

# Zerovalent metal-polymer composites via electroless deposition on functional polymers

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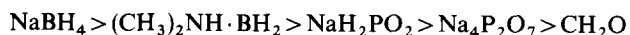
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Zerovalent metal-polymer composites are prepared under mild, aqueous conditions from functional polymers by sequentially forming a complex of the functional polymer with a noble-metal salt, e.g. tetrachloropalladate, removing uncomplexed noble metal and then treating with an electroless plating solution. If the functional polymer is soluble, metal-polymer microdispersions result. If it is a bead, then controlled particles with metallic properties result. Soluble functional polymer-noble metal complexes may be adsorbed on to inorganic oxide particles to prepare active Fischer-Tropsch catalysts. Metallization can occur by additive, subtractive or codeposition modes, affording great synthetic flexibility.

(Keywords: metal-polymer composites; electroless reduction; zerovalent metal-polymer microdispersions)

## INTRODUCTION

Recent literature contains numerous examples of metal or metal oxide dispersions and their properties<sup>1-9</sup>. We wish to report the metallization of soluble and insoluble functional polymers by a new method leading to metal or metal oxide microdispersions and suspensions (Figure 1). Functional polymers bind a noble metal (e.g. Pd<sup>2+</sup>) through complex formation or ion association. The polymer-associated Pd<sup>2+</sup> is reduced *in situ* to Pd<sup>0</sup>. Subsequent treatment with an electroless plating solution (EPS)<sup>10,11</sup> produces a metallized polymer. The reduction systems used to reduce Pd<sup>II</sup> to Pd<sup>0</sup> complexes have the following order of decreasing activity<sup>11,12</sup>:

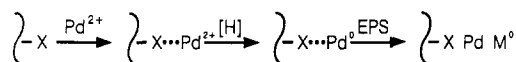


With NaH<sub>2</sub>PO<sub>2</sub> the reduction is complete within a minute at 25°C. A typical EPS consists of 0.1 M NiCl<sub>2</sub>, 0.65 M sodium gluconate and 0.2 M NaH<sub>2</sub>PO<sub>2</sub>, the reduction taking place at ambient conditions within an hour. Deposition of other metals, e.g. copper, can be direct or can follow premetallization with Ni (Figure 2). In the additive metal deposition mode, a second metal is deposited over the active nickel layer. Similarly codeposition of two metals is achieved simultaneously. In the subtractive metal deposition mode, replacement of the more electroactive nickel by copper occurs in the presence of dilute acid.

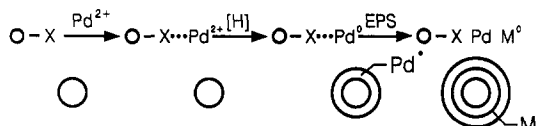
Metallization of soluble quaternary ammonium polymers<sup>12</sup> results in metal-polymer microdispersions (Table 1). Noble-metal sols of gold, palladium, platinum and silver were shown by SEM to range in size from 50 to 500 Å. The dispersions are coloured and stable for weeks. Metallization of ordered polymers, e.g. poly(L-lysine) (MW 50 000) and poly(L-glutamic acid) (MW 38 000), provides highly magnetic properties. An example

is a cobalt composite of poly(L-glutamic acid) incorporating 62% cobalt and showing specific magnetization ( $\sigma_m$ ) of 134 emu g<sup>-1</sup> and coercivity ( $H_c$ ) of 607 Oe. The stable noble-metal microdispersions were dialysed, freeze-dried and analysed. They show high metal incorporation values and e.s.c.a. binding energies consistent with known values for the corresponding bulk metals<sup>13</sup>.

### 1. Metallization of soluble polymers



### 2. Metallization of bead or latex



### 3. Metallization of immobilized beads and latices

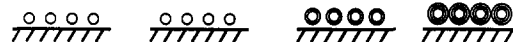
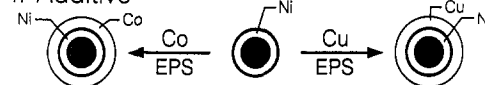
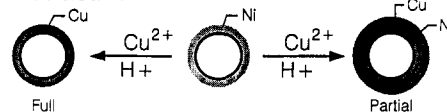


Figure 1 Metallization of functional polymers

### 1. Additive



### 2. Subtractive



### 3. Codeposition

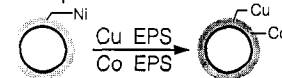


Figure 2 Modes of metal deposition

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**Table 1** Soluble polymer-zerovalent metal microdispersions,  $P\text{-CH}_2\text{N}^+\text{R}_3\text{Cl}^-\text{M}^0 \equiv (\text{P}_0\text{-100})\text{M}^0$ <sup>a</sup>

(M)	M/P <sub>0</sub> -100	Nitrogen (%)	Metal (%)	Colour	E.s.c.a. binding energy (eV)	
					P <sub>0</sub> -100]M <sup>0</sup>	M <sup>0</sup> (ref. 13)
Pd	1:1	3.7	12.3	Black	334.85	335.22
Pt	1:1	6.2	27.5	Black		
Au	2:1	3.9	47.4	Red	84.17	84.0
Ag	1:1	6.5	20.0	Brown	367.0	368.2
Cu <sup>b,c</sup>	1:1			Red	932.13	932.8
Ni <sup>b</sup>	1:1			Black		
Co <sup>b</sup>	1:2			Black		

<sup>a</sup> P<sub>0</sub>-100 is poly(*N,N,N*-trimethyl-*N*-(*m*- and *p*-vinylbenzyl)ammonium chloride); molecular weight 300 000

<sup>b</sup> Magnetic and sticky, not isolated

<sup>c</sup> Stabilized by polyacrylamide

We also report a new technique for the preparation of zerovalent metals supported on inorganic oxides. Catalysts were prepared in water by adsorption of a cationic polymer-noble metal salt complex on to an inorganic oxide surface, reduction to the zerovalent state, followed by deposition of cobalt metal from an EPS. When the oxide is Fe<sub>2</sub>O<sub>3</sub>, highly active Fischer-Tropsch catalysts result<sup>14</sup>.

