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Elaboration of Composite Electrodes based on Raney Nickel- and Pd/C for Electrosynthesis Applications

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Abstract: *Conductive composites of acrylamide and triethylene glycol dimethacrylate were prepared via frontal polymerization with various Raney nickel- and Pd/C content. These materials are proven to be applicable as electrodes in organic electrosynthesis. The incorporation of electrocatalytic metals results in a significant change in the chemoselectivity of the electroreduction of acetophenone, which indicates a change in the mechanism from electronation-protonation to electrocatalytic hydrogenation.*

Keywords: electroreduction, acetophenone, composite electrode, frontal polymerization

1. INTRODUCTION

In our previous article [1] we reported the synthesis and application of graphite filled AA-TGDMA composite electrodes for the electroreduction of acetophenone. It was shown that graphite containing composites could be used as electrodes in organic electrosyntheses. Both the product composition and the current efficiency of the electrolysis are influenced by the graphite content. These results led us to investigate the possibilities of metal incorporation into the polymer matrix using various metal powder additives.

In our study frontal polymerization was used for composite preparation. Frontal polymerization was first described by Checilo et. al. [2] in a liquid monomer. It is a special mode of polymerization, in which a reaction front travels through the monomer mixture, driven by the exotermicity of the reaction and leaves the polymer behind. The application of liquid monomers causes uncontrollable convection phenomena in the reaction front, which results in poor mechanical properties of the polymer. These problems can be overcome by the addition of acrylamide, a solid monomer [3]. The special method of composite preparation enables the incorporation of various additives into the polymer matrix. Because of the fast polymerization reaction there is not enough time for the additives with higher density to sediment. [4].

To continue our previous work, we have started to investigate the possible modifications of the physical and electrochemical properties of composite electrodes. Various methods are capable of modifying the selectivity of an electrode. We have chosen the incorporation of electrocatalytic metals into the composite electrode in order to extend the tuneability of the electrode properties through its composition. The high viscosity of the monomer mixture and the fast polymerization reaction enables the use of metal powders with high density as additives.

Hydrogenation of organic compounds is a very important reaction from the synthetic point of view. Electrocatalytic hydrogenation can be an advantageous alternative to heterogenous catalysis. The major difference between catalytic- and electrocatalytic hydrogenation mechanism is the way atomic hydrogen is formed on the catalyst surface [5]. In catalytic hydrogenation, the splitting of hydrogen molecules causes a kinetic barrier in the reaction, and mass transport of the hydrogen molecules present in low concentration in water limits the rate of hydrogen adsorption.

In aqueous phase electrocatalytic hydrogenation (ECH) water molecules are reduced, present in high concentration. The rate of charge transfer can be controlled by electrode potential, which does not necessitate the use of high pressures and temperatures, common in catalytic hydrogenation processes and this results in milder reaction conditions for ECH. The use of negative electrode potential can diminish or even prevent the adsorption of catalyst poisons [6].

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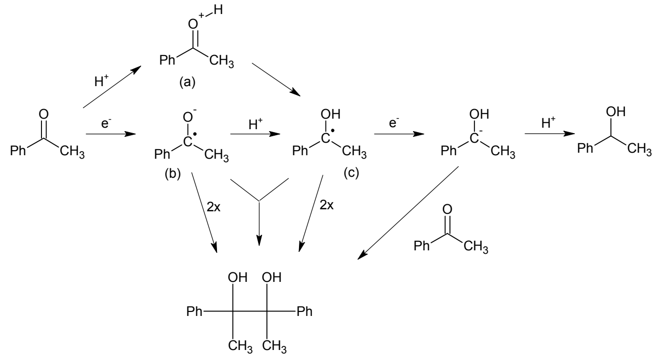

Figure 1. Electroreduction of acetophenone with EP mechanism, (a) acidic media, (b)-(c) basic or neutral media

The electroreduction of acetophenone was investigated extensively by various authors [7-12, 47] and the reaction mechanism was clearly established. Therefore this reaction was chosen here as the test reaction on these composite electrodes. The reduction of acetophenone in aqueous media proceeds via electronation-protonation mechanism on electrodes characterized by a large hydrogen overpotential and low surface coverage by adsorbed hydrogen such as mercury, lead, or graphite.

The two main products are 1-phenylethanol and 2,3-diphenyl-2,3-butanediol. The main factors, determining the chemo- and diastereoselectivity of the reaction, are the use of protic or aprotic conditions, pH, conducting salt, material and morphology of the electrode, and the cathode potential.

