Electroless Deposition for the Synthesis of Bimetallic Catalysts

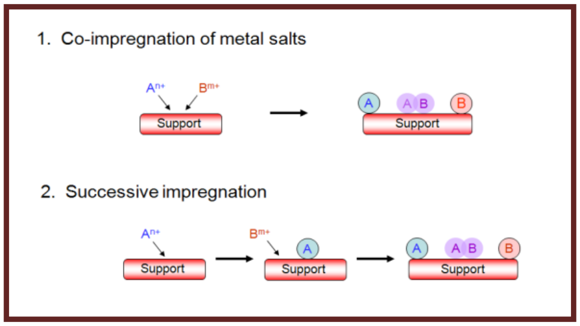
metals · inorganics · organometallics · catalysts · ligands · custom synthesis · cGMP facilities · nanomaterials

Why Bimetallic Catalysts?

The field of heterogeneous catalysis has recently turned its attention to the study of bimetallic catalysts because they offer the potential of increased **activities** and **selectivities** combined with enhanced **stability** as compared to their monometallic counterparts. Several families of bimetallic catalysts have been commercialized for use in industrial environmental treatment, chemical synthesis and petroleum refining processes.

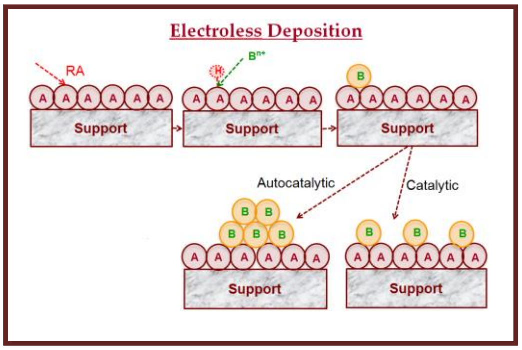
Why Electroless Deposition?

Currently, commercial scale methods for the production of bimetallic catalysts – typically involving successive impregnation or co-impregnation of two metal salts - suffer from an inability to carefully control the placement of the two different metals onto the substrate. As a result, a complex mixture of unwanted monometallic particles and bimetallic particles of varying compositions is obtained with no reproducibility from batch to batch. The catalytic performance of such mixtures is, not surprisingly, difficult to control.



Several alternative methods have been developed for the synthesis of bimetallic catalysts, but each of these approaches (ion exchange using a zeolite framework, polyvinyl alcohol or polyvinylpyrrolidone suspension/stabilization of bimetallic colloids, nanoparticles or clusters; and heteropolyatomic, organometallic complexes with a ligand-stabilized bimetallic core) also suffers to some extent from an inability to guarantee formation of the specific, desired bimetallic species as well as a limited combination of catalytically-activated metals.

Galvanic Displacement and **Electroless Deposition**, however, rely on redox chemical reactions to control the placement of a secondary metal onto a monometallic primary catalyst. Galvanic Displacement is limited to the deposition of noble metal salts with a higher reduction potential onto less-noble (or base metals with lower reduction potentials.



Electroless Deposition is more versatile, since all metals that can be deposited using electro-deposition can be used in this process as well. Any bimetallic composition can be prepared as long as the overall redox reaction of the reducible metal salt by the reducing agent is thermodynamically favorable. In addition, **Electroless Deposition** does not require high-temperature calcinations or reduction treatments and thus avoids the potential for restructuring effects. Furthermore, **Electroless Deposition** has been extensively used at commercial scale for the production of continuous film coatings with applications in electronics and corrosion protection.

Electroless Deposition has been demonstrated as a feasible method for the preparation of bimetallic catalysts with more targeted placement of even small amounts of the secondary metal. Bimetallic catalysts that have been prepared using **Electroless Deposition** have been shown to have more intimate contact between the metals than catalysts prepared using traditional wet methods. Most importantly, the secondary metal species in these new bimetallic compounds is preferentially deposited onto certain sites of the primary metal, leaving other active sites available for catalysis.

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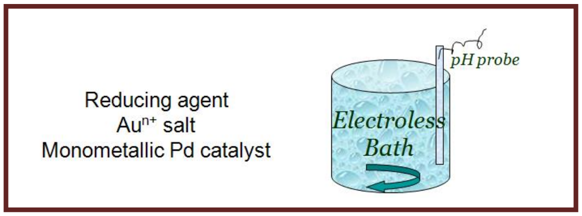
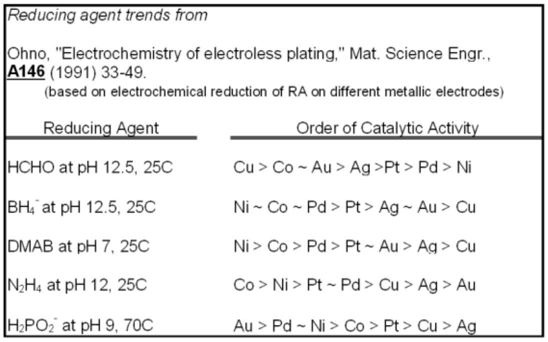
What is Electroless Deposition?

