

Highlights from Recent Literature

1 Analytical

1.1 New Technique to Observe a Time Evolution of a Gold Colloidal System In Nanochannels of MCM-41 Mesoporous Silica Using UV-Vis Spectroscopy

The authors report a possible application of UV-visible spectroscopy technique to study a time evolution of a Gold colloidal system in restricted geometry. H Tanaka, M McIntire, R Castillo-Garza from the Physics Department, University of California, Riverside, USA, *Microporous and Mesoporous Materials* 2005, **85(3)**, 374. The authors used a unique property of temperature and size dependence of the Gold surface plasmon band. The absorption spectra show the slow and faster-nucleation of the Gold atoms in the solution of H₂AuCl₄, Na citrate and MCM-41. The interfacial undercooling was estd. by comparing the absorption spectra of the bulk solution to the pore solution. Result is consistent with a Gibbs-Thomson const. $K = 54 \pm 2$ degree. nm, which is in good agreement with the values given by the previous experiments

1.2 Multilayer Approach to the Quantitative Analysis of X-Ray Photoelectron Spectroscopy Results: Applications to Ultrathin SiO₂ on Si and to Self-Assembled Monolayers on Gold

XPS is widely applied for the chemical characterization of surfaces and multilayers of thin films. To obtain quant. results, XPS peak areas generally are divided by sensitivity factors and normalized to 100 at% to obtain so-called raw concentrations. C van der Marel, M Yildirim, H Stapert from the Philips Research Laboratories, Eindhoven, NL, *Journal of Vacuum Science & Technology, A: Vacuum, Surfaces, and Films*, 2005, **23(5)**, 1456. For homogeneous materials, materials with randomly distributed atoms within the analyzed surface layer, these concentrations may be a useful quantity. Yet, for a material consisting of a substrate on top of which a number of chemical different layers are present, the raw concentrations depend on measuring details like the takeoff angle during the XPS analyses and clearly are not a satisfactory way to describe the sample.

The main purpose of this article is to present a calcination method that converts raw concentrations into more meaningful quantities. The method is applicable to a restricted but technology relevant class of samples: substrates on top of which one or more homogeneous layers are present. Examples are: gate dielects. on Si or GaAs, self-assembling monolayers on a metallic substrate, thin oxide films on metals with an org. contamination on top. The

method is based upon std. exponential attenuation of the photoelectron intensity as a function of travelled distance. For each element or chemical state in the system it has to be known to which layer(s) it belongs. Sensitivity factors are cor. for matrix effects and for intrinsic excitations. Starting from the raw concentrations, the method calculates in a self-consistent way the composition of all layers in the system and the thickness of each layer. Only one measurement at one measuring angle is required to obtain these results. To obtain insight into the accuracy of the calcination method, XPS results obtained on ultrathin SiO₂ layers on Si that were slightly contaminated with hydrocarbons were analyzed with the method. The obtained thicknesses were in good agreement with values for the thickness of the SiO₂ layer and the org. surface contamination as obtained by other methods. Consistent values were also obtained for the concentration ratio O/Si in the SiO₂ layers.

The calcination method also was verified for three types of self-assembled monolayers (SAM layers) on gold. Layers of C18 (octadecane-thiol) and of EG4 (a mercaptoalkyloligo-ethyleneglycol) deposited from solns. with different concentrations were examined Also, SAM layers deposited from mixtures with mols. with different chain lengths, mercapto-undecanol (MUO), and a biotinylated oligo-ethyleneglycol-alkyl thiol (BAT), were studied. The model anal. provided the thickness of the org. layers, the concentrations of the components in the layers, and the coverage of the gold with sulfur (in atoms/cm²). Rutherford backscattering spectrometry (RBS) was applied to det. (in an independent way) the amt. of sulfur at the gold surface. The RBS results correlated well with the XPS data. The obtained values for the concentration ratios of the SAM layers were in agreement with the theor. expected values. It is essential to model the mixtures of MUO and BAT as a three-layer system (gold substrate, aliph. interlayer, and top layer containing the ethylene oxide groups) to obtain agreement.

2 Catalysis

2.1 Tin Dioxide Supported Nanometric Gold: Synthesis, Characterization, and Low-temperature Catalytic Oxidation of CO

The Au/SnO₂ catalysts were prepared by a co-precipitation method. The structure of the sample treated at different temperatures was investigated by means of HRTEM and XPS. S Wang, J Huang, L Geng, B Zhu, X Wang, Z Shihua; W Huang, from the Department of Chemistry, NanKai University, Tianjin, Peop. Rep. China *Catalysis Letters* 2006, **108(1-2)**, 97. The structure of the samples after various treatments and their activity in the CO oxidation were compared. The results showed that the catalytic behaviour was related to the particle size of gold and surface oxygen species on the support. Highly dispersed gold particles and adsorbed surface oxygens and hydroxyl groups on the support were responsible for the high catalytic activity of the Au/SnO₂ catalyst.

2.2 Preparation and Catalytic Properties of Nanosized Gold Catalysts

A review; nanosized gold particles have been well known to possess extremely high activity for CO oxidation Y Chen, from the Department of Chemical and Materials Engineering, National Central University, Jhong-Li City, Taiwan, *Shiyou Jikan* 2006, **42(1)**, 13. The suitable supports are the metal oxides that can be partially reduced, such as TiO_2 , Fe_2O_3 , Co_3O_4 , etc. Gold particle size and its support have great effect on the catalytic properties of gold in various redox applications. However, the active sites and reaction mechanism are still in debate. This report reviews the preparation, characterization and catalytic applications of nanosized gold catalysts for various reactions.

2.3 Application of Gold Catalyst for Mercury Oxidation by Chlorine

This paper discusses a recent study of mercury catalytic oxidation by chlorinating reagents. Gold was chosen as the catalyst because of its reluctance to chemisorb some gases such as O_2 , NO , H_2O , and SO_2 . Y Zhao, M Mann, J Pavlish, B Mibeck, G Dunham, E Olson from the Chemical Engineering Department, University of North Dakota, USA, *Environmental Science and Technology* 2006, **40(5)**, 1603. This property, as demonstrated in this study, is instrumental to mercury oxidation by circumventing some undesired inhibitory reactions such as $\text{OH} + \text{NO} + \text{M}$. $\text{HONO} + \text{M}$ and $\text{OH} + \text{SO}_2 + \text{M}$. $\text{HOSO}_2 + \text{M}$, which were recognized under homogeneous situations at high temperatures in comparison to Cl_2 , HCl showed weak oxidizing capability but appreciable inhibition in mercury oxidation by Cl_2 , probably through the competition of active sites with Cl_2 . Overall, the mercury catalytic oxidation by Cl_2 on gold catalyst surfaces was viable, reaching 40-60% in this study under temperatures of 448-498 K, where the thermal decomposition of formed Hg^{2+} was effectively avoided.

2.4 Gold/Ferric Oxide Catalyst Assistants for Hydrogen-Rich Water-Gas Shift Reaction and its Additive Process

The gold/ferric oxide catalyst assistants comprise Al_2O_3 , ZrO_2 , and Nb_2O_5 at molar ratio of 0-0.6:0-0.6:0.1-0.6. Q Zheng, F Zhang, X Lin, J Li, T Chen, K Wei from the Fuzhou University, Peop. Rep. China, Patent application number CN 1748863, A, Mar 2006. The molar ratio of Gold: Fe_2O_3 : composite assistants is 1: 10-35:2-8. The catalyst is prepared by adding Nb_2O_5 powder to deionized water, ultrasonic treating, slowly dropping the mixt. solution of HAuCl_4 , $\text{Fe}(\text{NO}_3)_3$, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3$, and K_2CO_3 to Nb_2O_5 solution, ageing, washing, drying, roasting to obtain $\text{Au}/\text{Fe}_2\text{O}_3\text{-xAl}_2\text{O}_3\text{-yZrO}_2\text{-zNb}_2\text{O}_5$ catalyst.

