

# Highlights from Recent Literature

## Note:

A more comprehensive list of literature and patents, will be found in the searchable **Technical Database** on the World Gold Council website, [www.gold.org](http://www.gold.org) under science and Industry domain.

## 1 Analytical

### 1.1 Determination of Gold in Industrial Waste by Activated Carbon Concentration and Atomic Absorption Spectrophotometry

Gold in industry waste is detected by activated C concentration and atomic absorption spectrophotometry. X Li from the Analytical and Testing Research Center, Guangzhou Research Institute of Non-ferrous Metals, Guangzhou, Peoples Republic of China, Guangdong Youse Jinshu Xuebao 2004, **14(2)**, 151. The sample is oxidized with mixed acid, and the gold in it is dissolved with aqua regia. A part of the test solution is taken to concentrate gold completely with activated C. The activated C adsorbed gold is washed with HCl and  $\text{NH}_4\text{HF}_2$ , and meantime some impurities in it are removed. The results of this method conform to those of fire assaying. But the method was characterized with a low analytical cost, little pollution, fast analysis and relative std. deviation <1.20%.

## 2 Catalysis

### 2.1 Plasma/Gold Catalyst System for Selectively Removing Nitrogen Oxides from Exhaust Gas from Diesel Engine

A plasma/gold catalyst system for selectively removing nitrogen oxides from diesel exhaust gas is provided by J Hwang, B Jun, G Jun, D Jung, D Lee, G Lee, H Lee, J Ryu, E Yoon from the Blue Planet, Ltd., S. Korea PATENT NO. KR 2003011983, A, DATE 12/2/2003, to improve the  $\text{NO}_x$  conversion rate and the conversion rate from  $\text{NO}_x$  to  $\text{N}_2$  and selectively remove the  $\text{NO}_x$ . A plasma/gold catalyst system for selectively removing  $\text{NO}_x$  from diesel exhaust gas is composed of a plasma reactor to which a hydrocarbon besides those in the exhaust gas from the diesel engine is provided, and a catalytic reactor with a catalyst layer therein. The plasma/gold catalyst system induces the reduction reaction of the  $\text{NO}_x$  by connecting the plasma reactor and catalyst reactor in series. Thus, it is possible to improve the  $\text{NO}_x$  conversion rate and the conversion rate from  $\text{NO}_x$  to  $\text{N}_2$  and selectively remove the  $\text{NO}_x$ .

### 2.2 Activity and Stability of Low-Content Gold-Cerium Oxide Catalysts for The Water-Gas Shift Reaction

Q Fu, W Deng, H Saltsburg, S Flytzani- from the Department of Chemical and Biological Engineering, Tufts University, Medford, MA, *Applied Catalysis, B: Environmental* 2005, **56** (1-2), 57, report here on the high activity and stability of low-content gold-cerium oxide catalysts for the water-gas shift reaction (WGS). These catalysts are reversible in cyclic reduction.-oxidation treatment up to 400.degree.C, are non-pyrophoric, and are thus potential candidates for application to hydrogen generation for fuel cell power production Low-content (0.2-0.9 at.%) gold-ceria samples were prepared by single-pot synthesis by the urea gelation/coprecipitation method; and by sodium cyanide leaching of high-content (2-8 at.%) gold-ceria materials prepared by various techniques.

The low-content gold-ceria catalysts are free of metallic gold nanoparticles. Gold is present in oxidized form, as verified by a variety of analytical techniques. However, these materials display the same WGS activity as the high-content gold ones, and remain free of gold nanoparticles after use in a reaction gas stream composed of 11% CO-26%  $\text{H}_2\text{O}$ -26%  $\text{H}_2$ -7%  $\text{CO}_2$ -balance  $\text{H}_e$  up to 300 .degree.C. We show that the detg. factor for the retention of active gold in ceria is the surface properties of the latter. Measurements of lattice const. expansion indicate gold ion substitution in the ceria lattice. The turnover frequency of WGS under the assumption of fully dispersed gold is the same for a variety of low-content gold-ceria precipitations The stability of gold-ceria in various gas compositions and temperature was good. The most serious stability issue is formation of cerium hydroxycarbonate in shutdown operation.

### 2.3 Effect of Supports on the Gold Catalyst Activity for Catalytic Combustion of CO and HCHO

The deposition-precipitation method was used to prepare gold catalysts based on different supports. M Jia, Y Shen, C Li, Z Bao and S Sheng from the College of Chemistry and Environmental Science, Inner Mongolia Normal University, Peoples Republic of China, *Catalysis Letters* 2005, **99(3-4)**, 235

Their catalytic activities for combustion of carbon monoxide (CO) and formaldehyde (HCHO) were investigated. All these catalysts showed good activity for the two reactions and the Au/CeO<sub>2</sub>-a catalyst exhibited the highest activity for the two reactions. Furthermore, catalysts derived from the as-precipitated hydroxides exhibited higher activity than that from corresponding oxide supports. The BET, XRD, TEM and XPS were carried out. The results indicated that the gold dispersed more homogeneous on the as-precipitated hydroxide supports than that on the corresponding oxide supports.

## 2.4 Dismutation of Hg<sup>22+</sup> Catalyzed by Colloidal Gold

Colloidal gold in acetonitrile catalyzes the disproportionation of Hg<sup>22+</sup> to Hg<sup>2+</sup> and Hg<sup>0</sup>. H Kunkely, A Vogler from the Institut für Anorganische Chemie, Universität Regensburg, Regensburg, Germany, *Inorganica Chimica Acta* 2005, **358(2)**, 429.

This catalysis is apparently initiated by the amalgamation of the gold particles which is indicated by a concomitant change of the plasmon absorption of colloidal gold.

