
Highlights from Recent Literature

1 ANALYTICAL

1.1 *Flow-Injection Spectrophotometric Determination of Gold using 5-(4-Sulfophenylazo)-8-aminoquinoline*

Z. Zuotao, T. McCreedy and A. Townshend, Department of Chemistry, The University of Hull, UK, *Anal. Chim. Acta*, 1999, **401**(1-2), 237-241 have determined gold ($0-75 \mu\text{g ml}^{-1}$) spectrophotometrically at 605 nm in a flow injection (FI) system based on the reaction of Au(III) and 5-(4-sulfophenylazo)-8-aminoquinoline (SPA) in the presence of cetyltrimethylammonium bromide (CTAB). The carrier stream was 1% (wt/vol) disodium ethylenediaminetetraacetate and the reagent streams were 2.0×10^{-4} M SPA and 0.6% (wt/vol) sodium hydroxide solution.

2 CATALYSIS

2.1 *When Gold Is Not Noble: Nanoscale Gold Catalysts*

A. Sanchez, S. Abbet, U. Heiz, W.-D. Schneider, H. Haekkinen, R.N. Barnett and U. Landman, Institut de Physique de la Matière Condensée, Université de Lausanne, Switzerland have reported (*J. Phys. Chem. A*, 1999, **103**(48), 9573-9578) that whilst inert as bulk material, nanoscale gold particles dispersed on oxide supports exhibit a remarkable catalytic activity. Temperature-programmed reaction studies of the catalysed combustion of CO on size-selected small monodispersed gold clusters supported on magnesia, and first-principle simulations, reveal the microscopic origins of the observed unusual catalytic activity, with Au₈ found to be the smallest catalytically active size. Partial electron transfer from the surface to the gold cluster and oxygen-vacancy F-centre defects are shown to play an essential role in the activation of nanosize gold clusters as catalysts for the combustion reaction.

2.2 *The Catalytic Performance of Gold in Hydrogenation and Oxidation Reactions*

In a series of papers collected together in a Report entitled 'The Abilities and Potential of Gold as a Catalyst' members of the research group working with Dr Haruta in the Osaka National Research Institute (ONRI), AIST, Ikeda, Japan, described their results from April 1994 – March 1999) (see also *Gold Bull.*, 1999, **32**, 139). M. Haruta, *Osaka Kogyo Gijutsu Kenkyusho Hokoku*, 1999, **393**, 69-71, described selective oxidation of carbon monoxide in a hydrogen-rich stream using Au/MnO_x

catalysts (Au/Mn at. ratios: 1/19 and 1/50), prepared by coprecipitation and calcination in air at 573 K.

H. Sakurai (*ibid* pp 66 – 68), employed gold catalysts, prepared by deposition-precipitation or coprecipitation, and supported by TiO₂, Fe₂O₃, Al₂O₃ or ZnO, for the forward and reverse water-gas shift, using the commercial catalyst Cu/ZnO/Al₂O₃ as the reference. H. Sakurai (*ibid* pp. 56 – 58) also reviewed work on active supported gold catalysts for methanol synthesis from both CO₂ and CO. Effects of the kind of metal oxide supports and of the diameter of the gold particles on activity and selectivity for methanol synthesis were discussed.

M. Date (*ibid* pp. 38-43) reviewed the performance of Au/TiO₂, Au/Al₂O₃ and Au/SiO₂ catalysts for the CO oxidation reaction. TOF for Au/TiO₂ and Au/ α -Fe₂O₃ increased sharply with a decrease in diameter of gold particles below 4 nm.

2.3 *The Kinetics of CO Oxidation by Adsorbed Oxygen on Well-Defined Gold Particles on TiO₂(110)*

V.A. Bondzie, S.C. Parker and C.T. Campbell, Department of Chemistry, University of Washington, Seattle, USA, *Catal. Lett.*, 1999, **63**(3,4), 143-151, have described how very tiny gold particles on TiO₂ show excellent activity and selectivity in a number of oxidation reactions. They studied the vapour deposition of gold onto a TiO₂(110) surface using XPS, LEIS, LEED and TPD and found that they could obtain gold islands with controlled thicknesses from one to several monolayers. Studies on the titration reaction of oxygen adatoms with CO (to produce CO₂) show that this reaction is extremely rapid at room temperature, but its rate is slightly slower for the thinnest gold islands. Thus the association reaction (CO_g + O_a → CO_{2,g}) gets faster as the oxygen adsorption strength decreases, again as expected from Bronsted relations. For islands of about two atomic layers thickness, the rate increases slowly with temperature, with an apparent activation energy of 11.4 ± 2.8 kJ/mol, and shows a first-order rate in CO pressure and oxygen coverage, similar to bulk Au(110).