Heterogeneous multimetallic catalysts (Table 2) for alcohol synthesis based on synthesis-gas feedstocks were prepared and evaluated. A sample of iron oxide was used as a control. The catalysts were evaluated<sup>15</sup> in a single-pass, high-pressure flow reactor at 270°C using a feed composition of H<sub>2</sub>/CO = 2/1 at a total pressure of 800 psig.

The rates of formation of both alcohols and hydrocarbons follow the Schulz-Flory distribution of products<sup>16</sup>. Rhodium and Ir were exchanged with Co (subtractive deposition, see Figure 2) to yield the desired metal supported on iron oxide. The molar alcohol selectivity for the Rh catalyst was 34%, compared with 29% for Co, 27% for Ir and 25% for the Fe<sub>2</sub>O<sub>3</sub> control. All three catalysts were at least as active as the control and were stable over several days.

The rates of alcohol and hydrocarbon formation for the supported catalysts were less than those of the Fe<sub>2</sub>O<sub>3</sub> control, in agreement with known trends of Fischer-Tropsch activity; that is, Fe > Co > Rh > Ir<sup>15</sup>. The combined products of the supported catalysts were richer in alcohols than those produced by the iron oxide control. The molar selectivity for C<sub>1</sub>-C<sub>4</sub> alcohols was 29% for the Fe<sub>2</sub>O<sub>3</sub>]Co and 25% for the Fe<sub>2</sub>O<sub>3</sub> standard.

Additionally, metal-polymer composites characterized by cumulative properties were prepared, including functional beads incorporating both dyes and magnetic metals. The metallization of vesicles has been reported separately<sup>17</sup>.

#### EXPERIMENTAL: GENERAL METALLIZATION PROCEDURE

Bead dispersions, stable aqueous latex microgel dispersions or soluble polymers are used directly. Dry particles are dispersed by sonification for 1-5 min. The polymer is reacted with a dilute solution of PdCl<sub>4</sub><sup>2-</sup> (0.01%) in H<sub>2</sub>O. The polymer: Pd ratio is between 1000:1 and 100:1 (weight ratio). Formation of the complex proceeds for 30 min. Beads (>1 μm) are filtered and

**Table 2** Multimetallic alloys from Fe<sub>2</sub>O<sub>3</sub>]P<sub>0</sub>-100]Ni by subtractive or additive metal deposition<sup>a,b</sup>

Entry	Composition	C	H	Ni	Cu	Fe	Co
1	Fe <sub>2</sub> O <sub>3</sub> ]Ni]Co			6.1		43.8	8.5
2	Fe <sub>2</sub> O <sub>3</sub> ]P <sub>0</sub> -100]Ni]Co]Cu	2.6	0.5	6.8	6.9	55.1	3.1
3	Fe <sub>2</sub> O <sub>3</sub> ]P <sub>0</sub> -100]Ni/Cu]Co	6.1	1.3	12.5	7.2	21.2	3.2
4	Fe <sub>2</sub> O <sub>3</sub> ]P <sub>0</sub> -100]Ni/Cu	7.7	1.2	13.5	20.5	25.4	

<sup>a</sup> M<sub>1</sub>]M<sub>2</sub> shows additive deposition where M<sub>2</sub> was deposited on M<sub>1</sub>. M<sub>1</sub>/M<sub>2</sub>] shows subtractive deposition where M<sub>2</sub> was deposited by exchange with M<sub>1</sub>. P<sub>0</sub>-100 is poly(*N,N,N*-trimethyl-*N*-(*m*- and *p*-vinylbenzyl)ammonium chloride)

<sup>b</sup> Typical EPS solutions:

*Nickel* 0.1 M NiCl<sub>2</sub> · 6H<sub>2</sub>O, 0.2 M NaH<sub>2</sub>PO<sub>4</sub> · H<sub>2</sub>O, 0.65 M gluconic acid, 0.75 M NH<sub>4</sub>OH, 0.5 M NaOH

*Cobalt* Part 1: 0.1 M CoCl<sub>2</sub> · 6H<sub>2</sub>O, 0.65 M sodium gluconate. Part 2: Add 3.5 ml conc. NH<sub>4</sub>OH/100 ml Part 1 and DMAB to make 0.1-5% solution

*Copper* Part 1: 0.1 M CuCl<sub>2</sub> · 2H<sub>2</sub>O, 0.65 M sodium gluconate; add 35 ml conc. NH<sub>4</sub>OH prior to use to one litre solution. Part 2: 1-5% DMAB is prepared and added gradually until a slight molar excess, relative to metal ions, has been added

washed with H<sub>2</sub>O; latices and soluble polymers are dialysed vs. deionized H<sub>2</sub>O.

The polymeric PdCl<sub>4</sub><sup>2-</sup> complexes are treated with a 0.1% reductant solution in water, at ambient conditions for a period of 5 to 500 s. At completion, excess reductant is eliminated by filtration or dialysis. The active Pd<sup>0</sup> beads can be used immediately or stored.

The active beads are placed in an EPS and the reaction allowed to proceed at 20-70°C until the desired amount of metal is deposited, controlled by adjusting the EPS/bead ratio. The reaction is accompanied by hydrogen gas evolution, and disappearance of the coloured metal ions. At completion, the beads are filtered and washed with H<sub>2</sub>O whereas latices or soluble polymers are dialysed and freeze-dried.

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