## 2.5 Nanocrystalline and Mesostructured Y<sup>2</sup>O<sup>3</sup> as Supports for Gold Catalysts

The structure of yttrium oxide influences the CO oxidation activity of Au/Y<sup>2</sup>O<sup>3</sup> catalysts; nanocryst. Y<sup>2</sup>O<sup>3</sup> stabilizes more active species of gold and increases the activity of the gold catalyst in comparison with mesostructured and precipitated Y<sup>2</sup>O<sup>3</sup>. J Guzman, A Corma, from the Instituto de Tecnologia Química, UPV-CSIC, Universidad Politecnica de Valencia, Valencia, Spain, *Chemical Communications* 2005, **(6)**, 743.

## 2.6 Selective Oxidation of CO Over Model Gold-Based Catalysts in the Presence of H<sub>2</sub>

The model catalysts Au/Al<sub>2</sub>O<sub>3</sub>, Au/ZrO<sub>2</sub>, and Au/TiO<sub>2</sub> were produced by laser vaporization of a metallic gold rod followed by deposition of the formed clusters onto the support powders. C Rossignol, S Arrii, F Morfin, L Piccolo, V Caps, JL Rousset from the Institut de Recherches sur la Catalyse (CNRS), Villeurbanne, France, *Journal of Catalysis* 2005, **230(2)**, 476. This technique allows to obtain a narrow size distribution of highly dispersed gold particles on the support and, most importantly, similar sizes whatever the support. This makes it possible to accurately study the influence of the support identity on the catalytic reaction.

A detailed investigation of the preferential oxidation of CO in the presence of H<sub>2</sub> was undertaken. Catalytic performances in the PROX reaction were compared with those in the oxidation of CO in the temperature range of 25-420 .degree.C. A boost in the conversion of CO was observed in the presence of H<sub>2</sub> at low temperature; the extent of this boost is dependent on the support identity. Hence the reactivity order found for CO oxidation (Au/Al<sub>2</sub>O<sub>3</sub> .mchlt. Au/ZrO<sub>2</sub> < Au/TiO<sub>2</sub>) was changed. In fact, in the presence of H<sub>2</sub>, the reaction rates for the oxidation of CO become rather similar on all three systems.

## 2.7 Spectroscopic Evidence for the Supply of Reactive Oxygen during CO Oxidation Catalyzed by Gold Supported on Nanocrystalline CeO<sub>2</sub>

J Guzman, S Carrettin, A Corma, from the Instituto de Tecnologia Química, UPV-CSIC, Universidad Politecnica de Valencia, Valencia, Spain, *Journal of the American Chemical Society* 2005, **127(10)**, 3286. Nanocrystalline CeO<sub>2</sub> supplies reactive oxygen in the form of surface .eta.1 superoxide species and peroxide adspecies at the one-electron defect site to the supported active species of gold for the oxidation of CO.

## 2.8 Platinum-Catalyzed Synthesis of Water-Soluble Gold-Platinum Nanoparticles

The ability to control composition and size in the synthesis of bimetallic nanoparticles is important for the exploitation of the bimetallic catalytic properties. This paper reports findings of an investigation of a new approach to the synthesis of gold-platinum (AuPt) bimetallic nanoparticles in aqueous solution via one-phase reduction of AuCl<sub>4</sub><sup>-</sup> and PtCl<sub>4</sub><sup>2-</sup> using a combination of reducing and capping agents. P Njoki, J Luo, L Wang, M Maye, H Quaizar, CJ Zhong from the Department of Chemistry, State University of New York at Binghamton, Binghamton, USA, *Langmuir* 2005, **21(4)**, 1623.

Hydrogen served as a reducing agent for the reduction of Pt(II), whereas acrylate was used as a reducing agent for the reduction of Au(III). The latter reaction was found to be catalyzed by the formation of Pt as a result of the reduction of Pt(II). Acrylate also functioned as capping agent on the resulting nanocrystals. By controlling the feed ratios of AuCl<sub>4</sub><sup>-</sup> and PtCl<sub>4</sub><sup>2-</sup> and the relative concentrations of acrylate, an effective route for the preparation of AuPt nanoparticles with bimetallic compounds ranging from .apprx.4 to 90% Au and particle sizes ranging from 2 to 8 nm has been demonstrated. The composition, size, and shell properties were characterized using transmission electron microscopy, d.c. plasma-at. emission spectroscopy, Fourier transform IR spectroscopy, and X-ray diffraction. Implications of the results to the exploration of bifunctional catalysts are also briefly discussed.

## 2.9 Activity and Deactivation of Gold Catalysts Supported on Mesoporous Titania for Water-Gas Shift Reaction

Au/mesoporous titania catalysts were prepared and characterized by X-ray diffraction, TEM, N<sub>2</sub> adsorption analysis and TPD. V Idakiev, T Tabakova, P Konova, A Naydenov from the Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, Bulgaria, *Physical Chemistry* 2004, Proceedings of the International Conference on Fundamental and Applied Aspects of Physical Chemistry, 7th, Belgrade, Serbia and Montenegro, Sept. 21-23, 2004 **1**, 201. The WGS activity was tested at a wide temperature range (140-300 .degree.C). The slow deactivation of the catalysts was attributed to their ability to adsorb CO and accumulate it as carbonates. This deactivation is reversible and after heating in air the activity was restored

## 2.10 Catalysis by gold/platinum group metals. Mixed metal systems displaying increased activity

A review; by D T Thompson, *Platinum Metals Review* 2004, **48(4)**, 169. The recent surge of new interest in catalysis by gold has led researchers to investigate the effects of adding other metals to the gold. As a result, there are a no. of reactions with potential for industrial application where combinations of gold with a platinum group metal (pgm) have been shown to have advantages over either gold or the

pgm alone. These findings are expected to lead to applications in chem. processing, pollution control and fuel cell applications. Here, a no. of catalytic processes that have benefited from the synergy between a pgm and gold are described, and some interesting reports from recent conferences are highlighted.