In the **Electroless Deposition** process for the preparation of bimetallic catalysts, a reducible metal salt (cation or anion) is deposited onto the catalytically active sites of a monometallic primary metal surface through a controlled chemical reaction with a liquid-phase reducing agent. The reaction can be catalyzed by the pre-existing metal or undergo autocatalysis by the metal that is being deposited. The primary metal is typically supported on a substrate.



Reducing agent trends for different metals



Reducing agent trends from

Ohno, "Electrochemistry of electroless plating," Mat. Science Engr., **A146** (1991) 33-49.

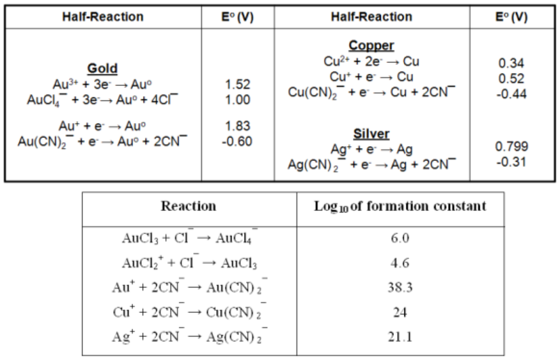
(based on electrochemical reduction of RA on different metallic electrodes)

Reducing Agent	Order of Catalytic Activity
HCHO at pH 12.5, 25C	Cu > Co ~ Au > Ag >Pt > Pd > Ni
BH_4^- at pH 12.5, 25C	Ni ~ Co ~ Pd > Pt > Ag ~ Au > Cu
DMAB at pH 7, 25C	Ni > Co > Pd > Pt ~ Au > Ag > Cu
N_2H_4 at pH 12, 25C	Co > Ni > Pt ~ Pd > Cu > Ag > Au
$H_2PO_2^-$ at pH 9, 70C	Au > Pd ~ Ni > Co > Pt > Cu > Ag

The process is a combination of anodic and cathodic electrochemical partial reactions. The aqueous reducing agent is catalytically activated at the surface of the primary metal to produce an active hydrogen species that reduces the aqueous secondary metal salt on the surface of the primary metal.

The choice of the metal salt and the reducing agent provide a means for controlling the **Electroless Deposition** reaction. The reducing agent must be thermodynamically unstable yet kinetically stable in the absence of a catalyst, yet reactive enough to deposit a metal onto the pre-existing monometallic catalyst surface.

Effect of ligands on reduction potentials

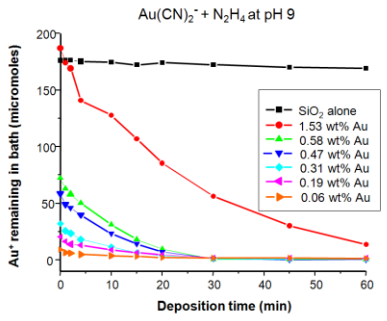


Half-Reaction	E° (V)	Half-Reaction	E° (V)
Gold		**Copper**	
$Au^{3+} + 3e^- \rightarrow Au^o$	1.52	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$AuCl_4^- + 3e^- \rightarrow Au^o + 4Cl^-$	1.00	$Cu^+ + e^- \rightarrow Cu$	0.52
$Au^+ + e^- \rightarrow Au^o$	1.83	$Cu(CN)_2^- + e^- \rightarrow Cu + 2CN^-$	-0.44
$Au(CN)_2^- + e^- \rightarrow Au^o + 2CN^-$	-0.60	**Silver**	
		$Ag^+ + e^- \rightarrow Ag$	0.799
		$Ag(CN)_2^- + e^- \rightarrow Ag + 2CN^-$	-0.31

Reaction	Log_{10} of formation constant
$AuCl_3 + Cl^- \rightarrow AuCl_4^-$	6.0
$AuCl_2^+ + Cl^- \rightarrow AuCl_3$	4.6
$Au^+ + 2CN^- \rightarrow Au(CN)_2^-$	38.3
$Cu^+ + 2CN^- \rightarrow Cu(CN)_2^-$	24
$Ag^+ + 2CN^- \rightarrow Ag(CN)_2^-$	21.1

Controlling the pH of the aqueous bath is critical for synthesizing desirable bimetallic catalysts using **Electroless Deposition**. Most reducing agents are effective under basic pH conditions that are above the point of zero charge (PZC) for most supports. Therefore, strong electrostatic adsorption (SEA) of positively charged metal salts on the negatively charged support surface can be an issue. The careful selection of the positively or negatively charged form of the reducible metal salt prevents SEA.