2.4 *Palladium/Gold Catalysts for the Manufacture of Vinyl Acetate*

A catalyst for the production of vinyl acetate by reaction of ethylene, oxygen, and acetic acid consists of metallic palladium and gold deposited on a porous support (T. Wang and J.A. Broussard, Celanese International Corporation, USA, WO Patent 9962632 A1 (1999)). The catalyst is prepared by

impregnating a porous support containing prereduced metallic palladium with a solution of potassium aurate, and reducing the potassium aurate to metallic gold or by impregnating with both gold and palladium salts and reducing to give both gold and palladium in metallic form.

2.5 Supported Gold/ MO_x Catalysts for NO/H_2 and CO/O_2 Reactions

M.A.P. Dekkers, M.J. Lippits and B.E. Nieuwenhuys, Gorlaeus Laboratories, Department of Heterogeneous Catalysis and Surface Chemistry, Leiden Institute of Chemistry, The Netherlands, *Catal. Today*, 1999, 54(4), 381-390, have investigated the reduction of NO with H_2 and the oxidation of CO with O_2 were investigated over silica- and alumina-supported gold/metal oxide catalysts (M: Co, La, Ce). In general, the silica supported samples were less active than the alumina supported ones, probably due to the presence of large gold particles. The presence of metal oxide was beneficial to the activity in the NO/H_2 reaction and the CO/O_2 reaction over Au/ SiO_2 . The opposite behaviour was observed with the NO reduction over Au/ Al_2O_3 where the metal oxide might cover active species. Addition of cobalt oxide and lanthana improves the selectivity towards N_2 .

3 CHEMISTRY

3.1 The 'Acac Method' for the Synthesis of Coordination and Organometallic Compounds: Synthesis of Gold Complexes

In this review, by J. Vicente and M.T. Chicote of the Facultad de Química, Departamento de Química Inorgánica, Grupo de Química Organometálica, Universidad de Murcia, Spain, *Coord. Chem. Rev.*, 1999, 193-195, 1143-1161, there are 119 references. The synthetic utility of acetylacetonato gold complexes as reagents for preparing Au(III) complexes with C, N and O donor ligands and Au(I) complexes with P ylide, methanide, methanediide, S ylide, amino, amido, nitrido, alkyl, phosphido, thiolato, hydrosulfido, trithiocarbonato, dithiocarbamato, 1,1 dithiolato and alkynyl (including ethynyl) ligands is shown.

3.2 Coordination Chemistry of Gold(II) Complexes

A. Laguna and M. Laguna, Instituto de Ciencia de Materiales de Aragón, Departamento de Química Inorgánica, Universidad de Zaragoza, C.S.I.C., Spain, *Coord. Chem. Rev.*, 1999, 193-195, 837-856, have described complexes with gold in a formal oxidation state of two. Examples have increased considerably in recent years and nowadays this oxidation state can be considered almost as a common oxidation state in gold chemistry. This review, with 118 references, covers the evolution of the knowledge of this oxidation state from the first dithiocarbamate derivatives. $[Au_2(S_2CNR_2)_2X_2]$, stable only at very low temperature, to the room temperature stable dinuclear

gold complexes $[Au_2(L-L)_2X_2]$ ($L-L = CH_2PPh_2CH_2$, CH_2PPh_2S , $C_5H_4PPh_2-2$; $X = \text{halogen}$). Although a dinuclear structure with an Au(II)-Au(II) bond supported by two equal bridging ligands were the first and most common, this review shows the present diversity as mononuclear, $[Au([9]aneS_3)_2](BF_4)_2$, dinuclear with two different bridging ligands, $[Au_2(S_2CNR_2)(CH_2PPh_2CH_2)_2X_2]$, with a unsupported metal-metal bond, $[Au_2(Ph_2PC_8H_6PPh_2)_2Cl_2](PF_6)_2$, and polynuclear Au(II) complexes either with chains of only Au centers or with other metals, such as $[(C_6F_3H_2)Au(CH_2PPh_2CH_2)_2Au]_2-Au_2(CH_2PPh_2CH_2)_2ClO_4$ or $[Au_2Pt(CH_2PPh_2S)_4X_2]$.