### 2.11 Support Effects on the Catalysis of Gold Nanoparticles and their Applications

A review by Masakazu, Haruta, Masatake from the Natl. Inst. Adv. Ind. Sci. Technol., Tsukuba, Japan, *Shokubai* 2005, **47(1)**, 8. Gold exhibits high catalytic activities when dispersed as nanoparticles with diameter less than 5 nm. Roles of the support are not only fixing the Au nanoparticles but also providing active sites as well as reactant O and moisture. Catalytic activities of the Au nanoparticles can be controlled by properly selecting the support for each reaction.

### 2.12 Gold Redox Catalysis for Selective Oxidation of Methane to Methanol

The activation and selective oxygenation of inert C-H bonds, as in methane, is a demanding problem. It is now shown, D De Vos, B Sels, from the Centre for surface Chemistry and Catalysis, K.U. Leuven, Louvain, Belgium, *Angewandte Chemie, International Edition* 2005, **44(1)**, 30, that the combination of Au as a catalyst and  $H_2SeO_4$  as the oxidant results in a 94% selectivity for  $CH_3OSO_3H$  at 28%  $CH_4$  conversion. These results mean that Au now claims its place alongside the other noble metals as a methane oxidn. catalyst.

### 2.13 Direct Evidence of Oxidized Gold on Supported Gold Catalysts

Supported gold catalysts have drawn worldwide interest due to the novel properties and potential applications in industries. However, the origin of the catalytic activity in gold nanoparticles is still not well understood. In this study, time-of-flight secondary ion mass spectroscopy (TOF-SIMS) has been applied to investigate the nature of gold in Au (1.3 wt %)/ $\gamma$ - $Al_2O_3$  and Au (2.8 wt %)/ $TiO_2$  catalysts prep'd. by the deposition-precipitation method. L Fu, N Wu, J Yang, F Qu, D Johnson, M Kung H Kung, P Dravid, from the Department of Materials Science & Engineering, Northwestern University, Evanston, USA, *Journal of Physical Chemistry B* 2005, **109(9)**, 3704. The SIMS spectrum of the supported gold catalysts presented  $AuO^-$ ,  $AuO_2^-$ , and  $AuOH^-$  ion clusters. These measurements show direct evidence for oxidized gold on supported gold catalysts and may be helpful to gaining better understanding of the origin of the catalytic activity.

### 2.14 Influence of Gold and Manganese as Promoters on Surface and Catalytic Performance of $Fe_2O_3/Al_2O_3$ System

The physicochemical, surface and catalytic properties of pure and doped  $Fe_2O_3/Al_2O_3$  solid catalysts with Au and  $Mn_2O_3$  calcined at 300, 500 and 700 .degree.C were investigated. N

Radwan, E El-Sharkawy, A Youssef, from the Faculty of Education, Department of Chemistry, Suez Canal University, Egypt, *Applied Catalysis, A: General* 2005, **281(1-2)**, 93. The dopant concentration of Au was varied between 0.4 and 1.6 mol%, while  $Mn_2O_3$  concentration was varied between 1.0 and 8.0 mol%. The techniques employed were DTA, XRD, TPR, EDX, nitrogen adsorption at -196 .degree.C, CO oxidation by  $O_2$  at 225-275 .degree.C and  $H_2O_2$  decomposition in aqueous solution at 30-50 .degree.C. The results obtained revealed that the doping of  $Fe_2O_3/Al_2O_3$  solids with different amounts of Au and  $Mn_2O_3$  changed the degree of crystallinity of  $Al_2O_3$  and  $Fe_2O_3$  phases.

The doping process led to a progressive increase in the sp. surface area of the treated solid catalysts to an extent proportional to the amt. of Au and  $Mn_2O_3$  added. This process led also to a progressive increase in the catalytic activities of the investigated solid catalysts towards CO oxidation by  $O_2$  and  $H_2O_2$  decomposition. The doping of solid catalysts with Au calcined at 300, 500 and 700 .degree. C exhibited catalytic activity in CO oxidation by  $O_2$  higher than those measured for solid catalysts doped with  $Mn_2O_3$  calcined at the same temps. Opposite results have been observed in case of  $H_2O_2$  decomposition. These findings indicate that the active sites taking part in CO oxidation by  $O_2$  are different from those involved in  $H_2O_2$  decomposition.

### 2.15 Titanium Oxide Nanotubes as Supports of Nano-Sized Gold Catalysts for Low Temperature Water-Gas Shift Reaction

Titanium oxide nanotubes (TNTs) have been synthesized via the reaction of  $TiO_2$  cryst. powders of either anatase or rutile phase and NaOH aq. soln. V Idakiev, Z Yuan, T Tabakova, B Su from the Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, Bulgaria, *Applied Catalysis, A: General* 2005, **281(1-2)**, 149. Their application as an active supports of gold particles prep'd. by deposition-pptn. (DP) method is investigated. The TNT supports and the gold catalysts were characterized by a range of methods including powder X-ray diffraction (XRD), transmission electron microscopy (TEM),  $N_2$  adsorption anal. and temp. programmed redn. (TPR). The catalytic activity of gold-supported titania nanotubes (Au/TNTs) was evaluated for the first time in water-gas shift reaction (WGSR) at wide temp. range (140-300.degree. C) and has been compared with Au/surfactant-templated- mesoporous-titania and  $Au/Al_2O_3$  catalysts under the same operating conditions. We try to establish a correlation between the catalytic performance of Au/TNTs and the nature of the support.

### 2.16 Gold on Titania Catalysts for the Oxidation of Carbon Monoxide: Control of Ph During Preparation with Various Gold Contents

$Au/TiO_2$  catalysts have been prepared by deposition-precipitation, with the initial pH of a  $HAuCl_4$  solution raised to various values between 4 and 11 by the addition of NaOH at room temp. F Moreau, G C Bond, A Taylor from the Institute for Materials Research, University of Salford, The Crescent

Salford, Greater Manchester, *Journal of Catalysis* 2005, **231(1)**, 105. The optimum pH for high activity proved to be 9; at this pH the main species in solution were anionic Au complexes, from which most of the chlorine had been removed by hydrolysis. At lower pH, the gold complexes contained more chlorine, Au particles were larger, and activities were lower.