It was concluded from the different diastereoselectivity found in acid or alkaline solutions that the dimerization proceeds via different mechanisms [13]. At low pH the combination of two neutral radicals leads to the same DL/meso ratio as the photopinacolization of acetophenone [14]. In alkaline solution the low proton availability alters the mechanism, the radicals formed as anions react with the neutral radicals being present in small concentration. During the coupling process, strong hydrogen bond is formed between the negatively charged oxygen of the anion and the hydroxyl group of the neutral radical. This interaction determines the DL preference of pinacol formation [15].

In neutral or weakly alkaline media acetophenone is reduced to alcohol in a single two-electron wave. With increasing substrate concentration dimerization becomes predominant [16]. Dimerization, being a second order reaction, is affected by the concentration of the radical intermediates. Efficient stirring enhances the transfer of radicals to the bulk of the solution, thus lowering their concentration near the electrode surface and preventing their further reduction. Cognet et. al. reached significantly higher pinacol yield by applying ultrasound during the electrochemical synthesis [17-18]. Decreasing the acetophenone concentration in the water by using a ternary system consisting of water, toluene and acetophenone, emulsified by sonication leads to increased phenylethanol ratio [19]. The low acetophenone concentration in the aqueous phase plays down the pinacolization by decreasing the probability of radical combination.

Electrode surface modification offers an alternative way in changeing the selectivity of the electrosynthesis, chemo- and diastereoselectivity are both influenced by chemical surface modification. Ishifune et. al. [20-21] has anodically oxidized carbon fiber and introduced â–cyclodextrin onto the surface. Both modified electrode showed DL preference in pinacol formation, which was ascribed to the interaction of surface hydroxyl groups with the intermediate radicals.

On graphite and mercury electrodes pinacol is obtained as main product, while in the case of nickel the selectivity inverted [22]. If the electrode metal has lower hydrogen overvoltage, chemisorbed hydrogen is formed in the electroreduction of water and the reduction proceeds via electrocatalytic hydrogenation (ECH) mechanism.

1. $H_2O + e^- + M \rightarrow M(H) + OH^-$
2. $C{=}O + M \rightarrow M(C{=}O)$
3. $2\,M(H) + M(C{=}O) \rightarrow M(CH\text{-}OH)$
4. $M(CH\text{-}OH) \rightarrow CH\text{–}OH + M$
5. $M(H) + e^- + H_2O \rightarrow H_2 + M + OH^-$
6. $2\,M(H) \rightarrow H_2 + M$

The adsorbed substrate reacts with atomic hydrogen on the surface of the catalyst. The formation of molecular hydrogen (eq. 5.-6.) competes with the addition to the double bond. This process decreases the current efficiency of the electrosynthesis.

ECH has some advantages, compared to electronation – protonation mechanism. The formation of chemisorbed hydrogen by water electrolysis requires less negative potential, than direct electroreduction of most substrates, and the reaction does not involve the formation of radicals, thus the formation of dimerization products can be avoided.

The adsorption energy of the substrate depends strongly on the nature of the metal and the substrate, but the state of the surface has remarkable effect too, the adsorption is stronger on porous surfaces [23]. On electrodes with high electrocatalytic activity, like platinised platinum, ethylbenzene is found to be the main product [24].

Besides electrode surface area and morphology, the interaction between the supporting material and the electrocatalyst can also play an important role in determining electrode selectivity [25]. It was found [26], that the electron density on platinum, deposited onto carbon increases, which results in weakening the bond between the platinum and hydrogen, enhancing hydrogen evolution and electroreduction. The current efficiency for the electroreduction of phenol to cyclohexanol was 85% at Pt/C electrode [27], and 74% at Pt/Pt electrode [28]. Increasing the Pt content of Pt/C electrodes over 60% decreases the current efficiency dramatically [29].

The advantage of the incorporation of metallic particles into a porous polymer matrix is that the matrix prevents aggregation and loss of the particles, and improves long term stability of the catalyst. Various noble metals were incorporated into a conducting polymer matrix by the polymerization of pyrrole derivatives, substituted with a positively charged group. The metals were immobilised via anion exchange of $PtCl_2^{2-}$, $PdCl_4^{2-}$, $RhCl_6^{3-}$ and $RuCl_6^{3-}$ followed by the electroreduction of the metal complexes [30-33].

