

Two-phase electrocatalysis by aqueous colloids

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Abstract

In this work, the combination of the advantages of two-phase catalysis, electrocatalysis and colloid catalysis is presented. It is shown that palladium or gold colloids prepared by citrate reduction can be charged negatively in a heterogeneous two-phase reaction and subsequently used as aqueous catalysts for dehalogenation reactions. This can be regarded as a new type of electrocatalysis. © 2002 Published by Elsevier Science B.V.

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1. Introduction

The interest in catalytic reactions taking place in biphasic systems where the two phases are immiscible liquids has been increasing constantly. The use of the two-phase method enables combination of the advantages of homogeneous and heterogeneous catalysis. The main advantages of homogeneous catalysis over heterogeneous catalysis in organic synthesis are the use of less aggressive reaction conditions and increased selectivity and activity while the disadvantage is costly and difficult process of separating the catalyst from the products and the solvents [1]. The use of two-phase systems overcomes these problems by introducing the catalyst and the substrates and later products in separate, mutually immiscible phases. Usually the catalyst is dissolved in water [1] or more recently fluorous [2] phase. This makes the recovery of the catalyst extremely simple: decantation. Most of the efforts in this field have been directed into developing suitable, water-soluble, often organometallic, catalysts [1]. In addition to molecular catalysts, water-soluble

[3,4] or fluorous phase soluble [5] metal colloids have been utilised as two-phase catalysts.

The interface between two immiscible electrolyte solutions (ITIES) offers the means to study charge transfer and adsorption phenomena at a liquid|liquid interface by well-established electrochemical techniques. The potential difference between the aqueous and organic phases can be controlled in a simple manner by the use of a potentiostat or potential determining ions [6,7]. The usefulness of the electrochemical approach has been demonstrated in the case of Phase-Transfer Catalysis [6,8–10] where the potential across the interface determined by the Phase-Transfer salt was shown to act as the driving force for the reaction. In the case of liquid|liquid interfaces, electrocatalysis is defined as interfacial catalytic reactions that require an electrical field across the interface.

In this communication we present a combination of two-phase catalysis, colloid catalysts and electrocatalysis. Metal colloids were prepared by traditional chemical reduction method. Electrochemical measurements are carried out to examine the charging of the colloid in a heterogeneous two-phase reaction. The charging of the colloid is verified with electrophoretic light scattering measurements. The colloids are shown to act as a catalyst in a two-phase reduction of 2-bromoacetophenone.

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2. Experimental

The Pd and Au colloids were prepared by the classical Turkevich [11] method. PdCl₂ (Aldrich), HAuCl₄ (Aldrich) and sodium citrate (Aldrich) were used as the starting materials for the colloids. The colloids were used in the voltammetric, charging and catalytic experiments as-prepared. The organic phase supporting electrolytes were tetraphenylarsonium tetrakis(4-chlorotetraphenyl) borate (TPAsTPBCl) or tetramethylammonium tetrakis(4-chlorotetraphenyl) borate (TMATPBCl), prepared as previously described [6]. 1,2-Dichloroethane was obtained from Rathburn Chemicals and used as received. All water used was distilled and run through the Millipore ion exchange system. All other chemicals used were of Analar grade.

The electrophoretic light scattering measurements were carried out with a Coulter DELSA 440SX equipment. An HP 6890 Gas Chromatograph equipped with an HP Innowax (30 m × 0.32 mm × 0.50 μm) capillary column was used for the chromatographic analyses. An Autolab potentiostat (EcoChemie) system with a positive feedback operation was used in four-electrode mode [12] to carry out the electrochemical measurements. The electrochemical measurements refer to the cell in Fig. 1. The potential is that of the water phase with respect to the organic phase, and a positive current is defined as the transfer of a negative charge from the organic to the aqueous phase or a positive charge in the opposite direction. The contribution of the reference junction to the measured potential was subtracted from the total cell potential as usual [13].