2.5 Metal-Support and Preparation Influence on the Structural and Electronic Properties of Gold Catalysts

Nanostructured gold catalysts supported on CeO_2 and SiO_2

were prepared by the deposition-precipitation (DP) and the solvated metal atom dispersion (SMAD) techniques. M Casaletto, A Longo, A Venezia, A Martorana, A Prestianni, Antonio from the Consiglio Nazionale delle Ricerche, Istituto per lo Studio dei Materiali Nanostrutturati, Italy, *Applied Catalysis, A: General* 2006, **302(2)**, 309. The structural and electronic properties of the catalysts were investigated by X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS) and XPS. Gold was found as small metal nanoparticles (cluster size .apprx.2 nm) in the SMAD-prepared samples and in ionic state in the DP catalysts. The catalytic activity of the samples was tested in the reaction of low temperature CO oxidation. Gold nanosized particles in a pure metallic state exhibited a worse catalytic performance, both on ceria and silica. The presence of non-metallic Gold species seems to be the main requisite for the achievement of the highest CO conversion at the lowest temperature. The higher activity of the Au/CeO_2 (DP) sample with respect to the Au/SiO_2 (DP) catalyst can be ascribed to a better stabilization of the Au^{+1} ions, probably as AuO^- species, by the cerium oxide.

2.6 CO Oxidation over Gold-Supported Catalysts-Coated Ceramic Foams prepared From Stainless Steel Wastes

A multilayer replication method has been used to prepare reticulated ceramic foams from steel making wastes. M Dominguez, M Sanchez, M Centeno, M Montes, J Odriozola from the Instituto de Ciencia de Materiales de Sevilla, Universidad de Sevilla, Seville, Spain *Applied Catalysis, A: General* 2006, **302(1)**, 96. These ceramic sponges have been used as support for prepreg. catalytic devices, after deposition of catalytic coatings of Al_2O_3 -gold and CeO_2 -gold. The obtained catalytic systems are active to the CO oxidation reaction and may be stable with no loss of activity as far as the amt. of residual water in the gaseous stream remains const. In the absence of water and reaction temperatures of 150 .degree.C the catalytic monolith shows 100% conversion of CO at least for 54 h. The metal content of the wastes has a pos. influence in the activity of the foams. The best catalytic results are obtained for the Au/CeO_2 -supported foams where the oxidation capability of gold atoms is combined with the redox properties of the ceria phase.

2.7 State of Gold on an $\text{Au}/\text{Al}_2\text{O}_3$ Catalyst Subjected to Different Pre-Treatments: an FTIR Study

An $\text{Au}/\text{Al}_2\text{O}_3$ sample was prepared by deposition-precipitation and characterized by different techniques (XRD, TEM, FTIR spectroscopy of adsorbed CO and catalytic test). IR spectroscopy of adsorbed CO on a sample evacuated at ambient temperature reveals no gold sites. T Venkov, H Klimev, M Centeno, J Odriozola, K Hadjiivanov from the Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria *Catalysis Communications* 2006, **7(5)**, 308. The results were explained by the fact that gold on this sample was present as Au_3^+

cations and these sites (as well as the Al_3+ sites) were blocked by water. When the sample was activated at 473 K, CO adsorption at 100 K produced: (i) carbonyl bands assocd. with the support and (ii) a band at 2167 cm^{-1} , stable towards evacuation and assigned to Au^+-CO species. Evacuation of the sample at 573 K led to auto-reduction of the Au^+ sites. Subsequent CO adsorption resulted in formation of two types of AuO-CO species (bands at 2112 and 2105 cm^{-1}). Only one kind of AuO sites (resp. carbonyl band at 2105 cm^{-1}) were detected with samples activated at 673 K. Re-oxidation of the sample at 673 K in O_2 atmosphere resulted in oxidation of all accessible metallic gold and appearance of (i) a small amt. of isolated Au^+ sites (resp. carbonyl band at 2175 cm^{-1}) and (ii) another kind of sites (resp. carbonyl band at 2139 cm^{-1} , disappearing during evacuation) assocd. with Au^+ cations on the surface of the metal particles. Both kinds of cations were stable at 573 K but gold cations were auto-reduced at 673 K. Comparison of the FTIR results with catalytic studies allowed some conclusions on the nature of the active sites in the CO oxidation reaction.

2.8 Low Temperature Oxidation of CO over Cluster-Derived Platinum-Gold Catalysts

The structural and catalytic properties of SiO_2 - and TiO_2 -supported Pt-Au bimetallic catalysts prepared by coimpregnation were compared with those of samples of similar composition synthesized from a $Pt_2Au_4(C.tplbond.CBut)_8$ cluster precursor. L Ortiz-Soto, O Alexeev, M Amiridis, from the Department of Chemical Engineering, University of South Carolina, USA, *Langmuir* 2006, **22(7)**, 3112. The smallest metal particles were formed when the bimetallic cluster was used as a precursor and TiO_2 as the support. FTIR data indicate that highly dispersed Gold crystallites in these samples, presumably located in close proximity to Pt, are capable of linearly coordinating CO mols. with a characteristic vibration observed at 2111 cm^{-1} . The cluster-derived Pt_2Au_4/TiO_2 samples were the only ones exhibiting low-temperature CO oxidation activity, indicating that both the high dispersion of Gold and the nature of the support are important factors affecting the catalytic activity for this system.

2.9 Relation between Nanoscale Gold Particle Structure and Activity for CO Oxidation on Supported Gold Catalysts

The CO oxidation activity of Au/TiO_2 , $Au/MgAl_2O_4$, and Au/Al_2O_3 catalysts, all containing approx. 4 wt% Au, was compared with the detailed size and shape of the gold particles in these supported catalysts. T Janssens, A Carlsson, A Puig-Molina, B Clausen from the Haldor Topsoe A/S, Lyngby, Denmark, *Journal of Catalysis* 2006, **240(2)**, 108. Based on the indications that CO oxidation on Gold catalysts requires low-coordinated Gold atoms, the turnover frequency per Au atom located at the corners of the Gold particles was calcd. A value of approx. 0.8 s^{-1} for both the Au/TiO_2 and the $Au/MgAl_2O_4$ catalyst was found. This represents an example

in which the difference in catalytic activity of a Gold catalyst with a reducible and irreducible support can be explained by a difference in Gold particle geometry only, without the need to invoke other support-induced effects. The turnover frequency per corner Gold atom in the Au/Al_2O_3 catalyst is approx. 4 times lower, indicating that other support-induced effects not related to the reducibility may play a role in this case.

2.10 The Effect of Gold Particle Size on Au-Au Bond Length and Reactivity toward Oxygen in Supported Catalysts

Gold catalysts with different metallic particle sizes and supported on silica, alumina, titania, zirconia, ceria, and niobia were prepared, and the reduced catalysts were characterized by EXAFS spectroscopy. J Miller, A Kropf, Y Zha, J Regalbuto, L Delannoy, C Louis, E Bus, J Van Bokhoven from the CS BP Research Center, Naperville, IL, 60565-8406, USA *SO Journal of Catalysis* (2006), **240(2)**, 222. As the Au-Au coordination number decreased, the interat. bond length decreased. The Au-Au bond length contraction appears to be independent of the support type. A correlation between the dispersion of Pt catalysts detected by hydrogen chemisorption and the EXAFS Pt-Pt coordination number was established and used to det. the dispersion of fully reduced Gold catalysts. In addition, the Gold particle size was established using a literature correlation of the EXAFS coordination number. For particles larger than about 40 \AA ., there was little change in the metallic bond length, whereas in catalysts with gold particles smaller than 30 \AA ., the Au-Au distance decreased with decreasing particle size, with a max. contraction of about 0.15 \AA .. Decreasing particle size also brought a decrease in the intensity of the white line of the XANES spectrum. Both the decrease in bond distance and white line intensity were consistent with an increase in the d-electron d. of Gold atoms in very small particles. Gold particles smaller than about 30 \AA .. were also reactive to air, leading to oxidation of up to 15% of the atoms of the gold particles, depending on the size; larger particles were not oxidized. These oxidized Gold atoms in small particles are suggested to be active for CO oxidation.

2.11 Gold Catalysts Supported on Mesoporous Zirconia for Low-Temperature Water-Gas Shift Reaction

Mesoporous ZrO_2 with high surface area and uniform pore size distribution, synthesized by surfactant templating through a neutral $[C_{13}(EO)_6-Zr(OC_3H_7)_4]$ assembly pathway, was used as a support of gold catalysts prepared by deposition-precipitation method. V Idakiev, T Tabakova, A Naydenov, Z Yuan and B Su from the Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, Bulgaria, *Applied Catalysis, B: Environmental* 2006, **63(3-4)**, 178. The supports and the catalysts were characterized by powder X-ray diffraction, scanning and transmission electron microscopy,

N₂ adsorption anal., temperature programmed reduction and desorption. The catalytic activity of gold supported on mesoporous zirconia was evaluated in water-gas shift (WGS) reaction at wide temperature range (140-300 .degree.C) and at different space velocities and H₂O/CO ratios. The catalytic behaviour and the reasons for a reversible deactivation of Au/mesoporous zirconia catalysts were studied. The influence of gold content and particle size on the catalytic performance was investigated. The WGS activity of the new Au/mesoporous zirconia catalyst was compared to the ref. Au/TiO₂ type A (World Gold Council), revealing significantly higher catalytic activity of Au/mesoporous zirconia catalyst. It is found that the mesoporous zirconia is a very efficient support of gold-based catalyst for the WGS reaction.