Polymer film electrodes have been widely synthetized and studied using diverse ways of electrode surface modifications; but the large scale of the use of these electrodes in electrosynthesis is limited by the stability of the polymer and it's attachment to the electrode surface. Any damage of the electrode coating leads to a decrease in selectivity of the electrode.

Composite electrodes consist of one- or more conducting phases, and one- or more insulator phases. [34]. They can be considered as solid analogues of graphite paste electrodes, where fine graphite powder is mixed with paraffin oil, to form a viscous paste [35].

Composite electrodes has significant advantages over paste electrodes as the mechanical resistance and the possibility of using them in non-aqueos media. Various polymers were used as agglutinant for composite preparation such as epoxy [36, 37], polyester [38, 39], PVC [40] or silicone rubber [41]. Calixto et al [42]found, that polyurethane, silicon rubber and epoxy matrix graphite containing composites can be used as voltammetric electrodes with a graphite content exceeding 50 w%.

The current efficiency of an electrochemical hydrogenation, proceeding via ECH mechanism depends on the relative rates of hydrogenation and hydrogen desorption. Several factors can influence these processes [43]. Among them, the electrode material and the electrode surface properties and composition have substantial effects.

Raney nickel was used at the first time in a powder form as a cathode material. It was spread on a metal plate that served as the electrical contact [44, 45]. Chiba et. al. [46] reduced several ketones besides aldehydes, Sciff's bases, oximes, nitriles, nitro compounds, olefines and acetylenes in nonaqueous media. They observed a significant increase in the current efficiency of the electroreduction, when the nickel plate electrode was covered with Raney nickel, and that the electrocatalytic reductions of the substrates led to higher product yields than catalytic hydrogenation did in the same system.

Lessard et. al. [47] have improved the elaboration of Raney-electrodes by electroplating Raney alloy particles onto the surface of a stainless steel grid in a nickel bath. The aluminium was leached out in aqoueous sodium hydroxide as in the preparation of classical Raney nickel catalyst. Raney nickel particles were obtained in this process, anchored to the metal surface by a layer of deposited nickel. This attachment prevents the deactivation of the catalyst by agglomeration. Various carbonyl compounds like ketones, aromatic aldehydes, acetoacetates and ketoacids were hydrogenated on Raney type- or spongy metal electrodes [43].

Acetophenone reduction was reported by Sakurai et. al. [45] on Raney nickel cathode. 1-phenylethanol was obtained as the only product, no formation of pinacol was observed. Senda et. al. [48] compared the electrochemical hydrogenation of 4-t-butylcyclohexanone at Raney nickel, cobalt and Pt/C, Pd/C powder electrodes. Higher conversion of the 4-t-butylcyclohexanone to the alcohol was observed on Raney metal, than on supported metal electrodes. Chen and Lasia [49] used Ni-Al powders as electrocatalysts to determine the origin of the high catalytic activity of Raney nickel. The electrocatalytic activity towards hydrogen evolution reaction of pressed and heated nickel and aluminium powder electrodes was studied, and it was found, that a dramatic increase in activity occours when the metal powders are heated above the melting point of aluminium, enabling the formation of new metallic phases, followed by leaching the aluminium out in sodium hydroxide. The main factor influencing the electrode activity was the roughness factor.

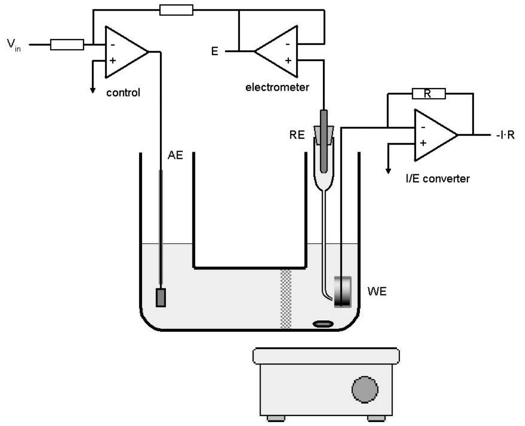

Figure 2. Experimental setup, used in electrosynthesis experiments
Vin: input voltage
E: measured electrode potential
- I·R: product of the current and „R" resistance

2. EXPERIMENTAL

Chemicals: Acrylamide (purum), from Sigma-Aldrich was ground in a ball-mill for 12 hours. Graphite (Merck, >95%) 50 µm powder, triethylene glycol dimethacrylate (>95%) and α,α'-azoisobutyronitrile (>98%) from Fluka were used as received. Acetophenone and dimethylformamide were distilled prior to use. Lithium bromide was dried at 110 ^{o}C. Raney alloy (50% Ni, 50% Al) was obtained from Sigma-Aldrich. W2 type Raney nickel was prepared from Raney alloy by leaching in sodium hydroxide solution [50]. It was washed with absolute ethanol and dried under argon in a Schlenk tube. It was mixed with a preweighed amount of TGDMA in a dry bag, under argon atmosphere, preventing the oxidation of the reactive metal. After mixing with the other components, the mixture was frontally polymerized.