Whereas other workers have used catalysts with more than 2% gold, the authors have focused on lower loadings: catalysts containing only 0.05-1.9 wt% gold were prepared, and the pH was kept const. at 9 throughout the preparation. When their activities for CO oxidation were detected under conditions of kinetic control, all of them had about the same activation energy and the same high specific activity, suggesting that their method of preparation gave similar distributions of gold particle sizes at all loadings.

Their activities were unchanged by calcination up to 573 K; however, a catalyst prepared at pH 6 lost activity progressively as the calcination temperature was raised. By withdrawing samples at critical points during the preparation, the authors have shown that the adsorbed precursor (the form of which det. the size of the gold particles) is in fairly rapid equil. with gold species in solution. This permits easy control of the gold particle size during the preparation and even allows the poor activity of a dried catalyst initially prepared at non-optimum pH to be substantially improved.

### 3 Chemistry

#### 3.1 Gold-Nickel Hydroxide Multi-Layers with Selective Absorption in the Visible Range

This work reports the growth of layered nickel hydroxide/gold films by sol-gel and dip-coating methods to obtain colored films for applications in switchable optical devices. P Haddad, F Ferreira, G Brito, M Fantini from the Instituto de Fisica, Sao Paulo-SP, 05315-970, Brazil, *Journal of Sol-Gel Science and Technology* 2004, **30(3)**, 179. The nickel and gold-based films were deposited on mica and glass plates from alc. sols. The distribution of electron d. inhomogeneities (voids, nickel and gold particles) in the films was detd. by means of small angle X-ray scattering (SAXS).

The SAXS measurements were used to det. the nickel and gold particle sizes and to give guidelines to the appropriate chem. route to deposit homogeneous colored films. X-ray diffraction (XRD) was used to monitor the cryst. properties. Transmission electron microscopy (TEM) was used to observe the nanostructure of the gold particles and at. force microscopy (AFM) to analyze the film surface. Spectral transmission was used to investigate the optical properties in these different layered systems, which present an absorption band in the visible region due to the gold aggregates. The composite material is deep blue. The analyses of SAXS data, TEM and AFM pictures are consistent, i.e., the formed Au particles are polydisperse in size and their clustering depends on the NiOxHy layer. The Au particles are polycryst., with [111]-preferred orientation, as detd. by XRD. The nickel oxy-hydroxide matrix is amorphous.

## 4 Electrochemistry

### 4.1 Electrochemical Nucleation of Gold Nanoparticles in a Polymer Film at a Liquid-Liquid Interface

Simultaneous nucleation of Au nanoparticles and polymn. of tyramine was carried out at an immiscible electrolyte interface. R Knake, A Fahmi, S Tofail, J Clohessy, M Mihov, V Cunnane, Vincent from the Materials and Surface Science Institute, University of Limerick, Limerick, Ireland, *Langmuir* 2005, **21(3)**, 1001-. By transferring the Au ion of tetraoctylammonium tetrachloroaurate (TOAAuCl<sub>4</sub>) from the org. to the aq. phase, a fast homogeneous electron transfer from the tyramine monomer reduces the Au ion. Electropolymn. then proceeds, and Au nanoparticles form. The newly formed nanoparticles act as nucleation sites for the deposition of the oligomers/polymer (and possibly vice versa). This results in Au nanoparticles stabilized in a polytyramine matrix. The size of the nanoparticles is controlled by the concn. of oligomers/polymer in soln. The polymer nanoparticle composite film was analyzed with TEM, XPS, and AFM.

### 4.2 Size and Crystallographic Orientation Controls of Gold Nanoparticles Electrodeposited on GC Electrodes

Au nanoparticles were electrodeposited onto glassy C-electrodes (nano-Au/GC) in the presence of 2 different additives, namely, cysteine and iodide ions. The electrochem. characterization of the electrodeposited nano-Au/GC electrodes was performed via the measurements of the reductive desorption patterns of a thiol (e.g. cysteine) self-assembled monolayer as well as the cyclic voltammetric response toward the oxygen redn. reaction in alk. medium. M El-Deab, T Sotomura, T Ohsaka from the Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Midori-ku, Yokohama, Japan, *Journal of the Electrochemical Society* 2005, **152(1)**, C1-C6.

The structural characterization of the electrodeposited Au nanoparticles was performed by the scanning electron microscope. The nano-Au/GC electrodes prepd. in the presence of 100 .mu.M cysteine were surprisingly found to be enriched in the Au(100) and Au(110) facets and are characterized by a relatively big particle size up to 300 nm as well as low particle d. (no. of particles per unit area). The Au nanoparticles prepd. in the presence of 100 .mu.M I- ions are much enriched in the Au(111) facets and are characterized by a relatively narrow particle size distribution range (10-40 nm) as well as a high particle d. Anal. of the x-ray diffraction data revealed a significantly decreased ratio of Au(111) domains of the Au nanoparticles electrochem. deposited in the presence of cysteine. These preliminary results suggest a simple way to control the size as well as the preferential crystallog. orientations of Au nanoparticles.

## 5 Electronics and Sensors

### 5.1 A Novel Gold Deposition Process for Wafer Applications

A review by N Brown and E Douglass from the Shipley Company, LLC, Freeport, NY, USA IEEE/CPMT/SEMI International Electronics Manufacturing Technology Symposium, 28th, San Jose, CA, United States, July 16-18, 2003, 323. The deposition of Ni and Au layers as under bump metallurgy (UBM) for wafer bump applications was established as a viable means of ensuring adhesion and bond reliability. These Ni/Au layers can be used in subsequent processes that employ either wire bonding directly to die pads or screened and reflowed solder paste for connectivity to next level substrates. This paper will discuss the process chemistries used to produce Ni/Au metallurgies over Cu or Al die pads. Conventional immersion Au processes deposit Au from solution via a displacement reaction with the surface of the Ni layer. This reaction continues until the Au completely covers any available Ni sites.