2.12 Hydrogen Production by Partial Oxidation of Methanol Over Gold Catalysts Supported on TiO₂-MOx (M=Fe, Co, Zn) Composite Oxides

Hydrogen prodn. by partial oxidation of methanol (POM) has been investigated over Au/TiO₂-MOx (M = Fe, Co and Zn) catalysts in the temperature range of 423-548 K. F Chang, H Yu, L Roselin, Y Selva; O-Chang; T Cheng CS Department of Chemical and Materials Engineering, National Central University, Taiwan, *Applied Catalysis, A: General* 2006, **302(2)**, 157. The catalysts were characterized by ICP, BET, XRD, TEM and XPS analyses. The XRD anal. confirms the desired structure and phase purity of Fe₂O₃, Co₃O₄, ZnO and TiO₂ samples and the presence of gold in these materials. TEM observations show that the gold particles are stabilized against sintering during calcination and after catalytic tests, in the presence of MOx in Au/TiO₂ catalysts. The XPS anal. detects the existence of metallic gold (Au⁰), non-metallic gold (Au. δ +) and Au₂O₃ species in the uncalcined catalyst samples both before and after reaction, and the existence of metallic gold (Au⁰) and Au₂O₃ species in the calcined catalyst samples. The catalytic activity of Au/TiO₂ for the POM reaction to produce hydrogen is improved by using addnl. support (MOx), probably due to a combination of factors, such as increasing the mobility of the lattice oxygen, maintaining the adequate oxidation state of the active gold particles and controlling the sintering of gold particles. Therefore, MOx can act as a structural promoter and/or as a cocatalyst. The most active catalyst is Au/TiO₂-Fe₂O₃. Although Fe₂O₃ in Au/TiO₂ catalysts increases the catalytic activity, a surfeit of Fe₂O₃ lowers the activity for hydrogen formation. Calcination of the catalyst samples results in a decrease of the catalytic activity. The sample dried at 373 K in air exhibits the highest activity for POM reaction. Both methanol conversion and hydrogen selectivity are increased with increase in reaction temperature. The reaction pathway is suggested to consist of consecutive methanol combustion, partial oxidation, steam reforming and decomposition CO produced by methanol decomposition and/or by reverse water gas shift is subsequently transformed into CO₂ and H₂ by the water gas shift and/or CO oxidation.

2.13 CO Oxidation Activity of Gold Catalysts Supported on Various Oxides and Their Improvement by Inclusion of an Iron Component

A number of oxide-supported gold catalysts have been prepared by deposition-precipitation, with variation of the pH over a wide range, the optimum pH for high activity being 9 for TiO₂, 7.5 for Fe₂O₃, and 7 for SnO₂ and CeO₂. F Moreau, G Bond from the Institute for Materials Research, University of Salford, Salford, Greater Manchester, UK, *Catalysis Today* 2006, **114(4)**, 362. Whereas the activity shown by Au/TiO₂ and Au/Fe₂O₃ decreased linearly with time, Au/CeO₂ and Au/SnO₂ underwent an initial major deactivation. Addition of iron in the preparation lowered the rate of deactivation when TiO₂, SnO₂ and CeO₂ were used as supports, and imparted activity when as with Bi₂O₃ it was previously lacking. XPS revealed the existence of a broad multi-state iron-containing region, and TEM and STEM/EDX indicated that small gold particles (1.5-4 nm) were partly in contact with it. Improved stability is therefore due to gold particles being in contact with an iron phase such as FeO(OH); calcination removed the stabilization.

2.14 Total Oxidation of Propene and Propane over Gold-Copper Oxide on Alumina Catalysts

Propene and propane oxidation to CO₂ and water over Au/Al₂O₃ and two Au/CuO/Al₂O₃ (4 wt. percent Gold and 7.4 wt. percent Au) catalysts was studied and compared with the catalytic behaviour of Au/Co₃O₄/Al₂O₃ (4.1 wt. percent Au) and Pt/Al₂O₃ (4.8 wt. percent Pt) catalysts. A Gluhoi, N Bogdanchikova, B Nieuwenhuys from the Department of Heterogeneous Catalysis and Surface Chemistry, Leiden Institute of Chemistry, Leiden University, Netherlands, *Catalysis Today* 2006, **113(3-4)**, 178. Characterization methods (x-ray diffraction, high resolution TEM, temperature-programmed reduction, diffuse reflectance UV-VIS spectroscopy) showed the presence of metallic Au, along with a highly dispersed CuO (6 wt. percent CuO), or more cryst. CuO phase (12 wt. percent CuO). A higher CuO load did not significantly affect catalyst performance for propene oxidation; Gold load appeared to be more important. A 7.4Au/CuO/Al₂O₃ was almost as active as Pt/Al₂O₃; Au/Co₃O₄/Al₂O₃ performed less than any CuO-containing, Au-based catalysts. Light-off temperature for propane oxidation was significantly higher than for propene. For this reaction, the particle size effect appeared to prevail over the Gold load effect. The most active catalysts were 4Au/CuO/Al₂O₃ (gold particles <3 nm) and 4Au/Co₃O₄/Al₂O₃ (gold particles <5 nm).

2.15 Application of Alumina Supported Gold-Based Catalysts in Total Oxidation of CO and Light Hydrocarbons Mixture

Al₂O₃-supported Gold nano-particles were produced using an anion exchange method and NH₃ washing procedure. S Ivanova, C Petit, V Pitchon from the Surfaces et Procédés

pour la Catalyse, Laboratoire des Materiaux, Strasbourg, France, *Catalysis Today* 2006, **113(3-4)**, 182. Catalysts were tested for total oxidation of a mixt. of light hydrocarbons and CO to assess the possibility of their application to reduce of cold start exhaust emissions. Results were promising according to the observed temperature range for unsatd. hydrocarbon oxidation. Acetylene results confirmed the difference of oxidation of this hydrocarbon over Gold catalysts. An ageing procedure was also examined, the procedure did not affect catalyst behaviour vs. hydrocarbon oxidation.

2.16 Stabilization of Cationic Gold Species on Au/CeO₂ Catalysts under Working Conditions

IR spectroscopy of CO adsorption at low temperature has shown the presence of oxidized gold species (Au⁺ and Au³⁺) on nanocryst. Au/CeO₂ catalyst. P Concepcion, S Carretin, A Corma from the Instituto de Tecnologia Quimica, Universidad Politecnica de Valencia, Spain, *Applied Catalysis, A: General* 2006, **307(1)**, 42. This species are quite stable even under reduction conditions like the CO oxidation reaction. The concentration of this species decrease by increasing the pre-treatment temperature of the Au/CeO₂ catalyst which is in accordance with a decrease in the catalytic activity of the sample. In accordance oxidized gold species are involved in the catalytic activity of Au/CeO₂ catalyst for CO oxidation although the participation of metallic sites cannot be excluded.

2.17 Synthesis of Supported Gold Catalysts for Selective Oxidation Of Cyclohexane with Air

The selective oxidation of cyclohexane with air to produce cyclohexanol and cyclohexanone without using any additional organic solvent or activator was investigated over silica gel supported nano-gold catalysts with a conversion of 10.8% and a selectivity of 90.8%. H Xiong, F Shi, JJ Peng, YQ Deng from the Centre for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, Peop. Rep. China, *Fenzi Cuihua* 2005, **19(3)**, 204. The gold content of the catalyst is only 0.032%, and its TOF number reached to 5.2.times.10⁴. The structure properties of the catalysts were characterized by AES, XRD, BET and TEM.