4 COATINGS, FILMS, MEMBRANES AND WIRES

4.1 Z-Scan Measurement of the Nonlinear Absorption of a Thin Gold Film

D.D. Smith, Y. Yoon, R.W. Boyd, J.K. Campbell, L.A. Baker, R.M. Crooks and M. George of the Space Sciences Laboratory, NASA Marshall Space Flight Center, Huntsville, AL, USA, *J. Appl. Phys.*, 1999, 86(11), 6200-6205, have used the z-scan technique at a wavelength (532 nm) near the transmission window of bulk gold to measure the nonlinear absorption coefficient of continuous *ca* 50 Å-thick gold films, deposited onto surface-modified quartz substrates. For highly absorbing media such as metals, determination of either the real or imaginary part of the third-order susceptibility requires a measurement of both nonlinear absorption and nonlinear refraction, *ie*, both open- and closed-aperture z scans must be performed.

4.2 Laser Writing on Gold-Containing Hydrocarbon Matrix Films

Conducting metal tracings have been achieved on gold-containing hydrocarbon matrix films deposited on glass and silicon substrates using a technique combining cathodic sputtering with an rf glow discharge: C. Guyard and B. Despax, Laboratoire de Genie Electrique de Toulouse, Université Paul Sabatier, France, *Surf. Coat. Technol.*, 1999, 116-119, 638-642. The metal tracings were formed using laser irradiation of the films, which permitted the generation of localized heating which decomposed the hydrocarbon matrix and agglomerated the gold particles leaving conducting patterns. The authors studied the influence of some interfaces (nickel-chromium and titanium) in order to improve the adhesion and mechanical resistance of the gold line. The acquired gold features were mainly characterized by 'scotch and scratch test' and SEM microscopy.

5 COLLOIDS AND NANOPARTICLES

5.1 *Preparation of Cationic Gold Nanoparticles and their Monolayer Formation on an Anionic Amphiphile Layer*

The reduction of AuCl_4^- by NaBH_4 in the presence of a quaternary ammonium disulfide has been used by T. Yonezawa, S.-Y. Onoue and T. Kunitake, Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka, Japan, *Chem. Lett.*, 1999, (10), 1061-1062, to give an aqueous dispersion of cationic gold particles in nano-dimension. These cationic nanoparticles could be assembled effectively on an anionic amphiphile layer with a close-packed structure.

5.2 *Colloidal Dispersions of Gold Rods*

The colloidal stability of nearly monodisperse aqueous dispersions of rod-shaped gold particles was studied using dynamic light scattering and electrophoresis by B.M.I. Van der Zande, J.K.G. Dhont, M.R. Boehmer and A.P. Philipse of the Van't Hoff Laboratory for Physical and Colloid Chemistry Debye Institute, Utrecht University, The Netherlands, *Langmuir* 2000, 16(2), 459-464. The average length of the gold particles is adjusted between 39 and 730 nm, and the diameter is about 17 nm. The translational diffusion coefficients are consistent with calculations for single non-aggregated rods with a 10-15 nm thick poly(vinylpyrrolidone) (PVP) adsorption layer. This supports the colloidal stability observed. Electrophoresis measurements show that the PVP-stabilized gold rods are negatively charged with a zeta-potential of about -47 mV, which according to interaction calculations is sufficient for double-layer stabilization. Gold-sphere dispersions were investigated for comparison. It turns out that PVP-stabilized gold spheres have a zeta-potential similar to that of the colloidal rods.

