Gold 2018

July 15-18, 2018 – Paris, France

ABSTRACTS
-
ORAL PRESENTATIONS
SESSION 1- Catalysis

S1 O1

Zahraa SHAHIN, Claude Bernard University-Lyon1-France

Elaboration of composite materials from gold thiolate clusters and MOFs as catalysts for valorization of hexoses

S1 O2

Toru MURAYAMA, Research Center for Gold Chemistry, Tokyo Metropolitan University

Polyoxometalate-Supported Gold Nanoparticulate Catalysts Prepared by sol immobilization method and their catalytic activity

S1 O3

Tanya SHIRMAN, Harvard University

Modular Design of Advanced Catalysts Using Au-based Bimetallic Nanoparticles

S1 O4

Ranin ATWI, Univ. Lyon - CNRS

Stable Au-Ag alloy nanoparticles encapsulated in single crystal multi-hollow zeolites: application to CO removal at low temperature studied by operando IR spectroscopy

S1 O5

Satoshi KAMEOKA, Tohoku University

Highly catalytic performance of porous gold with twin boundary defects

S1 O6

Katia FAJERWERG, Laboratoire de Chimie de Coordination, CNRS University of Toulouse

Controlled growth of high-density nanoparticles on zinc oxide thin films by photo-deposition

S1 O7

Evgeniy REDEKOP, University of Oslo

Catalyst Design: Scaling from UHV Models to Operating Conditions

S1 O8

Shi JUNJIE, Yantai University

Atomic Observation of Praseodymia-Titania Mixed Oxides Functionalized Nanoporous Gold as Stable Catalysts for Water-Gas Shift Reaction

S1 O9

Adrian CHMIELEWSKI, Laboratoire Matériaux et Phénomènes Quantiques - Université Paris Diderot

In-situ E-TEM study of the morphology of TiO_2 supported gold nanocatalysts under oxidizing (O_2) and reducing (H_2) atmosphere

S1 O10

Marie-Claire SAINT-LAGER, Institut Néel - CNRS

Pd and CO oxidation on Au30Pd70(110) upon O_2 and CO elevated pressure

S1 O11

Jessi VAN DER HOEVEN, Debye Institute for Nanomaterials Science, Utrecht Universtiy

In situ observation of metal redistribution in gold-silver nanorods

S1 O12

Shi CHUAN, Dalian University of Technology

Catalytic removal of formaldehyde at room temperature over supported gold catalysts

S1 O13

Hazar GUESMI, Institut Charles Gerhardt - CNRS/ENSCM- UMR5253-Equipe MACS

Toward an Accurate Theoretical Description of Gold-based Nanocatalysts Under Reactive Media

S1 O14

Fu SHI-EN, National Taiwan University of Science and Technology

Role of Water on CO oxidation over Boron-Nitrogen sheet supported Gold Clusters (Au9) -A First Principles study

S1 O15

Simon DAWSON, Cardiff Catalysis Institute, Cardiff University
In situ study of single-site gold catalyst during acetylene hydrochlorination using synchrotron radiation

S1 O16
Li JUN, Department of Chemistry, Tsinghua University
Stability and Reactivity of Gold Single-Atom Catalyst (SAC)

S1 O17
Lukasz WOLSKI, Adam Mickiewicz University in Poznań
The influence of gold and copper on activity and selectivity of Nb_2O_5 in photocatalytic methanol oxidation

S1 O18
Valérie CAPS, ICPEES (CNRS UMR 7515, University of Strasbourg)
Hydrogen-promoted CO oxidation over hydrophobic Au/FLG catalysts

S1 O19
James CARTER, Cardiff University
The Activation and Deactivation of $Au/CeZrO_4$ in the Low-Temperature Water-Gas Shift Reaction

S1 O20
Shi CHUAN, Dalian University of Technology
Atomic-layered Au clusters on α-MoC as catalysts for the low-temperature water-gas shift reaction

S1 O21
Rodolfo ZANELLA, Center for Applied Sciences and Technological Development-UNAM
Synergetic Effect of Bimetallic $Au-Ru/TiO_2$ Catalysts for CO and Methanol Complete Oxidation

S1 O22
Ali NASRALLAH, Cardiff University
Au-Pd Alloy Catalysts for the Oxidation of Organic Compounds

S1 O23
Yanan GAO, Eindhoven University of Technology
Gas-phase oxidative dehydrogenation of cyclohexanol to cyclohexanone over $Au/MgCuCr_2O_4$ catalyst

S1 O24
Mingyue LIN, Tokyo Metropolitan University
Efficient Elimination of Ammonia over Niobium Oxide Supported Gold Catalyst at Room Temperature

S1 O25
Gao LI, State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, CAS, Dalian, China
Non-Metallic Gold Clusters for Oxygen Activation and Aerobic Oxidation

S1 O26
Petra DE JONGH, Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University
Superior Stability of Au/SiO_2 Compared to Au/TiO_2 Catalysts for the Selective Hydrogenation of Butadiene

S1 O27
Jhonatan FIORIO, IQ-USP
Design of gold nanoparticle catalysts for chemoselective hydrogenations: N-doped carbon as support

S1 O28
Hidehiro SAKURAI, Division of Applied Chemistry, Graduate School of Engineering, Osaka University
Size Effect on Reduction of Aryl Chlorides with PVP-stabilized Gold/Palladium Bimetallic Nanoclusters Catalyst

S1 O29
Maela MANZOLI, Department of Drug Science and Technology, University of Turin
From biomass to value-added chemicals: microwave-assisted levulinic acid conversion over gold catalysts

S1 O30
Liane ROSSI, University of São Paulo

Hydrogenation on gold catalysts made easy: activation of H2 via frustrated Lewis pairs

S1 O31
Caixia QI, Yantai University
Catalytic Cracking of Light Diesel Over Au/ZSM-5 : An Application of Gold Catalysts Under Severe Conditions

S1 O32
Shishido TETSUYA, Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University
Supported Gold-Palladium Alloy Catalysts for Highly Efficient Hydrogen Storage System Based on Ammonium Bicarbonate/Formate Redox Equilibrium

S1 O33
Tamao ISHIDA, Tokyo Metropolitan University
Gold Nanoparticles as Soft Lewis Acid Catalysts for Transfer Vinylation

S1 O34
Pengfei HAN, Queensland University of Technology
Assembling Ni2+ complexes and gold nanoparticles on γ-Al2O3 as visible light photocatalysts for hydrogenolysis of lignin model compounds

S1 O35
Feng LIN, Gold Catalysis Research Center, State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences
Synergistic Effect of Gold Plasmonic Resonance and Solid Acid in Photocatalysis

S1 O36
Valérie KELLER, ICPEES (CNRS UMR 7515, University of Strasbourg)
Visible light photocatalytic H2 production from water over optimized Au/TiO2-gC3N4 nanocomposites

S1 O37
Déborah DE MASI, UMR 5215 - LPCNO
Bimetallic Gold-Ruthenium nanoparticles for catalysis

S1 O38
Eduardo BARBOSA, Universidade de São Paulo
Harvesting Gold Plasmonic Properties to achieve Selective Hydrogenations under Visible-Light in Au@AgPt Nanorattles

S1 O39
Marina RODIO, Hamburg Centre for Ultrafast Imaging (CUI); Physical Chemistry Department, Hamburg University
Gold nanoparticles: impact of surface chemistry on photocatalytic activity

S1 O40
Qi XIAO, CSIRO Manufacturing
Plasmonic Super Absorber of Light for Photocatalysis

S1 O41
Naoki MIMURA, National Institute of Advanced Industrial Science and Technology (AIST)
Gold Catalysts for Liquid-Phase Flow Reactor: Catalytic Oxidation of Glycerol into Functional Molecules

S1 O42
Laura PRATI, università degli studi di milano
GOLD-SILVER CATALYSTS: EFFECT OF CATALYST STRUCTURE ON THE SELECTIVITY OF GLYCEROL OXIDATION

S1 O43
Qingyi GU, Laboratoire de Chimie, ENS de LYON
Density functional theory on ethanol oxidation catalyzed by gold: unraveling the role of base

S1 O44

Baira DONOEVA, Utrecht University
Strong effect of the surface properties of carbon supports in Au-catalysed reactions

S1 O45
Nishtha AGARWAL, Cardiff Catalysis Institute, Cardiff University
Selective oxidation of methane to methanol with molecular oxygen using aqueous Au-Pd colloids at low temperature

S1 O46
Samuel PATTISSON, Cardiff University
Supported gold catalysts for the low temperature solvent-free oxidation of cyclohexene to cyclohexanediol using molecular oxygen as oxidant

S1 O47
Ayako TAKETOSHI, Research Center for Gold Chemistry, Tokyo Metropolitan University
Oxidative Esterification of Aliphatic Aldehydes by Gold Nanoparticle Catalysts in a Continuous Flow Reactor

S1 O48
Jun-Ichi NISHIGAKI, Research Center for Gold Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University
Redox Reaction of NAD+/NADH by Au Cluster Catalysts Related to the Coenzyme Regeneration for Dehydrogenases

Elaboration of composite materials from gold thiolate clusters and MOFs as catalysts for valorization of hexoses

Zahraa SHAHIN[1], Rodica CHIRIAC[2], Franck RATABOUL[1], and Aude DEMESSENCE[1*]

(1) *Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), UMR 5256, CNRS / Université de Lyon 1, 2, avenue Albert Einstein – 69626, Villeurbanne, France.*

(2) *Laboratoire des Multimateriaux et Interfaces (LMI), UMR 5615, CNRS / Université de Lyon 1, 22, avenue Gaston Berger – 69622, Villeurbanne, France.*

Atomically well-defined gold nano-clusters (GNCs), due to their size related properties, are known to be active in oxidation catalysis at relatively low temperature.[1] Besides, Metal-Organic Frameworks (MOFs) are hybrid materials that have shown interest in various fields from selective adsorption to catalysis due their large surface area and pore size tunabiliy.[2,3] Thus coupling these two materials will lead to get multisite composite catalysts for the conversion of hexoses. In our study we aim at combining the properties of both MOFs (texture, stability, acidic features) and GNCs (oxidation abilities) in one composite solid to generate two catalytic sites and synergetic effects, for the selective valorization of biomass into value-added products.[4,5]

Thus we prepared nanoparticles of a Lewis acid-based MOF: the MIL-101(Cr), made of terephthalate and Cr(III) cations, and different thiolate functionalized $Au_{25}(SR)_{18}$. The new composite materials (GNC@MOF) have been synthesized to support the clusters on the surface or inside the pores of the MOFs (see Figure 1). Then the initial results on heterogeneous catalysis will be presented using hexoses (glucose, fructose) as substrates for their valorization into valuable chemicals in oxidative conditions. We particularly investigated first the distinct effect of MOFs and GNCs followed by their synergy on the substrate reactivity. In addition, the effect of calcined and non-calcined GNCs supported on MOFs will be tested on catalysis, to study the effect of the presence of the thiolate ligands.
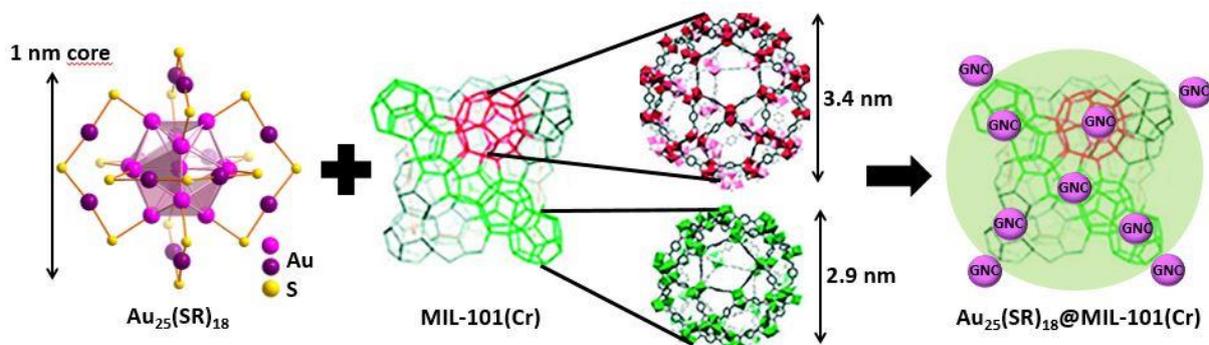

Figure 1. Composite materials for biomass valorization.

References
1- R. Jin, C. Zeng, M. Zhou, Y. Chen, *Chem. Rev., 116*, 10346-10413 (2016).
2- A. Herbst, C. Janiak, *Chem. Soc. Rev., 43*, 6011-6061 (2014).
3- H. Furukawa, K. E. Cordova, M. Okeeffe, O. M. Yaghi, *Science*, 341, 1230444 (2013).
4- C. Lavenn, A. Demessence, A. Tuel, *J. Catal*., *322*, 130-138 (2015).
5- C. Lavenn, A. Demessence, A. Tuel, *Catal. Today*, *235*, 72-78 (2014).

Corresponding author email: Zahraa.shahin@ircelyon.univ-lyon1.fr

Polyoxometalate-Supported Gold Nanoparticulate Catalysts Prepared by sol immobilization method and their catalytic activity

Toru Murayama[1*], Takuya Yoshida[1], Mingyue Lin[1], Norihito Sakaguchi[2], Tamao Ishida[1], Masatake Haruta[1]

(1) *Research Center for Gold Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo, Japan*
(2) *Center for Advanced Research of Energy and Materials, Hokkaido University, Sapporo, Hokkaido, Japan*

Polyoxometalates (POMs) are molecular metal oxide salts that have attracted considerable attention and the preparation of POM-based materials has been studied in various fields. However, there have been few reports on utilization of POMs as support materials for the deposition of gold.[1] However, the reported procedures for the preparation of Au/POMs have several problems. Many POMs are easily decomposed in an alkaline condition. Therefore, it is difficult to deposit gold NPs of less than 2 nm in size (so-called clusters) on the POM by the DP method in an alkaline condition. We used the sol immobilization (SI) method with thiolate-protected gold colloids to prepare POM-supported NPGCs under chloride-free and non-alkaline conditions.

SI was performed according to the literature[2] with slight modification. A dark brown solution of thiolate-protected gold colloids dissolved in 15 mL of toluene was added dropwise into a solution of Cs-SiW ($Cs_4SiW_{12}O_{40}$) dispersed in 10 mL of toluene. The dried catalyst was calcined at 300°C for 2 h in air. Gold colloids of several sizes (2.0, 4.2 and 10.7 nm = x) were prepared and the size was determined by HAADF-STEM images. The obtained samples were denoted as Au(x)/Cs-SiW. The gold loadings determined by atomic absorption spectroscopy were 0.66wt% for Au(2.0)/Cs-SiW, 0.93wt% for Au(4.2)/Cs-SiW and 0.67wt% for Au(10.7)/Cs-SiW. The catalytic activity for CO oxidation was measured by using a fixed-bed flow reactor. The reactant gas, 1 vol% CO in air (50 mL min^{-1}), was fed to the catalyst (0.15 g).

The results for CO oxidation over Au(x)/Cs-SiW (x = 2.0, 4.2 and 10.7) are shown in Figure 1. The activity of Au(2.0)/Cs-SiW for CO oxidation was very high, and the conversion of CO was 100% even at −20°C. The temperature for 50% CO conversion ($T_{1/2}$) was −67°C. Au(2.0)/Cs-SiW is a very active NPGC for CO oxidation compared to previously reported NPGCs such as Au/TiO$_2$, Au/Fe$_2$O$_3$ and Au/Co$_3$O$_4$. The activity of Au(4.2)/Cs-SiW was drastically decreased compared to that of Au(2.0)/Cs-SiW, and $T_{1/2}$ was 16°C. Au(10.7)/Cs-SiW showed very little activity for CO oxidation. The results clearly showed that deposition of smaller gold NPs is essential to obtain an active Au/Cs-SiW catalyst for CO oxidation reaction. Interestingly, the activities of Au/Cs-SiW catalysts decreased with increase in the reaction temperature to more than 40°C. When the reaction temperature was higher than 140°C, the conversion gradually increased. The apparent activation energy (Ea) of Au(2.0)/Cs-SiW also varied depending on the temperature. Within the temperature range from −60 to 40°C, Ea was 20.9 kJ mol^{-1}. In the temperature range from 40 to 140°C, Ea was −25.0 kJ mol^{-1}. At the reaction temperatures of more than 140°C, Ea was 9.3 kJ mol^{-1}. These results indicate that there is a U-shape for the temperature dependence of activity. The Au(2.0)/Cs-SiW catalyst showed full conversion with reaction for at least 840 h (35 days) at 0°C. The turnover number (TON) was more than 200,000 based on gold for 35 days.
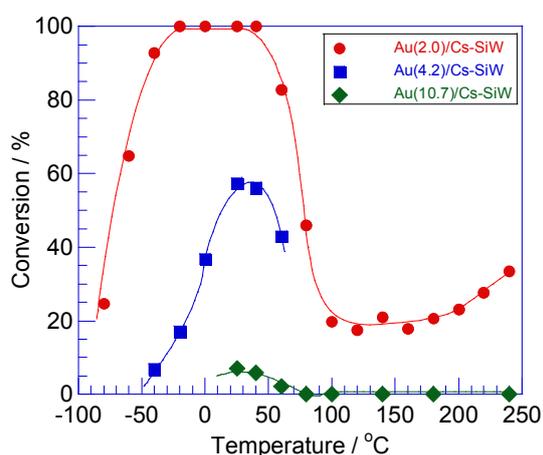
Figure 1. *Effects of reaction temperature on CO oxidation over Au(2.0)/Cs-SiW, Au(4.2)/Cs-SiW and Au(10.7)/Cs-SiW catalysts.*

References
1- T. Yoshida, T. Murayama, N. Sakaguchi, M. Okumura, T. Ishida, M. Haruta, Angewandte Chemie, 2018 in press.
2- T. Murayama, W. Ueda, M. Haruta, ChemCatChem, 2016, 8, 2620–2624.
Corresponding author email: murayama@tmu.ac.jp

Modular Design of Advanced Catalysts Using Au-based Bimetallic Nanoparticles

T. Shirman[1,2], J. Lattimer[1,2], M. Luneau[3], C. M. Friend[1,3], J. Aizenberg[1,2,3]
(1) John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, USA. (2) Wyss Institute for Biologically Inspired Engineering, Harvard University, Cambridge, USA. (3) Department of Chemistry and Chemical Biology, Harvard University, Cambridge, USA.

Bimetallic catalysts have been used in various reactions including reforming, pollution control, and selective chemical transformations.[1] In particular, gold-based bimetallic nanoparticles have emerged as promising catalysts for selective oxidation of alcohols, esterification, and amidization reactions.[2] Control over the composition and morphology, as well as an efficient incorporation of metallic NPs are critical factors for obtaining efficient catalysts. Herein we describe a material platform based on hybrid colloid templated porous (CTP) materials featuring a high degree of control over the composition of the various components and placement of the functional nanoparticles.[3] Our approach is based on the co-assembly of metal NPs-decorated polymer colloids as sacrificial templates and a matrix precursor material. Removal of the polymer via calcination produces a fully interconnected porous network with metal NPs present exclusively at the pore-matrix interface, which in turn results in superior mass transport within the catalyst and improved accessibility of the metal NPs. Importantly, the composition, morphology and size of the metal NPs can be predesigned for specific catalytic reactions, preserved during the fabrication processes and maintained by matrix stabilization during operation. The versatility of these types of materials will be demonstrated for a number of selective chemical transformations using AuAg and AuPd bimetallic nanoparticles. The presented approach creates immense possibilities in terms of the catalyst composition towards efficient and selective chemical transformations in a sustainable and material-efficient way.
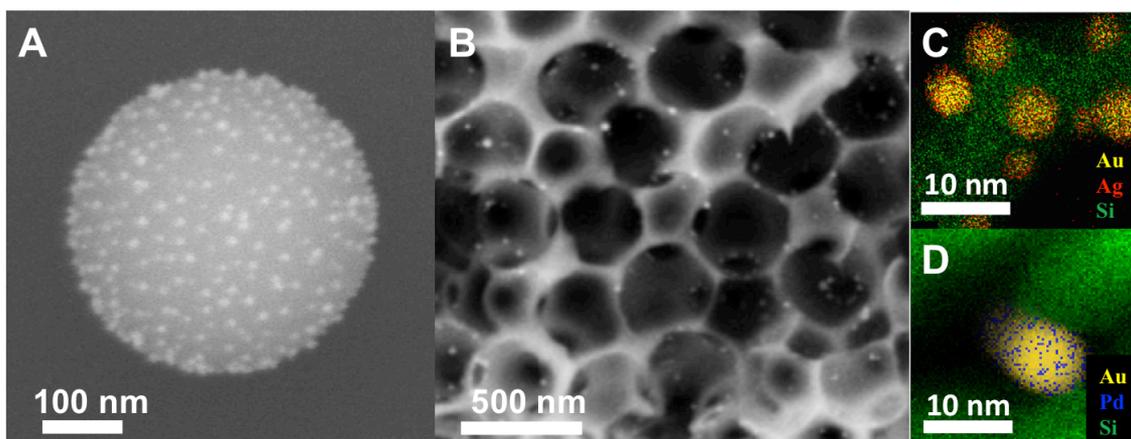

Figure 1. (A) Representative TEM image of templating polymer colloid decorated with $Au_{96}Pd_4$ bimetallic nanoparticles. (B) Representative SEM image of CTP SiO_2-AuPd. (C-D) Representative STEM-EDS maps of (C) CTP SiO_2-$Au_{90}Ag_{10}$ and (D) SiO_2-$Au_{96}Pd_4$.

References
1- D. Kyle, A. Gilroy, A. Ruditskiy, H-C. Peng, D. Qin, Y. Xia. Chem. Rev. **16**, 10414 (2016).
2- T. Shirman, J. Lattimer, M. Luneau, E. Shirman, C. Reece, M. Aizenberg, R. J. Madix, J. Aizenberg, C. M. Friend. Chemistry – A European Journal, **23,** 1 (2017).
3- E. Shirman, T. Shirman, A. V. Shneidman, K. R. Phillips, H. Whelan, E. Bulger, M.Abramovitch, J. Patil, R. Nevarez, A. Grinthal, J. Aizenberg. Adv. Funct. Mater. (2017) DOI: 10.1002/adfm.201704559.

Corresponding author email: tshirman@seas.harvard.edu

Stable Au-Ag alloy nanoparticles encapsulated in single crystal multi-hollow zeolites: application to CO removal at low temperature studied by *operando* IR spectroscopy

R. Atwi, A. Tuel, M. Maffre, L. Burel, F.C. Meunier[*]

University of Lyon - CNRS, IRCELYON, UMR 5256, Villeurbanne, France

The preparation of well-defined and stable alloy nanoparticle remains a challenge. We have shown that it was possible to prepare well-defined alloy nanoparticles encapsulated in single crystal hollow zeolite nanoboxes that were stable at 500°C in the presence of steam[1]. The overall metal loading in these single hollow nanoboxes had yet to be kept low if the preparation of small particles was sought. We have recently reported a novel method to prepare well-dispersed nickel nanoparticles at high loading (i.e. 6 wt.%) using multi-hollow single crystal zeolites[2].

The present contribution reports for the first time the preparation of Au and Au-Ag nanoparticles dispersed in multi-hollow silicalite-1 single crystals, derived from the method reported earlier[2]. Highly dispersed Au (not shown) and Au-Ag (Fig. 1, left) nanoparticles with a diameter around 3 nm were obtained, even after calcination at 550°C.

The CO oxidation activity and the species present at the surface of the catalyst were evaluated using a diffuse reflectance FT-IR spectroscopic (DRIFTS) cell described elsewhere[3]. The Au and Au-Ag materials exhibited a maximum of activity (Fig. 1, Middle), as expected[1]. Surprisingly, the Au-only sample was as active as the Au-Ag sample at lower temperatures, possibly due to a large fraction of low coordination sites that are able to adsorb and activate CO. This was confirmed by the operando DRIFTS data (Fig. 1, Right), which showed a significantly higher band at 2134 cm^{-1}, corresponding to CO adsorbed on step and corner sites[4]. The proportion of these sites was lower on the Au-Ag sample, but the alloy exhibited partially oxidised Ag sites (bands at 2189 and 2172 cm^{-1}) that could too adsorb CO. The activity of an Ag-only sample was significantly lower over this temperature range (Fig. 1, Middle), stressing again the synergy existing between Au and Ag for CO oxidation.