2.18 Gold Catalysis

A review; on the study of Gold catalysis. Gold can be highly dispersed on metal oxides by coprecipitation and deposition-precipitation methods to form Au- supported catalysts. Y Tao, Z Gao from the Shanghai Research Institute of Chemical Industry Science and Technology Information, Shanghai, 200020, Peop. Rep. China, *Huaxue Shijie* 2005, **46(2)**, 114. The supported catalysts with Gold particles <5 nm were highly active for many chemical reactions. The gold-supported catalysts were successfully used for catalysis of CO oxidation, acetylene hydrochlorination, crotonaldehyde selective hydrogenation, water-gas conversion reaction, and NOx reduction.

3 Chemistry

3.1 Optimization of the Dispersion of Gold and Platinum Nanoparticles on Indium Tin Oxide for the Electrocatalytic Oxidation of Cysteine and Arsenite

Gold and Pt nanoparticles (NPs) were prepared by chemical reduction of the corresponding metal complex bound by ion-exchange to generation-4 poly(amidoamine) dendrimers (PAMAM). D Ca, L Sun, J Cox from the Department of Chemistry and Biochemistry, Miami University Center for Nanotechnology, Hughes Laboratory, Miami University, Oxford, OH, USA, *Electrochimica Acta* 2006, **51(11)**, 2188. Arrays of the NPs on In Sn oxide (ITO) electrodes were formed by adsorbing a monolayer comprising a controlled ratio of NP-PAMAM to PAMAM on ITO that was modified with (3-aminopropyl)triethoxysilane; subsequently, the org. components were thermally destroyed. Varying the above-defined ratio resulted in a commensurate change of the d. of the NPs on the surface. Using an electrode modified in a solution with a mole fraction of Au-PAMAM (relative to total of Au-PAMAM and PAMAM) of 0.06, which gave NPs sepd. by 200 nm, the current for the catalytic oxidation of cysteine reached a value that did not increase when more nanoparticles were present. The analogous experiment on the oxidation of AsIII with PtNPs as the catalyst was optimized at a mole fraction of 0.2. Calculations assuming hemispherical diffusion suggested that the diffusion domains during cyclic voltammetry at 5 mV s⁻¹ were less than the distance between the NPs.

3.2 Theoretical Study of Co Adsorption on Gold/Alumina Substrates

Aiming to understand the role of the substrate in the adsorption of CO on Gold clusters supported on metal-oxides, E Fernandez, L Balbas, from the Departamento de Fisica Teorica Atomica y Optica, Universidad de Valladolid, Valladolid, Spain, *Journal of Physical Chemistry B* 2006, **110(21)**, 10449, have started a study of that process on 2 different Al₂O₃ substrates: an amorphous-like fully relaxed stoichiometric (Al₂O₃)₂₀ cluster and the Al terminated (0001) surface of .alpha.-(Al₂O₃) crystal. We present first principles calculations for the adsorption of one Gold atom on both Al₂O₃ substrate and the adsorption of Au₈ on (Al₂O₃)₂₀. We study the CO adsorption on the min. energy structure of these 3 different Au/Al₂O₃ systems. A single Gold adsorbs preferably on top of an Al atom with low coordination, the binding energy being higher in the case of Au/(Al₂O₃)₂₀. CO absorbs preferably on top of the Gold atom, but in the case of Au/(Al₂O₃)₂₀, Gold forms a bridge with the Al and O substrate atoms after CO adsorption. The authors find other stable sites for CO adsorption on the cluster but not on the surface. The Gold activity toward CO may be larger for the amorphous cluster than for the crystal surface substrate. For the most stable Au₈/(Al₂O₃)₂₀ configuration, 2 Gold atoms bind to Al and a O atoms respectively and CO adsorbs on top

of the Gold which binds to the Al atom. We find other CO adsorption sites on supported Au₈ which are not stable for the free Au₈ cluster.

4 Electrochemistry

4.1 Electrochemical Oxidation of Ferulic Acid in Aqueous Solutions at Gold Oxide and Lead Dioxide Electrodes

A kinetic study of the electrochemical oxidation of ferulic acid (3-methoxy-4-hydroxycinnamic acid) by direct electron transfer at treated Gold disk was combined with results of electrolyzes to produce total degradation into CO₂ and H₂O at Ta/PbO₂ anode. S Trabelsi, T Kallel, T Belhadj, R Abdelhedi from the Electrochimie et Environnement, Ecole Nationale d'Ingenieurs de Sfax, Tunisia, *Journal of Applied Electrochemistry* 2005, **35(10)**, 967. The oxidation of ferulic acid at Gold electrode was studied by cyclic voltammetry. At low concentration, ferulic acid shows one irreversible anodic peak. The peak current shows adsorption characteristics. For ferulic acid concentrations >0.02 mmol dm⁻³, the voltammogram shows 2 anodic peaks. The effect of experimental conditions on the ratio of these 2 peaks was examined. The proposed mechanism is based on the hypothesis of 2-electron oxidation of ferulic acid mol. involving a 3 intermediate cation mesomers. Hydrolysis of these mesomers gives caffeic acid, methoxyhydroquinone and 3,4-dihydroxy-5-methoxycinnamic acid. Then ferulic acid was quantitatively oxidized by electrolysis on lead dioxide to produce, via intermediate aromatic compounds, maleic acid, oxalic acid and formic acid whose oxidation leads to CO₂.

4.2 Synthesis, Structures, and Electrochemistry of Gold(III) Ethylenediamine Complexes and Interactions with Guanosine 5'-Monophosphate

[Au(en)Cl₂]Cl.cntdot.2H₂O was synthesized, and its structure was solved for the first time by the single-crystal x-ray diffraction method. S Zhu, W Gorski, D Powell, J Walmsley from the Department of Chemistry, University of Texas at San Antonio, San Antonio, USA, *Inorganic Chemistry* 2006, **45(6)**, 2688. The complex has square-planar geometry about Au(III), and the anionic Cl⁻ is located in the apical position and at a distance of 3.3033(10) .ANG. compared to 2.2811(9) and 2.2836(11) .ANG. for the coordinated Cl⁻. [Au(en)Cl₂]Cl.cntdot.2H₂O belongs to the space group Pbc_a with a 11.5610(15), b 12.6399(17), c 13.2156(17) .ANG., and Z = 8. Bond lengths of Au-N are 2.03 .ANG.. [Au(en)Cl₂]Cl.cntdot.2H₂O is less thermally stable than [Au(en)₂]Cl₃ because of the replacement of two Cl ligands by a 2nd en ligand in the latter. Cyclic voltammetry shows that the formal potential of Au(III)/Au(0) becomes more neg. in the series [AuCl₄]⁻, [Au(en)Cl₂]⁺, and [Au(en)₂]₃⁺. 1H, 13C, and 31P NMR reveal that in an aqueous solution [Au(en)Cl₂]⁺ bonds to 5'-GMP (1:1 mol ratio), via N(7), although the stability is not

very great. NMR data also indicate that N(7)-O(6) or N(7)-phosphate 5'-GMP chelation, as found in some Au(III) nucleotide complexes, is not present. The Au(III) complex undergoes hydrolysis at pH >2.5-3.0 and, therefore, N1 coordination to 5'-GMP is not observed. No direct coordination between 5'-GMP and [Au(en)₂]Cl₃ is observed.

4.3 Comparative Electrochemistry and Electrocatalytic Activities of Cobalt, Iron and Manganese Phthalocyanine Complexes Axially Co-Ordinated to Mercaptopyridine Self-Assembled Monolayer at Gold Electrodes

Comparative surface electrochemical and electrocatalytic properties of solid ultrathin monolayer films of metallophthalocyanine (MPc) complexes of Co (CoPc), Fe (FePc) and Mn (MnPc) self-immobilized, via axial ligation reaction, onto preformed 4-mercaptopyridine self-assembled monolayers (SAMs) on Gold electrodes were described. K Ozoemena, T Nyokong from the Chemistry Department, Rhodes University, Grahamstown, S. Africa *Electrochimica Acta* 2006, **51(13)**, 2669. Surface electrochemical parameters of the modified electrodes showed that these MPc-SAMs are densely packed with flat orientations. The electrochemical, electrocatalytic and stability properties of these MPc complexes follow this order: FePc > MnPc > CoPc. This finding is remarkable as probably the success of using this method of self-assembling of MPc onto Gold electrode is largely dependent on the bond distance between the pyridine linker and the central metal of the MPc; the shorter the distance, the faster the coordination and the better the electrocatalytic properties towards L-cysteine and thiocyanate. Thus, the superiority of FePc-based SAM over those of the MnPc and CoPc, probably is the result of the more favorable axial coordination properties of FePc with pyridine (i.e. shorter Fe-N(pyridine)) bond length.