6 ELECTROCHEMISTRY

6.1 *Determination of the Kinetic Parameters for the Electrothermal Atomization of Gold with and without Chemical Modifiers*

The effects of various experimental parameters and chemical modifiers on the atomization kinetics of gold in aqueous solution have been investigated by N.S. Thomaidis and E.A. Piperaki, Chemistry Department, Laboratory of Analytical Chemistry, University of Athens, *Spectrochim. Acta*, 1999, 54B, 1303-1320. The dissipation process of the atomized vapour was also studied, and the diffusion parameters were calculated in the absence and in the presence of chemical modifiers. The chemical modifiers studied were ascorbic acid, rhenium, palladium and rhodium. In the absence of chemical modifiers, a two-precursor atomization mechanism was observed in distinctive different temperature regions. When a long pyrolysis step and low masses of gold are

employed, atomization from dispersed particles with low E_a value was observed in the low-temperature region. At high masses of gold, a fractional order atomization from gold agglomerates with high, mass-dependent E_a values approaching the heat of vaporization was observed in the high-temperature region.

6.2 *Gold Plating*

A. Blair, *Plat. Surf. Finish*, 1999, 86(11), 48-50, has reviewed this topic. Gold is a noble metal with very good electrical properties, which makes it the logical choice for electronic interconnection applications. The relatively high price restricted its use to applications where its use was essential, combined with a reduced deposited uniform thickness, and a selective deposition. Gold is applied to surfaces of electronic components by electroplating, thermal decomposition of a screen-printed paste, vacuum deposition or thermal decomposition of an organometallic compound, or by mechanical rolling of inlay material. Electroplating consumes the highest amount of gold among these techniques. The plating solution usually contains $\text{KAu}(\text{CN})_2$ together with substances for the stabilization of the conductivity and buffers. Grain refining additives such as As^{3+} , Tl^{2+} , and Pb^{2+} were added in the plating solutions at low concentrations.

6.3 *Tensile Bond Strength of Electroformed Gold and Four Different Bonding Systems*

The tensile bond strengths of four different resin bonding systems to pure gold, electroformed by three different devices, have been tested before and after storage in water for 150 days at 36°C by H. Lu and F.-J. Faber, Zentrum Zahn-, Mund-, Kieferheilkunde, Universität Köln, Germany, *Dtsch. Zahnärztl. Z.*, 1999, 54(10), 648-650. The results show that irrespective of the electroforming procedure used, the bonding strengths were >20 MPa. No influence of water storage on samples bonded with the Panavia 21 EX system could be detected. The bonding strengths achieved with the Rocatec-System increased, while those of the Silicoater MD and Siloc systems decreased after 150 days.

7 ELECTRONICS

7.1 *Electroless Nickel-Gold Process for Finishing Printed Circuit Boards*

This review, by F. Koster and O. Meisriemel, Forschungs-Entwicklungsabteilung Galvanotechnik, AMI Doduco, Pforzheim, Germany, *Metalloberfläche*, 1999, 53, 17-19, describes two techniques for the surface finishing of printed circuit boards which were developed by AMI Doduco GmbH: electroless nickel/gold plating and electroless tin plating. The electroless plating techniques are compared with other surface-finishing techniques, like hot-air levelling and organic surface protection. The advantages of the electroless plating techniques for the

manufacture of further miniaturized printed circuit boards are summarized. The requirements for printed circuit boards regarding soldering, bonding, and contacting are fulfilled by the electroless coating techniques.

7.2 Process for Flip-Chip Bonding a Semiconductor Die Having Gold Bump Electrodes

P. Poenisch, J.A. Matthews and T. Tsao, Microunit Systems Engineering, Inc., US Patent 5985692 A 991116, have described a method for flip-chip bonding an integrated circuit die to a substrate. The method includes the steps of providing the integrated circuit die with at least one gold bump, forming a barrier layer on the gold bump, forming a bronzing agent on the barrier layer, and providing the substrate with at least one conductive bonding area, which is also covered with gold. The bronzing agent on the integrated circuit die is then aligned on the conductive bonding area, and a compression force is applied to the die and substrate so as to establish contact between the bronzing agent and the conductive bonding area. While maintaining position between the gold bump and conductive bonding area, the structure is alloyed such that the bronzing agent and the gold on the conductive bonding area form an intermetallic compound, thereby forming a bond between the die and the substrate. The barrier layer functions to prevent the bronzing agent from diffusing with the gold bump.

