

CATALYTIC MICROPARTICLES

FIELD OF THE INVENTION

The present invention relates generally to catalytic particles and more particularly, to catalytic microparticles containing electroactive polymers and a transition metal. The present invention further contemplates methods for the preparation of catalytic particles and their use in catalysing chemical reactions.

BACKGROUND OF THE INVENTION

There has been considerable interest in using polymeric matrices, and particularly electroactive polymers, to immobilize catalyst particles. Generally, the catalyst particles have been deposited onto a pre-formed polymer film. Methods involving the electrodeposition of catalyst particles onto pre-formed electroactive films are described in the following articles:

- (i) Chandler and Pletcher, *"The Electrodeposition of Metals onto Polypyrrole Films from Aqueous Solutions"*, *J. Appl. Electrochem.*, **16**, 62, 1986.
- (ii) Leone, et al., *"Electrodeposition and Electrochemical Behaviour of Palladium Particles at Polyaniline and Polypyrrole Films"*, *J. Electrochem. Soc.* **39**, 438, 1992.
- (iii) Bartak et al, *"Electrodeposition and Characterization of Platinum Microparticles in Poly(4-vinylpyridine) Film Electrodes"*, *Anal. Chem.* **58**, 2756, 1986.
- (iv) Tourillon et al., *"Electrochemical Inclusion of Metallic Clusters in Organic Conducting Polymers"*, *J. Electroanal. Chem.*, **158**, 181, 1983.

- (v) Vork et al., "Oxidation of Hydrogen at Platinum-Polypyrrole Electrodes", *Electrochimica Acta*, **31**, 1569, 1986.
- (vi) Gholamian and Contractor, "Oxidation of Formic Acid at Platinum Microparticles Dispersed in a Polyaniline Matrix", *J. Electroanal. Chem.*, **289**, 69, 1990.
- (vii) Kost and Bartak, "Electrodeposition of Platinum Microparticles into Polyaniline Films with Electrocatalytic Applications", *Anal. Chem.*, **60**, 2379, 1988.

However, a major disadvantage of using a catalyst incorporation procedure, in which the metal ions are electroreduced onto a pre-existing polymer film, is the confinement of the particles to the surface of the film. To circumvent this problem, attempts have been made to incorporate the catalyst particles into a growing polymer film. For example, Nougé *et al* (*J. Electrochem. Soc.*, **130**, 2126, 1983) incorporated RuO_4^{2-} dopant anions into polypyrrole during synthesis and subsequently reduced the RuO_4^{2-} to generate RuO_2 *in situ*. In US Patent No 5,334,292, a method is disclosed for producing electroactive polymer film with nanodispersed catalytic particles. The method involves the preparation of a colloidal suspension of catalytic particles in a solution containing an electroactive polymer precursor and the subsequent electrosynthesis of the electroactive film with the incorporation of the colloidal catalytic particles. Liu *et al* (*J. Electroanal. Chem.* **158**, 181, 1983) described the incorporation of finely divided and dispersed Pt particles in polymers such as Nafion[®] while the electrochemical dispersion of Pt microparticles in polymeric matrices such as poly(vinylacetic acid) was described by Kao *et al* (*J. Am. Chem. Soc.* **106**, 473 1984).

The examples above involve the incorporation of catalyst particles into films. European Patent No 0 665,265 describes a composition containing metal particles, a polymer and a particulate base material which involves the reduction of metal salts in the presence of a dissolved polymer such as polyvinylpyrrolidinone and a sol of the base material.

US Patent No 5,254,656, describes a method of preparing curable organosiloxane compositions containing organotitanate/microencapsulated platinum co-catalysts. US Patent

No 5,411,573 describes a process for accumulating and recovering metals in their elemental form, *i.e.* an oxidation state of zero, from an acidic solution by contacting the solution with an electroactive polymer.

In accordance with the present invention, the instant inventors have now developed a process for synthesizing catalytic microparticles containing an electroactive polymer and a transition metal in a form such that the oxidation state of the transition metal is greater than zero.