Time dependent deposition of Au on Pd/SiO_2



With appropriate **Electroless Deposition** baths, it is possible to prepare a series of bimetallic catalysts with increasing amounts of the deposited secondary metal and thus a range of activities and selectivities. By providing such control, **Electroless Deposition** provides a means for the rational design and synthesis of novel bimetallic catalysts with potentially novel catalytic properties.

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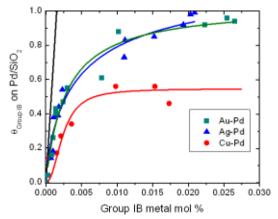
Performance of Bimetallic Catalysts prepared via Electroless Deposition

Coverage of Group IB metals on silica-supported Pd

Black line denotes mono-disperse IB metal on Pd at 1 : 1 ratio.



Electroless Deposition baths have been formulated for the deposition of both partial and multiple metal layers.

Silica-supported Ag–Pt, Au–Pd, and Cu–Pd compositions have been synthesized for use as catalysts for chemical transformations.

Carbon-supported Pt–Pd, Pt–Rh, Pt–Ru, and Pt–Co compositions have also been prepared for use in fuel cells.

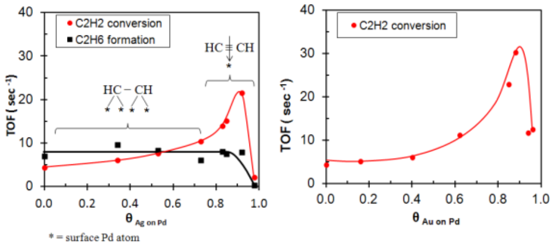
Electroless Deposition has also been used to synthesize H_2-selective Pd, Pd/Ag, and Pd/Cu alloy membranes for the production, separation and purification of ultrahigh purity H_2 for membrane reactor applications.

Bimetallic catalysts such as Ag–Pt/SiO_2 and Cu–Pd/SiO_2 have shown improved performance for the selective hydrogenation of 3,4-epoxy-1-butene (EpB), a highly functional olefin.

Au–Pd/SiO2 catalysts with incremental coverages of Au on Pd have exhibited interesting catalytic performance in the hydrogenation of propylene, which is typically a structure-insensitive reaction. It was found, however, that elevated fractional coverages of Au on Pd resulted in enhanced turnover frequencies (TOFs).

Effect of Ag and Au Coverage on Performance

Reaction conditions:
T = 65°C
Feed = 1% C_2H_2, 20% C_2H_4, 5% H_2, balance He.
GHSV = 6.0 x 10^5 hr^{-1}, except for θ_{Ag} = 0.98.



In many cases, these bimetallic catalysts were prepared using an **Electroless Deposition** bath containing the reactive yet selective cyano salt of the secondary metal and N_2H_4 as a strong reducing agent in combination with careful control of the pH and the reaction temperature.

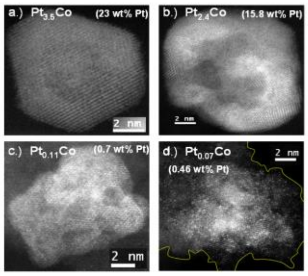
Electroless Deposition for Fuel Cell Catalysts

The commercial potential of proton exchange membrane (PEM) fuel cells has been limited in part by the high cost of the electrocatalysts necessary for the oxygen reduction reaction (ORR). The typical catalyst is platinum supported on electrically conductive porous carbon because it is corrosion resistant under the acidic conditions present in the fuel cell and is also exhibits a high activity toward oxygen reduction. High loadings (> 20 wt% Pt) are often required, however, which contributes to the high cost.

Core-Shell Structure for PEM Fuel Cells

Example of catalytic and auto-catalytic deposition of Pt on 2 wt% Co/carbon

$PtCl_6^{2-}$ + $(CH_3)_2NH$-BH_3 $\xrightarrow{\text{Co/carbon}}$ Pt-Co/carbon



To reduce the Pt loadings, and thus the electrocatalyst cost, either the dispersion of Pt on the surface can be increased, or the specific activity of the deposited platinum for the ORR can increased.