This work shows that it is possible to prepare highly dispersed and stable Au and Au-Ag nanoparticles in multi-hollow zeolites that exhibit interesting activity for CO oxidation at room temperature.
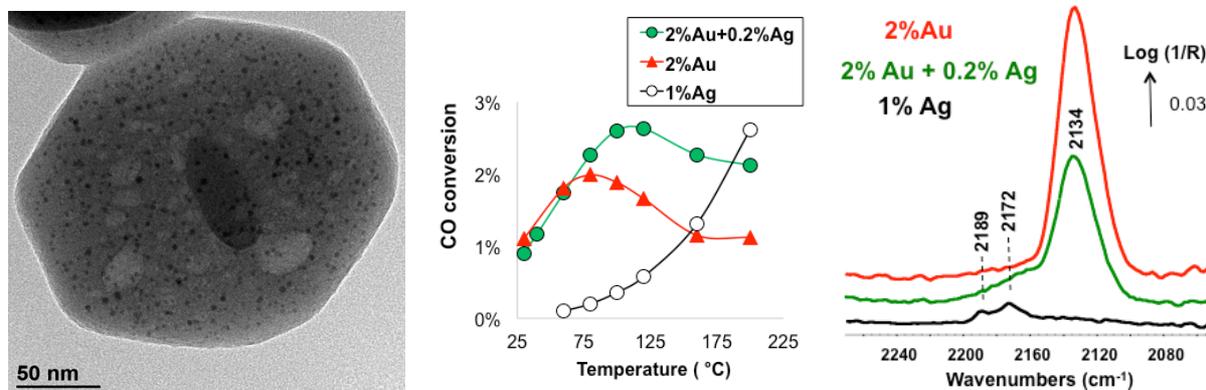

Figure 1. (Left) TEM picture of the 2 wt.%Au+0.2wt.%Ag@silicalite-1 sample calcined at 550°C. (Middle) CO conversion as a function of temperature. Feed: 2.8% CO + 40% O_2 in He, total flow rate 50 mL min^{-1}, 10 mg of catalyst. (Right) Operando DRIFTS spectra at 100°C corresponding to the catalytic data reported the previous figure.

References

1- S. Li, A. Tuel, J.-L. Rousset, F. Morfin, M. Aouine, L. Burel, F. Meunier, D. Farrusseng, ChemNanoMat **2**, 534 (2016).
2- D. Laprune, A. Tuel, D. Farrusseng, F.C. Meunier, ChemCatChem **9**, 2297 (2017).
3- A. Paredes-Nunez, D. Lorito, L. Burel, D. Motta-Meira, G. Agostini, N. Guilhaume, Y. Schuurman, F. Meunier, Ang. Chem. Int. Ed. **57**, 547 (2018).
4- T. Venkov, K. Fajerwerg, L. Delannoy, H. Klimev, K. Hadjiivanov, C. Louis, Appl. Catal. A: Gen. **301**, 106 (2006).

Corresponding author email: fcm@ircelyon.univ-lyon1.fr

Highly catalytic performance of porous gold with twin boundary defects

S. Kameoka[1*], M. Krajčí[2], A.P. Tsai[1]
(1) *IMRAM, Tohoku University, Sendai, Japan*
(2) *Institute of Physics, Slovak Academy of Sciences, Bratislava, Slovak Republic*

Since discovery of extraordinary catalytic properties such as CO oxidation [1] of porous gold (PG) this remarkable material has become a new class of catalysts with potential applications in a wide range of fields [2]. Samples of PG can be prepared, e.g., by leaching from alloys of Au with less noble elements such as Ag, Cu or Al. The origin of the catalytic activity of porous gold has been in literature widely discussed. To date, it is generally accepted that just the residual elements as, e.g., Ag which binds oxygen and its traces always remain in samples of porous gold play very important role in explanation of the extraordinary catalytic activity of porous gold. Recently, we reported that porous gold (PG(Al_2Au)) prepared by de-alloying the Al_2Au compound (i.e., despite missing Ag) with 10% NaOH aqueous solution which exhibited highly active for CO oxidation [3]. The mechanism of formation of the catalytically active sites described in our work represents thus a different contribution to the catalytic activity of porous gold than the effect of the residual elements. At this presentation, we will report high catalytic performance of PG(Al_2Au) for CO oxidation and selective hydrogenation of acetylene and propose their possible reaction mechanism.

As shown in Fig. 1(a), PG(Al_2Au) exhibited the higher catalytic performance than a conventional supported gold nanoparticles catalyst (Au/TiO_2 (WGC)). The origin of these high activities of PG(Al_2Au) is attributed to the high density of defects in the three-dimensional network of nanoscale ligaments (Fig. 1(b)). In high-resolution TEM images of the ligaments we observed high density of twin boundaries (TB) with nanoscale domain sizes (ca. 3 -10 nm). As shown in Fig. 1(c), these TB defects in the fcc lattice of PG(Al_2Au) are able to form active sites for the catalytic reaction on the surface because low-coordinated Au sites created by the TB defects (Colors indicates the coordination numbers (CN) of surface atoms). The twinning defects on the {211} surfaces of PG(Al_2Au) can create highly reactive closed-packed rows of Au sites with coordinations CN = 6 and CN = 5 as the W-chains (Fig. 1(c): see Top view). Using DFT methods, it is shown that on these under-coordinated atomic sites oxygen or hydrogen adsorption, and subsequent reaction can proceed via Langmuir-Hinshelwood (LH) mechanism. The reactivity of the W-chains in the PG(Al_2Au) can thus explain not only the catalytic activity toward the CO oxidation but also toward the semi-hydrogenation of C_2H_2. Twinning in the fcc lattice is a new systematic mechanism for formation of highly reactive under-coordinated surface atoms (*i.e.*, CN = 6 and 5) in nanostructured catalysts.
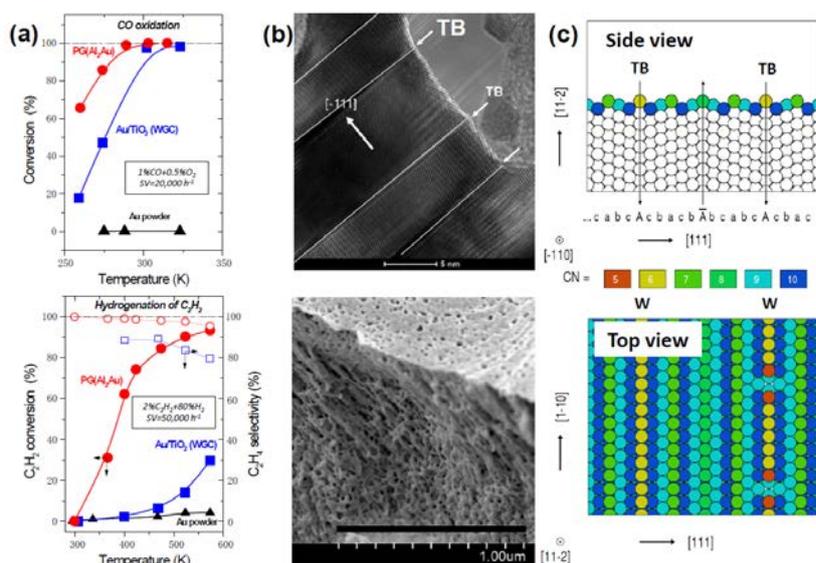

Figure 1. (a) Catalytic properties of various gold catalysts, (b) HRTEM and SEM images of PG(Al_2Au) and (c) Schematic views of the fcc Au(11-2) surface with the twin boundary (TB) defects.

References
1- V. Zielasek et al., Angew. Chem. Int. Ed. **45**, 8241 (2006); C. Xu et al., J. Am. Chem. Soc. **129**, 42 (2007).
2- *For example,* J. Biener, M. Biener, R.J. Madix, C.M. Friend, ACS Catal. **5**, 6263 (2015).
3- M. Krajčí, S. Kameoka, A.P. Tsai, J. Chem. Phys. **145**, 084703 (2016); **147**, 044713 (2017).

Corresponding author email: satoshi.kameoka.b4@tohoku.ac.jp

Controlled growth of high-density nanoparticles on zinc oxide thin films by photo-deposition

J.Cure[1], H. Assi[2], K. Cocq[2], L. Marin[1], K. Fajerwerg[2,3*]
P. Fau[2,3], E. Bêche[4], Y. Chabal[5], A. Esteves[1], C. Rossi[1]

(1) Laboratoire d'analyse et d'architecture des systèmes, LAAS-CNRS University of Toulouse, 7 Avenue du Colonel Roche, F-31077 Toulouse, France
(2) Laboratoire de Chimie de Coordination, LCC-CNRS University of Toulouse, 205 Route de Narbonne, F-31077 Toulouse, France
(3) University Toulouse III-Paul Sabatier, University of Toulouse, 118, Route de Narbonne, F-31077 Toulouse, France
(4) PROMES-CNRS, 7 Rue du Four Solaire, 66120 Font Romeu, France
(5) Department of Materials Science & Engineering, University of Texas at Dallas, Richardson, Texas 75080, United States

Since Faraday in the 1850s, gold nanoparticles (AuNPs) have been the subject of growing interest. AuNPs are now commonly used in many applications such as such as sensors, photocatalysis, photovoltaic devices, and biological labeling.
The deposition of gold nanoparticles (AuNPs) on zinc oxide films a key step for (photocatalysis)catalysis or photovoltaic applications, still remains difficult to master.

The deposition of Au NPs on ZnO films was explored to achieve small AuNPs size and homogeneous shape, high areal density, high purity, and good chemical grafting with the metal oxide film. Among three possible methods to deposit AuNPs on ZnO−spin coating, deposition precipitation with urea and photodeposition (P-D) only P-D achieved good enough results to be useful for most applications. The modified P-D technique developed herein produces homogeneously and dispersed spherical Au NPs (7.5 ± 3 nm in diam.) with a high packing density (3500 ± 10 NPs/μm^2). The high density of AuNPs has a direct impact on the activity of photocatalytic reactions. We demonstrate that high densities of Au NPs embedded within ZnO film enhance the production of hydrogen by photo- reduction of water. Furthermore, most of the AuNPs are intercalated into the 25 nm ZnO layer with only 1/5 of their volume emerging out of the metal oxide layer[2]. While the confinement of nano-objects in small volume remains a great challenge in nanotechnologies in general, the photodeposition process is able to deposit AuNPs on ZnO thin films. This photodeposition process makes it of great interest for many applications needing high purity materials such as photovoltaics, photocatalysis, water purification, or biosensors.
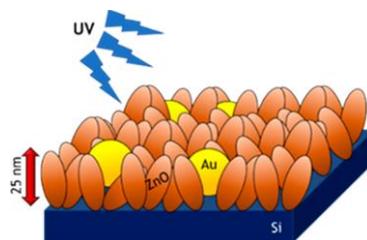

Figure 1. Representation of the high density of AuNPs obtained by deposition-precipitation (DP) for catalysis used for photocatalytic activity

References
1- Koh, S. J., Nanoscale Res. Lett. **2**, 519 (2007).
2- J.Cure, H. Assi, K. Cocq, L. Marin, K. Fajerwerg, P. Fau, E. Bêche, Y. Chabal, A. Esteves, C. Rossi, Langmuir, **DOI:** 10.1021/acs.langmuir.7b04105 (2018).

Corresponding author email: katia.fajerwerg@lcc-toulouse.fr

Catalyst Design: Scaling from UHV Models to Operating Conditions

R. J. Madix[1], Christian Reece[1], Evgeniy Redekop[2]

(1) Harvard University, School of Engineering and Applied Science, Cambridge, MA, USA
(2)   University of Oslo, Department of Chemistry, Olso, Norway

Studies of oxygen-assisted coupling of methanol on single crystal gold were used to reveal the catalytic cycle responsible for the oxygen-assisted coupling of alcohols to form their corresponding ester. This reaction is initiated by adsorbed oxygen atoms - so-called "active" oxygen. These model studies correctly predict the patterns of reactivity observed under catalytic conditions over nanoporous gold *catalysts* at 1 atm and 100-150 C. To understand more precisely the connection between the UHV studies and the reactor performance, fast, metered, pressure pulses of methanol were passed over a small amount of the catalyst at 100-150 C (TAP reactor) over a wide range of prescribed oxygen coverages, and the transient responses of the products utilized to determine the product selectivity. The dependence of the selectivity on oxygen coverage and temperature were assessed using rate constants obtained from the studies in UHV in combination with theoretical computations. Regression of the transient response information using the mechanism obtained from UHV reproduced the selectivity patterns precisely with modest adjustments to the rate constants. Differences in selectivity with respect to steady flow reactor results at 1 atm and 150 C were observed, however. These differences were explained entirely by a pressure effect, the origin of which is the variation in the surface concentration of adsorbed methoxy due to the kinetics of the elementary steps of the mechanism. When adjusted from the TAP conditions to 1 atm pressure, the mechanistic analysis accounts for the reactor performance exactly. The relationship between these kinetic studies and the mechanistic determinations from the model studies will be discussed.
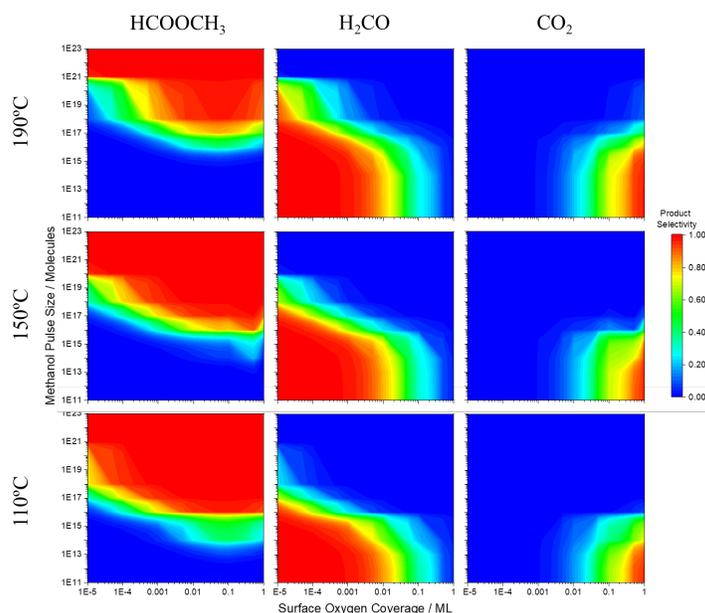

Figure 1. Selectivity contours for increasing reactant pressure (methanol) at varying active oxygen coverage on npAu catalysts from mechanistic analysis and fundamental rate constants

Corresponding author email: rmadix@seas.harvard.edu

Atomic Observation of Praseodymia-Titania Mixed Oxides Functionalized Nanoporous Gold as Stable Catalysts for Water-Gas Shift Reaction

Junjie Shi[12], Caixia Qi[1*], Christoph Mahr[3], Andreas Rosenauer[3], Marcus Bäumer[2], Arne Wittstock[2]

(1) Shandong Applied Research Centre of Gold Nanotechnology, School of Chemistry & Chemical Engineering, Yantai University, Yantai, China

(2) Institute of Applied and Physical Chemistry and Center for Environmental Research and Sustainable Technology, University Bremen, Leobener Str. UFT, 28359 Bremen, Germany

(3) Institute of Solid State Physics, University Bremen, Bremen, Germany

Dealloyed nanoporous metals hold great promise in the field of heterogeneous catalysis, however their tendency to coarsening at elevated temperature or under catalytic reaction conditions limit their further applications.[1-4] Here, we report highly stable praseodymia-titania mixed oxides functionalized nanoporous gold synthesized by a sol-gel method.[2] Specifically, we used aberration-corrected transmission electron and energy-filtered TEM imaging (EFTEM) to study the morphology and interface of the oxide and npAu substrate from an atomic-level. The further electron energy loss spectroscopy (EELS) point Pr-TiO$_x$ mixed oxides can form a solid solution. The flow reactor tests show that the Pr-TiO$_x$ functionalized nanoporous gold are not only highly active but also distinctively stable for water gas shift reaction in both low and high temperature range. Our atomic-scale observations provided compelling evidence that the formation of Pr-TiOx mixed oxide solid solution on the stepped surface of npAu play a key role in preventing the nanopore coarsening by lowering the free energy of the catalyst. The results demonstrate the potential of engineering the compositions of oxides coatings for advanced functional systems. We expect that such a catalyst design methodology will open the door to a new area of catalyst development.
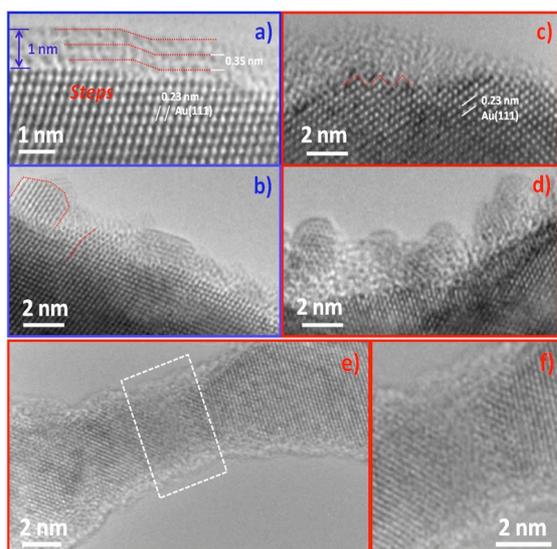

Figure 1. Surface atomic structure of oxides covered nanoporous gold.
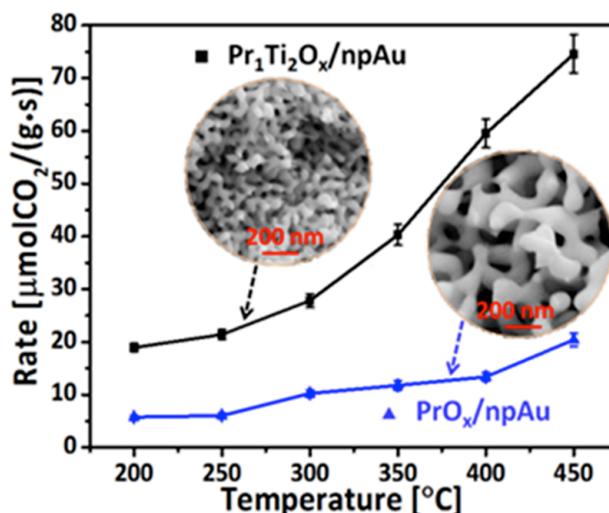
Figure 2. Water-Gas Shift activity of Pr$_1$Ti$_2$O$_x$/npAu and PrO$_x$/npAu as a function of temperature.

References
1- Wittstock, A.; Zielasek, V.; Biener, J.; Friend, C. M.; Baumer, M., Science, 327 (2010).
2- Shi, J.; Baumer, M.; Wittstock, A., JPCC, (118) 29270-29277(2014)
3- Shi, J.; Bäumer, M.; Wittstock, A., Catal. Sci. Technol (2016).
4- Shi, J.; Baumer, M.; Wittstock, A., PCCP, (19) 8880--8888 (2017).

Corresponding author email: qicx@ytu.edu.cn

In-situ E-TEM study of the morphology of TiO$_2$ supported gold nanocatalysts under oxidizing (O$_2$) and reducing (H$_2$) atmosphere

Adrian Chmielewski[1,*], Jaysen Nelayah[1], Hélène Prunier[1,4], Catherine Louis[2], Laurent Delannoy[2], Pavel Afanasiev[3], Damien Alloyeau[1], Guillaume Wang[1] and Christian Ricolleau[1]

(1) *Université Paris Diderot, Sorbonne Paris Cité, CNRS, Laboratoire Matériaux et Phénomènes Quantiques, UMR 7162, 75013, Paris, France.*
(2) *Laboratoire de Réactivité de Surface, Sorbonne Universités, UMR 7197, 4 Place Jussieu, 75005, Paris, France.*
(3) *Institut de recherches sur la catalyse et l'environnement de Lyon (IRCELYON), UMR 5256 CNRS & Université Claude Bernard – Lyon 1, 2 avenue Albert Einstein, 69626 Villeurbanne, France.*
(4) *Université Paris Diderot, Sorbonne Paris Cité, CNRS, Laboratoire Matière et Systèmes Complexes, UM4 7057, 75013, Paris, France.*

Since the discovery of the capabilities of nanometer sized gold clusters for the oxidation of carbon monoxide by Haruta *et al.* [1], supported-gold nanoparticles (NPs) are being intensively studied in the field of heterogeneous catalysis. Despite this on-going interest, the link between catalytic activity and morphology of the NPs is still not completely clear. This results from the lack of direct observations of these NPs in their reaction environments. In this contribution, we present *in situ* gas TEM studies of the morphological transformation of Au NPs supported on rutile-TiO$_2$ nanorods under oxidizing (O$_2$) and reductive (H$_2$) atmospheres as function of gas pressure and temperature.

Monometallic gold NPs were fabricated by pulsed laser deposition and deposited on rutile-TiO$_2$ nanorods. *In-situ* gas TEM up to atmospheric pressure and 400 °C was performed in an environmental gas-cell from Protochips Inc. Figure 1 shows a series of dark-field images of TiO$_2$-supported Au NPs under 750 Torr of O$_2$ between room temperature and 400 °C. Above 200°C, the NPs present truncated octahedron-like shape bounded by (100) and (111) facets. Below 200°C, the NPs present more rounded-like shape. This implies a change in surface energies of the (111) and (100) facets that form the truncated octahedron shape as well as a growth of (110) facets that make the NPs look more rounded.
The influence of the reaction medium (O$_2$, H$_2$) as well as the gas pressure and the temperature on the morphology of Au NPs will be discussed in this presentation.
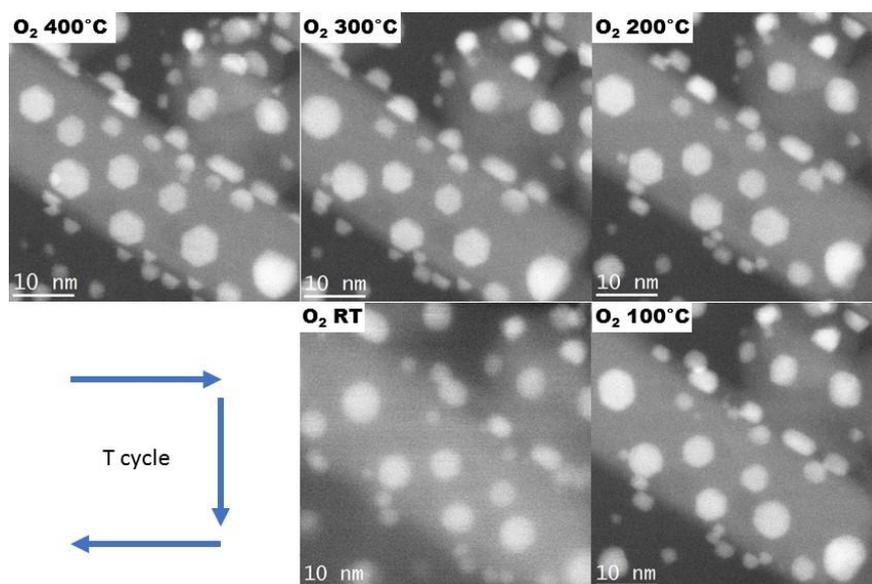

Figure 1. TiO$_2$ supported gold NPs under 750 Torr of O$_2$ at 400°C, 300°C, 200°C, 100°C and RT.