SUMMARY OF THE INVENTION

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise" and variations such as "comprising" and "comprises", will be understood to imply the inclusion of a stated integer or step or group of integers but not the exclusion of any other integer or step or group of integers of steps.

One aspect of the present invention contemplates a method for the preparation of catalytic microparticles containing a transition metal in a form such that it has an oxidation state greater than zero, comprising the steps of:

- a) providing an electroactive polymer with a reduced oxidation state; and
- b) contacting the polymer with an acidic solution of a transition metal compound; for a time and under conditions sufficient to incorporate the transition metal, having an oxidation state greater than zero, onto the polymer.

Another aspect of the present invention provides catalytic microparticles prepared by a process comprising the steps of:

- a) providing an electroactive polymer with a reduced oxidation state; and
- b) contacting the polymer with an acidic solution of a transition metal compound; for a time and under conditions sufficient to incorporate the transition metal, having an oxidation state greater than zero, onto the polymer.

Yet another aspect of the present invention is directed to catalytic microparticles comprising

an electroactive polymer and a transition metal in a form such that the transition metal has an oxidation state greater than zero.

Still yet another aspect of the present invention relates to a method for catalyzing a chemical reaction comprising a step of contacting catalytic microparticles, which comprise an electroactive polymer and a transition metal in a form such that the transition metal has an oxidation state greater than zero, with the chemical components required for said reaction, for a time and under conditions sufficient to catalyze said reaction.

In yet another aspect of the present invention, there is contemplated a use of a transition metal compound in the preparation of catalytic microparticles comprising an electroactive polymer and a transition metal in a form such that the transition metal has an oxidation state greater than zero.

Another aspect of the present invention provides a use of catalytic microparticles prepared by a method comprising the steps of:

- a) providing an electroactive polymer with a reduced oxidation state; and
 - b) contacting the polymer with an acidic solution of a transition metal compound;
- in catalyzing a chemical reaction.

A further aspect of the invention is directed to a use of catalytic microparticles, comprising an electroactive polymer and a transition metal in a form such that the transition metal has an oxidation state greater than zero, in catalyzing a chemical reaction.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides catalytic microparticles, in particular, catalytic microparticles comprising an electroactive polymer and a transition metal in a form such that the transition metal has an oxidation state greater than zero, and methods for producing same.

Accordingly, one aspect of the present invention contemplates a method for the preparation

of catalytic microparticles containing a transition metal in a form such that it has an oxidation state greater than zero, comprising the steps of:

- a) providing an electroactive polymer with a reduced oxidation state; and
- b) contacting the polymer with an acidic solution of a transition metal compound; for a time and under conditions sufficient to incorporate the transition metal, having an oxidation state greater than zero, onto the polymer.

The present invention is also directed to catalytic microparticles comprising an electroactive polymer and a transition metal in a form such that the transition metal has an oxidation state greater than zero and to such particles when prepared by the steps of :

- a) providing an electroactive polymer with a reduced oxidation state; and
- b) contacting the polymer with an acidic solution of a transition metal compound; for a time and under conditions sufficient to incorporate the transition metal, having an oxidation state greater than zero, onto the polymer.

As used herein, the term "microparticles" refers to particles having an average size of about 10 μm or less. Preferably the microparticles have an average size of about 5.0 μm or less, more preferably about 1.0 μm or less and most preferably, about 0.5 μm or less.

As used herein, the term "electroactive polymer" is taken to refer to an electrically conductive or semiconductive polymer or combinations thereof. A number of electrically conductive or semiconductive polymeric materials are known. They have been described, for example, in *"A Handbook of Conducting Polymers"* Vols I and II, edited by T. Skotheim, Marcel Dekker, N.Y. (1986). Polymers with conjugated backbones are of particular interest. The electrical conductivities of such materials may be made to undergo a metal-like transition, via the process of chemical or electrochemical doping. Four main classes of such conjugated polymers have been identified, viz., poly(acetylene) and its derivatives, poly(phenylene) and its derivatives, poly(heterocyclic) polymers, and poly(aniline) and its derivatives. Preferred classes are the poly(heterocyclic) and poly(aniline) polymers.