This mechanism, therefore, limits the possible thicknesses obtainable from immersion Au processes to approximately 0.10-0.15  $\mu\text{m}$ . A new Au deposition process will be described that operates in a similar way but is not limited by the displacement mechanism. This chemistry is capable of depositing significantly higher thicknesses of Au over Ni substrates, thus allowing this technology to be used for many new applications that normally would require electrolytic deposition of Au. The advantages of using an immersion process are its ability to deposit very uniform deposit thicknesses across a wafer surface, no requirement for elec. continuity across the plateable surface and the practicality of processing a large no. of wafers at one time. Performance results and operating characteristics of the new Au process will be reviewed. Pretreatment processes necessary to ensure optimum reliability will also be discussed.

### 5.2 Voltammetric Behavior of Ethopropazine and the Influence of Sodium Dodecylsulfate on its Accumulation on Gold Electrodes

Surfactants are sometimes used to improve the accumulation of some electroactive org. compds., but anionic surfactants have seldom been utilized for such a purpose yet. In this paper, the influence of the anionic surfactant SDS on the accumulation of ethopropazine (EPZ) at a polycryst. gold electrode was studied. EPZ exhibits an anodic peak at  $\approx 0.67$  V (vs. SCE) and a shoulder in pH 3.5 citric acid-biphthalate buffer soln. L Huang, L Bu, F Zhao, B Zeng from the Department of Chemistry, Wuhan University, Wuhan, People's Republic of China, *Journal of Solid State Electrochemistry* 2004, **8(12)**, 976. In the absence of SDS, the peak is small and ill defined, but it becomes high and well shaped when SDS is added.

This results from the adsorption of EPZ in the SDS membrane, which forms spontaneously on the gold electrode surface. For both cases EPZ shows the same electrode reaction mechanism, which is similar to that of promethazine (PMZ). The influence of other factors, such as

pH value, variety and concn. of buffers, other surfactants, accumulation potential and time etc was discussed. Only the anionic surfactants had an enhancement effect on the EPZ accumulation. Also, the soln. should be acidic or neutral so as to maintain the interaction due to its electrostatic nature. The optimum SDS concn. for EPZ accumulation is  $\approx 0.1$  mM regardless of whether or not an accumulation potential is adopted. When all the expt. conditions are optimized, the peak current of the anodic peak changes linearly with the concn. of EPZ over the range 0.4-4  $\mu\text{M}$ , and is thus of anal. significance.

## 6 Medical and Dental

### 6.1 Precious Metal Dental Alloys with High Gold Content and Complying with the Bio Sensation Requirement

The invention, by H Rueckert, from Dentagold Edelmetalle GmbH, Germany Patent No. DE 10317425, A1, 10/2/2005, concerns precious metal dental alloys with high gold, silver and platinum content and complying with the bio sensation requirement; the alloy is composed of (wt./wt.%): gold 73.0-76.0; silver 10.0-13.0; platinum 8.0-10.0; zinc 2.0-5.0; niobium 0.1-1.0; iridium 0.1-0.5; rhodium 1.0-2.0; tantalum 0.1-1.0; indium 0.1-1.0. The alloys do not contain toxic metals; their hardness and heat expansion coeffs. (16.2-16.4) enable good combinations with dental ceramics.

### 6.2 Gold Ion-Generating Therapeutic Cork Sheets or Textile Sheets with Quick-Acting Analgesic Effect

Patent by A T Akita, Patent No. JP 2005029555, A2 3/2/2005 describes Cork sheets, useful for treatment of neck pain, back pain, etc., contain Au ion-generating substances, anion generating substances (e.g. tourmaline), and far IR-radiating substances (e.g. ceramics). Preferably, the Au ion generators exit on the surface, and other substances inside of the sheets. The 3 substances synergically activate cells and promote circulation, thus exhibiting analgesic effect quickly.

### 6.3 Production of Gold Colloid

The inventor, S Oh from the Nano Bio Co., Ltd., S. Korea Patent No, KR 2003038871, A, 17/3/2003 provides a method of preparing a nano-particle sized gold colloid which has been found to possess a greater efficacy on various diseases such as cold, conjunctivitis, gonorrhoea, leprosy, pneumonia, rheumatism, endotoxemia, warts, acne, etc. Therefore, the gold colloid can be added to various liquors such as rice wine, distd. spirit (soju, Korean native name), refined rice (jeongjong), whisky or the like, or health drinks. The method of preparing a nano-particle sized gold colloid comprises the steps of: adding a solution of water sol. Au salt to boiling water; adding a trace amount of a surfactant which is harmless to the human body thereto; and boiling them at predetermined temperature.

## 7 Metallurgy, Materials and Coatings

### 7.1 Method for Manufacture of Fine-Grain Metal Particles, Gold Particles, and Pastes, Colloids, Films, and Optical Filters Containing Gold Particles

Manufacture of fine-grain metal particles having uniform grain size is carried out by irradiation of a metal ion solution with ultrasonic wave, under presence of a reducing agent. Y Hayashi, H Hirata, T Takahagi, S Niimiyahara, H Sakagami from the Mitsubishi Materials Corp., Japan Patent No. JP 2005036316, A2 10/2/2005. Fine-grain Au particles of size variation coeff.  $\pm 12\%$  may be manufactured by the said process. Also claimed are Au particles of average size 4-20 nm and size variation coeff.  $\pm 12\%$ , and pastes, colloids, films, and optical filters containing the Au particles. Metal particles suitable for wirings, colorants, optical filters, catalysts, etc. are obtained.