References
1- M. Haruta *et al.*, J. Catal. **115**, 301, (1989)

Corresponding author email: adrian.chmielewski@univ-paris-diderot.fr

Pd and CO oxidation on $Au_{30}Pd_{70}$(110) upon O_2 and CO elevated pressure

Marie-Claire SAINT-LAGER[1], Marie-Angélique Languille[2], Francisco J. Cadete Santos Aires[2], Pierre Dolle[1], Stéphanie Garaudée[1], Aude Bailly[1], Eric Ehret[2], Odile Robach[3]

(1) Institut Néel, 25 avenue des Martyrs, BP 166, F-38042 Grenoble cedex 9
(2) Institut de Recherche sur la Catalyse et l'Environnement, CNRS, Villeurbanne, France
(3) DRF//INAC/MEM/NRS, 17 Avenue des Martyrs, 38000 Grenoble

The pioneering work by Haruta *et al*[1] on low-temperature CO oxidation catalyzed by supported Au nanoparticles has stimulated numerous studies, among them the choice of Au_xPd_{1-x} alloy to improve the catalytic performance of both elements.

It was shown that Pd preferential segregation to the AuPd surface allows to form contiguous Pd sites that are necessary to O_2 dissociation and the presence of gold in the Pd neighboring facilitate CO desorption; therefore the PdAu alloys reactivity is superior compared with pure Pd below 200°C[2].

In this frame, we performed a detailed structural study of $Au_{30}Pd_{70}$(110) surface from UHV up to near ambient pressure of oxygen and CO as well as reactive conditions for CO oxidation (CO + O_2) at moderate temperatures (from RT to 200°C). We coupled *in situ* by GIXRD (grazing incidence x-ray diffraction) to gas analysis by mass spectroscopy, thanks to an homemade setup[3]. This was completed by chemical analysis by AES for each of the mains state of the system and by STM measurements.

The (1x1) Au rich surface in UHV, at room temperature, strongly evolves under oxygen when increasing the pressure up to 500 mbar. It induces the Pd enrichment with structural modifications with several (P,T) domains : two kinds of (1X2) reconstructions were identified, then the oxygen insertion in subsurface region before the growth of a fairly well defined film of strained PdO(100).

High pressures of CO also induce palladium segregation[4] therefore it appears that under (semi) realistic conditions gold tends to disappear from the $Au_{30}Pd_{70}$(110) surface. It was followed under reactive conditions at moderate temperature. The strained PdO was found highly active in oxygen-rich conditions and it turns out to be a very interesting model to study the mechanism of the CO oxidation on pure palladium surface that remains still very debated[5].

References

1 - M. Haruta *et al*, N. *Chem. Lett. 2*, 405 (1987) ; *J. Catal. 115*, 301, (1989).
2 - F. Gao *et al*, *JACS,* 131 , 5735 (2009).
3 - M.C. Saint-Lager *et al*, Rev. Sci. Instrum., 78 , 083902 (2007).
4 - M.A Languille *et al,* Catal. Today, 260, 39 (2016).
5 - M. Che*n et al, Top Catal 56 (2013) 1299: Kondoh et al Catal Today, 260,14 (2016); M. A. Van Spronsen et al, Chem. Soc. Rev.,* 46, 4347 (2017)

Corresponding author email: marie-claire.saint-lager@neel.cnrs.fr

# In situ observation of metal redistribution in gold-silver nanorods

J.E.S. van der Hoeven[1,2], T.A.J. Welling[2], T.A.G. da Silva[3], J.E. van den Reijen[1], X. Carrier[3], C. Louis[3], A. van Blaaderen[2], P.E. de Jongh[1]
(1) *Inorganic Chemistry and Catalysis, Utrecht University, Utrecht, Netherlands*
(2) *Soft Condensed Matter, Utrecht University, Utrecht, Netherlands*
(3) *Laboratoire de Réactivité de Surface, l'Université Pierre et Marie Curie, Paris, France*

Bimetallic Au-based nanoparticles receive much attention for their application in gas-phase catalysis [1,2]. Generally, the catalytic properties of such bimetallic nanoparticles critically depend on the distribution of the two metals. However, it remains very challenging to characterize the evolution of the atomic distribution within the particles under catalytic reaction conditions and at elevated temperatures. To study thermally driven metal redistribution in bimetallic nanoparticles *in situ*, we developed a well-defined model system consisting of Au-core Ag-shell nanorods encapsulated in a mesoporous silica shell [3,4]. This allowed us to control the Ag-Au ratio, shape and size of the nanoparticles, while the silica shell prevented deformation and sintering of the rods at elevated temperatures. We specifically chose Au-Ag based nanoparticles to study the kinetics of the metal redistribution, since Au-Ag alloy formation is thermodynamically favourable at all compositions. We studied the influence of the Au-Ag ratio on the alloying process in situ in the electron microscope and with EXAFS, and with electron microscopy ex situ after heating in an oven. We show that the alloying kinetics in the nanorods are, just as in bulk crystals, strongly influenced by the Au-Ag ratio, whereby a higher Ag-content leads to higher alloying temperatures. In addition, smaller particle volumes lead to lower alloy temperatures. Based on our experimental results a theoretical model was developed which accurately describes the alloying temperatures of Au-Ag based nanoparticles as a function of composition and volume.
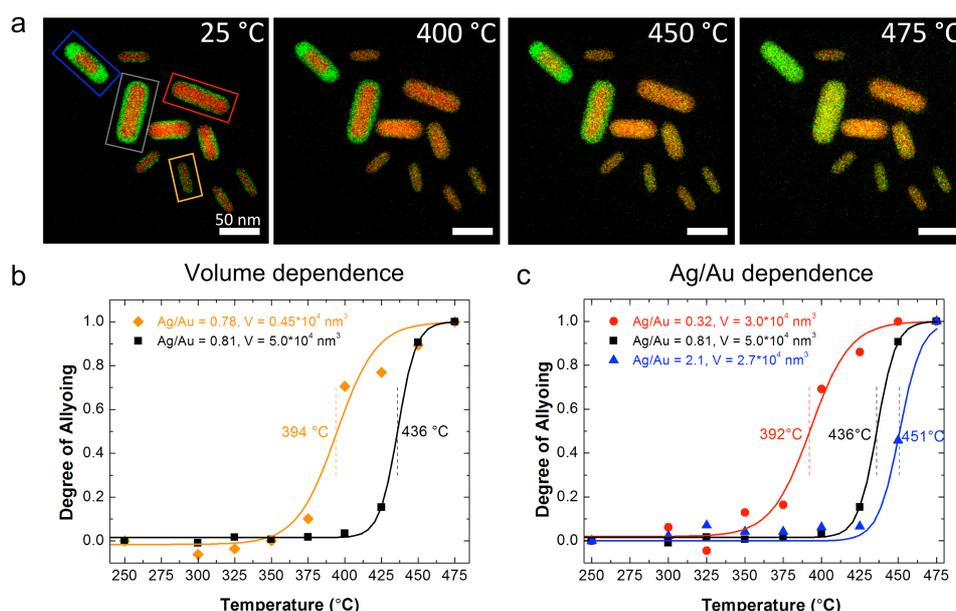
Figure 1. In situ heating of silica coated Au-core Ag-shell NRs in an electron microscope.
A) EDX maps with Au in red and Ag in green acquired at 25, 400, 450 and 475 °C. B) Plot of the degree of alloying for NRs as a function of particle volume and C) Ag/Au ratio

References

1- N. Masoud, L. Delannoy, C. Calers, J-J. Gallet, F. Bournel, K.P. de Jong, C. Louis, and P.E. de Jongh, ChemCatChem, 2017, 9, 2418 –2425
2- A. Sandoval, L. Delannoy, C. Méthivier, C. Louis, R. Zanella, Applied Catalysis A, 2015
3- W.A. Albrecht and J.E.S. van der Hoeven, T. Deng, P.E. de Jongh, A. van Blaaderen., Nanoscale, **9,** (2017), 2845-2851
4- T.S. Deng, J.E.S. van der Hoeven, A. Yalcin, H.W. Zandbergen, M.A. van Huis, A. van Blaaderen, Chem. Mater. 27, (2015), 7196-7203

Corresponding author email: j.e.s.vanderhoeven@uu.nl

Catalytic removal of formaldehyde at room temperature over supported gold catalysts

Bingbing Chen, Chuan Shi[*]

Laboratory of Plasma Physical Chemistry, Dalian University of Technology, Dalian, People's Republic of China.

Formaldehyde (HCHO) as a common indoor pollutant exposes great threat to human health. Long term inhaling of air with HCHO even at ppm level could lead to severe body diseases. With the strengthened environmental consciousness as well as the stricter regulations, HCHO abatement has been attracted more and more attention[1,2]. Catalytic removal at room temperature remains as a big challenge.

Series of gold nanoparticles stabilized on various supports[3-6] (CeO_2, FeO_x, γ-Al_2O_3 and SiO_2) were studied in our group as active catalysts for HCHO oxidation at room temperature under high GHSV of 600000 ml/(g·s). The results shown that the particle size of Au NPs plays crucial role in determining the initial activity. Au/γ-Al_2O_3 and Au/SiO_2 catalysts with the higher Au dispersion and smaller Au particle size render better catalytic HCHO oxidation activities. While the support has more significant influence on catalysts' stability. Owing to the strong surface interactions between Au NPs and the reducible oxides (like CeO_2), the gold NPs could be anchored over the oxides through the abundant of surface oxygen species (O_{ads}) and therefore exhibits a better stability for HCHO oxidation. However, due to the weak interaction between Au NPs and SiO_2, the aggregation of gold particles occurred during the reaction, which results in the fast deactivation[7].

By employing the technique of in situ DRIFTs, we investigate the reaction mechanism of HCHO oxidation over supported gold catalysts. The rate limiting step is oxidation of $HCOO^-_{(s)}$ into CO_2 and H_2O, which was catalyzed by Au NPs and being promoted by the presence of humidity.
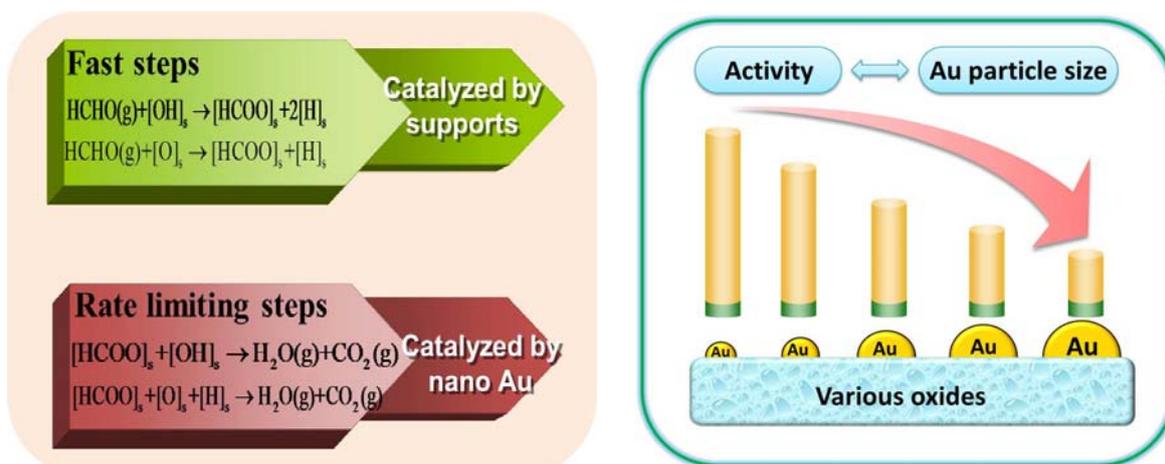

Figure 1. Catalyze the HCHO oxidation on various supports

References
1- Y. Wang, S. Yao, C. Shi et al., Catal. Sci. Technol. **5,** 4968 (2015).
2- Y. Wang, B. B. Chen, C. Shi et al., Catal. Commun. **59,** 195 (2015).
3- B. B. Chen, C. Shi, M. Crocker et al., Appl Catal., B **132-133**, 245 (2013).
4- B. B. Chen, Y. Wang, C. Shi et al., Appl. Catal., B **154-155,** 73 (2014).
5- B. B. Chen, Y. Wang, C. Shi et al., Catal. Commun. **42**, 93, (2013).
6- B.B. Chen, X.B. Zhu, C. Shi et al., Catal. Today **281,** 512 (2017).
7- B. B. Chen, X.B. Zhu, C. Shi et al., Chin. J. Catal. **37**, 1729 (2016).

Corresponding author email: chuanshi@dlut.edu.cn

Toward an Accurate Theoretical Description of Gold-based Nanocatalysts Under Reactive Media

M. Dhifallah[1,2], I-C Oguz[1], J. Meng[3], B. Zhu[3] and H. Guesmi[1*]

[1]Institut Charles Gerhardt Montpellier, CNRS/ENSCM, 8 Rue de l'Ecole Normale, 34296 Montpellier, France.
[2]Université de Gabes, Unité de recherche environnement, Catalyse et Analyse des Procédés, 6072 Gabes, Tunisie.
[3]Division of Interfacial Water and Key Laboratory of Interfacial Physics and Technology, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China.

Nano-alloy catalysts typically operate under high-pressure and high-temperature conditions, and this reactive environment may substantially influence the structure and the surface composition and therefore the reactivity of these nano-materials. Theoretical studies of catalytic properties are often investigated on model systems (extended surfaces and/or small nanoparticles) where the effect of the oxide support is neglected and where no account is taken for the possibility that the catalyst surface composition can be modified after the gas exposure [1]. This is a serious drawback that may prevent reliable description of the catalyst reactivity that mainly depends on the configuration of the surface. Nowadays, modeling the equilibrium structure and the shape of nano-alloys in a "realistic" reactive environment is still a barely studied subject and remains an extremely challenging task.

Recent works in the group have been focused on the study of the structural changes of gold-based nanocatalysts under reactive gas and on their related catalytic properties [2-5]. Different theoretical approaches from Density Functional Theory (DFT) calculations combined with Monte Carlo simulations (MC) to multiscale structure reconstruction (MSR) methodology were developed to predict and to reproduce the effect of adsorbed gas on the surface. Based on DFT-Ising model, CO adsorption induced segregation phenomenon in bimetallic Au-Pd systems (Figure 1) was explained and the different chemical ordering on the surface as a function of the temperature and the gas pressure were predicted [2]. In addition, to compare with experimental data, a complete phase diagram of the formed ordered phases as well as the overall reaction pathways toward CO oxidation reaction were predicted [3]. From MSR model, quantitative predictions of the equilibrium geometries of free monometallic gold nanoparticles [4] (Figure 2) and more recently on free and supported bimetallic ones were achieved at different temperatures and gas pressures. Simulation results of the shape evolution changes under reactive media have shown high concordance with experimental observations.
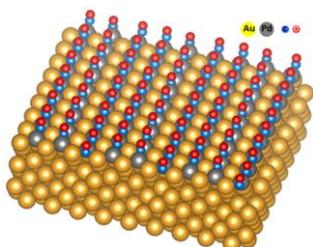

Figure 1: CO adsorption-inducing Pd segregation in Au-Pd surface and formation of stable ordered phases [2]. Pd linear chains (big grey balls) separated by Au linear chains (big yellow balls) with CO bridging Pd atoms. Carbon and oxygen atoms are represented by small blue and red balls, respectively.
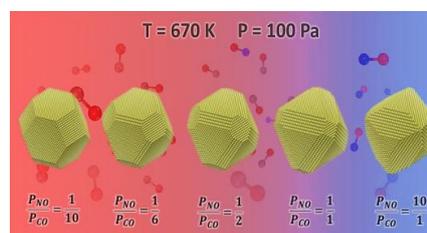
Figure 2: The shape evolution of gold nanoparticles in presence of mixed gas pressure from MSR model [4].

References

1- H. Guesmi, Gold Bulletin **46**, 213 (2013).
2- B. Zhu, J. Creuze, C. Mottet, B. Legrand, H. Guesmi, J. Phys. Chem C **120**, 350 (2016).
3- I-C OGUZ, T. Minéva and H. Guesmi, J. Chem. Phys. **148**, 024701-10 (2018).
4- B. Zhu, J. Meng, Yi Gao J. Phys. Chem. C **121**, 5629 (2017).

Corresponding author email: hazar.guesmi@enscm.fr

Role of Water on CO oxidation over Boron-Nitrogen sheet supported Gold Clusters (Au$_9$) -A First Principles study

Shi-En Fu, Jyh-Chiang Jiang*

Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan, R.O.C

Carbon monoxide (CO) is a highly toxic gas for human because of its high affinity with hemoglobin, and it causes many illnesses, suffocation, and sudden death. Therefore, the elimination of CO is attracted practical importance to control the environment. In many processes, the catalytic oxidation of CO to CO_2 over a heterogeneous catalyst surface is the suitable method in CO elimination. Due to the groundbreaking work of Haruta et al., [1] the use of gold nanoparticles as a catalyst to oxidize CO to CO_2 has become an interesting topic. Previously, many theoretical and experimental studies have explored the catalytic activity of Au clusters on pure metals and metal oxide surfaces. [2] Here we considered Au$_9$ clusters supported on a boron-nitrogen sheet (BN) and investigated its catalytic activity towards CO oxidation using first-principles calculations. Furthermore, we also explored the effect of water on the CO oxidation on Au clusters supported on the boron-nitrogen sheet. Our results indicate that Au$_9$ cluster is stably adsorbed on BN surface and the catalytic activity of Au$_9$ cluster is enhanced through electron transfer from BN to Au$_9$ cluster. We found that the stretching vibration of adsorbed CO on Au$_9$/BN surface is blue-shifted with the increase of water content, which is in agreement with the previous experimental observation. [3] By exploring the all possible CO oxidation pathways, we found that in presence with water on the Au$_9$/BN surface, the reaction barrier of rate determining step of CO oxidation is only 0.40eV, which is significantly lower than the previously studies. Our calculated results suggest that Au$_9$ clusters supported on BN surface could be a promising catalyst for CO oxidation at low-temperature conditions.

References
1- M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M. J. Genet, B. Delmon, J. Catal 144, 175-192 (1993).
2- H. An, S. Kwon, H. Ha, H. Y. Kim, J. Phys. Chem. C 120, 9292-9298 (2016).
3- T. M. Tran-Thuy, C. C. Chen, S. D. Lin, ACS Catal 7, 4304−4312 (2017).

M10506136@mail.ntust.edu.tw

In situ study of single-site gold catalyst during acetylene hydrochlorination using synchrotron radiation

G. Malta[1], S. J. Freakley[1], S. A. Kondrat[2], E. Gibson[4], P. Wells[4], C. J. Kiely[3] and G. J. Hutchings[1]

(1) *Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, CF10 3AT, UK*
(2) *Department of Chemistry, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK*
(3) *Department of Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania, PA 18015, USA*
(4) *UK Catalysis Hub, Research Complex at Harwell Rutherford Appleton Laboratory Harwell, Oxon, Didcot, OX110FA (UK)*

Vinyl chloride monomer (VCM) is a major commodity chemical with over 30 million tons produced annually; ca. the 90% of the VCM production is used in the manufacture of polyvinyl chloride (PVC). One of the main route for the production of VCM is the direct hydrochlorination of acetylene, a single step process, traditionally catalysed by carbon-supported mercuric chloride.

In 2013, the "Minamata convention on mercury", prohibited the use of mercury in VCM plants constructed after 2017, while the already existing reactors must be mercury-free by 2022.

Following the prediction of Hutchings in 1985,[1] Au supported on carbon has recently been validated as a replacement catalyst for this large scale industrial process.[2] Even though it was predicted and demonstrated in 1985 that gold supported on activated carbon is the most active catalyst for the acetylene hydrochlorination reaction, so far, the absence of operando studies of the acetylene hydrochlorination reaction has hindered the understanding of these systems.

In this study, the nature of the active species in carbon-supported gold catalysts has been investigated using X-ray Absorption spectroscopy (XAS) and Transmission Electron Microscopy (TEM).

We show that the active species comprise single-site cationic Au entities. In particular, during the time online studies, distinct changes in the X-ray Absorption Near Edge Structure (XANES) were observed (Figure 1 A), which clearly correlate to the reaction profile. [3] This observation, together with the analysis of the Extended X-ray Absorption Fine Structure (EXAFS) and supported by TEM, lead us to the conclusion that the active site for this reaction is a supported gold cation, including both Au (I) and Au (III), showing analogies with the single-site homogeneous catalysis.

The role of reactants was also taken into consideration in the deactivation mechanism of gold on carbon catalyst *via* an in situ XAS sequential gas flow experiment. Finally, tests performed on high metal loading catalyst allow to observe the deactivation of the catalyst due to the formation of inactive nanoparticles (Figure 1 B).

Finally, we reaffirm that in situ XAFS is important for studying the properties of this single site Au catalyst under various gas compositions and during deactivation.
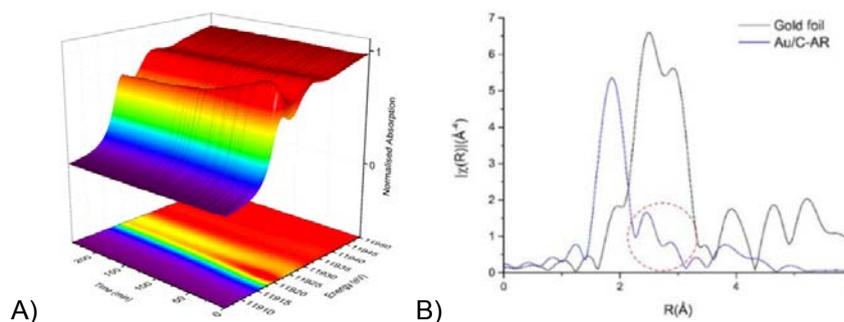

Figure 1. A) Three-dimensional profile plot of successive Au L$_3$ edges from XANES spectra acquired in situ as a function of reaction time. B) In situ EXAFS Fourier transform of the same catalyst compared to the refence material (Gold foil)

References
1- G.J. Hutchings, J. Catal, **96**, 292 (1985).
2- P. Johnston, N. Carthey, G. J. Hutchings, J. Am. Chem. Soc. **137**, 14548-14557 (2015).
3- G. Malta, S. A. Kondrat, S. J. Freakley, C. J. Davies, L. Lu, S. Dawson, A. Thetford, E. K. Gibson, D. J. Morgan, W. Jones, P. P. Wells, P. Johnston, C. R. A. Catlow, C. J. Kiely and G. J. Hutchings, Science **355**, 1399–1403 (2017)

*Corresponding author email: maltag@cardiff.ac.uk*

Stability and Reactivity of Gold Single-Atom Catalyst (SAC)

Jun Li[*]

Department of Chemistry, Tsinghua University, Beijing, China

Single-atom catalysis is a hot topic recently in the field of heterogeneous catalysis [1,2]. Fundamental understanding of support effects and metal–support interaction is critical in single-atom catalysis and general heterogeneous catalysis as well. In this work, theoretical investigations are carried out to study the nature of support effects of different tetravalent-metal dioxides of MO_2 (M = Ti, Zr, Ce, Hf, Th) in gold SACs using density functional theory with on-site Coulomb interactions (DFT+U). The properties of gold adatom on the stoichiometric (MO_2) and reduced (MO_{2-x}) surfaces as well as CO adsorption on Au_1/MO_2 and Au_1/MO_{2-x} have been studied systematically. The fundamental *quantum primogenic effect* that causes the radial contraction and low orbital energies of 3d and 4f orbitals in these MO_2 oxides is found to play a vital role in determining the valence states and charge distribution of gold single atoms (SAs) as well as the adsorption modes of CO on Au SAs with various MO_2 supports. We find that gold SAs supported on different surfaces exhibit oxidation states from Au(−I) to Au(0) to Au(I), depending on the nature of the metal oxide supports. The support-dependent oxidation states and charge distribution of Au can further influence the adsorption mode of CO. These results provide essential understanding on the nature of support effects of metal oxides in heterogeneous catalysis [3].