Preferably, the electroactive polymer itself may be formed by polymerizing conjugated monomers containing nitrogen, in the form of imine and/or amine moieties, and may exist in a number of intrinsic redox states arising from the imine/amine nitrogen ratios. Desirably, the electroactive polymer is selected from the group consisting of synthetic aniline polymers, synthetic pyrrole polymers, and their derivatives, and combinations thereof.

The electroactive polymer used in the present invention may be prepared according to art-recognized techniques, including oxidative chemical polymerization and electrochemical polymerization.

Reducing the oxidation state of the electroactive polymer to provide an electroactive polymer with a reduced oxidation state can be carried out by deprotonation followed by reduction by a reducing agent. Most effective incorporation of the transition metal into the electroactive polymers is achieved when the polymers are reduced to their lowest oxidation state.

Accordingly, another aspect of the invention provides a method for the preparation of catalytic microparticles containing a transition metal in a form such that it has an oxidation state greater than zero, comprising the steps of:

- a) providing an electroactive polymer with a reduced oxidation state; and
- b) contacting the polymer with an acidic solution of a transition metal compound; for a time and under conditions sufficient to incorporate the transition metal, having an oxidation state greater than zero, onto the polymer; wherein step a) further comprises the step of first deprotonating and reducing the oxidation state of a microparticulate electroactive polymer to afford the electroactive polymer with a reduced oxidation state.

In a preferred method, the desired reduced oxidation state of the electroactive polymer can be achieved by deprotonation, followed by reduction with a reducing agent.

As used herein, the term "base" refers to any substance which can accept a proton or donate an electron pair. Organic bases are defined as bases which contain the element carbon.

Inorganic bases are those which do not. An alkaline solution is defined as having a pH greater than about 7.

Deprotonation may be carried out by any suitable means using any known inorganic and organic bases which may include amines such as alkyl substituted amines including triethylamine, and diisopropylamine; and metal (Li, Na K, Ca and Mg) hydroxides, hydrides, alkoxides, acetates, carbonates and hydrogen carbonates. Preferred bases include aqueous alkaline solutions, such as NaOH, LiOH and KOH. Especially preferred is NaOH.

Suitable reducing agents are known to those skilled in the art and include those based on metals such as Fe, Sn, Al and Zn, for example, hydrides such as LiAlH_4 , NaBH_4 ; H_2 /catalyst; and the hydrazines. Preferred reducing agents are the hydrazines which include phenylhydrazine or hydrazine itself.

As used herein, the term "transition metal" refers to the elements defined as having partially filled *d* or *f* shells in their elemental form or having partially filled *d* and *f* shells in compounds (as defined in *Basic Inorganic Chemistry*, F. A. Cotton and G. Wilkinson, page 203, 1st Edition) and are further capable of catalysing a chemical reaction when they have an oxidation state greater than zero. Suitable elements may be selected from elements 21-29, 39-47, 57-79 and 89-107 as depicted in the PERIODIC TABLE OF ELEMENTS in the CRC HANDBOOK OF CHEMISTRY AND PHYSICS (73RD EDITION 1992-1993). Preferred transition metals are elements 21-29, 39-47, 57-79 (known to those skilled in the art as *d* block elements) and even more preferred elements include ruthenium (Rh), osmium (Os), rhodium (Ro), iridium (Ir), palladium (Pd) and platinum (Pt). Most preferably, the transition metal is palladium.

The oxidation state greater than zero is dependent upon the transition element and the allowable oxidation states for each element. These are known to those skilled in the art. Preferably the oxidation state is between +1 and +8. Preferred oxidation states for Ru are +2, +3 and +8; for Os, +3, +4 and +8; for Rh, +1 and +3; for Ir, +1, +3 and +4; for Pd, +2 and for Pt, +2 and +4.

Suitably, the transition metal compound is an oxide, complex or salt of the transition metal such that the transition metal has an oxidation state greater than zero. Appropriate forms are known to those skilled in the art and include halide salts (fluoride, chloride, bromide, and iodide salts, particularly chloride salts), oxides and other complexes formed from ligands. A preferred transition metal compound is palladium chloride (PdCl_2).