4.4 Electrochemical Capacitance of Mesoporous Gold

The surfaces of nanoscale Gold particles and components are oxide-free under normal ambient conditions. M Cortie, A Maarooof, G Smith from the Institute for Nanoscale Technology, University of Technology Sydney, Broadway, Australia, *Gold Bulletin (London, United Kingdom)* 2005, **38(1)**, 14. This unusual attribute permits the exploration of microstructures and functionalities that would not be feasible for less noble metals. Here the authors consider the electrochemical properties of mesoporous Gold sponges, prepared by de-alloying an AuAl₂ precursor. The sponges have a high sp. surface area, with an average pore diameter of 12 nm, but are prone to sinter. They may be prepared in bulk, or, more usefully, as coatings. Their electrochemical capacitance divided by their nominal surface area is high and, at a cell voltage of 0.6 V, reaches 100 mF/cm² for bulk samples and 2 mF/cm² for coatings. This is up to a thousand times greater than the 50 to 100 .mu.F/cm₂ exhibited by a planar Gold surface.

5 Electronics and Sensors

5.1 Well-Dispersed Gold Nanowire Suspension for Assembly Application

A method for fabricating well-dispersed nanowire suspension was demonstrated. C Xu, L Zhang, H Zhang, H Li from the College of Chemistry and Chemical Engineering, Lanzhou University, Peop. Rep. China, *Applied Surface Science* 2005, **252(4)**, 1182. Thin Gold nanowires were prepared by template synthesis, and then functionalized with sulfonate group-terminated thiols before suspended in different solvents. The degree of aggregation of the obtained suspension was evaluated with transmission electron microscopy (TEM) and UV-vis spectroscopy. The degree of aggregation was predominated by the solvents, and the best degree of dispersion was obtained when iso-Pr alc. (IPA) was used as the solvent. The Gold nanowires from the suspension can be selectively assembled onto chemical patterned substrates. This well-dispersed nanowire suspension is potentially useful for fabricating novel nanodevices.

5.2 Gold-Based Screen-Printed Sensor for Detection of Trace Lead

The application of a novel gold-based screen-printed sensor to lead detection is described. S Laschi, I Palchetti, M Mascini from the Dipartimento di Chimica, Polo Scientifico, Università di Firenze, Italy, *Sensors and Actuators, B: Chemical* 2006, **B114(1)**, 460. The sensor consists of a screen-printed three electrode cell: a gold working electrode, a silver pseudo-ref. electrode and a graphite counter electrode. It is used in combination with square wave anodic stripping voltammetry (SWASV). Sensor characterization experiments as well as the optimization of the anal. procedure are reported. The optimized parameters allow the detection of micrograms per L of lead concentrations following short anal. time (detection limit 0.5 $\mu\text{g L}^{-1}$ at 120 s deposition). Measurements of other metals such as copper, cadmium and mercury are reported.

5.3 Effects of Gold on the Properties of Tin-Antimony Solder in Flip-Chip-Pin-Grid-Array (FCPGA) Packages

The phys. characteristics of tin-antimony solder used in FCPGA semiconductor packages change with the diffusion of gold from the gold plated layers in the solder pads or pin. S Kee, L Hussain, K Nair, Y Khong, D Kumar, P Chandran from the School of Materials & Mineral Resources Engineering, Univ Science Malaysia. *Journal of Microelectronics and Electronic Packaging* 2005, **2(4)**, 281. This must be considered in the setting of parameters for subsequent re-flow processes and also possible impact on the quality and reliability of the solder joints. This paper describes phys. and micro-structural properties of the 95Sn₅Sb parent material alloyed with 1, 2, 2.5, 3, 3.5, 4 and 5 wt% of gold. In particular, the paper documents the decrease in the solidus and liquidus temperatures, increase in the Brinell hardness, and increase in both the electrical and thermal conditions of 95Sn₅Sb solder doped with gold.

6 Medical and Dental

6.1 Photothermal Treatment of Human Carcinoma Cells Using Liposome- Encapsulated Gold Nanoshells

The authors report the application of liposome-encapsulated gold nanoshells for *in vitro* photo-induced hyperthermia in human mammary carcinoma cells. P Kasili, T Vo-Dinh from the Advanced Biomedical Science & Technology Group, Oak Ridge National Laboratory, Oak Ridge, USA *NanoBiotechnology* 2005, **1(3)**, 245. In addition to evaluating their effects *in vitro*, the authors compared the application liposome-encapsulated gold nanoshells and free-standing gold nanoshells for NanoPhotoTherapy (NPT). NPT-induced hyperthermia was performed using a 785-nm near-IR light from a diode laser and the *in vitro* effects were evaluated using nucleic acid mol. probes by fluorescence microscopy. Additionally, the authors monitored the effectiveness of NPT by detecting apoptosis via caspase-9 activity.

6.2 Gold-Coated Stents

Surface modification of stents using pure gold as a biocompatible and hemocompatible coating material was expected to provide a solution to the complications of coronary stenting. J Rodermann, N Reifart from the West German Heart Centre, Department of Cardiology, University Hospital Essen, Germany, *Local Drug Delivery for Coronary Artery Disease* 2005, 433. The NIROYAL (Boston Scientific) was the last available gold coated stainless steel stent on the market. It was different from previous gold-coated stents in that it featured high purity and a two-step plating process to ensure complete coating and to eliminate pores, flakes and cracks with stent expansion, exposing the underlying material. Optimal radiopacity was the most evident benefit of the NIROYAL stent. Results of the 1998 non randomized, prospective, multi-center trial indicated comparable acute and long-term outcomes of the NIROYAL and the NIR stent (stainless steel). Furthermore, an increase in percent diameter stenosis of the NIROYAL-stent, a smaller minimal lumen diameter, a higher late loss and similar major adverse cardiovascular event rates were observed in another study compared to the NIR stent. Despite the superiority of gold coating to uncoated stainless steel stents *in vitro*, the clin. results were disappointing, probably due to an incomplete gold coverage after stent expansion.

6.3 Colloidal Gold Nanoparticles: A Novel Nanoparticle Platform for Developing Multifunctional Tumour-Targeted Drug Delivery Vectors

A review. Nanotechnology applied to biological problems represents an emerging field with the potential to offer extremely sensitive diagnostics and targeted cancer therapies. G Paciotti, D Kingston, L Tamarkin, from the CytImmune Sciences, Inc., Rockville, USA, *Drug Development Research* 2006, **67(1)**, 47. However, to achieve these goals,

nanoparticle delivery systems must outwit the many barriers that are intrinsic to the body's defenses, as well as those that develop during the growth and progression of tumours. The science is advancing and, for example, true nanoscale tumour-targeted drug delivery vectors are now able to reduce the likelihood of opsonization in the bloodstream and uptake by the reticuloendothelial system. Other advances hold promise for delivering multiple therapeutic agents to non-homogeneous populations of cancer cells in solid tumours. The authors briefly summarize herein the authors' attempts to build such multifunctional nanotherapeutics using colloidal gold nanoparticles. Specifically the authors discuss the development of colloidal gold-based drugs that are designed to target the delivery of TNF and paclitaxel to solid tumours.

7 Metallurgy, Materials and Coatings

7.1 Synthesis and Diameter Control of Multi-Walled Carbon Nanotubes over Gold Nanoparticle Catalysts

The synthesis of multi-walled carbon nanotubes was performed by the chemical vapour deposition of carbon source (C_2H_2 , C_2H_4 , methanol, or benzene) using dodecanethiol-stabilized gold nanoparticles (Au-DT) with monodispersity in size from 3 to 10 nm supported on SiO_2 - Al_2O_3 as a catalyst. M Yamada, M Kawana, M Miyake from the School of Materials Science, Japan Advanced Institute of Science and Technology, Ishikawa, Japan, *Applied Catalysis, A: General* 2006, **302(2)**, 201. The influences of reaction temperature, size of Au-DT, and carbon sources on the formed multi-walled carbon nanotubes were investigated. The diameter of multi-walled carbon nanotubes could be rationally controlled by changing the size of Au-DT only when C_2H_2 was used as a carbon source.