We have constructed a general thermodynamic model of chemical potentials and applied DFT electronic structure and *ab initio* molecular dynamics simulations, as well as kinetic Monte Carlo analysis, to probe the dynamical, reactive, and kinetic aspects of metal SACs on oxide support [4]. It is shown that, under realistic conditions, various factors such as temperature, pressure, particle size, and the reducibility of the support can strongly affect both the stability and the reactivity of SACs by altering the relative chemical potentials between SAs and metal nanoparticles (NPs). Remarkably, under reaction conditions, Au SAs can be dynamically created at the interface of small-size Au NPs on ceria support even without step sites, which accounts for the puzzling significant size effect in gold catalysis [5]. Our work underscores an unrecognized critical role of dynamic Au SAs in gold nanocatalysis and provides a general methodology for designing the metal SACs on oxide supports.
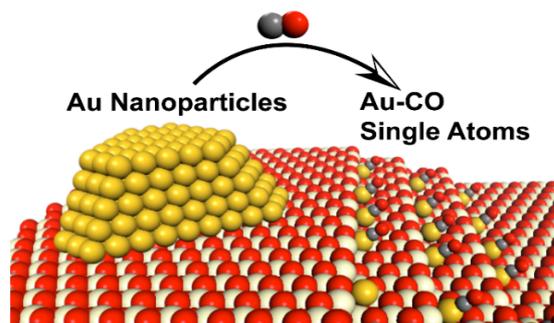
References

1- B. Qiao, A. Wang, X. Yang, L.F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li, T. Zhang, Single-Atom Catalysis of CO Oxidation Using Pt_1/FeO_x, *Nature Chem.* **3**, 634−641 (2011).

2- X. Yang, A. Wang, B. Qiao, J. Li, J. Liu, T. Zhang, Single-Atom Catalysts: A New Frontier in Heterogeneous Catalysis, *Acc. Chem. Res.* **46**, 1740-1748 (2013).

3- Y. Tang, S. Zhao, B. Long, J.C. Liu, J. Li, On the Nature of Support Effects of Metal Dioxides MO_2 (M = Ti, Zr, Hf, Ce,Th) in Single-Atom Gold Catalysts: Importance of Quantum Primogenic Effect, *J. Phys. Chem. C* **120**, 17514-17526 (2016).

4- J.C. Liu, Y.G. Wang, J. Li, Toward Rational Design of Oxide-Supported Single Atom Catalysts: Atomic Dispersion of Gold on Ceria, *J. Am. Chem. Soc.* **139**, 6190 (2017).

5- Y.G. Wang, D. Mei, V.A. Glezakon, J. Li, R. Rousseau, Dynamic Formation of Single-Atom Catalytic Active Sites on Ceria-Supported Gold Nanoparticles, *Nature Commun.* **6**, 6511 (2015).

Corresponding author email: junli@tsinghua.edu.cn

The influence of gold and copper on activity and selectivity of Nb₂O₅ in photocatalytic methanol oxidation

L. Wolski[1,2*], M. El-Roz[2], M. Daturi[2], M. Ziolek[1]

(1) *Adam Mickiewicz University in Poznań, Faculty of Chemistry, Poznań, Poland*
(2) *Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, Caen, France*

In recent years a lot of attention has been paid to development of active and selective catalysts for photocatalytic methanol oxidation. So far, detailed studies on this reaction allowed the investigation of the mechanism of photocatalytic process and to determine the factors affecting the catalyst activity and selectivity [1]. Our studies are part of these efforts due to investigation of the influence of gold and copper, as well as gold-copper interaction on the photocatalytic activity of semiconductors. The selection of Nb₂O₅ as a model support resulted from its high Brønsted acidity that is important factor for the obtainment of high selectivity towards the most valuable products, e.g. dimethoxymethane [2].

The studies included synthesis of mono (Au, Cu) and bimetallic (Au-Cu) photocatalysts supported on Nb₂O₅. Copper was deposited by wet impregnation, while for the deposition of gold two different approaches were applied, i.e. deposition-reduction (DR) and grafting with (3-Aminopropyl)trimethoxysilane (APTMS). The catalysts prepared were characterized with ICP-OES, XRD, N₂-adsortion/desorption, UV-vis, XPS, STEM-EDX, and in situ adsorption of pyridine and methanol. Photocatalytic activity of materials was studied in operando system under the irradiation with different light sources (monochromatic UV light, λ = 365 nm; polychromatic UV light with different intensity and polychromatic visible light, λ > 390 nm).
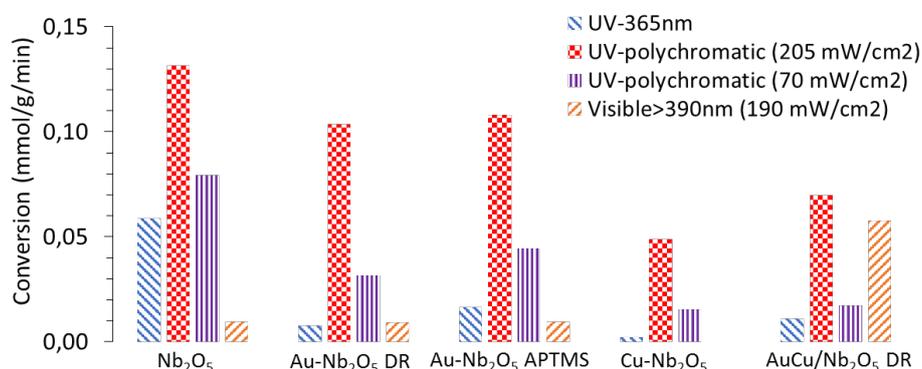

Fig. 1. Activity of catalysts in photocatalytic methanol oxidation depending on light source.

The results of photocatalytic activity of materials are shown in Fig. 1. From among all the catalyst prepared the highest activity in methanol photooxidation under polychromatic UV irradiation showed unmodified Nb₂O₅. The method of gold deposition has not affected the catalyst activity, but had significant impact on products distribution. Deposition of gold by anchoring allowed obtainment a high selectivity to dimethoxymethane, while deposition of gold by deposition-reduction led to the formation of CO₂ as the main product. It was observed that copper-containing catalysts (Cu/Nb₂O₅ and AuCu/Nb₂O₅) exhibited the lowest activity in MeOH oxidation under UV irradiation. Very interesting phenomenon was observed under visible light irradiation. From among all the catalysts prepared the highest activity was observed for bimetallic Au-Cu catalysts, while Cu/Nb₂O₅ and Au/Nb₂O₅ were almost inactive. The detailed analyses of relationship between the activity and selectivity of catalysts and their surface and physicochemical properties are the main issue of our presentation.

Acknowledgements

References

[1] M. El-Roz, P. Bazin, M. Daturi, F. Thibault-Starzyk, Phys. Chem. Chem. Phys. **17**, 11277 (2015).
[2] M. El-Roz, L. Lakiss, I. Telegeiev, O.I. Lebedev, P. Bazin, A. Vicente, C. Fernandez, V. Valtchev, ACS Appl. Mater. Interfaces. **9**, 17846 (2017).

*Corresponding author email: wolski.lukasz@amu.edu.pl*

Hydrogen-promoted CO oxidation over hydrophobic Au/FLG catalysts

F. Vigneron, A. Rach, J.-M. Nhut, A. Piquet, C. Pham-Huu, <u>V. Caps*</u>

ICPEES (Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé), CNRS UMR 7515 / University of Strasbourg, 25 rue Becquerel, 67087 Strasbourg Cedex 02, France

Gold catalysts have been considered for the low temperature purification of hydrogen feeding proton-exchange membrane fuel cells via CO preferential oxidation (PROX) [1] for over a decade. In these catalysts, gold nanoparticles (Au NP) are generally supported over oxides of transition metals. High activity is ensured by a synergy between oxygen activation mediated by the support (or more precisely by the gold/support interface) [2] and oxygen activation mediated by hydrogen [3]. These OH-terminated catalysts however quickly deactivate with time-on-stream, via OH-mediated carbonate formation [4]. Methyl-terminated oxide supports have allowed us to evidence (1) the intrinsic activity of Au NP for hydrogen-mediated CO oxidation with no involvement of the support [5], and (2) the superior selectivity and durability of these hydrophobic materials, due to their low reactivity towards the water by-product [6]. More efficient PROX catalysts based on gold could thus be developed by optimizing hydrogen-mediated oxygen activation catalyzed by such hydrophobic materials.

In this communication, we will show that Au NP supported on highly graphitized, unfunctionalized few-layer graphene (FLG) [7] can activate oxygen at low temperature (< 300°C) in the presence of hydrogen. The kinetics of hydrogen oxidation exhibit a higher H_2 partial order (close to 1, Figure 1a), associated with lower O_2 partial order (0.16), as compared with those observed over OH-terminated gold catalysts. The implications for H_2-mediated CO oxidation will be discussed, as a function of the chemical composition of the catalyst, i.e. the type of heteroatoms present in the material (Figure 1b).
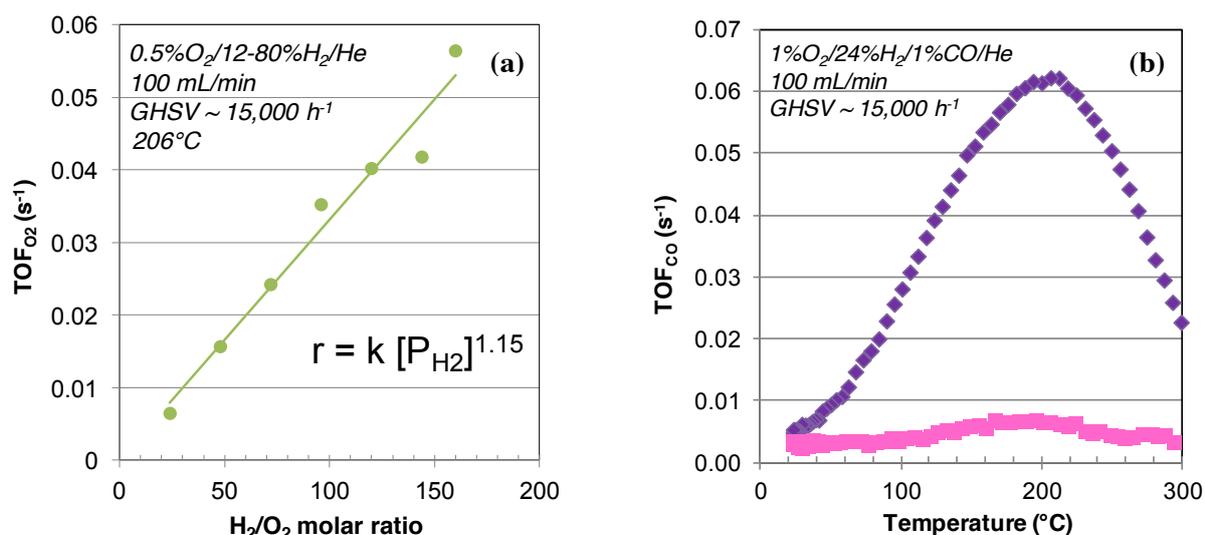
Figure 1. (a) Influence of H_2 partial pressure on Au/FLG-catalyzed oxygen activation and (b) PROX behavior of Au-FLG catalysts containing Na (◆) or not (■)

References

[1] S. Ivanova, C. Petit, V. Pitchon, V. Caps, ChemCatChem **2**, 556 (2010).
[2] G. C. Bond, D. T. Thompson, Gold Bull. **33**, 41 (2000).
[3] E. Quinet, L. Piccolo, F. Morfin, P. Avenier, F. Diehl, V. Caps, J.-L. Rousset, J. Catal. **268**, 384 (2009).
[4] C. K. Costello, M. C. Kung, H.-S. Oh, Y. Wang, H. H. Kung, Appl. Catal. A **232**, 159 (2002).
[5] D. Gajan, K. Guillois, P. Delichère, J.-M. Basset, J.-P. Candy, V. Caps, C. Copéret, A. Lesage, L. Emsley, J. Am. Chem. Soc. **131**, 14667 (2009).
[6] P. Laveille, K. Guillois, A. Tuel, C. Petit, J.-M. Basset, V. Caps, Chem. Commun. **52**, 3179 (2016).
[7] F. Vigneron, A. Piquet, W. Baaziz, P. Ronot, A. Boos, I. Janowska, C. Pham-Huu, C. Petit, V. Caps, Catal. Today **235**, 90 (2014).

Corresponding author e-mail: caps@unistra.fr

The Activation and Deactivation of Au/CeZrO$_4$ in the Low-Temperature Water-Gas Shift Reaction

James H. Carter,[a] Xi Liu,[b] Qian He,[a] Sultan Althahban,[c] Ewa Nowicka,[a] Simon J. Freakley,[a] Liwei Niu,[b] David J. Morgan,[a] Yongwang Li,[b] J. W. (Hans) Niemantsverdriet,[b,d] Stanislaw Golunski,[a] Christopher J. Kiely[a,c] and Graham J. Hutchings*[a]

[a]Cardiff Catalysis Institute, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK.
[b]SynCat@Beijing, Synfuels China Technology Co., Ltd, Beijing, 101407, China
[c]Lehigh University, 5 East Packer Avenue, Bethlehem, PA 18015-3195, USA.
[d]SynCat@DIFFER, Syngaschem BV, PO Box 6336, 5600 HH, Eindhoven, The Netherlands

The low-temperature water-gas shift (LTS) reaction has seen renewed interest in recent years in the context of fuel cell technology as a method of reducing the CO concentration in reformate streams. Au/CeZrO$_4$ is one of the most active catalysts reported for this reaction to date, but undergoes rapid deactivation on-stream.[1] The origin of the deactivation was previously studied it was inferred from EXAFS and XPS that particle de-wetting was the primary deactivation process and particle agglomeration was not considered an important deactivation process.[2] However, direct evidence for particle de-wetting has not been reported and detailed microscopy has not been carried out on this catalyst. Using *stop-start* scanning transmission electron microscopy (STEM) we were able to follow the *exact same nanoparticles* at different intervals of the reaction. Additionally, complementary X-ray photoelectron spectroscopy (XPS) was carried out to monitor changes in the Au oxidation state and speciation.

The time-on-stream profile of 2 wt% Au/CeZrO$_4$, prepared by deposition-precipitation, (Fig. 1, left), illustrates the rapid catalyst deactivation over the first 6 h. After this time, the rate of deactivation decreases but the activity continues to drop over 48 h.
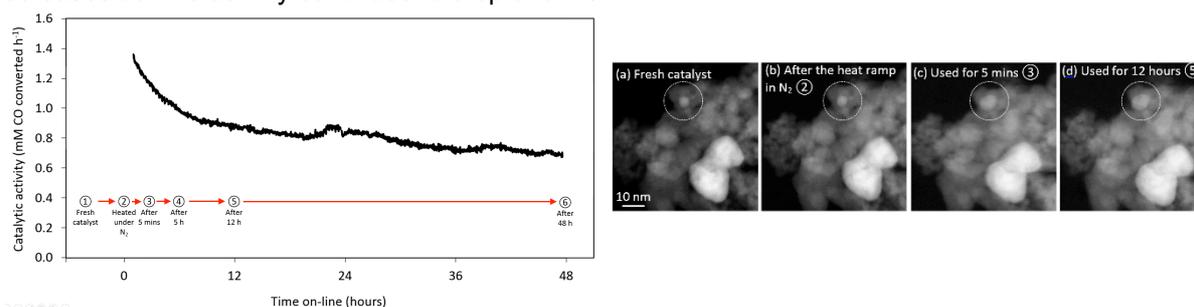

Fig. 1. Left: Time-on-stream profile of 2 wt% Au/CeZrO$_4$ under LTS conditions showing the intervals (1-6) at which the catalyst was characterized. Right: Systematic set of stop-start STEM-HAADF images of the same area in a 2 wt% Au/CeZrO$_4$ catalyst at different stages of the LTS reaction (150 mg, 2% CO, 2% CO$_2$, 7.5 % H$_2$O, 8.1% H$_2$ and 80.4% N$_2$. Total flow rate = 100 cm^3 min^{-1}).

The formation of small Au nanoparticles was observed during the heating up of the catalyst to reaction temperature, from Au species that were not resolvable by HAADF STEM. Additionally, particle agglomeration under reaction conditions was observed using stop-start HAADF STEM (Fig. 1, right). Complementary XPS revealed a decrease in Au^{3+} and a species ascribed to small Au nanoparticles after exposure to LTS reaction conditions. The stop-start STEM and XPS studies were fully consistent with the hypothesis that particle agglomeration is the primary mechanism of catalyst deactivation in the LTS reaction over Au/CeZrO$_4$.

These findings highlight the importance of a strong metal-support interaction in preparing stable catalysts, and will aid the future design of LTS catalysts. Additionally, the novel methodology of stop-start STEM has been shown to be a highly effective means of observing deactivation processes in catalytic reactions, while bypassing the challenge of conventional microscopy, which doesn't allow the same region of sample to be analyzed.

[1]   D. Tibiletti, A. Amieiro-Fonseca, R. Burch, Y. Chen, J. M. Fisher, A. Goguet, C. Hardacre, P. Hu, A. Thompsett, *Journal of Physical Chemistry B* **2005**, *109*.
[2]   A. Goguet, R. Burch, Y. Chen, C. Hardacre, P. Hu, R. W. Joyner, F. C. Meunier, B. S. Mun, A. Thompsett, D. Tibiletti, *Journal of Physical Chemistry C* **2007**, *111*.

Corresponding author email: carterj5@cf.ac.uk

Atomic-layered Au clusters on α-MoC as catalysts for the low-temperature water-gas shift reaction

Xiao Zhang, Chuan Shi[*]

Laboratory of Plasma Physical Chemistry, Dalian University of Technology, Dalian, 116024, People's Republic of China.

The water gas shift（WGS）reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$) is an essential step in the purification process for on-board fuel reforming and hydrogen production. From thermodynamic points of view, WGS is an exothermal reaction, low temperatures favor this process. However, the current industrial $CuO/ZnO/Al_2O_3$ catalysts exhibit poor activities under working temperatures lower than 250ºC. Therefore, considerable work has been focused on developing efficient catalysts for low temperature WGS reaction. Herein, we successfully synthesized layered gold (Au) clusters on a face centered cubicrystal (FCC) structured alpha-phase molybdenum carbide (α-MoC) substrate to create an interfacial catalyst system for the ultralow-temperature WGS reaction[1]. In this paper, we firstly compared the substrate properties of α-MoC with beta-phase molybdenum carbide (β-Mo_2C) which has a hexagonal closed packed (HCP) unit cell. As shown in Figure 1A, β-Mo_2C exhibited very poor WGS activity at whole temperatures. While α-MoC substrate could effectively catalyze the WGS reaction, exhibiting 65% CO conversion at 473 K. Surprisingly, the 2% Au/α-MoC shows 98% CO conversion at only 423K in the product-free gas feed, reaching 1.05 mol_{CO}/mol_{Au}/s, which was 20 times higher than the best activity previously reported in literature. In a single-run reaction (more than 140 h) under the full reformate gas feed, the 2% Au/α-MoC catalyst shows an excellent total turnover number (TTN), reaching up to 385,400 mol_{CO}/mol_{Au}.

Structural characterizations of 2% Au/α-MoC catalyst were further performed. HR-STEM images revealed layered Au clusters epitaxially grown on the substrate (Figure 1B, average diameter of 1-2 nm; thickness of 2-4 atomic layers (<1 nm)), which were in good agreement with the EXAFS fitting results (Figure 1C). Detailed crystal structure analysis also showed that these epitaxial Au clusters strongly aligned with the (111) planes of the α-MoC support. More astonishingly, no obvious structural difference was observed when the catalyst undergoes the high temperature activation (700ºC) process for 2h and the long-term reaction in WGS (more than 100h). Electron diffraction pattern proved that the contact angle of Au (200) and α-MoC (111) was calculated to be 42.7º, much smaller than Au particles over oxides surface, which implies the existence of strong Au-α-MoC interactions between the particles and the substrates. Benefiting from the strong metal-support interaction, water was activated over α-MoC at 30ºC. Adsorbed CO on adjacent Au sites were apt to react with surface hydroxyl groups formed from the water dissociation, leading to the high WGS activity at low temperatures.
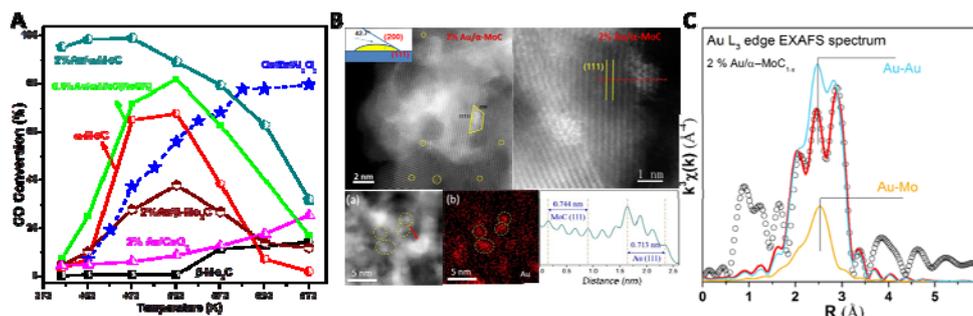

Figure 1. Catalytic properties and structural characterization of 2% Au/α-MoC catalyst. (A) The CO conversion of 2% Au/α-MoC and reference catalysts at various temperature. (condition: 10.5% CO, 21% H_2O, 20% N_2 in Ar; WHSV = 90,000 ml/g/h); (B) The HAADF-STEM images of 2% Au/α-MoC catalyst; (C) Fourier transformation (FT) EXAFS spectrum and fitting results of 2% Au//α-MoC catalyst.

References

1- Yao, S.; Zhang, X.; Zhou, W.; Gao, R.; Xu, W.; Ye, Y.; Lin, L.; Wen, X.; Liu, P.; Chen, B.; Crumlin, E.; Guo, J.; Zuo, Z.; Li, W.; Xie, J.; Lu, L.; Kiely, C. J.; Gu, L.; Shi, C.; Rodriguez, J. A.; Ma, D., Atomic-layered Au clusters on α-MoC as catalysts for the low-temperature water-gas shift reaction. Science **357**, 389 (2017).

Corresponding author email: Chuan Shi (chuanshi@dlut.edu.cn)

Synergetic Effect of Bimetallic Au-Ru/TiO$_2$ Catalysts for CO and Methanol Complete Oxidation

L. Calzada[1], S. Collins[2], L. Delannoy[3,] C. Louis[3], Ch W. Han[4], V. Ortalan[4], R. Zanella[1*]

(1) *Centro de Ciencias Aplicadas y Desarrollo Tecnológico, UNAM, Cd. Mx., Mexico*
(2) *Instituto de Desarrollo Tecnológico para la Industria Química, UNL, Santa Fe, Argentina*
(3) *Laboratoire de Réactivité de Surface, CNRS-Sorbonne Université, Paris, France*
(4) *School of Materials Engineering, Purdue University, West Lafayette, IN, USA.*

It is well known that gold nanoparticles supported on metal oxides are active in various reactions of environmental importance.[1] Particularly, supported Au nanoparticles is well known as very efficient catalysts for CO oxidation at low temperature.[1] It is also possible to perform the oxidation of some volatile organic compounds (VOCs) such as light hydrocarbons and alcohols at room temperature. The most efficient and low-cost method for their abatement is the catalytic combustion to CO$_2$ and H$_2$O, preferentially at low temperatures. On the other hand, the preparation of bimetallic catalysts has been proposed as an alternative to improve the activity, stability and/or selectivity of gold catalysts. In this way, the addition of a second metal could modify the physicochemical and electronic properties of the first metal.[2] Ruthenium-based catalysts have been studied in VOCs oxidation reaction, and in conjunction with gold, they exhibit an improvement in catalytic activity.[3,4]

Methanol is frequently employed as one of the model molecule for the total oxidation of VOCs; it has been investigated using gold catalysts supported on metal oxides.[4]

To study the effect of the addition of Ru to Au/TiO$_2$ catalysts, three types of Au-Ru/TiO$_2$ catalysts were prepared using methods involving deposition-precipitation with urea, with 3 wt% Au and 1.6 wt% Ru, i.e., with a 1:1 atomic ratio:
- co-deposition-precipitation,
- sequential deposition-precipitation with gold deposited first, then ruthenium,
- sequential deposition-precipitation with ruthenium deposited first, then gold.

They were tested in the reaction of CO oxidation performed at increasing temperature, from RT to 300 °C, and compared to monometallic 3 wt% Au/TiO$_2$ and 1.6 wt% Ru/TiO$_2$. Depending on the preparation method and the activation temperature, i.e., the temperature at which the samples were *in situ* reduced under H$_2$ before the reaction, the Au-Ru/TiO$_2$ (1:1) catalysts exhibited catalytic activity, either close to Au/TiO$_2$ or close to Ru/TiO$_2$, i.e., high or poor activity at low temperature, respectively. The most active catalyst was the one prepared by sequential deposition-precipitation with gold deposited first, then ruthenium, and HAADF and microEDS analysis showed that Ru core-Au shell type particles were formed. In contrast, for the poorly active catalysts, gold was in the core and Ru in the shell. For the most active sample, the Au:Ru atomic ratio was varied (1:1, 1:0.75, 1:0.5 and 1:0.25). The catalyst with the 1:0.75 atomic ratio exhibited the highest catalytic activity showing a synergetic effect due to the addition of ruthenium.