### 7.2 New Observations on Intermetallic Compound Formation in Gold Ball Bonds: General Growth Patterns and Identification of Two Forms of Au<sub>4</sub>Al

Relatively little information is available on the growth patterns and metallurgy of Au-Al intermetallics in fine-pitch and ultra-fine pitch ball bonding. A study of the growth pattern and chem. of intermetallic compds. is presented formed between a 25  $\mu\text{m}$  4 N gold wire and aluminum pad metalization after isothermal aging in air at 175.degree.. C Breach, F Wulff from the Materials and Applications Centre, Kulicke and Soffa (SEA) Pte. Ltd., Singapore, *Microelectronics Reliability* 2004, **44(6)**, 973.

The data show the intermetallics grow vertically and laterally under the ball and totally consume the Al in the bond pad in less than 20 h. Then, a third layer of intermetallic grows between Au<sub>4</sub>Al and Au<sub>5</sub>Al<sub>2</sub>. Measurements and observations made with energy-dispersive x-ray anal. and optical microscopy lead to the conclusion that the new compd. is a different form of Au<sub>4</sub>Al, most probably a low-temp. version of the  $\alpha$ -Au<sub>4</sub>Al intermetallic structure. Elec. resistance during intermetallic growth was not measured in this study but wire chem. and bonding conditions are found to affect the thickness of the intermetallic compds., which suggests that the resistance of ball bonds during molding and operation can change.

### 7.3 Gold-Alumina Cermet Photothermal Films

Cermet films of gold and aluminum oxide were sputter deposited onto silicon substrates. These films consisted of nanometer-sized gold grains embedded in a matrix of aluminum oxide and were designed to absorb visible radiation and minimally emit IR radiation. B Woods, D W Thompson, J Woollam, from the Department of Electrical Engineering, University of Nebraska, Lincoln, USA, *Thin Solid Films* 2004, 469. Ex situ and in situ spectroscopic ellipsometry were used to characterize film optical consts. from deep UV to middle IR.

The optical constants, for cermet films with gold vol. fractions ranging from 0 to 1, were used in predictive optical models. Thermal performance was optimized using a new algorithm based on energy balances. This algorithm wts. the parameter fit in predictive optical models to an ideal reflectance spectrum. This weighting factor emphasizes fitting in more significant spectral ranges and de-emphasizes fitting in less significant wavelength ranges. Absorptivity, emissivity, and their ratio were calcd. for optimized film structures.

### 7.4 Selective Electrochemical Recovery of Gold and Silver From Cyanide Aqueous Effluents Using Titanium and Vitreous Carbon Cathodes

A different approach to the electrochemical recovery of gold from Au-containing alloys is presented.

M Spitzer, R Bertazzoli, from the Departamento de Engenharia de Materiais, Faculdade de Engenharia Mecanica, Universidade Estadual de Campinas, Brazil, *Hydrometallurgy* 2004, **74(3-4)**, 233. A filter-press-type electrochemical flow reactor was used, and loosely adherent metal layers were obtained on highly polished vitreous carbon and titanium flat cathodes. On the former, the metal coating peeled off and was recovered as small flakes outside the reactor. On Ti, the metal coating was easily scraped off with a plastic spatula. Gold, silver and copper ions were recovered from real cyanide effluents under conditions such that the reduction reactions were mass transfer controlled. Cyclic voltammetry was used for identification of the potential range in which redn. of Au(I) was the main process to improve selectivity.

Subsequently, controlled potential electrolysis was carried out at potentials from -1.1 to -1.6 V vs. the SCE on vitreous carbon and from -1.0 to -1.2 V vs. SCE on the Ti cathode. Lower potentials favored greater selectivity and alloys containing 76 and 84% of gold were obtained on Ti and vitreous carbon, resp. Concn. decay profiles, as a function of potential and electrolysis time, presented pseudo-first-order kinetic and mass transfer coeffs. for Au(I) on the order of 10<sup>-5</sup> m/s on both cathodes in the region of potential in which electro-recovery presented a greater selectivity for gold. Cathodic efficiencies were higher on the Ti cathode in which 23% was obsd. for a gold alloy recovered at -1.0 V, and 15% when only gold was considered.

## 8 Nanotechnology

### 8.1 A Modified Nanosphere Lithography for the Fabrication of Aminosilane/Polystyrene Nanoring Arrays and the Subsequent Attachment of Gold or DNA-Capped Gold Nanoparticles

A modified nanosphere lithog. method for producing arrays of silanized structures at silicon surfaces is described. Polystyrene (PS) particles (600 nm or 1000 nm in diam.) were self-assembled onto a silicon substrate to form a hcp. pattern. The resultant patterned surface was then exposed to

a soln. of 3-aminopropyltriethoxysilane (APTS), which deposited gradually in the interstitial voids of the PS particle array. Y Wang, S Han, A Briseno, R Sanedrin, F Zhou from the Department of Chemistry and Biochemistry, California State University, Los Angeles, USA, *Journal of Materials Chemistry* 2004, **14(24)**, 3488.

When such a surface was sonicated in toluene to dislodge the PS particles, a mesoporous network contg. truncated PS nanorings/shells was produced. Gold nanoparticles or DNA-capped gold nanoparticles, which are both neg. charged, can be electrostatically attached onto the PS/APTS nanoring array. At. force microscopy (AFM) was used to image the surface pattern and structure after each step of the procedure, while x-ray photoelectron spectra (XPS) and UV-visible spectrometry were used to det. the compn. of the surface patterns. The mechanisms for forming the PS/APTS nanostructures are discussed. These structures could potentially be used as biosensors, heterogeneous catalysts, and functionalized.

