) in a 0.1 M NaOH solution (reference electrode materials). For the Ni/GC electrode (green line) the peaks corresponding to the $Ni(OH)_2$/NiOOH surface hydroxide transformation are seen at potentials of ca. + 0.50 V (anodic peak) and + 0.35 V (cathodic peak) in accordance with a long standing literature [25]. At the same time, the surface electrochemistry of bulk Ag (red dashed line) appears also similar to that reported in the literature [26]: the first set of anodic peaks in the + 0.15 - + 0.50 V range (with a maximum at ca. + 0.40 V) is attributed to the Ag/Ag_2O transformation and that at ca. + 0.70 V to the Ag_2O/AgO transformation, with their cathodic counterparts being at ca. +0.35 and -0.05 V respectively.

Fig. 6   Cyclic voltammetry at 50 mVs^{-1}of Ag bulk electrode (A), Ni/GC (A), as prepared Ag-Ni/GC (B) , cathodised Ag-Ni/GC (B), scanned in acid Ag-Ni/GC (B), Ag (Ni foam) (C), bulk Ni (C) and Ni foam (C) in 0.1 M NaOH

Figure 6(B) shows the voltammetry of the bimetallic Ag-Ni/GC electrodes and the overall features of Ag surface electrochemistry are clearly seen. The curves for the as prepared (black line) and cathodised in alkali (red dashed line) electrodes almost coincide with each other and the position of the first set of Ag anodic peaks is shifted with 70 mV to more positive potentials with respect to that of pure Ag (Figure 6, red dashed line), indicating that Ag oxidation to Ag_2O is easier in the presence of Ni. The small anodic peak at ca. + 0.45 V is most likely due to the oxidation of uncovered (or exposed during potential scanning) Ni areas (compare to Figure 6(A)). In the case of the acid-scanned Ag-Ni/GC electrode (Figure 6B, grey dotted line), the position and shape of the Ag peaks are similar to those of pure Ag and all oxidation peak are smaller. The ratio of the Ag/Ni related peaks shows a decrease in the amount of Ni from 6/1 until 10/1. Both trends are in line with the lower Ni content and lower Ni exposed surface of such electrodes as indicated by EDS result in the previous section. For all types of electrodes, the charge under the far cathodic

peak (corresponding to Ag oxides reduction to metallic Ag) was used for an estimate of Ag electroactive surface area. It can be seen that this charge is significant lower in the case of the acid-scanned electrodes, which is in line with the rougher surface seen in the SEM micrograph of Figure 3.

In addition, the surface electrochemistry of a practical Ag/Ni foam catalyst is investigated. Figure 6(C) presents cyclic voltammograms in alkali of Ag/Ni foam (red line) and Ni foam (black dotted line) electrodes. One can see that in this case a much larger Ni oxidation peak is observed as expected for a larger number of uncovered Ni areas on the much higher surface area of the Ni foam. Also, the Ag reduction peak at ca. 0.08 V is smaller (per nominal substrate area) than those observed for the Ni/GC supports. This is presumably due to the existence of uncovered Ni area within the tortuous volume of the Ni foam electrode.

3.3   Catalytic activity of Ag-Ni/GC and Ag/Ni foam for the benzylbromide reduction reaction.

Figure 7 shows the voltammetry of Ni, Ag and Ag-Ni/GC electrodes in acetonitrile solutions containing benzylbromide. The Ag-Ni/GC deposits are compared to bulk Ag and Ni electrodes subjected to the same pretreatment protocol. Peak-shaped current potential curves are observed in all cases, typical for an irreversible reaction (no anodic peak observed during the reverse, positive-going scan).