7.2 Computer Simulations in the Study of Gold Nanowires: The Effect Of Impurities

Suspended gold nanowires have recently been made in an ultra-high vacuum ambient and were imaged by electron microscopy. F Novaes, A da Silva, A Fazzio, E da Silva from the Instituto de Fisica, Universidade de Sao Paulo, Sao Paulo, Brazil, *Applied Physics A: Materials Science & Processing* 2005, **81(8)**, 1551. Two puzzles were presented: one atom thick wires are produced and some of the at. distances between these atoms before their breaking were too large. Simulations using realistic mol. dynamics method were able to unveil some processes to explain the mechanisms of formation, evolution, and breaking of these atomically thin Gold nanowires under stress. The calculations showed how defects induce the formation of constrictions that eventually will form the one-atom chains. Atomically thin chains, five atoms long were obtained, before breaking. The results were in excellent agreement with experimental results except for the large Au-Gold distances. In fact no theor. calcination of

pure gold nanowires have been able to produce such large distances. Light impurities that cannot be imaged in these experiments may be responsible for these large Au-Au distances. Using *ab initio* total energy calculations based on the d. functional theory, the authors have studied the effect of H, C, O, N, B, S, CH, CH_2 , and H_2 impurities on the nanowire electronic and structural properties, in particular how they affect the rupture of the nanowire. The authors find that the impurities tend to locally increase the nanowire's strength, in such a way that its rupture always occurs at an Au-Au bond and never at an Au-X bond (X being an impurity). In particular, oxygen seems to form very stable bonds that may be used to pull longer Au chains. Regarding the observed large Au-Au bond lengths, it was found, based on quasi-static calculations, that the best candidate to explain the large distances is H. However, some particular experimental conditions may lead to different results.

7.3 The Influence of the Surface Migration of Gold on the Growth of Silicon Nanowires

Interest in nanowires continues to grow, fuelled in part by applications in nanotechnology. The ability to engineer nanowire properties makes them esp. promising in nanoelectronics. Most silicon nanowires are grown using the vapour-liq.-solid (VLS) mechanism, in which the nanowire grows from a gold/silicon catalyst droplet during silicon chemical vapour deposition. J Hannon, S Kodambaka, F Ross, R Tromp from IBM Research Division, T. J. Watson Research Center, Yorktown Heights, NY, USA, *Nature (London, United Kingdom)* 2006, **440(7080)**, 69. Despite over 40 years of study, many aspects of VLS growth are not well understood. For example, in the conventional picture the catalyst droplet does not change during growth, and the nanowire sidewalls consist of clean silicon facets. Here the authors demonstrate that these assumptions are false for silicon nanowires grown on Si(111) under conditions where all of the experimental parameters (surface structure, gas cleanliness, and background contaminants) are carefully controlled. The authors show that gold diffusion during growth det. the length, shape, and sidewall properties of the nanowires. Gold from the catalyst droplets wets the nanowire sidewalls, eventually consuming the droplets and terminating VLS growth. Gold diffusion from the smaller droplets to the larger ones (Ostwald ripening) leads to nanowire diameters that change during growth. These results show that the silicon nanowire growth is fundamentally limited by gold diffusion: smooth, arbitrarily long nanowires cannot be grown without eliminating gold migration.

7.4 Effect of Glass Pre-Treatment on the Nucleation of Semi-Transparent Gold Coatings

Coatings of gold nanoparticles with a uniform film texture and a neutral blue hue may be applied to glass by an aqueous process and such coatings have recently been proposed for architectural applications. Here, X Xu, M B Cortie, M Stevens from the Institute for Nanoscale Technology, Department of

Chemistry, Materials and Forensics, University of Technology, Sydney, Australia, *Materials Chemistry and Physics* 2005, **94(2-3)**, 266, show that the optical transmission spectrum of these coatings is directly related to the interplay between the nucleation, growth and aggregation of the particles. In particular, prior treatments of the glass substrate in 1:1 sulfuric acid (H_2SO_4), 98% H_2SO_4 and buffered hydrofluoric acid (HF) exerted a strong influence on the subsequent particle size and coverage, which is explained here in terms of contact angle and its effect on rates of nucleation. The rate of nucleation on the surface treated with HF is estd. to be twice that of the surface treated with 98% H_2SO_4 . The color of the coatings is the result of inter-particle plasmonic interactions and is, therefore, also controlled by the nature of nucleation and growth process.

7.5 White Gold Alloys: Colour Measurement and Grading

A numerical grading system has been established for white gold alloys using the ASTM Yellowness Index D1925, an existing color quality std. S Henderson, D Manchanda from the Metallurgical Department, Cookson Precious Metals Ltd, Birmingham, UK, *Gold Bulletin* (London, United Kingdom) (2005), **38(2)**, 55. The Index is calcd. from the CIE (International Commission of Illumination) Tri-stimulus values, X, Y, and Z, and the scale is linear, so that as the number decreases, the alloy becomes whiter. This Index provides values that have good correlation with visual assessments and permits easy differentiation of color without knowledge of an alloys composition. The use of a spectrophotometer instrument provided a quick means of sample color measurement, with high precision and accuracy.

8 Nanotechnology

8.1 Direct Observation of Size Dependent Activation of NO on Gold Clusters

Vibrational spectra of NO ligands adsorbed on cationic gold clusters are obtained using IR multiphoton dissociation spectroscopy. A Fielicke, G von Helden, G Meijer, B Simard, D Rayner from the Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany, *Physical Chemistry Chemical Physics* 2005, **7(23)**, 3906. The authors observe a strong oscillation of the NO stretching frequency with increasing cluster size that reveals a clear odd-even dependence in the strength of the NO bond. For the corresponding CO complexes, no oscillation is found. This behaviour can be understood on the basis of the character and occupation of the frontier orbitals of the complexes.

8.2 Synthesis of Gold Nanowire And Nano-Dumbbell Shaped Colloids and Auc60 Nano-Clusters

A technique for the fabrication of colloidal Gold nanowire and nano-dumbbell shaped particles using carbon nanotubes and rod shaped viruses as templates is described.

P Landon, B Jarvis, C Gilleland, T Renfro, J Gutierrez, J Synowczynski, S Hirsch, R Glosser from the Department of Physics and Electrical Engineering, The Univ. of Texas at Dallas, Richardson, USA, Proceedings of SPIE-The International Society for Optical Engineering (2005), 5931 (Nanoengineering: Fabrication, Properties, Optics, and Devices II). The Gold encapsulation process was accomplished by the precipitation of Gold chloride from aqueous solns. When this process was conducted in the presence of hydroxylated C60, small pieces of phase-sepd. composites of AuC60 appeared to have formed. These nano-clusters may turn out to be large noble metal analogs of the alkali metal fullerenes with the smallest geometrically possible Gold aggregate consisting of 55 Gold atoms. The existence of noble metal fullerene composites was previously theorized. The alkali metal fullerenes are examples of phase-sepd. solids and have exhibited supercond. with temperatures as high as 33 K. The mechanism required for the binding energy between C60 and Gold was observed to exist between C60 and many of the mirror metals (Al, Ag, Au, Cu, Ni). This binding energy is a charge transfer from the metal Fermi level into the C60 LUMO. If this bonding energy is greater than the metals coagulation energy an Au/C60 size terminated mechanism during the formation of the Gold aggregates by the adhesion of C60 to the surface is energetically favorable.

8.3 Photocatalytic Preparation of Encapsulated Gold Nanoparticles by Jingle-Bell-Shaped Cadmium Sulfide-Silica Nanoparticles

Gold (Au) nanoparticles were deposited inside silica (SiO_2) shells containing cadmium sulfide (CdS) nanoparticles through photocatalytic reduction of potassium dicyanoaurate (I) by CdS. Photocatalytic B Pal, T Torimoto, S Ikeda, T Shibayama, K Sugawara, H Takahashi, B Ohtani, from the "Light and Control", PRESTO, Japan Science and Technology Agency, Saitama, Japan, *Topics in Catalysis* 2005, **35(3-4)**, 321. Gold deposition occurred only when core-shell nanoparticles having a void space between the core and shell, i.e., a jingle-bell-shaped structure, were used. These core-shell nanoparticles were prepared by size-selective photoetching of SiO_2 -covered CdS nanoparticles. The size of Gold nanoparticles could be controlled by adjustment of the void space in SiO_2 -covered CdS. Dissolution of CdS by acid treatment from the Au-deposited jingle-bell nanoparticles did not have any effect on the surface-plasmon absorption by Au. These facts indicate that Gold nanoparticles of adjustable size can be prepared in an SiO_2 shell that prevents mutual coalescence of Gold nanoparticles but allows permeation of molecules and ions.