Composites of acrylamide and triethylene glycol dimethacrylate in 1:1 molar ratio have been prepared, containing 25% graphite as additive, and 1% AIBN as initiator. The monomers and additives were homogenized in a mortar, and filled into a test tube, with an internal diameter of 9 mm, and a length of 100 mm. The polymerization was started by heating the top of the mixture using a soldering iron. Upon heating the initiator decomposes and starts a strongly exotermic chain reaction, which causes the decomposition of other initiator molecules in the neighbouring part of the reaction mixture. This results in a propagating polymerization front travelling through the whole mixture, leaving a highly crosslinked solid polymer behind. The composite rods, prepared via frontal polymerization were cut to 5 mm thick slices using a diamond cutting wheel. Copper wire was curled around these small disks, and insulated with a glue gun. These electrodes were used once, and discarded.

Electrosynthesis experiements were performed with acetophenone in order to determine the effects of metal incorporation on the selectivity of the composite electrodes. The electroreduction was performed in a two compartment glass cell, with 2 ml volume for each compartment and a glass frit as

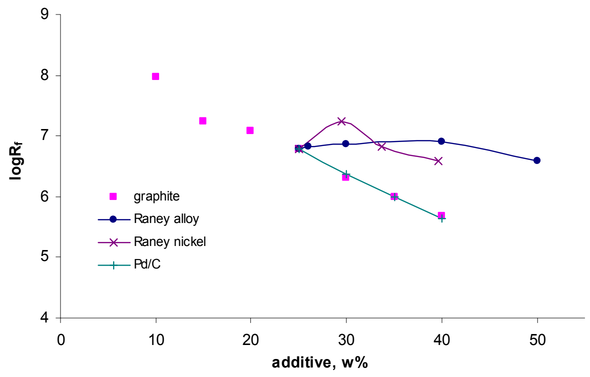

Figure 3. Effect of metal additives on the resistivity of graphite containing composites

separator. A home made potentiostat was used to keep the cathode potential constant. It was built according to the simplest circuit diagrams published in electrochemistry text books [51, 52]. It consisted of operational amplifiers type LM741 and CA3140, and had a current- and potential range of 40 mA and ±4V respectively. A Cole-Parmer 18200-10 USB data acquisition card was used as signal generator, and data logger.

Saturated calomel electrode (0,241V vs. NHE) was used as reference electrode, immersed into the catholyte in a Luggin-capillary. 0.3 M lithium bromide was used as electrolyte in water-DMF 1:1 mixture. 5 µl acetophenone was injected into the catholyte, and one hour electrolysis performed at constant cathode potential. The catholyte was stirred by means of a magnetic stirrer, set to 120 RPM. After the electrolysis, the product composition was determined by HPLC. 10 µl electrolyte was analysed without any sample preparation. (Waters Xterra RP18 5 µm, 4.6x150 mm column, eluent: acetonitrile/water 35/65, flow: 1 ml/min, detection: 220 nm). Every electrosynthesis experiement was performed twice. All thepresented data points are the average of two paralell measurements.

3. RESULTS

Raney alloy, Raney nickel and Pd/C were used as additives in various amount for the preparation of 25% graphite containing composites of acrylamide and triethylene glycol dimethacrylate in 1:1 molar ratio.

The specific resistance of the Raney alloy or Raney nickel containing composites were higher than that of composites containing the same amount of graphite as additive. This is due to the lower specific volume of metals in comparison to that of the graphite. This is responsible for the formation of fewer percolation paths in the composite resulting in higher resistivity. The resistivity of Pd/C containing composites, are approximately the same as the graphite containing ones. This verifies the relation between resistivity and additive volume.

On composite electrodes with various graphite content, different rates of hydrogen evolution was observed and a relation was found between the graphite content and the hydrogen overvoltage [1]. This effect is found to be more significant on the metal containing composites. The hydrogen overvoltage was measured in a three electrode system consisting of the composite working electrode, SCE as reference-, and platinum as an auxilliary electrode. 0.3 M LiBr in three different water-DMF mixtures was used as electrolyte.

