difference Fourier map and refined isotropically. Crystal dimensions: $0.44 \times 0.23 \times 0.21$ mm; $T = 173$ K; monoclinic, space group $P2_1$, $a = 7.7156(5)$, $b = 17.0039(11)$, $c = 7.8656(5)$ Å, $\beta = 98.133(1)°$, $V = 1021.55(11)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.112$ g cm^{-3}; 5330 reflections collected, 3229 independent; $2\theta_{max} = 50°$; 370 parameters; $R_1 = 0.0417$, $wR_2 = 0.0768$ for $I > 2\sigma(I)$; residual electron density: 0.145 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-105289. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[5] The typical normalization of O–H and B–H bonds to 0.96 and 1.21 Å, respectively, leads to the more realistic H–H distances of 1.62–2.28 Å.

[6] These corrections are still likely to overestimate the H–H contact distances as they represent typical values for noninteracting partners. A similar analysis of the three close BH···HO contacts in the X-ray structure of $NaBH_4 \cdot 2H_2O$ ($NaBD_4 \cdot 2D_2O$) yielded distances 0.04 Å longer on average than the final neutron diffraction values.

[7] We found the 1.73 Å as the shortest reliable H–H contact distance for a dihydrogen bond reported so far (ref. [1a]). Another value of 1.68 Å was reported, but the disorder of the proton donor solvent as well as the uncertainty in its N–H proton location make this distance somewhat less reliable. See: B. P. Patel, W. Yao, G. P. A. Yap, A. L. Rheingold, R. H. Crabtree, *Chem. Commun.* **1996**, 991–992.

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Contactless Electrodeposition of Palladium Catalysts[**]

Jean-Claude Bradley[*] and Zhongming Ma

In principle, electrodeposition offers a convenient method of modulating the properties of metal catalysts. It has been used extensively to prepare metal catalysts on conductive substrates such as carbon, metals, or conductive oxides.[1–4] Underpotential deposition to form surfaces with modified catalytic behavior could be considered a related technology.[5, 6] A critical limitation of electrodeposited catalysts is that the deposited area is essentially limited to the electrode surface. To increase the available surface area of electrodeposited catalysts, electrodeposition of metal structures within polymers such as polyvinylpyridine,[7, 8] poly(vinylacetic acid),[9] and nafion[10–13] has been actively explored. A recently developed, related approach is electrodeposition in thin gel coatings.[14] However, such approaches are limited to coatings only a few micrometers thick because of the difficulty of assuring an ohmic or electron-hopping contact with the growing electrodeposit while maintaining a highly permeable structure for rapid diffusion of the reagents and high surface area. Furthermore, small isolated deposits cannot usually be obtained by this method because of the necessity of having an electrically contiguous structure that extends from the electrode into the matrix. Here we describe an electric-field method for preparing electrodeposited catalysts which does not require physical contact between the power source and the deposits. This approach, referred to as bipolar electrodeposition, not only enables electrodeposition across several centimeters of the support but also allows the position of the deposit to be controlled.

Other attempts to increase the thickness of electrodeposited catalysts include the use of electrically conductive polymers such as polypyrrole,[15–17] polyaniline,[18–21] or viologen-based polymers.[22] However, due to anisotropic field distributions and the finite resistivity of the conductive polymer, it is unlikely that homogeneous electrodeposition will be possible in deposits more than a few micrometers thick with this approach. Furthermore, the choice of support is limited to conductive polymers in electrical contact with an electrode.

One method that avoids electrical contact with the conductive support is photoelectrodeposition onto semiconductor particles. This has been used extensively as a method of electrodepositing catalytically active metals (e.g. Au, Pt, Pd, Ag, Rh, Ir) onto a dispersed semiconducting support (e.g. TiO_2, ZnO, SnO_2, ZrO_2, ThO_2, CdS, WO_3).[23–39] In this case photons promote electrons from the valence band into the conduction band of the semiconductor particles to give a situation in which anodic and cathodic processes occur on different regions of the same particle. Although this method was successful in producing catalysts, it requires a semiconductor whose bandgap is tuned to the wavelengths that can penetrate into the sample. Furthermore, due to absorption of light, homogeneous exposure across large volumes is not possible without prolonged mixing.