These catalysts (sequential deposition-precipitation (gold first then ruthenium)), thermally treated at 300 °C in H$_2$, were also tested in the total oxidation of methanol. The catalytic activity showed a synergetic effect at room temperature mainly for the 1:1 and 0.75:1 atomic ratio.[5] TPR, UV-Vis spectra, XPS and DRIFTS-CO results also confirm the interaction between Ru and Au. Operando FTIR spectroscopy, performed during the oxidation of methanol as a function of the reaction temperature, showed that formates were the main reaction intermediates of the reaction, that they were already formed at RT on bimetallic Au-Ru/TiO$_2$ catalysts and that they were oxidized at lower temperatures than the monometallic Ru and Au counterparts.[4]

References
1- G.C. Bond, C. Louis, D.T. Thompson, Catalysis by Gold, Imperial College Press, London, 2006.
2- V. Dal Santo, A. Gallo, A. Naldoni, M. Guidotti, R. Psaro, Catal. Today 197, 190 (2012).
3- F.W. Chang, L.S. Roselin, T.C. Ou, Appl. Catal. A 334, 147 (2008);
4- T. Sreethawong, D. Sukjit, P. Ouraipryvan, J.W. Schwank, S. Chavadej, Catal.Lett. 138, 160(2010).
5- L.A. Calzada, S. E. Collins, C. W. Han, V. Ortalan, R. Zanella, Appl. Catal. B 207, 79 (2017).

Corresponding author email: rodolfo.zanella@ccadet.unam.mx

# Au-Pd alloy catalysts for the oxidation of organic compounds

Ali Nasrallah[1], David Willock[1], Richard Catlow[1, 2]
(1) *Cardiff University, Cardiff, United Kingdom*
(2) *University College London, London, United Kingdom*

The use of natural gas as a feedstock for chemical synthesis or for the synthesis of fuels currently relies on conversion to syngas and then further processing via Fischer-Tropsch catalysis.[1] A more elegant and lower cost route[2] would be possible if the partial oxidation of methane (the main component of natural gas) to more C_1 molecules such as methanol were available. Noble metals such as gold and palladium have been shown to be highly efficient catalysts for the partial oxidation of methane using H_2O_2 as the oxygen source.[3] Very recently it has been realised that once this catalysis is initiated with H_2O_2, it is possible to incorporate oxygen directly from O_2, which makes the economics of a process based on this reaction much more attractive.[4]

Aside from methane, Au-Pd alloy nanoparticles are highly efficient catalysts for the in-situ production of hydrogen peroxide and the partial oxidation of various organic substrates using hydrogen peroxide.[5, 6] However, the exact mechanism and reactive species in this reaction are unclear. It has been proposed that these oxidation reactions involve radical mechanisms where the oxygen is delivered via a hydroperoxide radical species. The exact form of this species is unclear as is the role of protonation by water to form the species from dioxygen. This project studies the partial oxidation of organic molecules using supported Au-Pd alloy catalysts. The aim is to use quantum chemical calculations to study the activation of oxygen and the role of the peroxide intermediates that are formed in the proposed mechanism. Moreover, the synergistic effect of Au and Pd in this reaction is investigated to rationalise the enhanced performance of the alloy catalyst. In this project, calculations on slab model surfaces of Au, Pd, and Au-Pd alloy are performed using the Vienna Ab Initio Simulation Package (VASP) code.
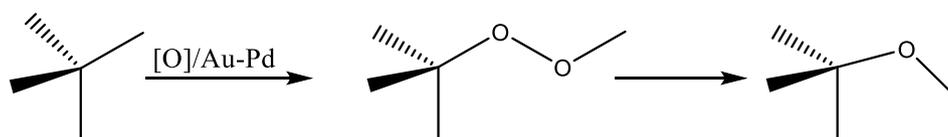
Adsorption of methyl hydroperoxide which is proposed to be the crucial intermediate of this reaction on the (111) and (100) surfaces of pure Au and Pd as well as an alloy surface is evaluated and compared. Based on these results, the cleavage of the O–O bond of the hydroperoxide on the metal surface is investigated by calculating the according transition states and activation energies to determine the activity of the different facets of the pure metal and alloy catalysts.

References
1. Dry, M. Catalysis Today 2002, 71, 227-241.
2. Mansuy, D. (1993). Activation of alkanes : the biomimetic approach. Coordination Chemistry Reviews, 125(1-2), pp.129-141.
3. Asencios, Y.; Marcos, F.; Assaf, J.; Assaf, E. Brazilian Journal of Chemical Engineering 2016, 33, 627-636.
4. N. Agarwal, S. J. Freakley, R. U. McVicker, S. M. Althahban, N. Dimitratos, D. J. Morgan, R. L. Jenkins, D. J. Willock, S. H. Taylor, C. J. Kiely and G. J. Hutchings, Science, 358, 223-226, (2017).
5. H. Alshammari, P. J. Miedziak, D. W. Knight, D. J. Willock and G. J. Hutchings, Catal. Sci. Technol., 3, 1531, (2013).
6. X. Liu, M. Conte, M. Sankar, Q. He, D. M. Murphy, D. Morgan, R. L. Jenkins, D. Knight, K. Whiston, C. J. Kiely, G. J. Hutchings, Appl. Catal. A: Gen., 504, 373, (2015).

Corresponding author email: NasrallahA@cardiff.ac.uk

Oxidative dehydrogenation of cyclohexanol to cyclohexanone over Au/MgCuCr$_2$O$_4$ catalyst

Y. Gao, Emiel. J. M. Hensen
Inorganic Materials Chemistry, Eindhoven University of Technology

Dehydrogenation of cyclohexanol (CH-ol) to cyclohexanone (CH-one) is an important industrial process, as cyclohexanone is an intermediate used in the production of caprolactam. Currently, in the industry Cu-based catalysts are widely used in the direct dehydrogenation process [1-2]. However, this reaction is endothermic and thus restricted by reaction equilibrium. In addition, catalysts used also suffer from serious deactivation. In contrast, oxidative dehydrogenation of CH-ol to CH-one is exothermic, therefore, in principle this process can reduce energy consumption and overcome the reaction equilibrium. More importantly, the introduction of oxygen can help remove some intermediate species which otherwise would lead to deactivation. Gold catalysis has attracted great interest in the past two decades because of its surprisingly high activity and selectivity in many reactions, especially in selective oxidation reactions [3]. However, to our knowledge there has been no report of a highly active, selective and stable catalyst for the gas-phase oxidative dehydrogenation of CH-ol to CH-one.
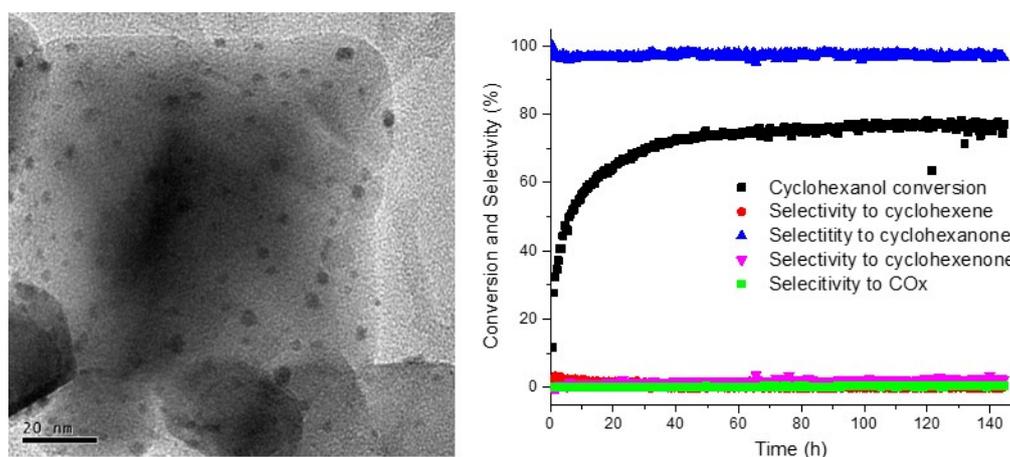

Figure 1. TEM images of fresh Au/MgCuCr$_2$O$_4$ catalyst (left) and catalytic performance of Au/MgCuCr$_2$O$_4$ catalyst in oxidative dehydrogenation of cyclohexanol (right)

In the present work, Au/MgCuCr$_2$O$_4$ catalyst was successfully prepared by deposition-precipitation method. TEM image (Fig.1) shows that gold nanoparticles are in the range of 2-4 nm and well-distributed. In the oxidative dehydrogenation of CH-ol to CH-one, there was an induction period at the initial stage of the reaction, probably due to surface reconstruction. At stable stage, CH-ol could be selectively converted to CH-one with CH-ol conversion of 71% and CH-one selectivity of 96% at 260 °C. Surprisingly, there was no deactivation even after 100 h of reaction, indicating the great advantage of oxidative process. The good catalytic performance can be attributed to the presence of well-dispersed and sinter-resistant nm-sized gold nanoparticles and a strong Au-Cu synergy. The effect of Mg/Cu ratio and residual Na in support were also studied systematically in our research in order to better elucidate the Au-support interaction and the underlying reaction mechanism.

References
1- N. P. Tangale, P. S. Niphadkar, S. S. Deshpandel. Appl. Cata. A, 2013, 467, 421- 429.
2- B. M. Nagaraja, V. S. Kumar, V. Shashikala. J. Mol. Catal. A. 2004, 223, 339-345.
3- A. S. K. Hashmi, G. J. Hutchings, Angew. Chem. Int. Ed. 2006, 45, 7896-7936.

Corresponding author email: y.gao@tue.nl

Efficient Elimination of Ammonia over Niobium Oxide Supported Gold Catalyst at Room Temperature

Mingyue Lin[1], Baoxiang An[1], Nao Niimi[2], Yohei Jikihara[2], Tsuruo Nakayama[2], Tamao Ishida[1], Masatake Haruta[1], Toru Murayama[1*]

(1) *Research Center for Gold Chemistry, Tokyo Metropolitan University, Minami-Osawa, Hachioji, Tokyo, 192-0397, Japan*
(2) *NBC Meshtec Inc, 2-50-3 Toyoda, Hino, Tokyo, 191-0053, Japan*

Ammonia is a well-known pollutant with the characteristic pungent smell which has adverse effects on human health and environment. Selective catalytic oxidation (SCO) of NH_3 with O_2 to harmless N_2, H_2O is a potentially efficient method to remove NH_3. Gold catalysts are well known for their high catalytic activities in ambient air at low temperatures[1]. It has been reported that the addition of Au can lead to a significant enhancement in NH_3-SCO because Au can enhance the band intensity of imide-like adspecies. Besides, acidic metal oxides can adsorb NH_3. Therefore, acidic metal oxides supported gold catalysts are the promising candidates for realizing NH_3-SCO at low temperatures. Niobium oxides (Nb_2O_5), which is a solid acid with a low isoelectric point, is attractive as an acidic support. However, it is very difficult to prepare nanoparticulate gold catalysts if the support's isoelectric point is below 5. We have recently developed a sol immobilization method[2] to deposit Au nanoparticle (diameter < 3nm) on Nb_2O_5 which will provide a new possibility for low-temperature SCO of NH_3.

Three Nb_2O_5 crystal structures[3] (layered-structure-type, orthorhombic and amorphous, denoted as Nb_2O_5-L, Nb_2O_5-T and Nb_2O_5-A) and different Au loading amount were synthesized and evaluated for selective catalytic oxidation of NH_3. As shown in Fig.1, Nb_2O_5-L showed no catalytic activity for NH_3 oxidation even at 250°C. In contrast, the catalytic activities of Au/Nb_2O_5 for NH_3 oxidation were greatly enhanced. The lattice oxygen species on Au/Nb_2O_5-L is good for the formation of active atomic oxygen species which may give an explanation of its high catalytic activity for NH_3 oxidation. In addition, the Au loading amount would greatly influence the catalytic activity of Au/Nb_2O_5-L for NH_3 oxidation. The catalytic activity increased with the increase of Au loading amount from 1wt% to 5wt% while the size of Au nanoparticles remaining the same. Au(5wt%)/Nb_2O_5-L showed a 60% conversion of NH_3 at 25°C which is the highest conversion of NH_3 oxidation reported yet at room temperature.

In conclusion, different kinds of Nb_2O_5 were used as supports for the preparation of Au/Nb_2O_5. Nb_2O_5-L was inactive for NH_3 oxidation. However, the catalytic activity was significantly enhanced by the deposition of Au nanoparticles. Moreover, the catalytic activity of Au/Nb_2O_5-L was much higher than other two kinds of Nb_2O_5 supported gold catalysts because of its large surface area and surface's lattice oxygen species. The effect of Au loading amount on the catalytic activity of Au/Nb_2O_5-L indicated that the periphery interface between Au and Nb_2O_5-L may be the active sites for NH_3 oxidation.
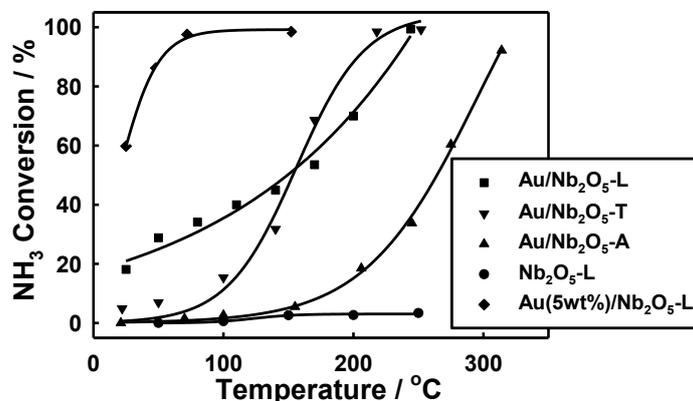
Figure 1. Effect of reaction temperatures on NH_3 conversion over different Nb_2O_5 supported gold catalysts. The Au loading amount was 1wt%. The amount of catalyst was 0.15 g. The reactant gas contained 50 ppm NH_3 and 20% O_2 balanced with Ar.

References

1- M. Haruta, T. Kobayashi, H. Sano H, N. Yamada, Chem. Lett. **16**, 405 (1987).
2- T. Murayama, W. Ueda, M. Haruta, ChemCatChem **8**, 2620 (2016).
3- T. Murayama, J. Chen, J. Hirata, K. Matsumoto, W. Ueda, Catal. Sci. Technol. **4**, 4250 (2014).

Corresponding author email: murayama@tmu.ac.jp

Non-Metallic Gold Clusters for Oxygen Activation and Aerobic Oxidation

Z. Li, G. Li[*]

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, CAS, Dalian, China

Non-metallic Au nanoclusters of atomic precision (Au_nL_m, where L = organic ligand: thiolate and phosphine) have been shown as a new promising nanogold catalyst. The well-defined Au_nL_m catalysts possess unique electronic properties and frameworks, providing an excellent opportunity to correlate the intrinsic catalytic behavior with the cluster's framework as well as to study the catalytic mechanisms over gold nanoclusters.[1]

Here, we only demonstrate the important roles of the gold nanoclusters in the oxygen activation (e.g., $^3O_2$ transfer to $^1O_2$ in the irradiation of light)[2] and their oxidations in the presence of oxygen, such as CO to CO_2, sulfides to sulfoxides, alcohol to aldehyde, styrene to styrene epoxide, amines to imines, and glucose to gluconic acid (Figure 1).[3-5] The size-specificity (Au_{25} (1.3 nm), Au_{38} (1.5 nm), Au_{144} (1.9 nm), etc), ligand engineering (e.g., aromatic vs aliphatic), and doping effects (e.g., copper, silver, palladium, and platinum) are discussed. The partial removal of protecting ligands to expose the gold atoms for reactants can largely improve the cluster's activity.[6,7] Finally, the proposed reactions' mechanism and the relationships of clusters' structure and activity at the atomic level also are presented.
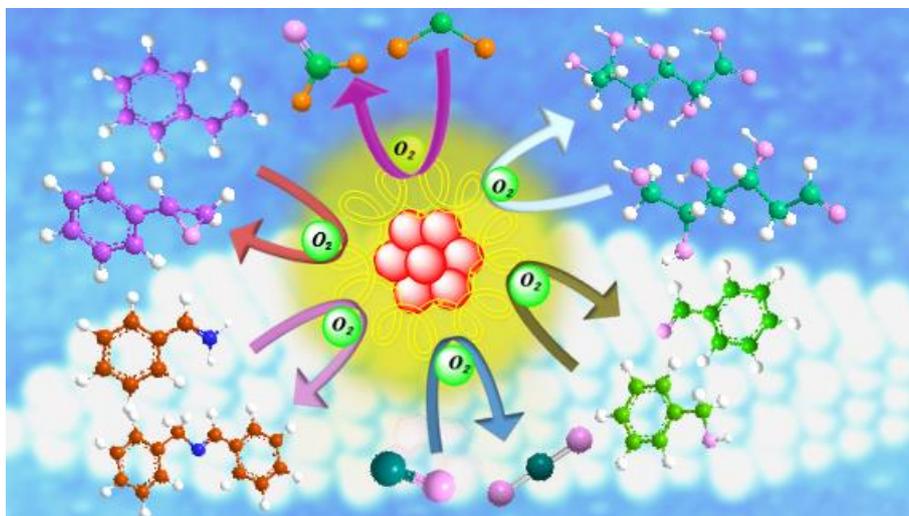
Figure 1. Aerobic oxidation over Au clusters.

References
1- G. Li, R. Jin, Acc. Chem. Res. **46**, 1749 (2013).
2- Z. Li, C. Liu, H. Abroshan, D. R. Kauffman, G. Li, ACS Catal. 7, 3368 (2017).
3- W. Li, C. Liu, H. Abroshan, Q. Ge, X. Yang, H. Xu, G. Li, J. Phys. Chem. C **120**, 10261 (2016).
4- C. Liu, J. Zhang, J. Huang, C. Zhang, F. Hong, Y. Zhou, G. Li, M. Haruta, ChemSuSChem 10, 1976 (2017).
5- H. Chen, C. Liu, M. Wang, C. Zhang, N. Luo, Y. Wang, H. Abroshan, G. Li, F. Wang, ACS Catal. 7, 3632 (2017).
6- G. Li, H. Abroshan, Y. Chen, R. Jin, H. J. Kim, J. Am. Chem. Soc. 137, 14295 (2015).
7- C. Liu, H. Abroshan, C. Yan, G. Li, M. Haruta, ACS Catal. 6, 92 (2016)

Corresponding author email: gaoli@dicp.ac.cn

Superior Stability of Au/SiO$_2$ Compared to Au/TiO$_2$ Catalysts for the Selective Hydrogenation of Butadiene

N. Masoud[1], L. Delannoy[2], K. P. de Jong[1], C. Louis[2], P. E. de Jongh[1*]

(1) *Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, 3584 CG Utrecht, The Netherlands*
(2) *Sorbonne Université, Campus Pierre et Marie Curie, Laboratoire de Réactivité de Surface, UMR CNRS 7197, F-75005 Paris, France*

Small Au particles are catalytically very active for several reduction and oxidation reactions, including the low-temperature oxidation of CO. In many cases reducible supports such as TiO$_2$ and CeO$_2$ lead to higher catalyst activities than when inert supports such as SiO$_2$ are used. Au is also a highly selective catalyst for the semi-hydrogenation of alkadiene impurities without further hydrogenation of the alkene stream, which is required for the production of industrial monomers. No large differences in activity have been observed on different supports, including TiO$_2$, CeO$_2$, ZrO$_2$ and Al$_2$O$_3$.[1] In this contribution we additionally report on using SiO$_2$ as a support, and especially discuss the influence of support properties on the longer term stability of these catalysts.

We compared supported gold catalysts with similar structural properties and morphology, and prepared using the same preparation strategy[2], but on supports of a different chemical nature: SiO$_2$ and TiO$_2$. We tested the activity, stability and selectivity of these 2−4 nm Au nanoparticulate catalysts for the hydrogenation of 0.3% butadiene in the presence of 30% propene (Figure 1). At full conversion of butadiene, only 0.1% of the propene was converted for both supported catalysts, demonstrating their high selectivity. The TiO$_2$-supported Au catalyst was initially much more active than the SiO$_2$ supported Au catalyst. However, a striking difference in catalyst stabilities was observed (Figure 1).
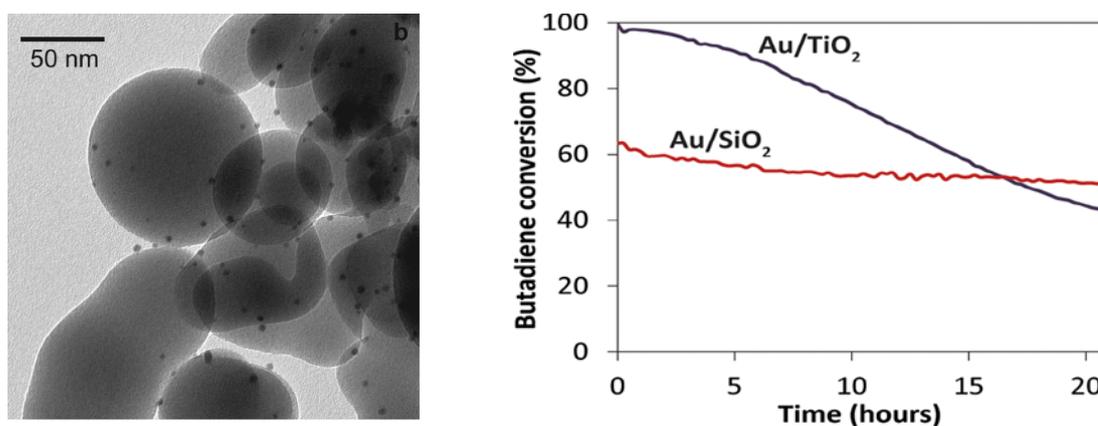
Figure 1. Left: electron micrograph of 0.6 wt% Au on SiO$_2$ (Aerosil50); Right: butadiene conversion at 200 °C comparing SiO$_2$ and TiO$_2$ (DegussaP25) catalysts, Feed: 0.3% butadiene, 30% propene, 20% hydrogen and He as a balance

The TiO$_2$-supported Au catalysts showed a steady loss of activity, which was recovered by heating in air. We found that the deactivation is not due to significant metal particle growth or strong metal−support interaction. We demonstrated that instead it is due to the deposition of carbonaceous species under reaction conditions. In contrast, all the SiO$_2$-supported catalysts were highly stable, with very limited formation of carbonaceous deposits. It shows that SiO$_2$-supported catalysts, despite their 2−3 times lower initial activities, clearly outperform TiO$_2$-supported catalysts within a day of run time.

References
1- A. Hugon, L. Delannoy, C. Louis, Gold Bull. **41,** 127 (2008).
2- X.Y. Liu et al. J. Chem. Mater. **21,** 410 (2009).
3- N. Masoud et al. ACS Catal. **7**, 5594 (2017).

Corresponding author email: P.E.deJongh@uu.nl

Design of gold nanoparticle catalysts for chemoselective hydrogenations: N-doped carbon as support

J. L. Fiorio[1*], R. V. Gonçalves[2], E. Teixeira-Neto[3], N. Lopez[4], L. M. Rossi[1]

(1) *Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748, 05508-000, São Paulo, SP, Brazil.*
(2) *Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970, São Carlos, SP, Brazil.*
(3) *Brazilian Nanotechnology National Laboratory (LNNano), Brazilian Center for Research in Energy and Materials (CNPEM), Zip Code 13083-970, Campinas, Sao Paulo, Brazil.*
(4) *Institute of Chemical Research of Catalonia, ICIQ, The Barcelona Institute of Science and Technology, Av. Països Catalans 16, 43007, Tarragona, Spain.*

Gold nanoparticles (Au NPs) have attracted a significant amount of interest as catalysts due to their exceptional selectivity and surprisingly high activity for some reactions, however gold was considered only a modest hydrogenation catalyst.[1] Recently, the combination of Au NPs with amine ligands was reported as effective way to catalyze the semihydrogenation of alkynes, due to a frustrated Lewis pair (FLP) interface formation that activates H_2 heterolytically allowing an unexpected high hydrogenation activity.[2] The main drawback of the previous catalytic system is the necessity of addition of external ligands, in large excess, for the activation of gold surfaces via FLP.