The size of the microparticles can be varied by the addition of a colloidal inorganic additive to a solution of the monomer during the formation of the electroactive polymer. By the addition of a colloidal inorganic additive during the polymerization of the corresponding monomer, electroactive polymer microparticulate composites of less than or about $0.5\text{ }\mu\text{m}$ can be formed. Suitable colloidal inorganic additives are the inorganic oxides such as SiO_2 and TiO_2 , preferably SiO_2 . Preferably, the inorganic colloidal additive is used at a weight ratio of additive to monomer of between about 0.1 to about 10, preferably about 0.5 to about 5 and more preferably about 1 to about 3.

In the absence of colloidal inorganic particles during the formation of the electroactive polymers, the average particulate size obtained after reduction of the polymer is preferably about $1\text{ }\mu\text{m}$.

Preferred concentrations of monomer in solutions are between about 0.01M and 1.0 M, more preferably between about 0.01 and 0.5 M and even more preferably between about 0.1M and 0.2M. Especially preferred concentrations for the monomers of aniline or pyrrole are about 0.1M to 0.2M.

In the oxidative polymerization of the respective monomers, preferably aniline or pyrrole, an oxidizing agent is used. Suitable oxidizing agents are known to those skilled in the art and may include oxidizing agents selected from ammonium persulfate, ferric chloride, $\text{K}_2\text{Cr}_2\text{O}_7$ and KIO_3 . The amount of oxidizing agent used in the polymerization process is dependent on the monomer used and suitable quantities in relation to the respective monomers are known to those skilled in the art. Preferably the oxidizing agent is employed

on a molar ratio of oxidizing agent to monomer of about 0.1 to 5, preferably about 0.5 to 3. The preferred oxidizing agent for aniline is ammonium persulfate and the preferred amount of the oxidizing agent is 2/3 of that of the aniline monomer on a molar basis. In the case of polymerization of polypyrrole, the preferred oxidizing agent is ferric chloride and the preferred amount is 2.5 times that of pyrrole monomer on a molar basis.

As used herein, the term "acid" refers to a substance which can donate a proton or accept an electron pair. Organic acids are defined as acids which contain the element carbon. Inorganic acids are those which do not.

The acidic solution from which the transition metal is incorporated into the electroactive polymeric particles can be a mineral acid, inorganic acid or organic acid solution such that the solution of the transition metal is contacted with the reduced electroactive polymer is at a pH of less than 7. Mineral acids which may be used include hydrochloric acid, and nitric acid. Preferably the acid is hydrochloric acid. Other suitable acids may include chloroauric acid, or any acid in which the transition metal is soluble. Preferably the acid is at a concentration of between 0.01 to 10M, more preferably 0.1 to 5.0M and more preferably 0.25 to 2.0M.

Suitably, the polymerization, reduction and transition metal uptake processes may be carried out at a temperature of between about 10°C - 60°C, more preferably at room temperature.

In yet another aspect, the present invention relates to a method for catalyzing a chemical reaction comprising a step of contacting catalytic microparticles, which comprise an electroactive polymer and a transition metal in a form such that the transition metal has an oxidation state greater than zero, with the chemical components required for said reaction, for a time and under conditions sufficient to catalyze said reaction.

Yet a further aspect of the invention is directed to a use of catalytic microparticles, comprising an electroactive polymer and a transition metal in a form such that it has an oxidation state greater than zero, in catalyzing a chemical reaction.

Chemical reactions which may be catalyzed by the catalytic microparticles of the present invention may include any chemical reaction which can be catalyzed by a transition metal having an oxidation state greater than zero. Suitable reactions include the reduction, by hydrogenation, of various functional groups such as carbon-carbon double and triple bonds; carboxylic acids, esters and amides; nitriles; nitrates; aldehydes; ketones as well as the reduction of molecular oxygen.

The present invention is further described by the following non-limiting examples. It will be understood, however, that the specific details given in each example have been selected for the purpose of illustration only and are not to be construed as being limitations on the scope of the invention.