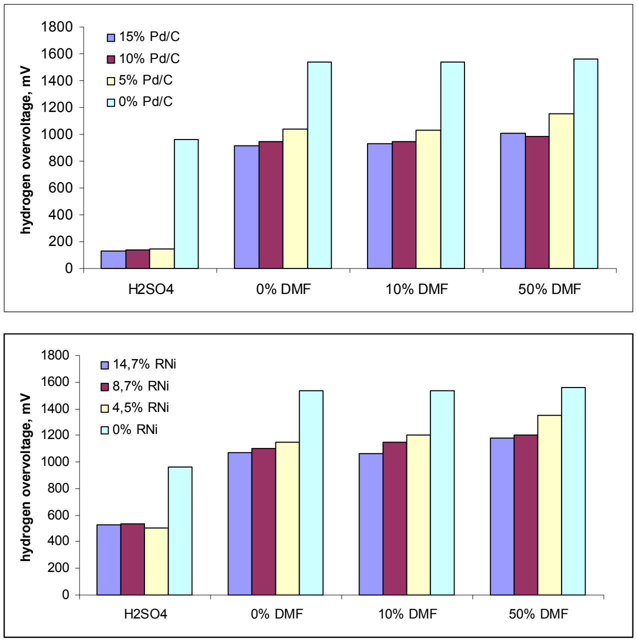

Figure 4. Effect of the electrolyte composition on hydrogen overvoltage at composite electrodes with different Pd/C or Raney nickel content in 0,5M sulphuric acid and 0,3M LiBr solutions with 0-10-50% dimethyl-formamide content.

Relatively high overvoltage values were observed on metal-free composite electrodes. This is due to the high resistivity of the composite materials, which is not unusual in the case of graphite containing composite materials, as shown by Oliviera et. al. [41], and Calixto et. al. [42]. They have applied these electrodes for volt-ammetry, because of their wide potential window. An other factor, raising the overvoltage is electrolyte pH, which was 6 for LiBr solutions. In 0,5M sulfuric acid the overvoltage is much lower, which is caused by the higher hydroxonium ion concentration [53].

The incorporation of metal additives significantly lowers the hydrogen overvoltage. Palladium and Raney nickel are effective catalysts for the reduction of water, even in small amounts. By increasing the ratio of additive, the overvoltage further decreases. The DMF content of the electrolyte has a minor effect on hydrogen overvoltage, which can be attributed to the blockage of catalitically active centers by the adsorption of amine impurities onto the electrocatalyst surface [54]. The hydrogen overvoltage on bright nickel cathode was found to be 660 mV in lithium bromide solutions, and 150 mV in sulfuric acid, which is in good accordance with the literature values [55].

Electrosynthesis experiements have been performed with Raney alloy containing composites and the effects of the metal content on the product composition have been examined. A significant increase was observed in the chemoselectivity to 1-phenylethanol

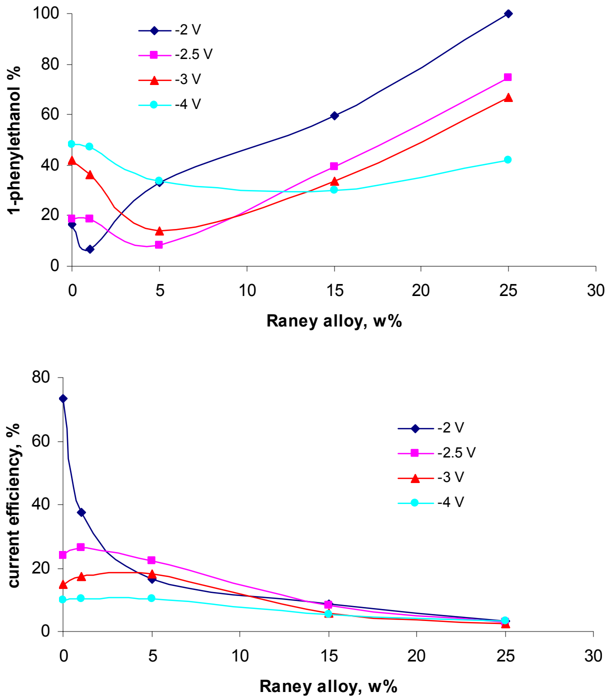

Figure 5. 1-phenylethanol yield and current efficiency of acetophenone reduction as a function of Raney alloy content at different cathode potentials (measured versus SCE)