8.4 Kinetic Study of Gold Nanoparticle Growth in Solution by Brust-Schiffrin Reaction

Nanoparticle growth in solution is a rather complicated process governed by many thermodynamic and kinetics factors. X Liu, J Worden, Q Huo, J Brennan, from the Nanoscience

Technology Center and the Department of Chemistry, University of Central Florida, Orlando, FL, 32826, USA SO *Journal of Nanoscience and Nanotechnology* (2006), **6(4)**, 1054. A better understanding of nanoparticle growth kinetics is of primary importance leading to a better control on the nanoparticle size and size distribution. In this work we conducted both experimental and theoretical study on the kinetics of Brust-Schiffrin reaction for the synthesis of gold nanoparticles. Using an excessive amounts of thiol ligands, the nanoparticle growth was stopped at different intermediate stages. The study revealed and confirmed that the reproducibility of Brust-Schiffrin reaction for the synthesis of gold nanoparticles with diams. around 2 nm is rather poor due to the intrinsic complexity of this two-phase reaction. The analytical results of each intermediate product by TEM showed that nanoparticles grew very rapidly at the early stage of reaction and reached a maximum value of 2.6 nm at reaction time of around 10 min. Further increase of reaction time led to a decrease of nanoparticle size. In addition to the experimental study, we proposed a kinetic model for nanoparticle growth in solution by assuming that the nanoparticle core expands through incremental addition of gold atoms to the existing nanoparticle nuclei. This model not only gave a relatively good fitting to the experimental data, but also provided further insight into the nucleation and core expansion stage of the nanoparticle growth, which had not been revealed in previous modeling studies.

8.5 Reproducible Interconnects Assembled from Gold Nanorods

By using cleanroom-based lithography procedures to produce identical electrode arrays, the authors have fabricated dielectrophoretic nanowires that vary in their conductance by $\pm 10\%$. Transmission electron microscopy established the presence of interconnect segments composed of densely aggregated nanoparticles and of individual nanorods lying in the current-carrying path. B Ozturk, C Blackledge, B Flanders, D Grischkowsky from the Department of Physics, Oklahoma State University, Stillwater, OK, USA SO *Applied Physics Letters* 2006, **88(7)**, 073108/1. The current-voltage profiles of these interconnects exhibited barriers to charge transport at temperatures less than ≈ 225 K; furthermore, their conductances increased exponentially with temperature with an activation energy comparable to the nanorod charging energy. These results indicate that the Coulomb blockade assocd. with individual nanorods in the interconnects is the primary conductance-limiting feature.

8.6 Structure and Thermal Stability of Gold Nanoplates

Gold (Au) nanoplates with an average thickness of ≈ 70 nm and several $10 \mu\text{m}$ in edge size have been mass synthesized through a solution-phase method. Structural studies demonstrate that the Gold nanoplates are single crystals with (111) planes as two basal surfaces.

Fragmentation of Gold nanoplates is found when temperature is higher than $450 \text{ }^\circ\text{C}$. C Kan, G Wang, X Zhu, C Li, B Cao, from the National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing, 210093, Peop. Rep. China SO *Applied Physics Letters* (2006), **88(7)**, 071904/1. Investigations on the thermal stability of Gold nanoplates suggest that the melting and breaking start mainly at the (110) bounded edges, while the (111) surfaces of Gold nanoplates show high stability. This work is valuable for Gold nanostructures applied at elevated temperatures.

8.7 Optical Properties of Star-Shaped Gold Nanoparticles

Here the authors report the synthesis, structure, and optical properties of ≈ 100 nm star-shaped Gold nanoparticles. C Nehl, H Liao, J Hafner from the Department of Physics & Astronomy, Department of Chemistry, Rice University, Houston, TX, USA, *Nano Letters* 2006, **6(4)**, 683. Single particle spectroscopy measurements revealed that these nanoparticles have multiple plasmon resonances resulting in polarization-dependent scattering with multiple spectral peaks, which correspond to the different tips on the star-shaped structure. The plasmon resonances also are extremely sensitive to the local dielec. environment.

8.8 New Preparation Method of Gold Nanoparticles on SiO₂

It is shown that adsorption of the $[\text{Au}(\text{en})_2]^{3+}$ cationic complex can be successfully employed for the deposition of gold nanoparticles (1.5 to 3 nm) onto SiO₂ with high metal loading, good dispersion, and small Gold particle size. R Zanella, A Sandoval, P Santiago, V Basiuk, J Saniger from the Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México (UNAM), Mexico City, Mexico *Journal of Physical Chemistry B* 2006, **110(17)**, 8559. When the solution pH increases (from 3.8 to 10.5), the Gold loading in the Au/SiO₂ samples increases proportionally (from 0.2 to 5.5 wt %), and the average gold particle size also increases (from 1.5 to 2.4 nm). These effects are explained by the increase in the amt. of neg. charged sites present on the SiO₂ surface, namely, when the solution pH increases, a higher number of $[\text{Au}(\text{en})_2]^{3+}$ species can be adsorbed. Extending the adsorption time from 2 to 16 h gives rise to an increase in the gold loading from 3.3 to 4.0 wt % and in the average particle size from 1.8 to 2.9 nm. Different morphologies of gold nanoparticles are present as a function of the particle size. Particles with a size of 3-5 nm show defective structure, some of them having a multiple twinning particle (MTP) structure. At the same time, nanoparticles with an average size of ca. 2 nm exhibit defect-free structure with well-distinguishable {111} family planes. TEM and HAADF observations revealed that Gold particles do not agglomerate on the SiO₂ support: gold is present on the surface of SiO₂ only as small particles. D. functional theory calculations were employed to study the

mechanisms of $[\text{Au}(\text{en})_2]^{3+}$ adsorption, where neutral and neg. charged silica surfaces were simulated by neutral cluster $\text{Si}_4\text{O}_{10}\text{H}_4$ and neg. charged cluster $\text{Si}_4\text{O}_{10}\text{H}_3$, resp. The calcination results are totally consistent with the suggestion that the deposition of gold takes place according to a cationic adsorption mechanism.

9 Refining

9.1 Study of Collectors for Mineral Flotation of Gold-Bearing Ores

The applicability of SGM series reagents in a scheme of collective-selective flotation was studied on sulfide ores containing Cu 1.7-2.0, Zn 0.9-1.15, S 29-31%, Gold 1.4-1.7, Ag 10-21 ppm. V Bocharov, V Ignatkina, G Lapshina, M Viduetskii, L Poltavskaya from MISiS, Russia, *Tsvetnye Metally (Moscow, Russian Federation)* 2005, (1), 12. With all of the collectors tried pos. beneficiation indexes with yields 100 ppm were obtained. With respect to pyrite, collector SGM-1 was more selective than xanthogenates. With use of the combination of Bu xanthogenate and collector SGM-1 at ratios of (1.0-0.5):1 the loss of Cu, Zn, and Gold to tailings was decreased and the grade of the collective conc. was increased. With collector SGM-2 the grade of the Cu conc. was higher but less Cu was extd. Increasing the alky. of pulp with > 300 mg/L CaO decreased metal extn. by all of collectors tried. Collector SGM-5 in comparatively small amt. (20-40% of the std. disbursement for xanthogenates) provides a high level of extn. of nonferrous and precious metals. Collectors SGM-1 and SGM-5 in combination with xanthogenates did not improve the flotation results. The new collectors are comparable with xanthogenates in their toxicity and can be made at Russian chemical manuf. facilities at a cost close to that of xanthogenates.

9.2 Intensification of Gold Extraction Process from Resistant Gold-Sulfide Concentrates

The use of chemical opening process for arsenopyrite products in acid-alkali solns. $\text{Fe}(\text{NO}_3)_3$; $\text{Fe}_2(\text{SO}_4)_3$; HNO_3 (H_2SO_4) is possible in gold hydrometallurgy, with consequent gold dissolution by non-cyanide solvents A Kholmogorov, Y Kononov, L Shashina, T Kadetova, from IKhKhT, RAN, Russia, *Tsvetnye Metally (Moscow, Russian Federation)* 2005, (3), 23.

9.3 The Autoclave Oxidizing Sample Preparation of Gold Ores

The method of autoclave leaching applied to gold detn. in mineral products. O Belousov, L Dorokhova, T Chmyshkova, A Zhyzhaev, from IKhKhT, RAN, Russia, *Tsvetnye Metally (Moscow, Russian Federation)* 2005, (3), 13. The autoclave break-downing gave the possibility of sample preparation time decreasing in three times. The ways of gold losing during this process were defined. An efficiency of the

autoclave oxidizing sample preparation of oxidized gold ores was shown in the present work. Optimal conditions of this process were detd.