EXAMPLE 1

A polyaniline microcomposite was synthesized using 2 ml of aniline, 3.14 g ammonium persulfate and 3 g colloidal silica in 100 ml of 1M HCl. The reactions were carried out at room temperature under constant stirring for several hours. The microcomposites were separated from the solution by centrifugation and redispersed in 1M HCl. The centrifugation-redispersion cycle was repeated twice. The polypyrrole microcomposite was synthesized using 1 ml of pyrrole, 9.1 g ferric chloride hexahydrate and 3 g colloidal silica in 100 ml deionized water. The reactions were carried out at room temperature under constant stirring for several hours. The microcomposites were separated from the solution by centrifugation and redispersed in deionized water. The centrifugation-redispersion cycle was repeated twice.

EXAMPLE 2

The electroactive polymer microcomposites synthesized according to the procedure in Example 1 were deprotonated by treatment with excess 0.5M NaOH for 1 h, followed by washing with deionized water and drying under dynamic vacuum. The reduction of the undoped polymers was carried out by reaction with excess hydrazine followed by washing with water and acetone. The electroactive polymer microcomposites prepared using the

colloidal silica and according to the procedures stated above, have a polymer content of about 50% by weight and a mean particle size of less than 0.5 μm .

EXAMPLE 3

The electroactive polymer microcomposites prepared according to the procedures in Examples 1 and 2 were treated with PdCl_2 in 0.5M HCl with Pd^{2+} concentration of 100 mg dm^{-3} and a N(from PAN and PPY)/Pd mole ratio of 4:1 for several hours under constant agitation. The microcomposites were then separated from the solution by centrifugation and washing with copious amounts of water. X-ray photoelectron spectroscopy analysis of the microparticles indicates that the Pd is present as Pd^{2+} rather than elemental Pd and the Cl/Pd ratio is close to 2.

EXAMPLE 4

The catalytic activity of the Pd-containing microcomposites synthesized according to procedures in Example 3 is demonstrated in the reduction of dissolved oxygen in water. In the reduction of dissolved oxygen using H_2 and 0.01 wt% of microcomposite in water, dissolved oxygen content was reduced to less than 20ppb.

EXAMPLE 5

Microcomposites containing Pd and electroactive polymer can be synthesized according to the procedures in Examples 1, 2 and 3, without the inclusion of colloidal silica. The mean particle sizes of the Pd-containing microparticles are less than 5 μm . The Pd exists as Pd^{2+} in these microcomposites.

EXAMPLE 6

The catalytic activity of the Pd-containing microcomposites synthesized according to procedures in Example 5 is demonstrated in the reduction of nitrobenzene by H_2 to aniline. With a molar ratio of Pd to nitrobenzene of 1/100, 99% of the nitrobenzene is converted to aniline within 2 h.

**CLAIMS:**

1. A method for the preparation of catalytic microparticles containing a transition metal in a form such that it has an oxidation state greater than zero, comprising the steps of:
 - a) providing a microparticulate electroactive polymer with a reduced oxidation state; and
 - b) contacting the polymer with an acidic solution of a transition metal compound for a time and under conditions sufficient to incorporate the transition metal, having an oxidation state greater than zero, onto the polymer.
2. A method of claim 1 wherein the oxidation state of the transition metal element is between +1 and +8.
3. A method of claim 1 or 2 wherein the electroactive polymer is selected from poly(acetylene), poly(phenylene), poly(heterocyclic) and poly(aniline) polymers and their derivatives or combinations thereof.
4. A method of claim 3 wherein the electroactive polymer is selected from poly(heterocyclic) and poly(aniline) polymers and their derivatives.
5. A method of claim 4 wherein the electroactive polymer contains imine and/or amine moieties.
6. A method of claim 4 wherein the electroactive polymer is poly(aniline), poly(pyrrole), a derivative thereof or a combination of said polymers or derivatives.
7. A method of any one of claims 1 to 6 wherein the electroactive polymer has been reduced to its lowest oxidation state.
8. A method of any one of claims 1 to 7 wherein step a) further comprises the step of first deprotonating and reducing the oxidation state of a microparticulate electroactive



polymer to afford the electroactive polymer with a reduced oxidation state.