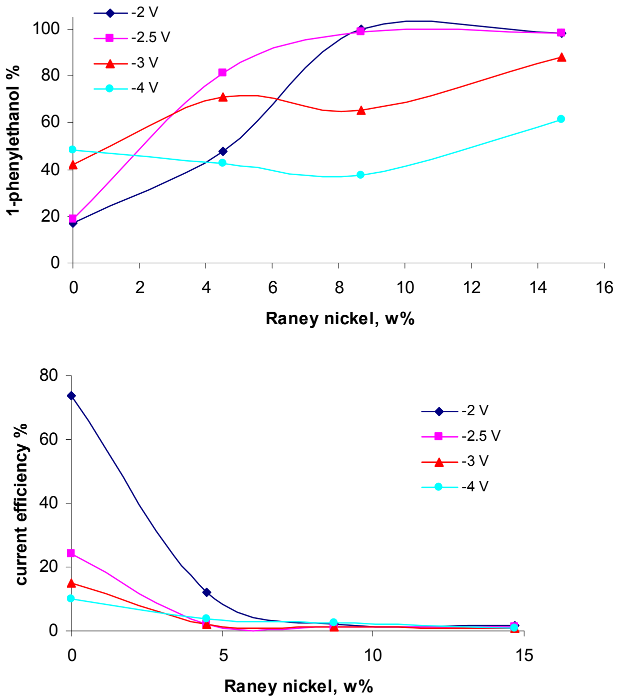

Figure 6. 1-phenylethanol yield and current efficiency of acetophenone reduction as a function of Raney nickel content at different cathode potentials (vs. SCE)

and a decrease in the current efficiency (fig. 5).

Composites with various Raney nickel content were prepared, which showed nearly 100% chemoselectivity to 1-phenylethanol, but current efficiency decreased to 1%. Phenylethanol yields expand with increasing metal content as a result of ECH mechanism gradually becoming predominant. The effect of metal content is the most significant on 2V, where the phenylethanol yield changes from 10% to 100% (fig. 6). At higher cathode potential, the phenylethanol/pinacol ratio is lower, which indicates a shift to the EP mechanism. The hydrogen overvoltage diminishes with the growing metal content, which results in a higher exchange current – and rate of hydrogen evolution – at a given cathode potential.

The mixing effect of hydrogen evolution enhances the transport of intermediate radicals from the electrode surface, and prevents the adsorption of acetophenone, as previously reported by Cognet et. al. [17-18]. The current efficiency drastically decreases with increasing metal content; the water reduction hampers the reduction of acetophenone.

The activation of Raney alloy on the composite surface was attempted by means of leaching the electrodes in diluted sodium hydroxide solution. We have observed vigorous hydrogen evolution in 5% NaOH solution, which ceased in an hour. Electrosynthesis experiments were carried out with these electrodes after thorough rinsing. The chemoselectivity to 1-phenylethanol did not grow significantly, but the current efficiency decreased to approximately halve of it's original value, which indicates some increase in electrocatalytic activity of the electrode for water reduction.

The preparation of Raney nickel from Raney alloy requires long-term leaching in concentrated sodium hydroxide solution [50]. This would attack and decompose the polymer. To overcome this problem, we have used previously activated Raney nickel as an additive for the preparation of composite electrodes. These cathodes showed increased electrocatalytic activity and less additive caused higher selectivity to 1-phenylethanol.

On -2 and -2.5 V cathode potentials almost 100% chemoselectivity can be reached (fig. 6). In this case the mechanism is probably clear ECH. Current efficiency is very low at higher metal contents.

In order to observe the differences in the electrode surfaces, scanning electron microscope images were taken of the Raney alloy and the Raney nickel containing composites (see figure 7. images).

The SEM images were collected by detecting back scattered electrons, so brighter shades correspond to higher atomic numbers. It can be seen on 100x magnification images, that the metal powders, used as additives are characterized by heterogenous size distribution. Particle size ranges from a few microns to a few tens of microns. On medium magnification the fragmentary structure of metal particles can be observed, which is probably due to the effect of the diamond cutting wheel, used for cutting of composites. Comparing the surfaces of a Raney alloy particle and an etched Raney nickel particle, the increased surface roughness can be observed, caused by the dissolution of the aluminium from the alloy.