Herein, pyrolysis of $Au(OAc)_3$ in the presence of phenanthroline over TiO_2 furnishes a highly active and selective Au nanoparticle (NP) catalyst embedded in a nitrogen-doped carbon support, Au@N-doped carbon/TiO_2 catalyst (Figure 1). Highly selective hydrogenation of numerous structurally diverse alkynes proceeded in moderate to excellent yield under mild conditions. The high selectivity toward the industrially important alkene substrates, functional group tolerance and the high recyclability makes the catalytic system unique. Both high activity and selectivity are correlated the combination of gold and nitrogen atoms of N-doped carbon that can serve as a basic site to promote the heterolytic activation of H_2 under very mild conditions. In comparison to previous gold hydrogenation catalysts, where N-containing ligands were added externally,[2] the present "full heterogeneous" and recyclable catalyst makes the whole process environmentally and economically attractive.
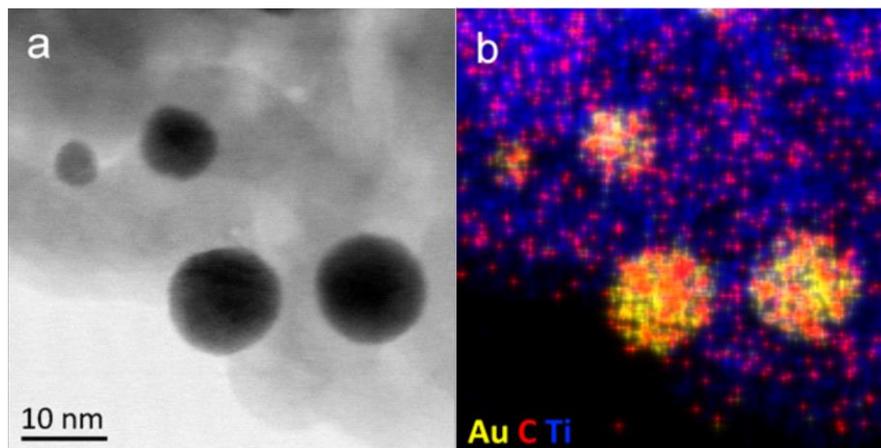
*Figure 1. Bright field STEM image (a) of a representative area of the Au@N-doped carbon catalyst (Au-L1/TiO₂ material after pyrolysis at 400 °C) and correspondent EDX elemental maps (b).*

References
(1)   Stratakis, M.; Garcia, H. *Chem. Rev.* **112**, 4469 (2012).
(2)   Fiorio, J. L.; López, N.; Rossi, L. M. *ACS Catal.* **7**, 2973 (2017).

Corresponding author email: jhonatan@iq.usp.br

Size Effect on Reduction of Aryl Chlorides with PVP-stabilized Gold/Palladium Bimetallic Nanoclusters Catalyst

H. Sakurai*[1], S. Mouri[1], S. Haesuwannakij[1]

(1) *Division of Applied Chemistry, Graduate School of Engineering, Osaka University,*
2-1 Yamada-oka, Suita, 565-0871, Japan

It is well recognized that the catalytic activity of metal nanoclusters depends on the size, and intensive studies have been carried out in the single-metal cluster system[1]. In contrast, comprehensive study on the size effect of the bimetallic clusters catalysts is still few partly because of the lack of the appropriate size-selective preparation of such bimetallic clusters. We prepared various size of Au/Pd-alloy nanoclusters stabilized by poly(*N*-vinyl-2-pyrrolidone) ranging 1 to 8 nm size by several methods including micro-flow technique[2,3]. The size effect of $Au_{0.5}Pd_{0.5}$:PVP nanoclusters[4] on catalytic activity for hydrodechlorination reaction of aryl chlorides[5] was investigated to find that the size effect showed a volcano shape tendency, and that the 3 nm-sized clusters gave the highest catalytic activity (Figure 1). Details of newly developed method of preparation, characterization of the clusters, and the possible reaction mechanism will be discussed in this presentation.
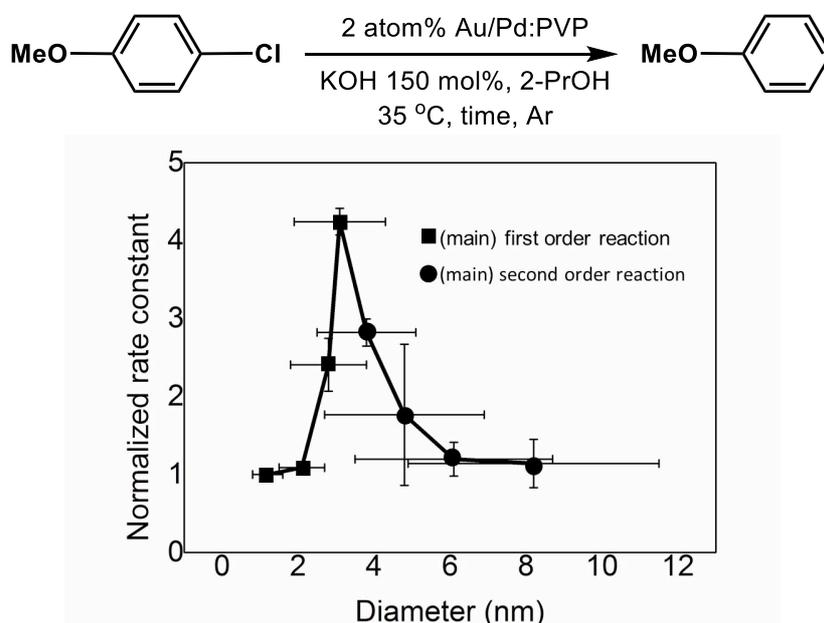
Figure 1. The size effect of Au/Pd NPs for hydrodechlorinaton reaction of p-chloroanisole.

References
1- For example, a report from our group; H. Tsunoyama, H. Sakurai, T. Tsukuda, Chem. Phys. Lett. **429,** 528 (2006).
2- S. Haesuwannakij, W. Karuehanon, V. L. Mishra, H. Kitahara, H. Sakurai, S. Kanaoka, S. Aoshima, Monatsch. Chem. **145**, 23 (2014).
3- N.Hayashi, Y.Sakai, H.Tsunoyama, and A.Nakajima, Langmuir **30**, 10539 (2014).
4- R. N. Dhital, C. Kamonsatikul, E. Somsook, K. Bobuatong, M. Ehara, S. Karanjit, H. Sakurai, J. Am. Chem. Soc. **134**, 20250 (2012).
5- S. Karanjit, A. Jinasan, E. Samsook, R. N. Dhital, K. Motomiya, Y. Sato, K. Tohji, H. Sakurai, Chem. Commun. **51**,12724 (2015).

Corresponding author email: hsakurai@chem.eng.osaka-u.ac.jp

From biomass to value-added chemicals: microwave-assisted levulinic acid conversion over gold catalysts

M. Manzoli[1*], S. Tabasso[1], G. Grillo[1], F. Bucciol[1], F. Menegazzo[2], M. Signoretto[2] and G. Cravotto[1]

(1) *Department of Drug Science and Technology and NIS—Centre for Nanostructured Interfaces and Surfaces, University of Turin, Via P. Giuria 9, Turin 10125, Italy*

(2) *Department of Molecular Sciences and Nanosystems, Ca' Foscari University Venice and INSTM Consortium RU Ve, Via Torino 155, 30170 Venezia Mestre, Italy*

Microwaves (MW) are currently applied as non-conventional enabling technology to promote fast chemical transformations producing rapid internal heating, that has been hypothesized to originate from a direct interaction of the electromagnetic field with specific molecules, intermediates, or even transition states in the reaction medium[1]. Indeed, the debate is still open and focused on discerning among thermal effects, due to the rapid heating, and high bulk reaction temperatures reached under MW dielectric heating, and other specific or non-thermal effects. Such effects, which are not linked to a macroscopic change in reaction temperature, involve the non-uniform heating at the surface of heterogeneous catalysts and the production of hot spots by MW irradiation, resulting in non-equilibrium local heating localized at the surface of the metal nanoparticles present on the catalysts[2]. Levulinic acid (LA) is among the most promising platform molecules obtained from biomass[3] and it can be converted into high value-added molecules that can be used as green solvents, biofuel additives, in pharmaceutical industry and in the synthesis of biopolymers[4]. In this study, we will focus on the MW-assisted LA hydrogenation over gold catalysts (commercial 1 wt% Au/TiO_2 by AUROlite™ and 1.25 wt% Au/ZrO_2 prepared by deposition-precipitation) to obtain γ-valerolactone (GVL) and 1,4-propanediol (1,4-PDO). LA hydrogenation was performed in water or without any solvent either by (i) H-transfer (using methanol, propanol or formic acid) or (ii) in the presence of molecular H_2. In the former case, Au/ZrO_2 gave lower conversion to GVL than Au/TiO_2, but higher selectivity, reaching 100 % with formic acid as H-donor. However, the Au/TiO_2 catalyst was able to convert completely the LA and to further reduce GVL to 1,4-PDO in the presence of 50 bar H_2 already at 150 °C (4 h reaction time). Interestingly, the selectivity to 1,4-PDO was complete at 200 °C. Complete ethyl levulinate reduction to 1,4-PDO was obtained at 160 °C using 1,4-dioxane as solvent (6h reaction time) with 60 bar H_2 over a CuAlZn catalyst[6]. Diffuse Reflectance UV-Vis analysis (Figure 1) revealed the presence of Au nanoparticles with similar size (~2 nm[5]) on the two catalysts, putting in evidence also a role played by the support. Further characterisation to establish structure activity relationships is ongoing and the results obtained on both fresh and used the catalysts will be illustrated.
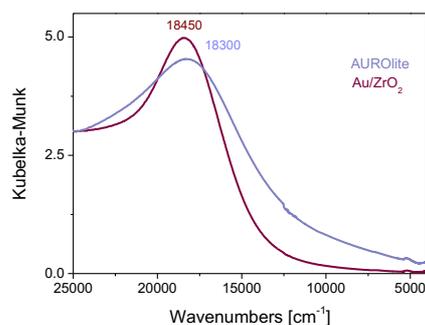
Figure 1. Diffuse Reflectance Uv-Vis spectra of Au/TiO₂ e Au/ZrO₂.

References

1- O.K. Kappe, B. Pieber, D. Dallinger, Angew. Chem. Int. Ed. **52**, 1088 (2013).
2- Y. Tsukahara, A. Higashi, T. Yamauchi, T. Nakamura, M. Yasuda, A. Baba, Y. Wada, J. Phys. Chem. C **114**, 8965 (2010).
3- T. Werpy, G. Petersen, A. Aden, J. Bozell, J. Holladay, J. White, A. Manheim, D. Eliot, L. Lasure, S. Jones, Office of Energy Efficiency and Renewable Energy, US Department of Energy: Washington, DC, USA **1**, 1 (2004).
4- D. W. Rackemann, W. O. S. Dohertyand, Bioprod. Bioref. **5**, 198 (2011).
5- A. A. Hakeem, Z. Zhao, F. Kapteijn, M. Makkee, Catalysis Today **244**, 19 (2015).
6- D. Ren, X. Wan, F. Jin, Z. Song, Y. Liu, Z. Huo, Green Chem. **18**, 5999 (2016).

Corresponding author email: maela.manzoli@unito.it

Hydrogenation on gold catalysts made easy: activation of H_2 via frustrated Lewis pairs

L. M. Rossi[1], N. López[2], R. J. M. Silva[1], J. L. Fiorio[1]

[1]*Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, São Paulo, Brazil*

[2]Institute of Chemical Research of Catalonia – ICIQ, Tarragona, Spain

The dissociation of molecular hydrogen, a crucial step in hydrogenation reactions, is not favorable on gold surfaces; though nanostructuring can improve it, high temperature is still required. The concept of 'frustrated Lewis pairs' (FLPs) was introduced a decade ago [1] to explain the activation of small molecules, such as H_2, through an 'encounter complex' where a Lewis acid (LA) and Lewis base (LB) are in close proximity, but prevented from forming a strong classical adduct. Stephan and co-workers [1] reported the heterolytic cleavage of H_2 at room temperature with FLPs of phosphorus and boron compounds. The concept has expanded rapidly from main group-FLP to metal-based FLP [2], in which the metal complex promotes the heterolytic cleavage of H_2 producing a hydride (delivered to a metal center) and the proton is incorporated into the ligand (e.g., amine protonation). FLP are also present in biological reactions, e.g. hydrogenases, where the heterolytic H_2 cleavage occurs under mild conditions. We recently proposed that heterolytic dissociation of H_2 is promoted by ligands adsorbed on gold surfaces, which expands the FLP concept to gold catalysis [3]. The heterolytic cleavage of H_2 contrasts with the homolytic cleavage of H_2 commonly observed on metal surfaces of traditional heterogenous catalysts (platinum group metals), but opens up the possibility to explore less active metals that are not prone to dissociate H_2. We first found that the addition of nitrogen-containing bases to silica supported Au NPs made hydrogenation reactions possible to occur under mild conditions. This activity was not seen in blank experiments with gold catalyst only. We proposed that H_2 is heterolytically activated on the gold-ligand interface and the so-formed tight-ion pair could be selectively transferred to an alkyne in a cis configuration controlled by electrostatic interactions leading to the corresponding Z-alkene. Using DFT calculations, we were able to show that the catalytic activity correlates with H_2 dissociation energy, which depends on the basicity of the ligand and on the reorganization energy of the ligand on the surface required to activate hydrogen. We were able to disclose a remarkable promotional effect of nitrogen-containing bases with two heteroatoms as a new ligand-based strategy to boost gold activity. After that, the versatile FLP concept applied to gold catalysis made easy the hydrogenation of many functional groups such as alkyne-to-alkene, epoxyde-to-alkene, aldehyde-to-alcohol, N-oxide-to-amine, etc. under mild conditions (Figure 1). Different ligands were explored and selected examples of successful hydrogenations catalyzed by gold will be discussed.

Figure 1. Activation of gold catalysts for hydrogenations via FLP.
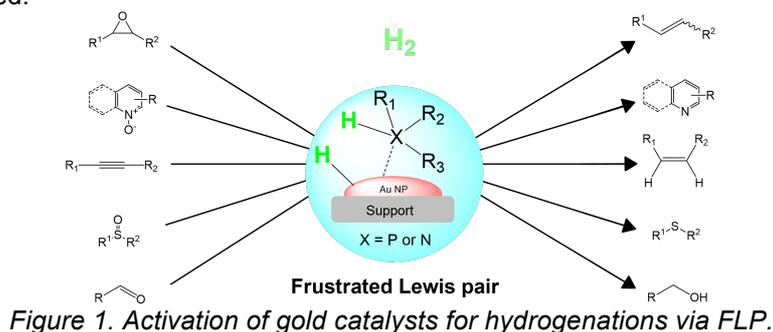
References

[1] GC Welch, RRS Juan, JD Masuda, DW Stephan, Science **314**, 1124 (2006).
[2] SR Flynn, DF Wass, ACS Catal. **3**, 2574 (2013).
[3] JL Fiorio, N Lopez, LM Rossi, ACS Catal. **7**, 2973 (2017).

Corresponding author email:lrossi@iq.usp.br

Catalytic Cracking of Light Diesel Over Au/ZSM-5 : An Application of Gold Catalysts Under Severe Conditions

Caixia Qi*, Yunxia Wang, Libo Sun, Miao Zhang

Shandong Applied Research Center for Gold Nanotechnology (Au-SDARC), School of Chemistry and Chemical Engineering, Yantai University, Yantai, PR China

Over the past decades, the gold based catalysts have become a vital new force in the field of green chemistry [1] The application of gold catalysts have extended from some simple reactions such as, CO oxidation, water gas shift[2], to more complex systems such as epoxidation of propylene[3], hydrogenation of acetylene[4-6]. However, most of the reported reactions are carried out under a relative mild reaction conditions.

In this study, we have investigated the application of Au modified ZSM-5 for the catalytic cracking of light diesel oil which is a relatively harsh catalytic reaction system (usually operated at high temperatures and pressure). Our study shows an improved selective production of propylene was achieved at a much low operation temperature(300° C) with the maintained realtively high cracking activity. The adding of small amount of gold don't destroy the regular structure of the zeolite substrate, In contrast, it modulated the acidity and pore structure of zeolite to an optimized.condition. It was found that the strong interactions between gold and ZSM-5 caused the transfer of some gold species to the aluminum skeleton which results in an increased concentration of the so called B acid. Therefore, an,increased yields of low carbon olefin can be achieved. Moreover, the introduction of gold favors the cracking of heavy components, and the longer the chain is, the easier it is to break. In general, the catalytic cracking of light diesel oil over Au/ZSM-5 shows a bi-catalytic effect of acid and gold catalysis. We expect that such a novel study will open the door to a new area of gold catalysts for more severe condition applications..

Production Distribution (%)	ZSM-5	Types of Au/ZSM-5 with theoretical Au loading (wt %)							
		a	b	c	d				
		1.0	1.0	1.0	0.5	0.8	1.0	1.2	1.5
Dry gas+LPG	40.4	33.7	26.7	33.7	55.8	44.9	46.7	24.2	23.9
Gasoline	8.6	10.0	4.9	4.7	3.1	8.4	6.8	11.1	10.2
Diesel oil	51.0	56.3	68.4	61.6	41.1	46.7	46.5	64.7	65.9
Conversion	46.0	28.1	40.4	34.1	67.1	50.1	50.4	30.9	29.6
MAT	49.0	32.1	43.8	38.3	56.1	53.3	53.5	35.3	34.1
Py# selectivity	29.6	27.9	31.4	40.8	38.4	32.5	52.8	41.4	68.6
$Au (wt %)	--	0.67	0.08	0.91	0.10	0.12	0.17	0.20	0.21
&W / S	4.6	0	22.5	2.3	3.4	3.35	3.8	4.07	4.5

Table 1 Product distributions of the catalytic cracking of light diesel oil at 460 °C over the Au/ZSM-5 catalysts
(LPG means liquefied petroleum gas. #: Propylene. $: The actual Au loading measured by ICP-AES analysis. &: The ratio of weak acid to strong acid based on NH3-TPD measurement.)

References
1- G. J. Hutchings，M. Brust，H. Schmidbaur, Chem. Soc. Rev., **37**, 1759 (2008).
2- M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M. J. Genet, B. Delmon, J. Catal., **144**, 175(1993).
3- C. Qi, J. Huang, S. Bao, H. Su, T. Akita, M. Haruta, J. Catal., **281,** 12(2011).
4- H. Wang, W. Fan, Y. He, J. Wang, J. N. Kondo, T. Tatsumi, J. Catal., **299,** 10(2013).
5- P. Rubio-Marques, J. C. Hernandez-Garrido, A. Leyva-Perez, A. Corma, Chem. Commun., **50**, 1645(2014).

Corresponding author email: qicx@ytu.edu.cn

Supported Gold-Palladium Alloy Catalysts for Highly Efficient Hydrogen Storage System Based on Ammonium Bicarbonate/Formate Redox Equilibrium

K. Nakajima[1], H. Miura[1,2,3], T. Shishido[1,2,3,4*]

(1) *Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, Tokyo, Japan*
(2) *Research Center for Hydrogen Energy-based Society, Tokyo Metropolitan University, Tokyo, Japan*
(3) *Elements Strategy Initiative for Catalysts & Batteries, Kyoto University, Kyoto, Japan*
(4) *Research Center for Gold Chemistry, Tokyo Metropolitan University, Tokyo, Japan*

Hydrogen (H_2) is considered to be an attractive candidate as a chemical energy carrier for a sustainable energy technology, because the only byproduct of its reaction with oxygen is water, and efficient energy conversion can be realized by combining with fuel cell technology. Recently, Beller and co-workers designed a reversible hydrogen storage cycle based on the redox system bicarbonate/formate [1]. Ammonium formate can storage hydrogen in the high density (3.2 wt%) and safety, and solid bicarbonates are easy to handle and highly soluble in aqueous media. Several research groups reported that both the hydrogenation of bicarbonate and the dehydrogenation of formate proceeded on Pd-based and Ru-based catalysts. However, further improvement in efficiency of catalyst at ambient conditions is still required, thus the development of a novel catalytic system that can operate at ambient temperature would be highly demanded. In this work, supported Au-Pd alloy catalysts were prepared and examined for the bicarbonate hydrogenation and formate dehydrogenation.

Figure 1 shows the result of ammonium bicarbonate hydrogenation over active carbon (AC) supported AuPd catalysts with various Au/Pd ratio (*x*Au*y*Pd | *x*:*y*=Au:Pd molar ratio). AuPd catalysts showed higher production rate of ammonium formate than that of Pd catalyst regardless of Au/Pd ratio. Production rate of HCO_2NH_4 per weight of catalyst increased with the Au/Pd ratio up to Au/Pd=5. On the other hand, the turnover number frequency (TOF) increased with the ratio of Au/Pd, monotonically. Figure 2 shows the result of ammonium formate dehydrogenation over supported AuPd catalysts with various Au/Pd ratio. AuPd catalysts showed higher activity than Pd catalysts. Both the production rate of H_2 per weight of catalysts and TOF increased with increasing the Au/Pd ratio up to 1 and then decreased.

Structural characterization results by XRD, EXAFS and HADDF-STEM of AuPd catalysts with different Au/Pd ratio revealed the formation of random Au–Pd alloy nanoparticles with a uniform size of around 3 nm on AC. Au L_3-edge XANES spectra and XPS of AuPd catalysts elucidated the charge-transfer from Pd to Au. These results indicate that the ratio of Au/Pd remarkably affected on the activity of supported Au-Pd alloy catalyst by the changes in electronic and local structure of Au and Pd.
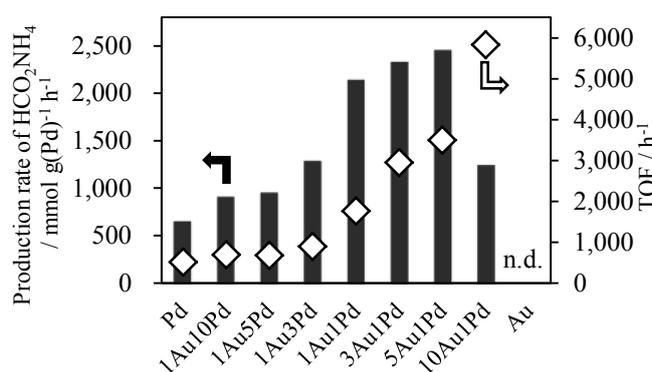
Fig.1 Production rate of HCO_2NH_4 over AuPd/AC
Conditions: H_2 5 MPa, 333 K
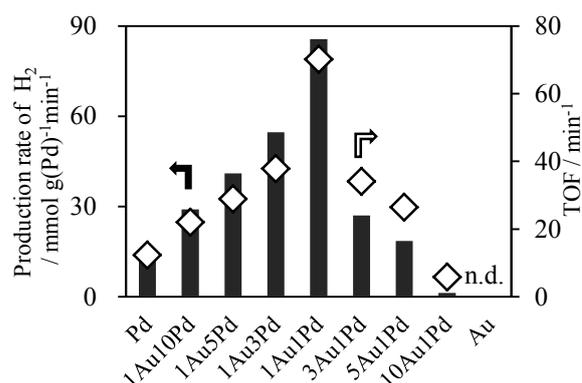
Fig.2 Production rate of H_2 over AuPd/AC
Condition : 313 K

References
1- A. Boddien, F. Gartner, M. Beller et al., Angew. Chem. Int. Ed. **50**, 6411 (2011).