9.4 High-Permeation Polyelectrolytes for Extraction of Ions of Gold and Accompanying Metals from Cyanide Solutions in Heap Leaching

Polyfunctional anionites of Ional series with different content of strong and weak basic groups were synthesized. E Ergozhin, B Kenzhaliev, T Chalov, K Akhmetova, T Kovrigina, from IKHN MON RK, Russia *Tsvetnye Metally (Moscow, Russian Federation)* 2005, (2), 43. The starting monomers were diglycidyl ethers of resorcin (DGER), hydroquinone (DGEH), and dioxydiphenylpropane (DGEDDFP) and also oligomers of epichlorhydrine (OEKHC), allyl bromide (AB), and allyl chloride (AKh). Ional-1 was synthesized by the condensation of DGER or DGEH with polyethylenimine. Other syntheses were: Ional-1A by DGER or DGEH in the presence of AB or AKh; Ional-3 by DGER, DGEH, or DGEDDFP with poly-2-Me-5-vinylpyridine (PMVP) in the presence of AB or AKh; and Ional-13 by the reaction of allyl glycidyl ether with PMVP in the presence of H_2O_2 as indicator. Ional-5, -5A, -7, and -10 were synthesized using various ratios of starting compounds and various conditions of reaction. The effectiveness of the Ional anionites and the com. available exchanger AM-2B for extg. Gold and other metals from cyanide solns. was studied. Principal indicators detd. sorption properties (ion-exchange capacity and selectivity, time needed to establish equil. desorption curves). The synthesized sorbents have better kinetic characteristics than AM-2B. Solns. of 3% H_2SO_4 (eluent-1) and 4% NaOH (eluent-2) were used to remove impurity metals from the satd. ionite under static and dynamic conditions. Eluent-1 sufficiently fully removed Zn, Fe, and Ni; eluent-2 removed the Cu.

9.5 Comparison of Variants of Cyaniding CIP And Rip Products after Bacterial Oxidation of Gold-Bearing Concentrates

With use of CIP (coal in pulp) sorption technology, over a 20 d period, the Gold content in the solid tailings remained at 0.03-0.09 mg/L and the Gold content in satd. sorbent was 6.1-6.9 mg/L. V Dement'ev, S Gudkov, Y Emel'yanov, OAO "Irgiredmet", Russia, *Tsvetnye Metally (Moscow, Russian Federation)* 2005, (2), 18. With use of RIP (resin in pulp) sorption technology, over a 28 d period, the Gold content in tailings interstitial solution varied over the range 0.04-0.43 mg/L and the capacity of the sorbent for Gold decreased from 5.9 to 2.7 mg/L. Gold extn. via CIP technology was higher by 1.7% at the min. than via RIP technology. The coal used for testing was coking activated and the resin used was AM 2B anion exchanger. The choice of technology of Gold extraction from cyanidation solutions should be determined by economic parameters at all stages of processing.

9.6 Gold Recovery from Chloride Solutions With XAD-7: Competitive Adsorption Of Fe(III) And Te(IV)

In this study, competitive adsorption of metal chloro complexes on the polymer adsorbent XAD-7 was investigated. Au(III), Fe(III) and Te(IV) dissolved in HCl and alkali metal chloride solns. were used as the model compounds. Adsorption equil. were measured for individual elements as well as for binary pairs and the data were correlated in terms of activities of the adsorbable complexes. M Laatikainen, E Paatero from the Laboratory of Industrial Chemistry, Lappeenranta University of Technology, Lappeenranta, Finland, *Hydrometallurgy* 2005, **79(3-4)**, 154. Finally, the equil. model together with the experimental detd. apparent diffusion coeffs. was utilized in simulation of breakthrough curves of multicomponent mixtures. Adsorption of gold and iron can be explained satisfactorily by taking into account the formation equil. of the tetrachloro complexes and the difference in their acid strengths. The uptake of the weakly acidic HAuCl_4 depends only slightly on the HCl concentration and adsorption was substantially stronger in NaCl solns. The opposite trends observed for iron were due to the lower stability and higher degree of dissociation of HFeCl_4 . The adsorbable complex of Te(IV), $\text{Te(OH)}_2\text{Cl}_4$, has lower affinity for the adsorbent, but at high concentrations it can reduce substantially the adsorption capacity for Au(III) and Fe(III). This effect was confirmed with the adsorption column runs, and the change in the breakthrough behaviour of Au(III) and Fe(III) can be explained quant. by the simulation model.

9.7 Processing of Residual Gold (III) Solutions via Ion Exchange

The processing of gold (III)-hydrochloric acid solns. by the anionic ion exchange Lewatit MP-64 resin was investigated. F J Alguacil, P Adeva, M Alonso, from the Centro Nacional de Investigaciones Metalurgicas (CSIC), Madrid, Spain, *Gold Bulletin (London, United Kingdom)* 2005, **38(1)**, 9. The influence of several variables such as the temperature, the hydrochloric acid and metal concentrations in the aqueous solution and the variation of the amt. of resin added was studied. Moreover, a kinetic study performed in the uptake of gold (III) by Lewatit MP-64 shows that either the film-diffusion and the particle-diffusion models fit the adsorption process on the resin. Results obtained from batch experiments were applied to a continuous system using a vertical column. The loaded resin could be eluted by an acidic thiourea solution at 20.degree. Various systems were investigated to ppt. gold from eluants, only the use of sodium borohydride allowed to accomplish the recovery of the metal from the pregnant solns. Gold was recovered as fine particles, which were characterized by optical and SEM.

9.8 Biological Processes for Gold Recovery

Bacterial oxidation of sulfide minerals is a familiar and com. available process to enhance gold recovery with problem

ores. Pintail Systems, a Colorado-based company had developed bio-processes for gold recovery based on natural mineral formation and transformation in a global mineral cycle. L Thompson, I MacCulloch, from Pintail Systems, Inc, Golden, CO, USA, *Publications of the Australasian Institute of Mining and Metallurgy* 2004, **6/2004**(Bac-Min 2004 Conference), 175. The biological recovery of precious metals from ore involves a number of mechanisms that are dependent on the metal-mineralogical assocn. These processes include: (1) partial bio-oxidation of sulfide ores; (2) oxidation of gangue minerals exposing gold to leaching; (3) surfactant properties of bacteria/nutrient solns. that improve wettability of ores and solution contact with leachable gold and silver; and (4) microbial prodn. and excretion of trace amts. of gold lixivants, and bio-fracturing or biol. alteration of ore minerals. Pintail has demonstrated enhanced recovery of precious metals during cyanide detoxification of spent heaps at the end of mine life. Biol. recovery processes also have the potential to be applied to *in situ* mining technologies. The *in situ* process application could recover gold from subgrade deposits, small deposits or those ore bodies with uneconomic stripping ratios for conventional mining. *In situ* biomining can be accomplished at a fraction of the cost of conventional mining and leaching and does not have the environmental liabilities assocd. with many conventional gold lixivants.

9.9 Method for Extracting Gold

The title method comprises: (1) adding water to gold-containing ore to obtain ore slurry, (2) adding chemical extractant and superfinely grinding into granules with a grain size of no larger than 1 .mu.m while dynamically extg., or superfinely grinding into granules with a grain size of no larger than 1 .mu.m and adding chemical extractant, (3) sepg. liq. phase from solid phase, and (4) carrying out desorption of the liq. to obtain the final product. S Bi from the South China University of Technology, Peop. Rep. China SO Faming Zhuanli Shenqing Gongkai Shuomingshu, PATENT No CN 1766136, A, May 2006. This method has the advantages of gentle operation conditions, no environment pollution, high extrn. rate, and low cost.

10 General

10.1 Preparation of Nanometered Gold Catalyzer

M Wang, Taiwan, PATENT No US 2006122057 A1, June 2006. A nanometered Gold catalytic coating material for use in gas mask, mouth-muffle, gasoline additive, filter for air cleaner and the like to eliminate the toxicity of CO is disclosed to be prepared by: adding Gold grains of diameter below 5 nm to an org. solution, and then adding O_2 to the solution, thereby causing Gold grains to form Au_2O_3 , and then adding porous metal carriers of diameter >5 nm to Au_2O_3 solution, for enabling Au_2O_3 to be adhered to the pores in the metal carriers, and thus a nanometered Gold catalyzer is thus obtained.