Besides Raney nickel, palladium on carbon or Pt-alloys on

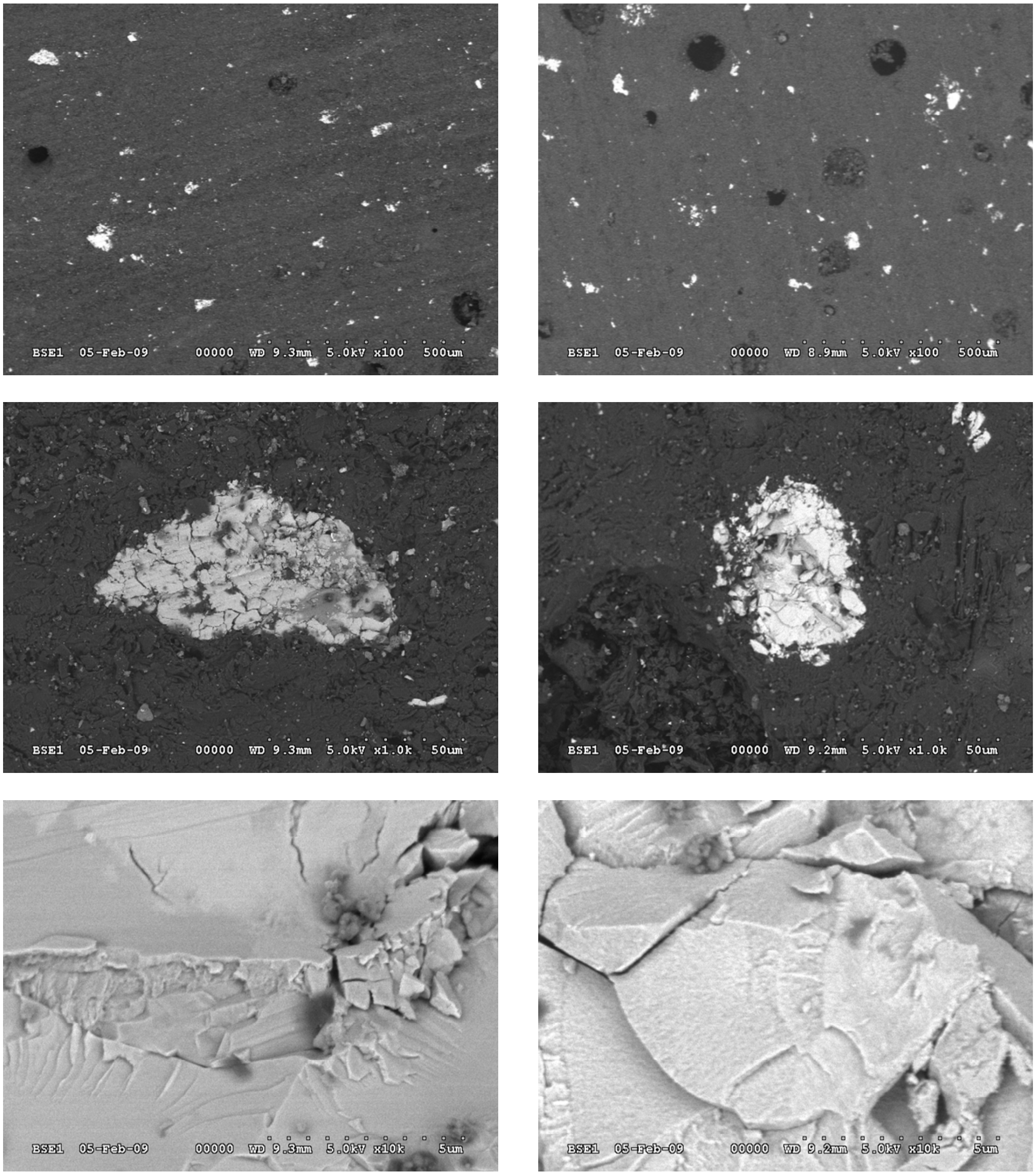

Figure 7. Sem images of Raney alloy (left) and Raney nickel (right) containing composites

carbon are very well known and widely used catalysts in hydrogenation [56]. 10% Pd on carbon was used as an additive in the electrode preparation.

Palladium containing electrodes are characterized by lower chemoselectivity and higher current efficiency values (2-3 times higher), which means lower electrocatalytic activity than that of Raney nickel (fig. 8). This can be ascribed – besides different electrochemical and adsorption properties – to the lower metal content. Lower electrocatalytic activity of Pd/C was also reported by Senda et. al. in ketone reduction [48]. High electrocatalytic activity of hydrogenation of phenol to cyclohexanol was also found on Pt-alloys depending of the catalyst composition and loading [25, 27, 29, 54, 57]. The results we obtained in this work, on the hydrogenation of acetophenone clearly show, that the composite electrodes are interesting alternative low cost and effeicient catalysts in electrosynthesis.