Using **Electroless Deposition**, it is possible to prepare platinum core/shell bimetallic electrocatalysts with increased specific ORR activity and stability in the corrosive PEM fuel cell environment. In one formulation, a base metal (Co) is at the core and is thus protected by the Pt shell. The core/shell structure enables a very high Pt dispersion, while possibly providing greater resistance to sintering, and allows for interaction between the Pt and the base metal atoms for enhanced activity.

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The result: preparation of Pt–Co/C catalysts with reduced Pt loadings and higher oxygen reduction activity.

Strem Products for Electroless Deposition

Strem offers a wide range of supported metals, reducible metal salts and reducing agents that are ideal for use in the synthesis of bimetallic catalysts via **Electroless Deposition**.

Supported Metals (see www.strem.com for extensive list)

Support Metal	Carbon	Alumina	Barium oxide	Titania	Silica	Calcium oxide	Zinc oxide
Palladium	X	X	X	X	X	X	
Platinum	X	X			X	X	
Rhodium	X	X					
Ruthenium	X	X					
Cobalt					X		
Gold		X		X			X
Silver		X					

Reducible Metal Salts

Gold		Palladium		Platinum		Silver		Perrhenate Salts	
$NH_4AuCl_4·XH_2O$	02-1000	Na_2PdCl_4·3H2O	93-4613	$Na_2PtCl_4·XH_2O$	93-7810	$KAg(CN)_2$	93-4739	NH_4^+	93-0249
$NaAuBr_4·XH_2O$	79-3505	K_2PdBr_4	93-4611	K_2PtBr_4	78-1967				02-0900
$HAuCl_4·XH_2O$	79-0500	Na_2PdCl_6	93-4612	$Na_2PtCl_6·_6H_2O$	78-1995			K^+	75-0500
$KAu(CN)_2$	79-3000	K_2PdCl_6	93-4610	K_2PtCl_6,	78-1960			Ag^+	47-1700
$KAuCl_4·XH_2O$	93-7906	$(NH_4)_2PdCl_4$	93-4602	K_2PtCl_4	78-1970	**Copper**		Na^+	93-7508
		K_2PdCl_4	46-2126	$(NH_4)_2PtCl_4$	93-7802	$KCu(CN)_2$	19-3025		
				$K_2Pt(NO_2)_4$	78-1985				

Reducing Agents

Compound	Chemical Formula	Catalog No.
Tetrabutylammonium borohydride	$(C_4H_9)_4NBH_4$	02-5000
Tetraethylammonium borohydride	$(C_2H5)_4NBH_4$	93-0573
Tetramethylammonium borohydride	$(CH_3)_4NBH_4$	93-0536
Sodium borohydride	$NaBH_4$	93-1118
Sodium triacetoxyborohydride	$Na(OOCCH_3)_3BH$	11-0595
Sodium cyanoborohydride	$NaBH_3CN$	11-2800
Sodium dihydrobis(2-methoxyethoxy)aluminate	$Na(CH_3OCH_2CH_2O)_2AlH_2$	93-1077
Potassium borohydride	KBH_4	93-1907
Potassium triethylborohydride	$KB(CH_2CH_3)_3H$	19-1970

If you do not see a supported metal, reducible metal salt or reducing agent of interest to you for use in the synthesis of bimetallic catalysts via **Electroless Deposition**, please contact Strem.

References:

1. J. Rebelli,, A.A. Rodriguez, S. Ma, C.T. Williams, J.R. Monnier, Catal. Today, 160 (2011) 170.
2. J. Rebelli, M. Detwiler, S. Ma, C.T. Williams, J.R. Monnier, J. Catal. 270 (2010) 224.
3. M. Ohashi, K.D. Beard, S. Ma, D.A. Blom, J. St-Pierre, J.W. Van.Zee, and J.R. Monnier, Electrochimica Acta 55 (2010) 7376.
4. K.D. Beard, D. Borrelli, A.M. Cramer, D. Blom, J.W. Van Zee, J.R. Monnier, ACS Nano 3 (2009) 2841.
5. K.D. Beard, J.W. Van Zee, J.R. Monnier, Appl. Catal., B 88 (2009) 185.
6. M.T. Schaal, A.Y. Metcalf, J.H. Montoya, J.P. Wilkinson, C.C. Stork, C.T. Williams, J.R. Monnier, Catal. Today 123 (2007) 142.
7. M.T. Schaal, A.C. Pickerell, C.T. Williams, J.R. Monnier, J. Catal. 254 (2008) 131.

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