Fig. 7   Cyclic voltammetry at 50 mVs⁻¹ for Ni, Ag and Ag-Ni/GC (as prepared (A)), cathodised in alkali (B) and scanned in acid (C) in acetonitrile + 0.1 M TBPA + 1 mM benzylbromide

Three observations can be made in all graphs of Figure 7. First, there is a pronounced effect of electrode pretreatment on Ag activity towards the reaction, as indicated by the relevant shifts of peak position. Second, the peak position for the Ag-Ni/GC electrodes is always less negative than that of the plain Ag electrodes (see also Table 1 where the peak

potential values are tabulated). This proves the beneficial effect of Ni on Ag catalytic properties (note that Ni itself is a poor catalysts as it can be seen by the voltammograms corresponding to pure Ni electrodes, given in the Figure 7A-B, blue dotted line). Finally, from all electrodes tested, it is the alkali-cathodised Ag-Ni/GC electrode that shows the best catalytic activity, showing a 100 mV positive shift of its peak potential with respect to an as prepared (simply polished) Ag electrode (Table 1). This shift is comparable to those found for other Ag-Ni systems [22]. The superiority of the cathodized sample is most probably due to the presence of Ni in its metallic form (note that the effect of cathodisation on Ag is adverse; see the corresponding voltammogram of Figure 7(B)). It seems therefore that metallic Ni modifies the electronic properties (and hence the adsorption affinity) of Ag in a way beneficial to benzyl bromide reduction (e.g. by decreasing the adsorption strength for some intermediates). This is in line with theoretical predictions that smaller and less electronegative transition metals lower the adsorption affinity of other transition metals towards small adsorbates. The peak shape of in acid scanned Ag/Ni-GC deposits (Figure 7C) differs significantly from the other two pretreatment protocols (Figure 7A-B). Bulk Ni is not given as a reference because pretreatment of bulk Ni in acid gives only anodic dissolution of Ni. For Ag-Ni/GC scanned in acid a peak can be observed for the reduction reaction of benzyl bromide at ca. -0.97 V and a shoulder peak at -1.14 V. It is assumed that by scanning in acid two reaction sites are obtained; one where a bimetallic system is formed Ag/Ni-GC and a second one where all Ni is resolved and a Ag/GC system remains.

Table 1 Peak potentials for as preapared, cathodised in alkali and scanned in acid bulk and Ag/Ni deposits

A much safer assessment of the intrinsic catalytic activity of the Ag electrodes can be obtained by looking into the currents at the kinetic control regime (i.e. at the "foot" of the voltammetric curves) and by normalizing those currents by an estimate of Ag electroactive area. Normalisation of the currents is done by correction through the charge of the Ag peak

at ca. 0.00 V obtained in the surface electrochemistry in alkali (Figure 6). The charge is an indicator of the Ag active surface area. Figure 8 present results for the best Ag electrode (alkali-cathodised Ag-Ni/GC) and the reference material of cathodised bulk Ag. It can be seen that currents normalized per charge are higher in the case of Ag-Ni/GC, i.e. even after correction for any surface variation effects.

Fig. 8   *Linear voltammetry at 50 mVs^{-1} of cathodised in alkali Ag-Ni/GC deposits in the kinetic controlled region in acetonitrile + 0.1 M TBAP and benzylbromide (1mM)*

Figure 9 shows the reduction of benzylbromide on a Ag/Ni foam modified electrode. An Ag/Ni foam catalyst would be of interest for practical applications due its higher surface area and open structure. It can be seen that a clear voltammogram is observed with, albeit shifted to higher potentials than that of a Ag (bulk Ni) electrode. This moderate shift may originate from the existence of uncovered Ni areas (note that Ni is a poorer catalyst for this reaction) and increased ohmic losses through the tortuous volume of the three dimensional electrode.