7.3 Contact Physics of Gold Microcontacts for MEMS Switches

D. Hyman and M. Mehregany, Electrical Engineering and Applied Physics Department, Case Western Reserve University, Cleveland, OH, USA, *IEEE Trans. Compon., Packag. Technol.*, 1999, 22(3), 357-364, have published a study of gold metallic contacts describing contact resistance, heat dissipation, and surface damage in the normal-force regime of tens to hundreds of μN , which is typical of the contact forces from microactuation. The purpose of this work is to present the micromechanical switch designer with practical information on gold contact phenomena in this force regime, as most work in micrometallic contacts has focused on contact forces >1 mN. Results indicate that actuation forces of several hundred μN are required for reliable fully metallic contacts, with resistance and current carrying ability primarily dependent on morphological, thermal management, and nm-depth material properties of the contact electrodes.

8 MATERIALS SCIENCE

8.1 Gold Paste for Decorating Glass and Ceramic Articles

K. Ito and K. Sugita, Katsushi, Narumi China Corporation, Japan, WO Patent 9961260 A1 991202, have patented a paste consisting of Au 82.0-99.1, Bi 0.4-5.0, Si 0.2-3.0, and Zr and/or Al 0.3-10.0 wt%. The gold paste can be used for forming a gold decorated part

which generates no electrical conductivity, causes no sparks upon exposure to an electromagnetic wave from a microwave oven, is almost free from suffering damage, has good texture and good gold colouring, and exhibits a feeling of high-class.

8.2 Gold Line Patterning on Glazed Alumina Substrate using Laser Decomposition of an Organometallic Compound

A gold organic compound coated on glazed Al_2O_3 substrates was thermally decomposed by irradiation of a continuous-wave argon laser, and the effects of laser power density and scan speed on formed gold line features, geometry, and electrical resistivity have been studied by E. Makino, A. Nakamura and T. Shibata, Graduate School of Engineering, Hokkaido University, Sapporo, Japan, *Hyomen Gijutsu*, 1999, 50(10), 933-938. Laser irradiation at a power density of 0.9-1.9 kW/cm^2 and a scan rate of 25 $\mu\text{m}/\text{s}$ produced a smooth, flat gold line. Lines were about 0.3 μm thick, whereas the initial compound layer was about 7 μm thick. Electrical resistivity was about 10 $\mu\omega/\text{cm}$, which was a little higher than that of bulk gold, probably due to a small amount of additive impurities for promoting adhesion. When the scan rate was increased and substrates were heated and cooled more quickly, cracks were induced in the glaze layer due to thermal expansion. At power densities higher than 2 kW/cm^2 , severe cracking occurred and gold vaporized.

8.3 Clear Lacquer Coating over Gold Plated Surfaces by Electrophoretic Method for Decorative Applications

A high performance electrophoretic cathodic clear lacquer system has been studied by P. Parthasarathy, Surface Chem Finishers, Bangalore, India, *Bull. Electrochem.*, 1999, 15(5-6), 179-182, in respect of its durability and toughness when coated upon gold-plated surfaces for decorative applications such as watch parts, imitation jewellery, and spectacle frame industries. The mechanism of cathophoretic lacquering and the important parameters for the process control are briefly described.

9 METALLURGY

9.1 Determination of the Critical Point of Gold

K. Boboridis, G. Pottlacher and H. Jager, Institut für Experimentalphysik, Technische Universität Graz, Austria, *Int. J. Thermophys.*, 1999, 20(4), 1289-1297, placed wire-shaped gold specimens in a new, improved high-pressure vessel, which is part of a fast capacitor-discharge circuit and in which static pressures above 600 MPa can be reached with distilled water as the pressure-transmitting medium. The specimens are self-heated resistively by a current pulse. The current through the specimen, the voltage drop across it, and its temperature are recorded as a function of time with submicrosecond resolution. The radial expansion of the specimen is determined with a CCD camera. Experiments are

performed at different pressures. When the critical pressure is exceeded, there is no liquid-gas phase transition; hence, no sudden change in the thermal expansion rate is observed. The results for temperature, pressure, and specific volume at the critical point of gold are as follows: $T_c = 7400 \pm 1100$ K, $p_c = 530 \pm 20$ MPa, and $v_c = 0.13 \pm 0.03 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$.