At -2 V cathode potential the chemoselectivity rises monotonously. On -2.5 V the increase is only slight, and on higher

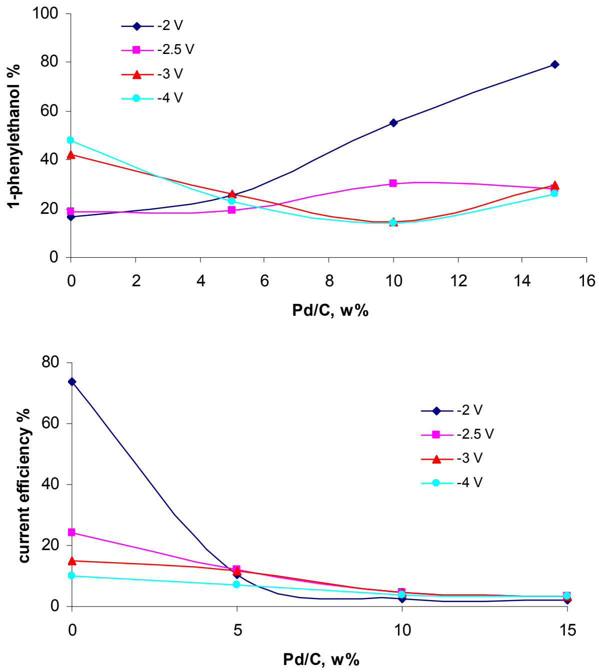

Figure 8. 1-phenylethanol yield and current efficiency of acetophenone reduction as a function of Pd/C content at different cathode potentials

potentials the dependence of 1-phenylethanol yield on metal content changes to a decreasing tendency.

On the SEM image with 10000x magnification, the Pd metal particles can be seen as small attached spheres with an average particle size of 100nm.

4. SUMMARY

It was shown, that frontal polymerization is an appropriate method for the preparation of metal containing conductive composites. The electrochemical properties of the graphite containing acrylamide – triethylene glycol dimethacrylate based composite electrodes can be altered by electrocatalytic metal powder addition. Incorporation of Raney nickel or Pd/C changes the mechanism of the reaction from electronation – protonation to electrochemical hydrogenation thus changing the chemoselectivity of the electrode. Besides electrode potential, electrode composition can be used to influence the product composition. The applied catalysts lowered the hydrogen overvoltage leading to an increase in the rate of hydrogen gas evolution and holding back ketone reduction.

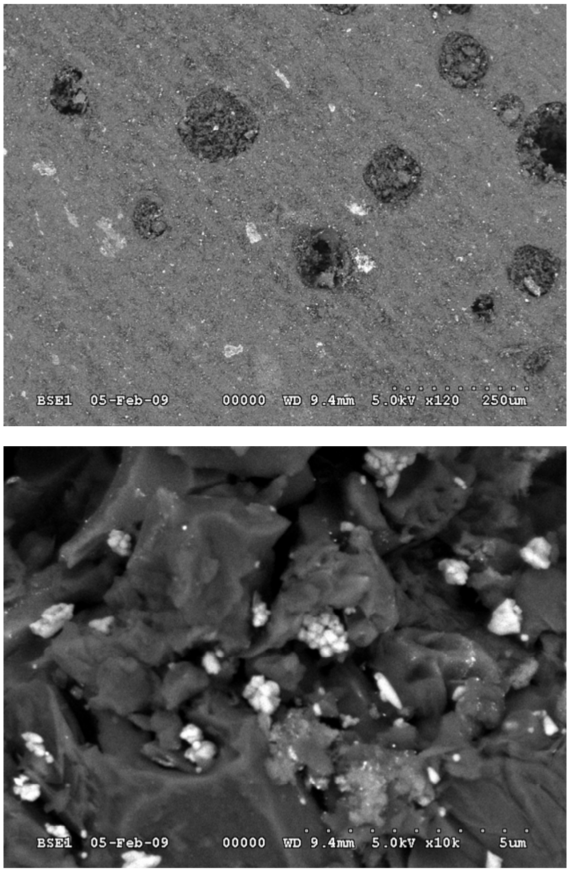

Figure 9. SEM images of 5w% Pd/C containing composites

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