Fig. 9   *Cyclic voltammetry at 50 mVs^{-1} of Ag/Ni foam and bulk Ag(bulk Ni) in acetonitrile + 0.1 M TBAP and benzylbromide (1mM)*

3.4   Bulk electrolysis of benzylbromide on Ag-Ni/GC and Ag/Ni foam electrodes

Next to the electrocatalytic activity, the electrosynthetic pathway for the reduction of benzylbromide on Ag-Ni/GC and Ag/Ni foam electrode is investigated. These experiments (Figure 10) are performed to investigate the efficiency of a catalyst with respect to the yield of the reaction of benzylbromide until toluene. The mechanism of dissociative electron transfer of aryl halides such as benzylbromide is already previously reported [27] and is known to proceed in a stepwise manner. Benzylbromide has low lying π orbitals in

which the incoming electron is accommodated. Depending on the potential the radical is further converted in an anion or undergoes a polymerisation reaction. At potentials not lower than -1.3V vs. Ag/AgCl the protonation of the radical is more favourable while at more negative potentials a competition between protonation and polymerisation occurs.

Fig. 10   Bulk electrolysis of Ag-Ni/GC deposits (A) and Ag/Ni foam (B) recorded at -1.05 V

Bulk electrolysis experiments are carried out at a potential of -1.05V vs. Ag/AgCl i.e. the reduction peak potential of benzylbromide on silver in the mass transfer control region. The results of bulk electrolysis experiments on Ag-Ni/GC deposits and a planar Ag disk electrode are shown in Figure 10A. At prolonged periods a steady state mass transfer regime of very low mass transfer rates is expected to be approached in the stationary solutions used, resulting to an apparent steady state yield. As expected, the chemical analysis results, in line with the reaction mechanism, indicate that only the conversion of benzylbromide to toluene takes place, without any polymerisation reaction at the applied potential. For all Ag-Ni/GC deposits a higher yield of toluene is found in comparison with bulk Ag. The highest yield (49 mol%) is found for Ag-Ni/GC deposits cathodised in alkali. Since the electrolysis is carried out under mass transfer control and all electrodes of Figure 10(A) have the same nominal substrate area, any differences should be attributed to differences in the morphology of the deposits that may result to non-linear diffusion edge effects. In Figure 10 (B) bulk electrolysis on the Ag (Ni foam) is compared with that on bulk Ag. It should be stressed out that bulk electrolysis on both the Ag/Ni foam and bulk Ag are carried out at -1.05 V. Although the selected potential is not equal to the reduction peak potential for Ag (Ni foam) a good yield of 59 mol% is obtained. Once again, only the formation of toluene took place without the occurrence of any polymerisation reaction. The higher yield (59 mol%) of the Ag (Ni foam) in reference with respect to bulk Ag (37 mol%) is most likely due to its larger geometric surface (6.42 cm²).

4. Conclusions

Bimetallic Ag-Ni/GC electrocatalysts were prepared by galvanic replacement of Ni surface layers through simple immersion of the latter into a silver ion containing solution. The Ag-Ni/GC deposits were subsequently subjected to three different pretreatment protocols; as prepared, cathodised in alkali and scanned in acid. Spectroscopic characterization showed that cathodising in alkali and scanning in acid has a clear influence on the surface reorganisation. By cathodising in alkali and scanning in acid a higher atomic ratio of Ag-Ni could be managed of 1÷13 and 1÷4 respectively in comparison with the 1÷17 for the as prepared electrodes. For all preparation protocols the Ag-Ni electrodes showed an improved catalytic activity toward the benzylbromide reduction in acetonitrile, indicating a beneficial effect of Ni on Ag catalytic properties. The best catalytic activity was found for Ag-Ni/GC electrodes cathodised in alkali. Bulk electrolysis experiments confirmed that at an applied potential of -1.05 V vs. Ag/AgCl the main benzylbromide reduction product at all Ag-Ni electrodes (as prepared, scanned in acid, cathodised in alkali) was toluene, with a yield comparable or better to that of bulk Ag electrodes. In addition a practical Ag/Ni foam was prepared in an identical manner as the Ag-Ni/GC electrode. The Ag/Ni foam catalyst exhibited a higher overpotential caused by the existence of some uncovered Ni areas and diffusion in the tortuous structure. The large surface area and higher current response resulted in a higher yield of 59 mol% towards the formation of toluene.

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