### 8.2 Formation of Silver Nanorods by Microwave Heating in the Presence of Gold Seeds

The authors report the use of rapid microwave (MW) heating to prep. silver nanorods. The procedure the authors describe is one in which a silver salt is reduced to silver metal by the action of sodium citrate in the presence of gold seeds. F Liu, P Huang, Y Chang, C Ko, F Ko, T Chu from the National Nano Device Laboratory, Hsinchu, Taiwan, *Journal of Crystal Growth* 2005, **273(3-4)**, 439-. The authors have characterized the silver products by UV-visible absorption spectroscopy, SEM, energy-dispersive x-ray anal., x-ray diffractometry, and electron diffraction. The key requirement for producing the silver nanorods in a high aspect ratio is an adequate MW heating time.

### 8.3 Formation of Molecular Rectifier with Gold Nanoclusters

Gold nanoclusters encapsulated with organic molecules are of great interest for its possible applications in various fields of nanotechnology like mol. electronics, catalysis, and medical science. Here, the authors demonstrate that the monolayer and bilayer films of thiol-capped gold nanoclusters can exhibit diode-like properties provided controlled spatial asymmetry is created between two tunnel junctions used to connect a gold nanocluster mol. S Pal, M Sanyal, N John, G Kulkarni from the Surface Physics Division, Saha Institute of Nuclear Physics, Kolkata, India, Los Alamos National Laboratory, Preprint Archive, *Condensed Matter* 2005 1-13.

Current-voltage characteristics of this mol. rectifier were obtained from conducting probe at. force microscopy measurements and also from conventional two-probe resistance measurements. Systematic x-ray reflectivity and at. force microscopy measurements were carried out to characterize the spatial asymmetry introduced by a monolayer of fatty acid salt gadolinium stearate used to deposit thiol-

capped gold nanocluster mols. on hydrophilic SiO<sub>2</sub>-Si(001) substrate by the Langmuir Blodgett technique. The prominent rectification property obsd. in these nano-structured films could be explained from the measured spatial asymmetry. An obvious application of this work will be to form an array of memory dots with gold nanoclusters by depositing these on a monolayer of org. mols. having desired "tail length".

### 8.4 Synthesis of Branched Gold Nanocrystals by a Seeding Growth Approach

Synthesis of branched Au nanocrystals by a seeding growth approach is described. In this process, HAuCl<sub>4</sub> aqueous solution was supplied stepwise to grow the Au seeds (.apprx.2.5 nm) into larger nanoparticles with a highly faceted particle structure (.apprx.15-20 nm in diam.). Na dodecyl sulfate (SDS) served as a capping agent to facilitate the formation of highly faceted nanoparticles, and ascorbic acid was used as a weak reducing agent.

The highly faceted nanoparticles then transformed into branched nanocrystals (.apprx.40 nm in length) by further addn. of the SDS-HAuCl<sub>4</sub> soln. and ascorbic acid for particle growth. The branched nanocrystals show bipod, tripod, tetrapod, and pentapod structures and are composed of mainly (111) lattice planes. These multipods appear to grow along the twin boundaries of the initially formed highly faceted Au nanoparticles, as the twin boundaries on the pods originate from the centers of the branched nanocrystals. The concn. of ascorbate ions in the soln. has a profound influence on branch formation. These branched nanocrystals are stable to storage at low temp. (i.e., 4.degree.), but they may slowly evolve into a multitwinned faceted crystal structure (i.e., pentagonal-shaped decahedral structure) when stored at 30.degree..

### 8.5 Morphology of Si Nanowires Fabricated by Laser Ablation Using Gold Catalysts

Si nanowires (NWs) were fabricated successfully by laser ablation using Au as catalyst. Si wafers were used as the collector. K Wang, S Chung, D Kim from the Physics Department and Electron Spin Science Center, Pohang University of Science and Technology, Namku, S. Korea, *Applied Physics A: Materials Science & Processing* 2004, **A79(4-6)**, 895. The diameters of Si NWs ranged from 20 to 150 nm. Different forms of Si NWs were observed at different local sites inside a furnace: Si NWs with a high aspect ratio of length to diameter, Si NWs with defects and Si NWs with embedded Au-containing nanoparticles. Esp., a nanoparticle-embedded Si NW is a new nanostructure that is observed for the first time.

### 8.6 Method for Manufacturing Nano-Grade Gold Particles

The present invention provides a novel method for manufacturing nano-grade Au particles, where glyoxylate ion obtained by adjusting pH value of glyoxylic acid solution serves as a reducing agent to reduce trivalent Au ions, such

as  $\text{HAuCl}_4$ , to nano-grade Au particles; immersing a substrate containing aminosilane on a surface thereof in the Au particle solution; and depositing the Au particles. S Hu, R Ye, Y Liou, R Liou, D Huang, Patent No. TW 567091, B, 21/12/2003. The nano-grade Au particles obtained from this method may be implemented in the manufacturing of single electron transistors.

## 9 Refining

### 9.1 The Phased Metallurgical Upgrade Strategy at Gold Fields Limited South African Operations

The approach adopted to upgrade the current metallurgical facilities at both the Driefontein and Kloof Gold Mines in the Republic of South Africa is discussed. B Taunyane, A Phillips from the Gold Fields Mining Services Limited, Parktown, S. Africa, *Publications of the Australasian Institute of Mining and Metallurgy* 2003, **4/2003** (Eighth Mill Operators' Conference, 2003), 143. Gold Fields Ltd. operates eight metallurgical plants within South Africa of which three have recently been upgraded to replace the older technol. previously installed, with modern equipment.

This upgrade was undertaken to improve the extn. efficiencies and reduce operating costs. The upgrade was undertaken in a phased approach with the first phase focused on replacement of the filtration/zinc pptn. processes with modern pump-cell carbon-in-pulp technol. Included in this upgrade phase was the installation of an automated hands-free electrowinning cell. The second phase of the upgrade entailed replacement of the multiple comminution stages previously installed with large semi-autogenous/ball mill combinations. Due to the rapid return on these projects, a fast-track approach was adopted which necessitated the purchase of available conditioned second-hand mills from both within South Africa and in Australia.