Here we describe a novel method for creating electrodeposited catalysts over large volumes of nonconductive supports with a much more homogenous distribution than available by other electrodeposition techniques. Our method relies on the polarization of conductive micrometer-scale particles in a nonconductive matrix. This represents another application of our approach to toposelectively (site-selectively) functionalize or otherwise modify particles by using electric fields. We earlier demonstrated toposelective electrodeposition onto isolated millimeter-[40, 41] and micrometer-sized[42] copper particles to form wires with diameters as small as 0.3 μm. We refer to the objects generated from such toposelective manipulation as toposomes.[43]

The preparation of the catalyst is shown schematically in Figure 1. Graphite particles (nominally 1–2 μm in diameter) were dispersed onto one side of 60-μm-thick cellulose paper by nebulizing an acetone suspension of the particles. The papers were then stacked to a thickness of 0.5 cm and sandwiched between two flat graphite electrodes with dimensions of 2 × 2 cm. After immersion in a 1 mM solution of $PdCl_2$

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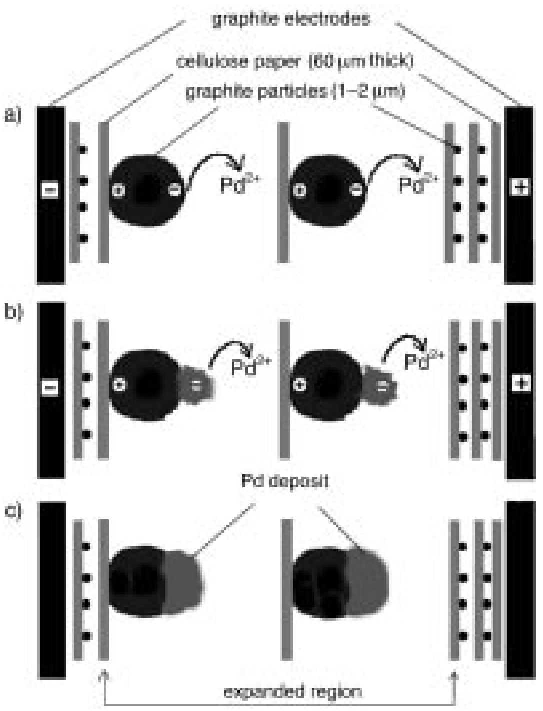

Figure 1. Schematic representation of the preparation of the bipolar electrodeposited catalyst. a) An electric field is generated across graphite particles sandwiched between layers of thin cellulose paper by applying a voltage drop with two flat graphite electrodes. b) Since the system is bathed in a 1 mM solution of $PdCl_2$ in toluene/acetonitrile (1/1), Pd is electrodeposited on the cathodically polarized region of each graphite particle. c) After the field is removed, the catalyst is washed and dried. It can now be used as a catalytically active material.

in toluene/acetonitrile (1/1), an electric field of controlled intensity and duration was applied by imposing a voltage drop between the graphite electrodes. The paper support was then washed thoroughly with acetone to remove unchanged salt and dried.

Application of an electric field polarizes the electrically isolated graphite particles and results in separate anodic and cathodic regions on the same particle (Figures 1 and 2). As expected, the reduction process involves electrodeposition of the metal. Although we have not yet identified the oxidation processes, the involvement of the solvents, the halide counter-ions, or adventitious water is likely.

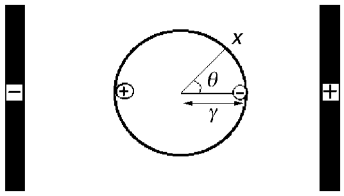

Figure 2. Polarization of a sperical particle in an electric field. See text and Equations (a) and (b).

To a first approximation, for a spherical particle of radius r exposed to an electric field E, an overpotential η is induced at a position x, expressed as an angle θ relative to the direction of the applied electric field.[44, 45] [Eq. (a)]. It follows that the maximum potential difference $\Delta V_{\max}$ across the particle is given by Equation (b). Significant deviations from Equation (b) are expected for nonspherical particles such as the graphite platelets in the present work. However, Equation (b) does suggest that the particle radius and the electric field required to induce electrodeposition in a given system are inversely proportional to one another.

$$\eta_x = Er\cos\theta \tag{a}$$

$$\Delta V_{\max} = 2\,Er \tag{b}$$

Since each particle serves as both anode and cathode, the process is referred to as bipolar electrochemistry.[44–54] This phenomenon has been investigated for applications in metal recovery,[46–49] electrosynthesis,[50–53] and electrochemical etching of diamond.[54] However, in these cases, millimeter-scale particles or disks were used because the field required to induce a sufficient overpotential at the particle surface increases with diminishing particle radius [see Eq. (b)]. This is particularly difficult in aqueous salt solutions, for which high conductivity prevents the application of high fields at the feeder electrodes. Micrometer and submicrometer metal particles have been used to carry out bipolar electrochemistry, but aprotic solvents or conductivity water must be used.[55–57] Bipolar electrodeposition onto electrically isolated micrometer-scale particles has received limited attention.[42] Although aqueous media are generally too conductive for particles of this size, organic solvents such as toluene/acetonitrile offer a sufficiently resistive environment for high fields (5000 V cm^{-1}) to be applied while still allowing electrodeposition to occur.