Corresponding author email: shishido-tetsuya@tmu.ac.jp

Gold Nanoparticles as Soft Lewis Acid Catalysts for Transfer Vinylation

T. Ishida[1*], R. Sodenaga[1], T. Honma,[2] M. Haruta[1]
(1) *Tokyo Metropolitan University, Tokyo, Japan*
(2) *Japan Synchrotron Radiation Research Institute, Hyogo, Japan*

Homogeneous Au(I, III) catalysts have been intensively studied as soft Lewis acid catalysts for such as hydration of alkynes and hydroamination. Recently, supported Au nanoparticles (Au NPs) catalysts have been reported to be active for hydroamination and oxidative C–H bond coupling that cationic Au may be involved in the reaction mechanism. In addition, Bistoni et al. reported that Au NPs can work as soft Lewis acid catalysts by theoretical study, although the acidity is expected to be lower than that of Au(I, III).[1] In this study, we aimed to develop highly active heterogeneous Au catalysts that can be used as soft Lewis acid catalysts. Transfer vinylation of carboxylic acids with vinyl acetate[2] was chosen as a model reaction (Scheme 1), because vinyl esters are one of the valuable compounds and frequently used as intermediates in organic syntheses.

Some 1 wt% Au catalysts were purchased from Haruta Gold Inc. and 0.3 wt% Au catalysts were prepared by deposition-precipitation (DP). To a glass vial, benzoic acid (0.5 mmol), Au catalyst (Au 1 mol%), vinyl acetate (1 mL), and tridecane as an internal standard were charged. After the reaction at 100 °C, the reaction mixture was analyzed by gas chromatography.

A screening test of metal oxide supports revealed that ZrO_2 gave the highest yield (82%) of vinyl benzoate, while basic (ZnO, NiO, and CeO_2) and acidic (SiO_2) supports showed low catalytic activity. Moreover, Au on a mixed metal oxide, CeO_2-ZrO_2, the yield was improved up to 92%. Although the reaction temperature is relatively higher than that for homogeneous Au catalysts,[2] the target product was obtained in the same yield as the previous report with lesser amount of Au and without any additives such as silver salt.

Because the basicity of CeO_2-ZrO_2 was almost similar to that of ZrO_2 estimated by a temperature-programmed desorption of CO_2, the difference in the activity between ZrO_2 and CeO_2-ZrO_2 might by probably due to the chemical state or the size of Au particles. Therefore, several Au/CeO_2-ZrO_2 catalysts having different Au(III)/Au(0) ratio were also prepared by changing the reduction conditions to elucidate the Au active species (Table 1). The Au(III)/Au(0) ratio was estimated by Au L_{III}-edge X-ray absorption near edge structure spectra using Au foil and Au(OH)$_3$ as references. Au/CeO_2-ZrO_2 prepared by DP followed by only drying contained Au(III) as a major species and showed the lowest activity. In contrast, Au/CeO_2-ZrO_2 prepared by DP followed by reduction with H_2 contained Au(0) as a major species and showed much higher catalytic activity than Au/CeO_2-ZrO_2_dry. In addition, smaller Au NPs showed higher activity. This result suggests that Au NPs worked as a soft Lewis acid catalyst as well as Au(I) complexes and its catalytic activity was higher than larger ones.

On the other hand, transfer vinylation of alcohols with vinyl acetate to give vinyl ethers by Au NPs catalysts were failed due to the alcohol oxidation, which contrasts to the results obtained by homogeneous Au(I) complexes.
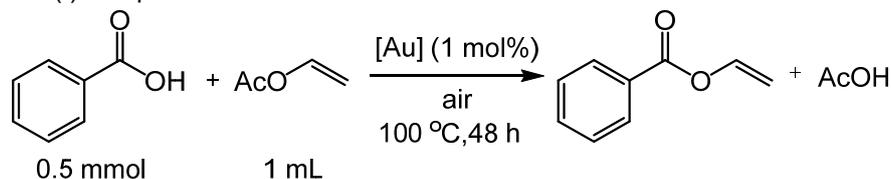
Scheme 1. Transfer vinylation of benzoic acid by gold catalysts.

Table 1. Transfer vinylation of benzoic acid by Au/CeO_2-ZrO_2.

	Au(III) (%)	Au(0) (%)	Au NP size (nm)[a]	Vinyl benzoate yield (%)[b]
Au/CeO_2-ZrO_2_dry	65	35	4.9	17
Au/CeO_2-ZrO_2_air	11	89	5.8	36
Au/CeO_2-ZrO_2_H_2	2	98	3.2	53

a) Estimated by HAADF-STEM and XAFS. b) GC yield after 2 h.

References
1- C. Bistoni, P. Belanzoni, L. Belpassi, F. Tarantelli, J. Phys. Chem. A 120, 5239 (2016).
2- A. Nakamura, M. Tokunaga, Teterahedron Lett. 49, 3729 (2008).

Corresponding author email: tamao@tmu.ac.jp

Assembling Ni^{2+} complexes and gold nanoparticles on $γ$-Al_2O_3 as visible light photocatalysts for hydrogenolysis of lignin model compounds

**Pengfei Han**[1], **Sarina Sarina**[1], **HuaiYong Zhu**[1]*

[1]*School of Chemistry, Physics and Mechanical Engineering, Faculty of Science and Technology,*

Queensland University of Technology, Brisbane, QLD 4001, Australia

Lignin is a main constituent (15-30% by weight, 40% by energy) of lignocellulosic biomass,[1] which refers to the most abundantly available raw material on the earth for the production of bio-fuels. Besides, a large volume of lignin waste is produced annually by the paper industry. However, the aryl ether bonds of lignin are relatively unreactive, depolymerisation of lignin into small molecules is challenging, so more than 98% of lignin is currently simply burned to provide heat for other industrial processes.

The major repeating units of lignin are orthomethoxy-substituted C_9 phenolic moieties, which are cross-linked by relatively unreactive C-O bonds, contributed by $β$-O-4 (45-62%), $α$-O-4 (3-12%), and 4-O-5 (4-9%) linkages.[2] The conversion of lignin into high-volume and low-molecular weight aromatic molecules has become the center of interest for scientists worldwide.

Nickel has been found as an effective element in catalyzing C-O bond cleavage of lignin models by hydrogenolysis,[3-6] but the operating temperature (>150 ^{o}C) is still high that over-reduction could easily happen and by-products like saturated cycloalkanols would be obtained inevitably.[4]

Herein, the photocatalytic performance of the Au-Ni^{2+} system for the cleavage of benzyl phenyl ether and 2-phenyl phenyl ether that have $α$-O-4 and $β$-O-4 linkages, respectively, is investigated. The catalytic activity of Ni complexes can be enhanced by the localized surface plasmon resonance (LSPR) effect of nearby Au nanoparticles under visible light irradiation, thus making the reactions happened at a mild condition (90°C).
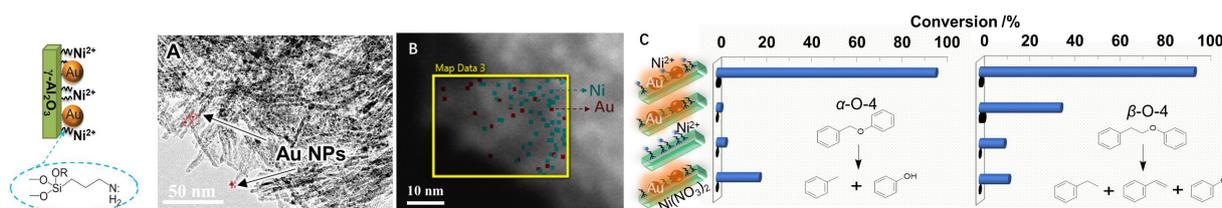
Figure 1. The Schematic illustration of the synthesized nAu@Al_2O_3-silane-NH_2-Ni^{2+} photocatalyst, A) TEM image and B) EDS mapping of the photocatalyst, C) Comparison of the catalytic performance of the Au-Ni^{2+} composite catalyst with the monometallic catalysts (supported Au NPs and immobilized Ni^{2+}) and the mixture (supported Au NPs mixed with Ni salt) for C-O bond cleavage of lignin model compounds under visible light irradiation (blue) and in the dark (black). Reaction conditions: lignin model compounds (0.05 mmol), KOH (0.15 mmol), 2 mL of IPA solvent, 1 atm argon atmosphere, 20 mg of catalysts, under 90 ^{o}C for 24 h, halogen light intensity: 0.96 and 1.11 W cm^{-2} in $α$-O-4 and $β$-O-4 reaction respectively.

References

1. Perlack, R. D. et al. Biomass as feedstock for a bioenergy and bioproducts industry: the technical feasibility of a billion-ton annual supply. DTIC Document 12, 4 (2005).
2. Sarkanen, K. V. & Ludwig, C. H. Lignins: occurrence, formation, structure and reactions. Lignins: occurrence, formation, structure and reactions. Wiley-Interscience (1971).
3. Sergeev, A. G. & Hartwig, J. F. Science 332, 439 (2011).
4. Molinari, V., Giordano, C., Antonietti, M. & Esposito, D. J. Am. Chem. Soc. 136, 1758 (2014).
5. Kelley, P., Lin, S., Edouard, G., Day, M. W. & Agapie, T. J. Am. Chem. Soc. 134, 5480 (2012).
6 He, J., Zhao, C. & Lercher, J. A. J. Am. Chem. Soc. 134, 20768 (2012).

Corresponding author email: hy.zhu@qut.edu.au

Synergistic Effect of Gold Plasmonic Resonance and Solid Acid in Photocatalysis

Feng. Lin[1]*, Masatake Haruta[1,2], Jiahui Huang[1]*

(1) Gold Catalysis Research Center, State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, P. R. China
(2) Research Center for Gold Chemistry, Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, Tokyo, Japan

It is highly desired to remove sulfur-containing organic compounds such as thiophene/thiol from fuel oils and organic pollutants such as rhodamine B and phenol from the polluted wastewater. To mitigate these environmental problems, solar driven catalysis by semiconductors is considered as a promising route. In particular, surface plasmon resonance (SPR) may contribute greatly to improve the limited efficiency of photocatalysts.

Herein we synthesized the SPR-mediated visible-light-responsive photocatalyst, 0.5 wt.% Au/SO_4^{2-}-TiO_2, which can achieve over 99% conversion of pollutants (thiophene, thiol, rhodamine B and phenol) during photocatalytic oxidation with air as oxidant under visible light irradiation. The great enhancement of photocatalytic activity can be attributed to the synergistic effect of Au SPR and SO_4^{2-}-TiO_2 acting as a Lewis acid, which are beneficial for the efficient separation and transfer of the photo-generated electrons and holes (Figure 1). Such a strategy would be important to the design and preparation of highly photocatalytic active semiconductor catalysts.
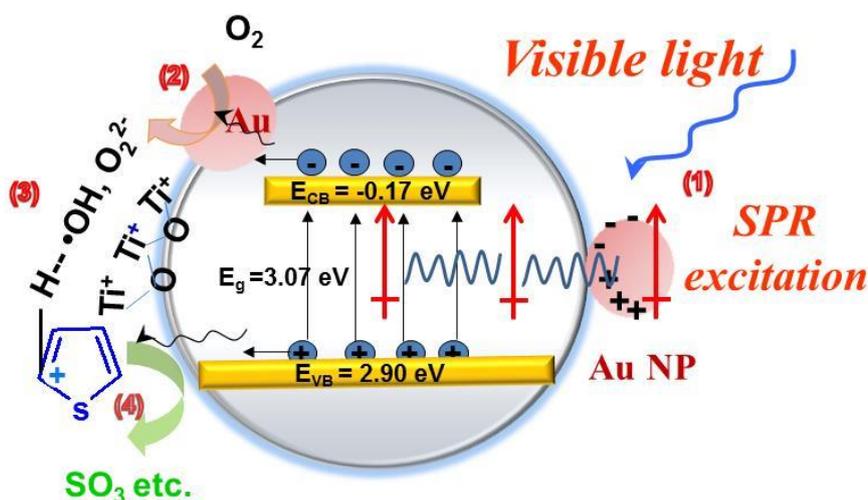
Figure 1. Schematic description of the mechanism for the photocatalytic oxidation of pollutans (e.g. thiophene) on 0.5 wt.% Au/SO_4^{2-}-TiO_2 photocatalyst.

References

1- F. Lin, B. Shao, Z. Li, M. Haruta*, J. H. Huang*, *etc.* Applied Catalysis B: Environmental, **218**, 480 (2017).
2- T. Takei, T. Akita, I. Nakamura, J. H. Huang, M. Haruta, *etc.* Advances in Catalysis, **55**, 1 (2012).

Corresponding author email: jiahuihuang@dicp.ac.cn

Visible light photocatalytic H_2 production from water over optimized Au/TiO$_2$–gC$_3$N$_4$ nanocomposites

C. Marchal[1], T. Cottineau[1], M. G. Méndez-Medrano[2], C. Colbeau-Justin[2], V. Caps[1], V. Keller[1*]

(1) *ICPEES (Institut de Chimie pour l'Energie, l'Environnement et la Santé), CNRS UMR 7515 / University of Strasbourg, 25 rue Becquerel, 67087 Strasbourg Cedex 02, France*
(2) *Laboratoire de Chimie Physique, CNRS UMR 8000 / Université Paris-Sud, Bâtiment 349, 91405 Orsay Cedex, France*

TiO$_2$–gC$_3$N$_4$ composites have recently attracted a lot of attention due to their extended absorption properties in the visible range.[1-5] In particular, their association with plasmonic metal nanoparticles (NPs) makes them interesting candidates for the photocatalytic production of hydrogen from water under visible light.[1,5] However, large quantities of sacrificial agents, typically >10 vol.%, are still used in order to obtain a detectable activity. Here we will show that state-of-the-art activities can be obtained in the presence of a much lower amount of sacrificial agent (<1 vol.%), using optimized Au/TiO$_2$-gC$_3$N$_4$ nanocomposites. In particular, we will discuss the method of synthesis of such composite, which involves the pyrolysis of C$_3$N$_4$ melamine and dicyandiamide precursors in the presence of pre-crystallized, high surface area titania and the sonochemical deposition of gold.[6] We will present the physico-chemical characterizations obtained (BET, XRD, TEM, XPS, UPS, UV-vis.) which clearly evidence the existence of specific TiO$_2$/C$_3$N$_4$, Au NPs/C$_3$N$_4$ and Au NPs/TiO$_2$ heterojunctions. Finally, we will discuss the mechanisms involved in solar and visible photocatalytic hydrogen production (see Figure 1) based on measurement of electrons mobility using time resolved microwave conductivity (TRMC).
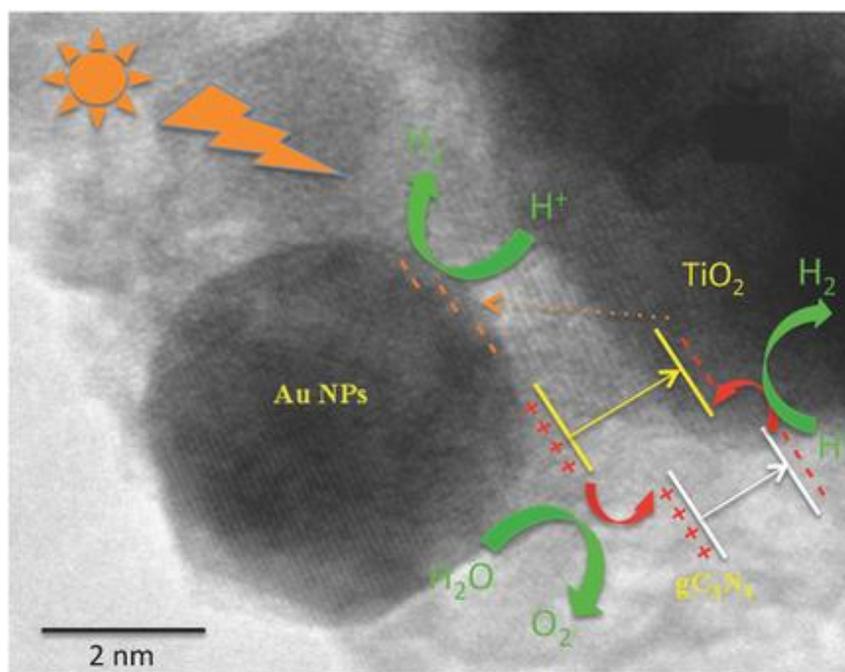
Figure 1. Mechanism of photocatalytic H_2 production over optimized Au/TiO$_2$–gC$_3$N$_4$ nanocomposites highlighting the efficient heterojunction between TiO$_2$ and C$_3$N$_4$ and the role of gold as co-catalyst.

References
1- B. Chai, T. Peng, J. Mao, K. Lia, L. Zan, Phys. Chem. Chem. Phys. **14**, 16745 (2012).
2- K. Sridharan, E. Jang, T. J. Park, Appl. Catal. B **142-143**, 718 (2013).
3- Y. Chen, W. Huang, D. He, Y. Situ, H. Huang, ACS Appl. Mater. Interf. **6**, 14405 (2014).
4- Z. Huang, Q. Sun, K. Lv, Z. Zhang, M. Li, B. Li, Appl. Catal B. **164**, 420 (2015).
5- X. Wei, C. Shao, X. Li, N. Lu, K. Wang, Z. Zhang, Y. Liu, Nanoscale **8**, 11034 (2016).
6- C. Marchal, T. Cottineau, M. G. Méndez-Medrano, C. Colbeau-Justin, V. Caps, V. Keller, Adv. Energy. Mater. DOI: 10.1002/aenm.201702142 (2018).

Corresponding author email: vkeller@unistra.fr

Bimetallic Gold-Ruthenium nanoparticles for catalysis

D. De Masi, J. Albero, L-M. Lacroix, P.F. Fazzini, H. García, B. Chaudret

Université de Toulouse, LPCNO, UMR 5215 INSA CNRS UPS, Toulouse, France
Universidad Politécnica de Valencia, Instituto de Tecnología Química (UPV-CSIC), Avenida de los Naranjos s/n, 46022 Valencia, Spain

The development of technologies using renewable energy sources becomes a necessity to reduce our use of fossil fuel and greenhouse gas emissions. However these renewable sources, whether solar cells or windmills, are intermittent. It is therefore important to work on ways to store them efficiently.

Sabatier reaction, the transformation of CO_2 and H_2 in methane, may be a solution to store chemically renewable energies. This reaction requires a catalyst as well as temperature higher than 250°C to achieve measurable reaction rates due to the high-energy barrier of the process. Ruthenium NPs, due to their high selectivity towards CH_4, are one of the best candidates to catalyze the conversion of CO_2.

In this contribution, we evaluate the role of plasmonic heating[1] in this reaction. Two materials both containing Au[2] and Ru nanoparticles supported on a commercial support have been synthesized. Through light irradiation, Au plasmon band absorbs energy, which is transferred to the Ru Nps, in contact or in close contact, increasing locally their temperature and, therefore, the rate of CH_4 production.
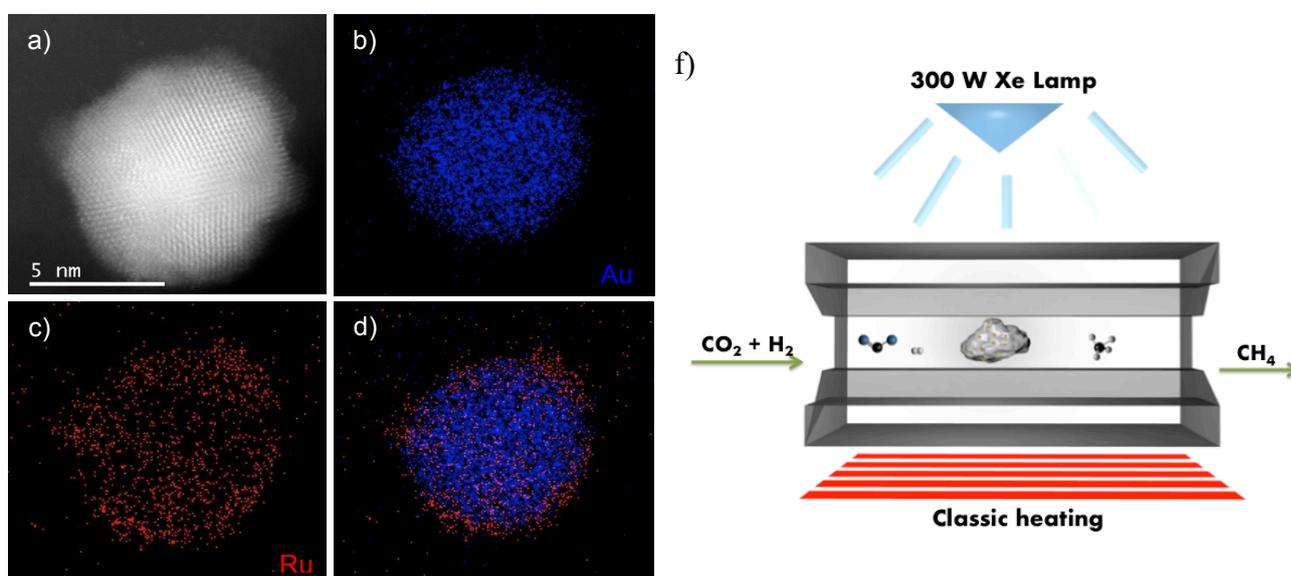
a)HAADF-STEM image of an individual Au-Ru nanoparticle showing a brighter contrast Au core and darker contrast RuNPs. b-d), STEM-EDX elemental maps of Au, Ru and superimposed Au and Ru atome distribution f) Phtotothermal reactor assited with classic heating

References

1- Hiroki Hiramatsu and Frank E. Osterloh, Chem. Mater. 16, 2509 (2004)
2- Alexander O. Govorov and Hugh H. Richardson, nanotoday 7, 30 (2007)

Harvesting Gold Plasmonic Properties to achieve Selective Hydrogenations under Visible-Light in Au@AgPt Nanorattles

Jhon Quiroz, Eduardo C. M. Barbosa, Thaylan P. Araujo, Jhonatan L. Fiorio, Liane M. Rossi and Pedro H. C. Camargo

Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo
Av. Prof. Lineu Prestes, 748, 05508-000, São Paulo-SP, Brazil

The efficient use of solar energy has received wide interest due to the increase of energy and environmental concerns. A promising alternative in chemistry is sunlight-driven catalytic reactions. Recent scientific reports have shown that plasmonic metal nanoparticles (Au, Ag, and Cu) promotes catalytic reactions through photoexcitation of localized surface plasmon resonance (LSPR)[1,2]. However, single component plasmonic nanocatalysts can only drive a limited range of chemical reactions when compared to traditional metal catalysts (Pt, Pd and Rh). In this context, the concept of plasmon-catalysis hybridization emerges as an intuitive strategy in order to simultaneously achieve efficient light harvesting and widespread catalytic applications[3]. This work seeks to boost the understanding of the plasmon-catalysis hybridization phenomenon. To accomplish this, we propose to integrate the active phases in the form of nanorattles (NRT), comprised of Au nanosphere inside a Ag/Pt with different Pt shell compositions. The NPs were characterized, supported on commercial SiO_2 and used for photochemical mediated alkyne semi-hydrogenation reactions.