### 9.2 Lihir Gold Five Years on - Maximizing Throughput and Capital Utilization

During the first five years of operation, the Lihir gold mine has steadily increased its plant throughput rate to >4 Mton/yr, well above the original design capacity of 2.8 Mton/yr for ore containing 7.2% S. A McDonald from MAusIMM, C/- Lihir Management Company, Brisbane, Qld, Australia, *Publications of the Australasian Institute of Mining and Metallurgy* 2003, **4/2003** (Eighth Mill Operators' Conference, 2003), 115. Understanding how future variations in ore type impact on plant performance has been an integral part of the Lihir development program. The key drivers for significant improvements in the plant include a second oxygen plant, pilot flotation plant, autoclave heat recovery circuit, pebble crushing circuit and addnl. autoclave feed pumping capacity. The result is a process plant with the flexibility to accommodate variations in ore type without significant loss of throughput.

### 9.3 Method for Recovering Gold and Silver from Acidic Thiourea Aqueous Solution Using Iron Powder

A method for recovering gold and silver from acidic thiourea aq. solution using iron powder is provided to environment friendly and efficiently recover and separate gold and silver from the acidic thiourea aq. solution containing gold, silver and other trace of impurities by using iron powder as precipitant. S Kim, H Lee, J Oh from the Korea Institute of Science and Technology, Patent No. A, 30.8.2003.

The method for recovering gold and silver from acidic thiourea aq. solution using iron powder comprises the steps of adding iron powder as precipitant to the acidic thiourea aq. solution as injecting nitrogen gas into an acidic thiourea aq. solution in which gold ore is leached; and selectively precipitated gold and silver in the acidic thiourea aq. solution by stirring the acidic thiourea aq. solution as continuously injecting the nitrogen gas into the acidic thiourea aq. solution, wherein the nitrogen gas is injected into the acidic thiourea aq. solution at a flux of 200 to 400 mL/min, wherein size of the iron powder corresponds to a sieve size of 100 to 200 meshes, and the iron powder is added to the acidic thiourea aq. solution in an amt. of 3 to 5 g/L, wherein temperature of the precipitation is maintained to 20 to 30.degree., wherein speed of the stirring is maintained to 200 to 300 rpm, and wherein time of the precipitation is maintained to 30 to 40 min.

### 9.4 Effect Of Copper on Gold Recovery by Zinc from Leach Liquors

$\text{Cu}^{2+}$  in cyanidation leaching liquor at high concentrations (838.0 mg/L) seriously interferes with the replacement of Au with powdered Zn. H Cao from the Dept. Chem., Weinan Teachers College, Weinan, Peoples Republic of China, *Baoji Wenli Xueyuan Xuebao, Ziran Kexueban* 2003, **23(1)**, 39. The yield of Au displacement was improved up to 99.83% and only 1.5% Cu was reduced when CaO was added to the leaching liquor and the leaching liquor was stirred for 24 h at room temp. to maintain the CaO concn. at 400 mg/L.

### 9.5 CIP – Who needs it? A Combination Circuit of Gravity, Flotation and intensive leach may provide the optimal environmental and cost outcome for Gold Plants – stage II – results

The authors challenge the traditional thinking that whole ore cyanidation followed by carbon in pulp (CIP) or carbon in leach (CIL) should be applied as a std. process in the majority of gold processing flow sheets. A Gray, J Abols, A McCallum, G Patrick, G Johansen, N Grigg, from Gekko Systems Australia, Australia, *Publications of the Australasian Institute of Mining and Metallurgy* 2004, **1/2004** (AusIMM New Leaders' Conference, 2004), 149. The concept of whole ore leaching by using cyanide can result in unnecessary environmental and capital risk. Alternative, currently available technologies can be used to provide the desired level of gold recovery at a much lower installed cost and less impact on the environment.

Gravity concentration, alone or in conjunction with flotation, can produce a gold bearing concentrate that can then be fed directly to a batch or continuous intensive cyanidation unit. The in-line leach reactor is an intensive cyanidation unit, and this technol. include significantly reduced capital outlays for Greenfield plants or plant upgrades and increased investor returns. Redn. of on-site cyanide and carbon inventories improves plant safety, materials handling and site security. By using direct electrowinning to treat the gold bearing solutions produced, the need for a conventional carbon stripping circuit is removed. The potential also exists to increase grind size to save energy, further decreasing capital and operating costs and decreasing the environmental impact of a mill. Detoxification of cyanide before the release of the soln. to the tailings dam can minimize tailings disposal and containment requirements. When used in the right application, the proposed process will have little or no impact on gold recovery and may actually increase recovery for complex ores. Areas applicable to this type of treatment include plants in environmentally sensitive regions, lower tonnage higher grade deposits, coarse gold deposits, and preg robbing ores, some of which may not currently be economically feasible using std. processes and flow sheets. Two examples of such projects are provided in which an alternative to whole ore leaching and CIP or CIL has the potential to deliver these benefits.

## 10 General

### 10.1 Manufacture Of Glass-Gold/Silver-Glass Sandwich Structure

A method for preparing a gold or silver film-treated glass plate and a glass plate structure are provided, wherein the glass plate has an excellent heat insulation and is applied to a floor finishing material or a decoration material. J An, Patent No. KR 2003063971, A, 31/7/2003. The method comprises the steps of (S1) adhering a gold or silver foil to the surface of glass; (S2) standing the glass plate vertically to allow bubbles to be emitted, and fusing the two glass plates by heating; and (S3) cooling the fused glass plates. The glass plate structure is a sandwich-like structure comprising two glass plates and a gold or silver foil placed between the two glass plates, wherein the glass plates are fused. Preferably the upper plate is made of glass and the under plate is made of ceramic in the glass plate structure; and/or the glass plate structure contains an empty inner space for the heat insulation.