A key concept in the present work is to control the properties of catalytic systems by modulating electric field parameters during their preparation. As a first step, the hydrogenation of crotonaldehyde with palladium as catalyst was employed as a model reaction. Figure 3 A shows the effect of the electric field intensity on the amount of Pd deposited, as monitored by atomic absorption spectroscopy (AAS). A strong correlation between the amount of Pd deposited and catalytic activity for hydrogenation can be seen in Figure 3 B. Exposure to electric fields in the absence of graphite particles led to no increase in Pd content (see Figure 3 A, control curve). Apparently, some palladium is not removed by thorough washing, and there are contributions from the paper and from the graphite itself. This residual palladium is presumably still in ionic form as no catalytic activity is detected for such samples (Figure 3 B).

Two types of assay were used to investigate the effect of electric field strength on the activity of the catalyst. In Figure 3 B the same total weight of support was used, whereas in Figure 3 C the total amount of Pd was kept constant. Both methods clearly show a strong correlation between the electric field intensity during catalyst preparation and the catalytic activity. Note that in Figure 3 C, no background correction was made for the residual palladium ions that are present in the absence of an electric field. Such a correction is not straightforward because the application of the electric

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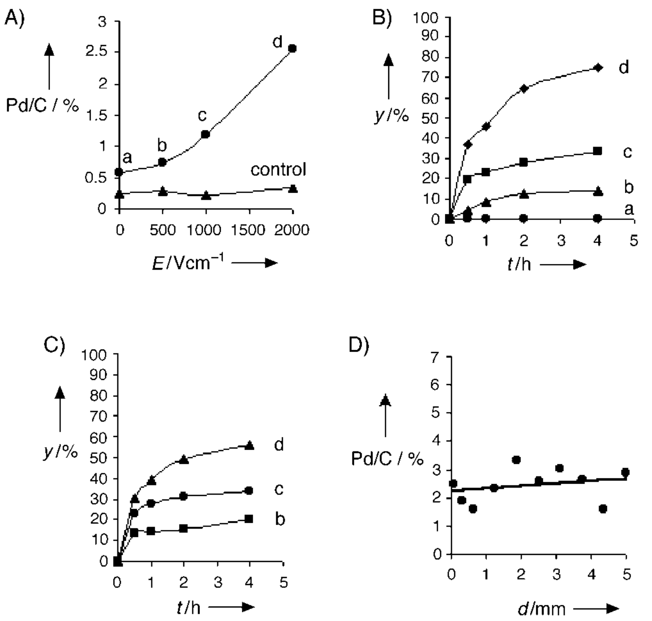

Figure 3. Characterization of four sets of catalysts, prepared by the method of Figure 1, at the following field strengths: a) 0, b) 500, c) 1000, d) 2000 $V\,cm^{-1}$. In all cases the duration of exposure to the field was 15 min, the solution was 1 mM $PdCl_2$ in toluene/acetonitrile (1/1), and the graphite powder amounted to 2.5 wt% of the total dry paper support. The two flat graphite electrodes (2×2 cm) were 0.5 cm apart. Immediately after application of the field the papers were washed exhaustively with acetone then dried and kept in a dessicator. A) The upper curve represents the Pd/C ratio for each catalyst as determined by AAS on samples digested in aqua regia. The control curve corresponds to the theoretical Pd/C percentage ratio for experiments carried out in the absence of graphite (calculated for the same amount of graphite as in the case of the upper curve). Presented are the results of three experiments. The average standard deviation was ± 0.16 for the upper curve and ± 0.04 for the control curve. B) Conversion y (GC analysis) of crotonaldehyde (60 mM in ethanol) to butyraldehyde under 1 atm of hydrogen for the same mass (400 mg) of total dry paper support and catalyst. Presented are the results of three experiments. The average standard deviation was ± 3.68. C) As for (B), except that the total amount of Pd (determined by AAS) was kept constant at 0.114 mg. Presented are the results of three experiments. The average standard deviation was ± 4.41. D) Pd content determined at various positions between the anode (leftmost point) and cathode (rightmost point). The field strength was 2.0 $kV\,cm^{-1}$.

field appears to substantially deplete this background level. This is evident from the atomic absorption data of the experiment at 500 $V\,cm^{-1}$, which show virtually the same loading as in the zero-field experiment but with vastly different catalytic activity (see Figures 3 A and B). A possible explanation may be the conversion of Pd ions adsorbed onto the graphite into catalytically active metal, without substantial additional plating from the surrounding solution under low-field conditions.