3. Results and discussion

3.1. Electrochemical studies at externally polarised interface

The voltammetric response of a system with an aqueous colloid and an electron donor in the organic phase was studied by cyclic voltammetry and the results are shown in Fig. 2. The results in Fig. 2 correspond to Pd colloid with 1 mM decamethylferrocene (DCMFC) in the organic phase (cell in Fig. 1). An irreversible response is obtained as the potential is swept positive. The response is only detected when both the DCMFC and

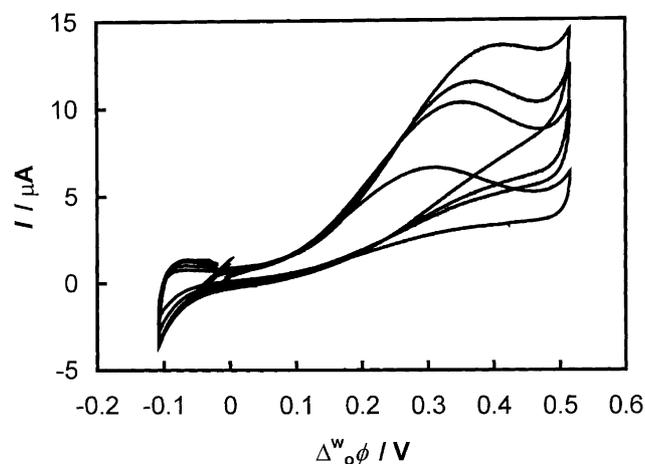
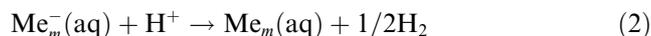
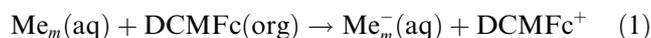


Fig. 2. Voltammetric response for the electron transfer reaction between 1 mM DCMFc in the organic phase and aqueous Pd colloid in the cell in Fig. 1. Sweep rates were 25, 50, 75 and 100 mV s⁻¹.

the Pd colloid are present in the cell. Otherwise, the response follows the baseline. The peak current depends linearly on the square root of the sweep rate. The peak potential shifts to slightly more positive values with increasing sweep rate. The precise position of the peak potential varied between different measurements. It is proposed that the response in Fig. 2 is the result of the heterogeneous charging of the aqueous colloid with electrons from DCMFc. The response for a gold colloid is similar to the Pd case. The reaction can be described as:



where Me_m is Pd or Au. The second reaction is much slower, so that the charge built in the aqueous phase is quite stable and can be detected by electrophoretic measurements even hours after the charging experiment.

It could be possible that a similar type of response as seen in Fig. 2 for the colloidal charging process would be obtained for the electrodeposition of the metal nanoparticles at the interface [14,15]. Some of the starting materials from the colloid synthesis can be present in the aqueous colloid phase. However, a similar response is observed using a sulfanilate ligand stabilised Pd colloid in the aqueous phase [16]. In that case the nanoparticles are obtained as a powder and redissolved in water phase to yield a colloid, therefore there should not be any starting materials present. Also, the response for a gold colloid is analogous to the one shown in Fig. 2. If there still were gold chloride present in the aqueous phase, a tetrachloroaurate ion transfer signal would be expected in the potential window.



Fig. 1. Schematic representation of the electrochemical cell.

3.2. Electrophoretic mobility

Electrophoretic measurements of small metal particles in aqueous solutions have been carried out to determine the charge of the particles [17,18]. Ung et al. [17] simulated the effect of cathodic polarisation of the colloid by adding borohydride to a polymer stabilised silver sol, and observed an increase in the electrophoretic mobility after the addition. In the present case, the cathodic polarisation is realised via a heterogeneous electron transfer reaction between the aqueous and the organic phases.

The electrophoretic mobility of the particles was determined to confirm the build up of negative charge on the colloid. In these measurements, the potential difference across the liquid|liquid interface was set with potential determining ions [6,7], therefore no external control of the interfacial potential by a potentiostat is needed. This approach is very suitable for catalytic studies because it enables controlling the interfacial potential in biphasic systems that can be stirred to maximise reaction rate. The aqueous phase in the measurements was the citrate colloid with 0.1 mM TMACl. The organic phase contained 5 mM TMATPBCl and the electron donor DCMFc. The concentrations of the supporting electrolytes TMACl and TMATPBCl were chosen so that the Galvani potential difference across the interface was 0.22 V. Electron transfer from DCMFc to the colloid takes place at this potential. In the experiment, 5 ml of each phase were combined in a small vial and stirred for an hour. The organic phase was separated and the electrophoretic mobility of the particles was determined. The citrate-stabilised colloids have a slight negative charge to start with due to the adsorbed citrate ions. Fig. 3 shows on the left axis the dependence of the electrophoretic mobility for the Au colloid as a function of the concentration of the electron donor DCMFc. As can be seen, the charge on the particles increases with the DCMFc concentration at low concentrations and reaches a plateau at higher concentrations. The results for the Pd colloid are similar. These results clearly show that the metal colloid is charged in the two-phase process.