10 REFINING

10.1 FTIR and EXAFS Investigations of Microstructures of Gold Solvent Extraction. Hydrogen Bonding Between Modifier and Au(CN)₂⁻

G. Ma, W. Yan, T. Hu, J. Chen, C. Yan, H. Gao, J. Wu, and G. Xu, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing, China, *Phys. Chem. Chem. Phys.*, 1999, 1(22), 5215-5221, have studied the structures of the loaded organic phases of three quaternary amine solvent extraction

systems for gold. N263-xylene, N263-tributyl phosphate (TBP)-dodecane and N263-2-ethylhexanol (isooctanol)-dodecane (N263 = trialkylmethylammonium chloride; alkyl = C₈-C₁₀) were studied by FTIR and EXAFS spectroscopy.

According to the EXAFS results, it was found that the gold coordination environment was the same before and after extraction. However, the C≡N stretching vibrations of Au(CN)₂⁻ in the three systems differed greatly.

10.2 The Effect of Galvanic Interaction on the Behaviour of Free and Refractory Gold During Froth Flotation

This paper, by A.J. Teague, J.S.J. Van Deventer and C. Swaminathan, Department of Chemical and Metallurgical Engineering, Royal Melbourne Institute of Technology, Australia, *Int. J. Miner. Process.*, 1999, 57(4), 243-263, provides new information on the effect of galvanic contact between metallic iron and free gold, and gold locked in refractory iron sulfide minerals such as pyrite and pyrrhotite.

BOOK REVIEW

The Chemistry of Organic Derivatives of Gold and Silver

Edited by Saul Patai and Zvi Rappoport. Published by John Wiley and Sons Ltd (Chichester, New, York, Weinheim), 1999, 734 pages, ISBN 0 471 98164 8. Price £300.00

The first chapter of this reference book is entitled 'General and Theoretical Aspects of Gold Compounds' by T. Hoz and H. Busch and includes data on a large number of Au(I) and Au(III) complexes, not all of which fall into a strict definition of what is usually taken to be organic derivatives – but the inclusion of related gold compounds does in fact add further interest to the chapter's content. The second chapter, by R.V. Parish, describes the Mössbauer spectroscopy of gold compounds, a technique used for determining the oxidation state of the gold. There is a chapter midway through the book on 'Synthesis and Uses of Organogold Compounds' by H. Schmidbaur, A. Grohmann, M.E. Olmos

and A. Schier, and this includes sections on the synthesis of σ -bonded organogold complexes, homo- and hetero-metallic gold clusters containing gold-carbon bonds, and the synthesis and properties of alkene, alkyne, carbene and related complexes of gold. Towards the end of the book there are valuable chapters on 'Gold-Thiol Self-Assembled Monolayers' by V. Chechick and C.M. Stirling and 'Medicinal Chemistry of Organogold Compounds' by S.P. Fricker – amongst the applications for monolayers are their use in microelectronics, sensor devices and for anchoring liquid crystals; and gold compounds are used in the treatment of rheumatoid arthritis and have potential for use with some other diseases.

Most of the remaining eleven chapters deal with various other aspects of both gold and silver chemistry, although one of them is solely on the synthesis and uses of organosilver compounds. The topics dealt with jointly include the thermochemistry of the organometallic compounds by J.F. Liebman, J.M. Simões and S.W. Slayden; their NMR and ESR spectroscopy by C.F. Shaw III; their photoelectron spectroscopy by I. Novak;

analytical aspects by J. Zabicky and S. Grinberg; their electrochemistry by A.A. Mohamed, A.E. Bruce and M.R.M. Bruce; their organic photochemistry by W.M. Horspool; the pyrolysis of organic derivatives by R.A. Aitken; their acidity, basicity and hydrogen bonds by T.M. Klapötke; their rearrangements by S. Wang and J.P. Fackler Jr; and the synthesis of isotopically labelled compounds by M. Zielinski, M. Kanska and R. Kanski.

Overall the book demonstrates that a wide range of different types of organic derivatives of gold and silver can be prepared and it is clear that further investigations will continue to enlarge the number and variety of such compounds available. There is a wealth of detailed information in this book with many useful tables, formulae, equations, graphs, and references; and there are good author and subject indices. This publication is to be recommended as a reference book for all those interested in gold chemistry, both in academia and industrial circles.

David Thompson