9. A method of claim 8 wherein the electroactive polymer is first deprotonated followed by reduction by a reducing agent.
10. A method of claim 9 wherein the deprotonation is achieved by an aqueous alkaline solution.
11. A method of claim 10 wherein the aqueous solution is a LiOH, KOH or NaOH solution.
12. A method of claim 11 wherein the aqueous solution is a NaOH solution.
13. A method of claim 8 wherein the reducing agent is hydrazine or phenyl hydrazine.
14. A method of any one of claims 1 to 13 wherein the catalytic microparticles further comprise an inorganic particulate additive.
15. A method of claim 14 wherein the inorganic particulate additive is an inorganic oxide.
16. A method of claim 15 wherein the inorganic oxide is TiO_2 or SiO_2 .
17. A method of claim 16 wherein the inorganic oxide is SiO_2 .
18. A method of any one of claims 1 to 17 wherein the catalytic microparticles have an average size of about $5.0\ \mu\text{m}$ or less.
19. A method of claim 18 wherein the catalytic microparticles have an average size of about $1.0\ \mu\text{m}$ or less.



20. A method of claim 19 wherein the catalytic microparticles have an average size of about 0.5 μm or less.
21. A method of any one of claims 14 to 17 wherein the inorganic particulate additive is incorporated into the catalytic microparticle during the synthesis of the electroactive polymers from their respective precursor monomers.
22. A method of claim 21 wherein the inorganic additive is used at a weight ratio of additive to an electroactive polymer precursor monomer of between about 0.1 and 10.
23. A method of claim 22 wherein the inorganic additive is used at a weight ratio of additive to an electroactive polymer precursor monomer of between about 0.5 and 5.
24. A method of claim 22 wherein the inorganic additive is used at a weight ratio of additive to an electroactive polymer precursor monomer of between about 1 and 3.
25. A method of any one of claims 1 to 24 wherein the transition metal is ruthenium, osmium, rhodium, iridium, palladium or platinum.
26. A method of claim 25 wherein the transition metal is palladium.
27. A method of any one of claims 1 to 26 wherein the transition metal compound is an oxide or halide salt of a transition metal.
28. A method of claim 27 wherein the transition metal compound is a chloride salt.
29. A method of claim 28 wherein the transition metal compound is palladium chloride (PdCl_2).
30. A method of any one of claims 1 to 29 wherein the acidic solution of step b) is a mineral acid.



31. A method of claim 30 wherein the mineral acid is selected from HCl or HNO₃.
32. A method claim 31 wherein the mineral acid is HCl.
33. A method of any one of claims 1 to 29 wherein the acid is an inorganic acid.
34. A method of any one of claims 1 to 29 wherein the acid is an organic acid.
35. A method of any one of claims 30 to 34 wherein the concentration of the acid solution is from about 1M to 10M.
36. A method of claim 35 wherein the concentration of the acid solution is from about 0.1M to 5M.
37. A method of claim 36 wherein the concentration of the acid solution is from about 0.25M to 2.0M.
38. A method of any one of claims 1 to 37 when performed at a temperature of between about 10°C - 60°C.
39. A method of claim 38 when performed at room temperature.
40. Catalytic microparticles comprising an electroactive polymer and a transition metal in a form such that the transition metal has an oxidation state greater than zero.
41. Catalytic microparticles of claim 40 when prepared according to the method of any one of claims 1 to 39.
42. A method for catalyzing a chemical reaction comprising the step of contacting catalytic microparticles, further comprising an electroactive polymer and a transition metal



in a form such that the transition metal has an oxidation state greater than zero, with the chemical precursors required for said reaction, for a time and under conditions sufficient to catalyze said reaction.

43. A method of claim 42 wherein the catalyst microparticles are prepared according to the method of any one of claims 1 to 39.

44. Use of a transition metal compound in the preparation of catalytic microparticles comprising an electroactive polymer and a transition metal in a form such that the transition metal has an oxidation state greater than zero.

45. Use of catalytic microparticles, prepared by a method according to any one of claims 1 to 39, in catalyzing a chemical reaction.

46. Use of catalytic microparticles, comprising an electroactive polymer and a transition metal in a form such that it has an oxidation state greater than zero, in catalyzing a chemical reaction.