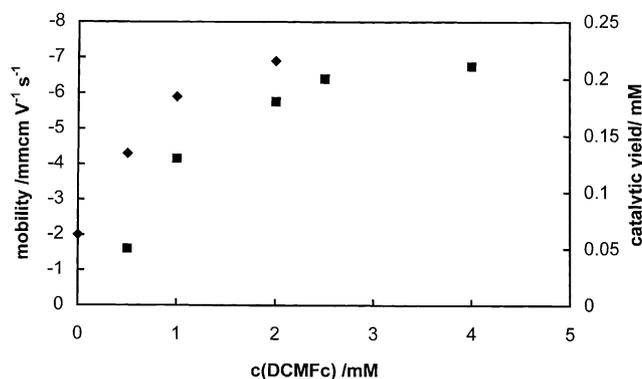


Fig. 3. Left axis (◆): the electrophoretic mobility of Au colloid as a function of DCMFc concentration. Right axis (■): catalytic yield of acetophenone as a function of DCMFc concentration.

3.3. Electrocatalytic dehalogenation reaction

A chargeable colloid is a very desirable type of catalyst due to its environmentally friendly nature. Catalytic experiments were conducted in order to study if the charged colloids can be used as an electron source in organic reactions. Dehalogenation of 2-bromoacetophenone (BrAc) was chosen as the model reaction. The reactions were carried out in a similar manner to the charging experiments in the previous section. 0.95 mM of BrAc was added to the organic phase. The Au colloid was used as the catalyst. The solutions were stirred for 2 h before analysing the yield of the product acetophenone (Ac) with GC. The right axis in Fig. 3 corresponds to the dependence of the Ac yield on the concentration of the electron donor. As can be seen, the yield follows the shape of the charge build-up in the colloid. It has to be noted though that the conversion in these experiments was not 100%. Higher conversion was achieved with increased reaction time. A control measurement in the absence of the colloid did not result in the reduction of the substrate. Also, it was noted that the presence of the base electrolytes was essential for a successful catalytic reaction.

The dehalogenation experiments clearly show the potential applications for this new type of catalytic system. This is illustrated in Fig. 4. Previously,

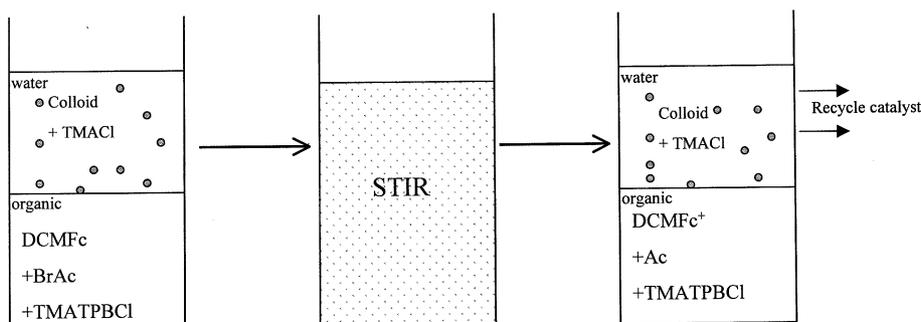


Fig. 4. Schematic illustration of the catalytic reaction.

electrochemically prepared Pd nanoparticles at ITIES have been shown to act as dehalogenation catalysts [19] as well as electron transfer mediators for a photoinduced reduction of an organic substance in the presence of a water-soluble porphyrin compound [20]. In these cases the recovery of the catalyst is not possible.

4. Conclusions

This report presents a novel combination of two-phase catalysis, electrocatalysis and colloid catalysis. It is shown by electrochemical four-electrode cell measurements and by electrophoretic light scattering measurements that the aqueous colloids can be charged with electrons by a two-phase process involving DCMFc as the electron donor. The catalytic activity of the colloids in a two-phase electrocatalytic system is demonstrated using dehalogenation of an organic substrate.

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