To ensure that the palladium was indeed deposited by a bipolar mechanism evenly throughout the volume of the inert matrix, the palladium content was analyzed at various positions between the two electrodes. If the palladium were simply deposited at the cathodic feeder electrode, then the palladium content should exhibit a maximum in the cathodic region and decrease rapidly towards the anode. As shown in Figure 3 D, the palladium is fairly evenly dispersed throughout; hence, the catalyst was prepared by bipolar electrodeposition.

Evidence for the toposelectivity of the bipolar electrodeposition was obtained by exposing the palladium-derivatized graphite particles to a solution of gold tribromide and reversing the field direction. A transmission electron micrograph of a particle obtained by such a treatment is shown in Figure 4. Energy dispersive X-ray analysis showed that the gold and palladium deposits are located at opposite ends of the particle.

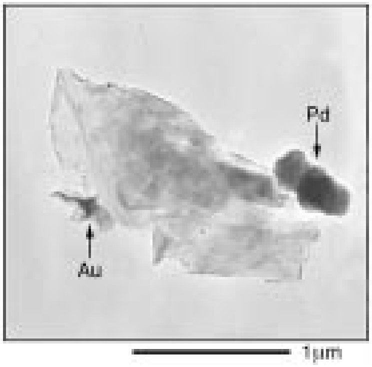

Figure 4. Transmission electron micrograph of an isolated graphite particle with Pd and Au introduced sequentially at opposite ends by bipolar electrodeposition with opposite field directions for each metal. Under the experimental conditions described in Figure 3, the powder was first exposed to 2.0 $kV\,cm^{-1}$ for 15 min in the presence of 1 mM $PdCl_2$ in toluene/acetonitrile (1/1) and then washed with acetone and drying. The procedure was then repeated with 0.25 mM $AuBr_3$ in toluene/acetonitrile with the same field strength and duration but opposite field direction. Energy dispersive X-ray analysis showed the presence of each metal only in the dark areas indicated by the arrows.

Taken together, the above results demonstrate the preparation of a bipolar electrodeposited catalyst (BEC), the catalytic activity of which can be modulated by means of the applied electric field strength. It is well known that various parameters in chemical reductions (type of reductant, temperature, pressure, additives) lead to modulation of catalyst activity and selectivity. Changes in catalyst particle morphology and size, as well as support interactions, are likely the dominant cause. It is therefore expected that in the production of catalysts by electric field mediated reduction, the catalyst activity, and perhaps selectivity will depend on electric field parameters (intensity, time, pulse sequence, and direction). The last parameter is particularly important because it offers the ability to control the position of metal deposition by means of the direction of an electric field vector. This type of microsegregation control on a particulate support would be difficult to obtain by conventional methods and may prove to have important implications for catalytic activity.

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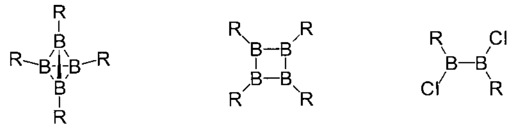
Blue Tetrakis(diisopropylamino)-*cyclo*-tetraborane and Yellow Tetrakis(tetramethylpiperidino)tetrabora-tetrahedrane[**]

Claus-Jürgen Maier, Hans Pritzkow, and Walter Siebert[*]

Dedicated to Professor Otto J. Scherer on the occasion of his 65th birthday

The chloro[1] and *tert*-butyl derivatives[2, 3] of tetraborane(4) (**1**) have a tetrahedral structure (B–B bond lengths in **1b**:[3] 1.699(6) – 1.714(4) Å), whereas an opening of the tetrahedron to a four-membered ring (**2**) is discussed for B_4Cl_4 (**1a**)[4, 5] and B_4Br_4[6] in solution. The reaction mixture obtained from di-*tert*-butyldichlorodiborane(4) and Na/K alloy was shown by Klusik and Berndt to contain **1b** ($\delta(^{11}B) = 135.7$) and the radical anion $[B_4tBu_4]^{\bullet-}$ (**2b**$^{\bullet-}$, observed by ESR spectroscopy), for which they postulated a bent ring structure.[7] Morrison[8] could not confirm the proposed planar structure



1	a	b	f
R	Cl	*t*Bu	TMP

2	c	d	e
R	NMe_2	NEt_2	N*i*Pr_2

3	e	f
R	N*i*Pr_2	TMP

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