The NRT synthetic protocol comprises first the obtention of Au seeds follow by deposition of Ag shell and finally the replacement of silver by platinum through a galvanic reaction. The change of color observed throughout the synthesis evidences an influence of metals hybridization in the optical properties of the NPs. LSPR extinction spectra confirm this observation (Figure 1). The Au seeds displayed a characteristic sharp plasmon band at 525nm. After coating with Ag a broad band appeared at 402 nm and the band ascribed to Au disappear, suggesting the formation of Au@Ag core shell. The Ag replacement by Pt red shifted the optical profile and increases the broadness of the LSPR spectra indicating plasmon resonance hybridization between Au and AgPt shell. Noticeably, for the sample with higher Pt content (Au@AgPt_3) the maximum of LSPR extinction corresponds with the observed for Au. TEM micrographs (Figure 1) confirm the formation of the Au@AgPt NRT. The obtained NPs are form by polyhedral particles with diameter of around 40-50 nm. It can be seen that increasing the Pt content creates more empty spots which is in agreement with the red shifted observed in the LSPR spectra by baring the gold extinction contribution. A representative SEM image of the supported NRT (Figure 1) shows a homogeneous distribution over the SiO_2.
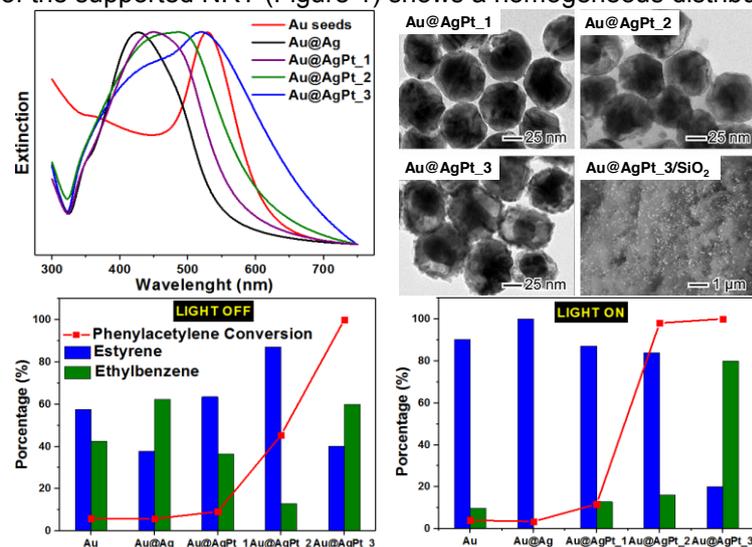
Figure 1. LSPR extinction spectra, TEM-SEM micrographs and phenylacethylene (PA) selective hydrogenation results.

Catalytic properties of the supported NPs were evaluated by liquid phase phenylacethylene hydrogenation. The conversion and selectivity data for different catalysts under light on and light off conditions are shown in Figure 1. For Au seeds and Au@Ag no catalytic activity was achieved after 8h. However, for the Pt NRT the PA conversion increases as a function of Pt content independent of light use. Noticeably, the Au@AgPt_3 sample reached 100% conversion without light but poor selectivity and over hydrogenation under light on. The intermediate NRT Au@AgPt_2 exhibits the desired catalytic performance, the PA conversion increase from 40% to 98% while maintaining the styrene selectivity >80% when illuminated.

References
1- P. Christopher, H. Xin, S. Linic, Nat. Chem. **3**, 467 (2011).
2- S.Mukherjee, F. Libisch, N. Large, O. Neumann, L. Brown, J. Cheng, J. Lassiter, E. Carter, P. Nordlander, N. Halas, Nano Lett. **13**, 240 (2013)
3- U. Aslam, S. Chavez, S Linic, Nat. Nanotech. **12**, 1000 (2017).
Corresponding author email: jhonquiroz@gmail.com

Gold nanoparticles: impact of surface chemistry on photocatalytic activity

M. Rodio[1,2]*, F. Schulz[2], E. Minutella[2], R. Intartaglia[3] and H. Lange[1,2]

(1) *Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, Hamburg, 22761, Germany*
(2) *Physical Chemistry, Hamburg University, Martin-Luther-King Platz 6, Hamburg, 20146, Germany*
(3) *Nanophysics, Istituto Italiano di Tecnologia, Via Morego 30, Genoa, 16163, Italy*

Because of their unique physicochemical properties, gold nanoparticles (Au-NPs) are studied in the context of various applications including surface-enhanced Raman scattering, biosensing, and photocatalysis (Figure 1a). Up to now different parameters, such as the size and shape of Au-NPs have shown to play a central role for their catalytic activity. Recently, it has been shown that the catalytic efficiency is also affected by the stabilizing ligands surrounding the Au-NPs. For instance, a direct relationship between the chain length and packing density of the ligand with respect to the Au-NPs catalytic activity was reported[1]. However, the effect of the Au-NPs surface chemistry on their localized surface plasmon resonance (LSPR) and interband excitations is presently not understood in detail. In our group, we recently investigated the relaxation of hot electrons in Au-NPs with different sizes[2] (Figure 1b).
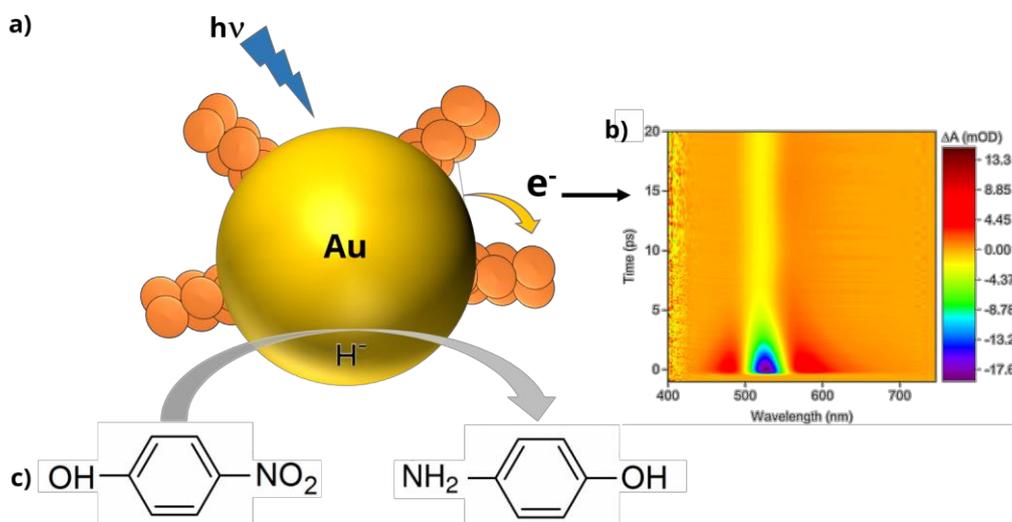
Figure 1. (a) Sketch of a plasmon-induced catalysis. Photoexcited electrons can support a redox reaction. (b) Time-evolution of the hot electron relaxation monitored by the change in contrast in a transient absorption experiment. (c) Sketch of 4-NP reduction to 4-AP mediated by Au-NPs.

In this work, we report on the impact of Au-NPs surface chemistry on their catalytic properties, under light driven excitation. A set of Au-NPs with different surface chemistry (ligand-free, citrate and PEG-based polymers) was prepared using femtosecond laser ablation in liquid[3] or chemical reduction method[4]. The catalytic activity was evaluated using the model reduction of 4-Nitrophenol (4-NP) to 4-Aminophenol (4-AP) in the presence of Au-NPs and NaBH₄ (Figure 1c). UV–Vis spectroscopy in the dark and under the irradiation of light with different wavelengths was employed to evaluate the 4-NP reduction rate. Transient absorption spectroscopy was used to better understand the processes related to the Au-NPs hot electron relaxation.

References
1- S.M. Ansar, ACS Catal. **6**, 5553 (2016).
2- E. Minutella, J. Phys. Chem. Lett. **8**, 4925 (2017).
3- R. Intartaglia, Phys. Chem. Chem. Phys. **15**, 3075 (2013).
4- F. Schulz, Langmuir **30**, 10779 (2014).

*Corresponding author email: rodio@chemie.uni-hamburg.de

Plasmonic Super Absorber of Light for Photocatalysis

Q. Xiao[1*], T. U. Connell[2], A. S. R. Chesman[1], D. E. Gómez[2]
(1) *CSIRO Manufacturing, Bayview Ave, Clayton, VIC 3168, Australia*
(2) *RMIT University, Melbourne, VIC 3000, Australia*

The direct utilization of solar energy to boost chemical reactions is an attractive approach to address increasing demand of renewable energy sources. Hot charge carrier extraction from plasmonic metal nanostructures to semiconductors is key to a number of proposed nanophotonics technologies for solar harvesting.[1] Favourable materials and catalytic properties make systems based on plasmonic metal gold (Au) and traditional semiconductor TiO_2 particularly interesting. However, the efficient usage of hot carriers in these systems is still challenging, especially in the visible range of solar sppectrum.[2] Therefore, strategies to improve the hot carrier generation rate and the efficiency have to be developed, which can extend the light harvesting range of the nanostructures to sub-bandgap photon energies. An emerging class of plasmonic metamaterial is super-absorbers.[3] In these systems, it is found that the mirror/semiconductor/nanoparticle metamaterials could achieve broadband strong light confinement at the metal interface across the broadband spectrum. These nanostructures significantly improve the hot carrier generation rate and the collection efficiency.[3] However, the practical realization and application of the super-absorber in organic synthesis have not yet been developed; a number of open questions still remain regarding the fundamental understanding of the physics and chemistry of plasmon-induced hot carrier harvesting and how does the harvested hot carrier boost the efficiency in a photocatalytic organic reaction.

Here we demonstrate that a Au mirror/TiO_2/Au nanoparticle super-absorber system can be direct used in the transformation of organic reactants into desired products in a highly selective manner, through low intensity visible irradiation.[4] The super-absorber capable of absorbing near-unit incident light and the resulting photocatalyst achieves a significant catalytic rate for the selective oxidation of benzylamine into corresponding imine, at room temperature and atmospheric pressure. (Figure 1) We show that using the enhanced light absorbance of our super-absorber leads to ~29-fold increases in the photocatalytic efficiency by the plasmonic nanostructures. This study developed a model that successfully captures the essential physics of the plasmonic hot electron charge generation and separation in plasmonic super-absorber, and applied this effect in photo-catalytic organic synthesis. Plausible reaction mechanisms involving hot carrier transfer were discussed.[4]
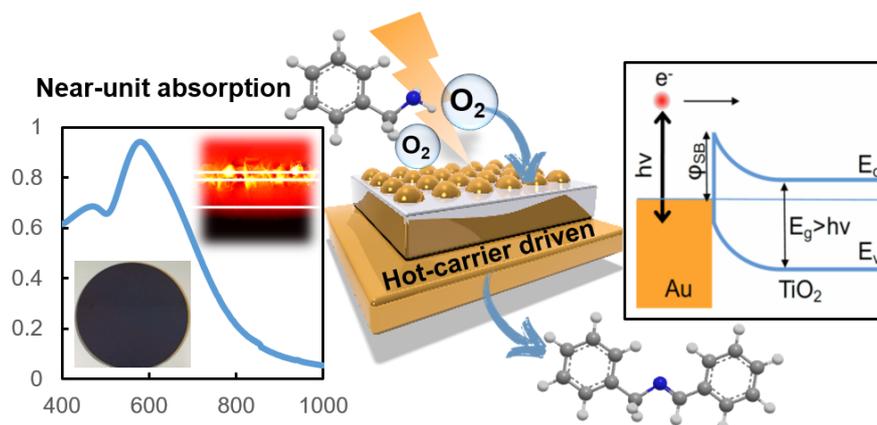
*Figure 1. Hot carries extraction in super absorber for photocatalysis*

References
1- M. Moskovits, Nat. Nanotechnol. **10**, 6 (2015).
2- J. Y. Park, et al. Acc. Chem. Res. **48**, 2475 (2015).
3- C. Ng & D. E. Gómez, et al. ACS Nano **10**, 4704 (2016).
4- Q. Xiao & D. E. Gómez, et al. **Submitted** (2018).

Corresponding author email: kevin.xiao@csiro.au

Gold Catalysts for Liquid-Phase Flow Reactor: Catalytic Oxidation of Glycerol into Functional Molecules

N. Mimura[1*], N. Muramatsu[1], T. Nagase[1], N. Hiyoshi[1], O. Sato[1] and A. Yamaguchi[1]
(1) *National Institute of Advanced Industrial Science and Technology (AIST), Sendai, Japan*

Gold catalysts are very effective for not only gas phase reaction but also liquid phase one. Here, we would like to focus on the oxidation of glycerol over gold catalysts. The usages of target molecules, such as glyceric acid and tartronic acid, are additive of ink, activator of cell, moisturizing agent and so on. There are many previous studies of the glycerol oxidation. Au, Au-Pd and Pt-Bi catalysts are typical reported catalysts[1]. The catalytic reactions were carried out in a batch-type reactor in almost cases. We believe that flow reactors are important for biomass conversion, considering large amount processing in the future. Accordingly, we would like to present the developments of gold catalysts for liquid-phase flow reactor, including screening of catalysts, long-term tests and microscope analysis.

The Au/alumina catalysts were prepared by deposition-precipitation (DP) method[2]. Catalytic reaction tests were conducted by using a stainless-steel liquid-phase flow reactor (inside diameter = 9.4 mm, length = 50 mm) with Teflon filters at the inlet and outlet of the reaction chamber. Products were identified by means of high-performance liquid chromatography.

Table 1 shows the catalytic performances of Au/alumina catalysts prepared under different pH conditions. The pH value affects the Au contents and activities of the catalysts. Catalyst No. 4 indicates the best performance among the tested catalysts.

Table 1. *Catalytic oxidation of glycerol by using flow-type reactor over various Au/Al$_2$O$_3$ catalysts*

No.	Au content (ICP results) (wt %)	Initial pH of Au solution in DP method	Conversion (GLY[a]) (%)	Selectivity (GLYA[b]) (%)	Selectivity (TA[c]) (%)
1	0.27	7.0	38.6	36.8	44.5
2	0.38	5.6	33.7	37.6	38.9
3	0.69	4.6	40.4	37.6	35.5
4	0.88	3.6	38.8	41.0	44.3
5	0.89	3.2	21.5	39.2	43.3

a : glycerol, *b* : glyceric acid, *c* : tartronic acid. Temperature =358 K. Reactant solution: glycerol, 0.6 mol/L, NaOH, 2.4 mol/L (glycerol/NaOH=1/4 (mol/mol)). Flow rate of reactant= 0.25 mL/min. Flow rate of oxygen= 6.0 mL/min. Catalyst weight= 0.5 g.

Figure 1 shows a result of long-term catalytic test using catalyst No. 4 in Table 1. An induction period was observed. The reason of induction period is considered to be slow reduction of gold species to more suitable state by mild reductant such as glycerol. Figure 2 shows the scanning transmission electron microscope (STEM) images of fresh catalyst. There are three types of gold species, which are nanoparticle (8-12 nm), cluster (1-2 nm) and atomic gold. We are now investigating the details of the active species. And we would like to present several useful ingenuities about catalysts for the flow reactor at the conference.
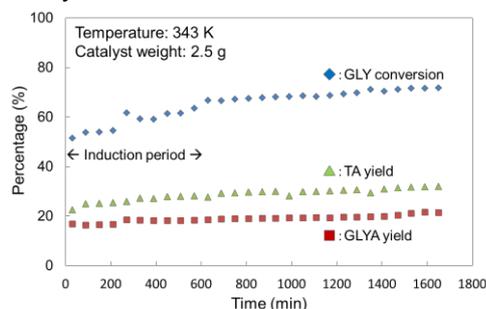
Figure 1. Long-term catalytic test
Parameters were same as Table 1 except catalyst weight and temperature.
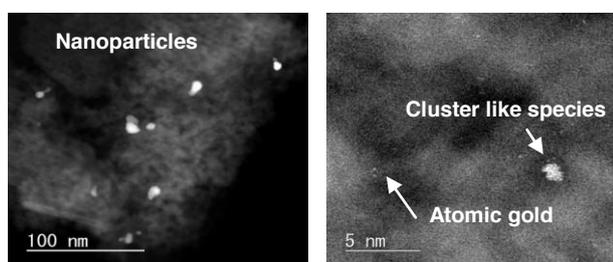
Figure 2. STEM images of fresh catalyst (No.4)

References
1- (*a*) B. Katryniok, *et al.*, *Green Chem.*, **13**, 1960 (2011). (*b*) N. Mimura, *et al.*, *RSC Adv.*, **4**, 33416 (2014). (*c*) N. Mimura, *et al.*, *Catal. Lett.*, **144**, 2167 (2014).
2- M. Haruta, *et al.*, *J. Catal.*, **144**, 175 (1993).

Corresponding author email: n.mimura@aist.go.jp

Gold-Silver Catalysts: Effect Of Catalyst Structure On The Selectivity Of Glycerol Oxidation.

A. Jouve[1], M. Stucchi[1], S. Cattaneo[1], A.Villa[1], C. Evangelisti[2], A. Beck[3], R. Zanella[4], L. Prati[1][*]

(1) Dipartimento di Chimica, Università degli Studi di Milano, via C.Golgi 19, 20133 Milano, Italy
(2) Istituto di Scienze e Tecnologie Molecolari (ISTM-CNR), Via G. Fantoli 16/15, 20133 Milano, Italy
(3) Centre for Energy Research, MTA, Konkoly Thege Miklós út 29-33, 1121 Budapest, Hungary
(4) UNAM Centro de Ciencias Aplicadas y Desarrollo Tecnológico, UNAM, Circuito Exterior S/N, Ciudad Universitaria, Apartado Postal 70-186, Delegación Coyoacán, C.P. 04510 Cd. de México, Mexico

Glycerol constitutes a very useful, renewable platform molecule which can be transformed in a huge amount of chemicals of industrial interest. Particularly under oxidative conditions in a basic medium it has been shown that the main product is glyceric acid. Its subsequent oxidation to tartronic acid has been shown to be promoted by Bi-modified systems (1,2) which however normally present low stability undergoing easy leaching of the promoter. Therefore, the development of long-life catalysts allowing a sustainable production of tartronic acid could be not only of scientific but also of industrial interest. Tartronic acid is indeed used as an oxygen scavenger in food industries.

This contribution deals with the modification of gold catalyst, a well-recognized catalyst for glycerol oxidation, with silver investigating the impact of the bimetallic structure on the selectivity (and activity) of the reaction in order to develop a stable, highly selective catalyst.

Three different synthetic methods (namely sol immobilization (3), solvated metal atom deposition (4), deposition-precipitation (5) have been used to prepared AuAg bimetallic catalysts. Despite a very similar particle size distribution and composition a strongly different selectivity in glycerol oxidation (0.3M solution, 50°C, 3atm O2, glycerol/metal 2000 mol/mol, glycerol/NaOH 4 mol/mol) has been revealed. In particular, we revealed by XPS, Auger and XANES analyses different bimetallic structures which are promoting different reaction pathway.

References

1- P. Fordham, M. Besson, P. Gallezot Appl.Catal. A: General 1995, 133, LI79-LI84
2- A.Villa, D.Wang, G.M. Veith, L.Prati J.Catal. 2012, 292, 73-80
3-T. Benkó, A. Beck, K. Frey, D. F. Srankó, O. Geszti, Gy. Sáfrán, B. Maróti, Z. Schay Appl. Catals A: General 2014, 479, 103–111
4.-a) C. Evangelisti, E. Schiavi, L.A. Aronica, R. Psaro, A. Balerna, G. Martra, "Solvated Metal Atoms in the Preparation of Supported Gold Catalysts" in "Gold Catalysis: Preparation, Characterization, and Applications", Ed. L. Prati, A. Villa, Pan Stanford Publishing Pte. Ltd., Singapore, 2016, pp. 73-92; b) L.A. Aronica, E. Schiavi, C. Evangelisti, A.M. Caporusso, P. Salvadori, G. Vitulli, L. Bertinetti, G. Martra, J. Catal. 2009, 266, 250-257
5- C. Louis, 2016. Deposition Reduction. In: L. Prati, A. Villa. Gold Catalysis – Preparation, Characterization and Applications, 1-38.

Corresponding author email: laura.prati@unimi.it

Density functional theory on ethanol oxidation catalyzed by gold: unraveling the role of base

Q. Gu[1*], P. Sautet[1,2], C. Michel[1]

(1) *Univ Lyon, Ens de Lyon, CNRS, Université Lyon 1, Laboratoire de Chimie UMR 5182, F-69342, Lyon, France*

(2) *Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, Los Angeles, California 90095, United States*

Alcohol oxidation to acid in water catalyzed by Au with O_2 as the oxidant is a quite green and ideal reaction with a high selectivity and conversion up to 90%[1]. However, the reaction necessitates the addition of a base, which results in carboxylates and disobeys the atom economy. When it is catalyzed by Pt, the reaction can still occur without base although with a much lower conversion[2], and it also faces the problem of instability caused by overoxidation and poisoning of the surface[3]. To get rid of the addition of base, we need to understand the role of base first. We took ethanol as an example and used DFT method to study oxidation reaction both on Au and Pt to unravel the role of base, and try to finally propose a way of performing reaction without base.

Electrons from ions are considered as one of the main effects of the electrolyte[4], in basic environment, the electrons comes from OH^-. So in the following calculation, periodic symmetric model with addition of electrons are taken as the modeling of basic environment as described in *Figure 1.* All the calculations are performed at PBE level with dDsC dispersion correction in implicit solvent through Poisson-Boltzmann continuum approximation. Microsolvation method is used to obtain a proper adsorption and desorption free energy in water. It is found that the adsorption of OH^- both on Au and Pt are exothermic reactions which confirms the possibility of the electron donation from the base to the surface.

In our study, the whole reaction pathway both in neutral and basic environment on Au and Pt are computed, *Figure 1* shows the reaction on Au in basic environment. In neutral environment, 4OH should be produced by O_2 activation to assist the oxidation, then the oxidation goes through an aldehyde intermediate and finally produces acid. Computing the energies of corresponding intermediates and transition states, we found the rate determining step on Au is O-O cleavage with an energetic span of 1.22 eV, while the rate determining step on Pt is the desorption of the products with an energetic span of 1.23eV. These show the neutral environment kills the oxidation on Au at the very beginning while the main problem for Pt is the poisoning by the product, which are consistent with the experimental results[2,3]. We also computed reactions in basic environment on Au, the energetic span decreased to 0.91eV and the reaction energy also decreased by 0.69eV compared to the neutral environment. This can explain the necessity of base in alcohol oxidation catalyzed by Au. It also validates the fact that the key role of base lies in the electron donated by OH^-.

From the important role of electron in alcohol oxidation, we propose to find electron donors like support, additives to obtain a base free reaction.
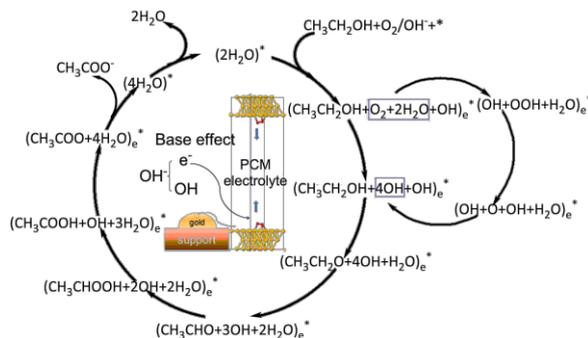
Figure 1. Catalytic circle of ethanol oxidation in basic environment

References

1- C. Bianchi, F. Porta, L. Prati, M. Rossi, Top. Catal. **13,** 231 (2000)
2- B. N. Zope, D. D. Hibbitts, M. Neurock, et al. Science, **330(6000)**, 74-78 (2010).
3- T. Mallat, A. Baiker, Catal. Today **19,** 247 (1994)
4- P. Wang, S. N. Steinmann, G. Fu, C. Michel, P. Sautet, ACS Catal. **7,** 1955−1959, (2017)

Corresponding author email: qingyi.gu@ens-lyon.fr

Strong effect of the surface properties of carbon supports in Au-catalysed reactions

B. Donoeva[1]*, N. Masoud[1], P. E. de Jongh[1]*

(1) *Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Utrecht, 3584 CG, the Netherlands*

Gold nanoparticles supported on carbon materials demonstrate remarkable activity and/or selectivity in various reactions. However, the surface properties of carbon materials can greatly differ depending on the preparation method and post-treatments. For example, carbon surface can be easily functionalized by incorporating other elements, such as oxygen and nitrogen,[1,2] which in turn would affect carbon surface polarity and acid-base characteristics. These parameters are expected to strongly influence the activity, selectivity and stability of supported gold catalysts.

In this work, we prepared and characterized a set of Au catalysts (2-4 nm particle size) supported on high surface area graphite (HSAG) materials with different surface characteristics, but the same morphology.[3] The catalysts have been investigated for the oxidation of 5-hydroxymethylfurfural (HMF) and hydrogenation of butadiene.

Study of the Au catalysts for HMF oxidation showed that the activity (TOF_{Au}) and the yield of furandicarboxylic acid (FDCA) strongly increased with the point of zero charge (PZC) of the support (Figure 1). On the other hand, Au catalysts supported on acidic HSAG (HSAG and HSAG-ox, PZC < 7) were highly selective towards the intermediate HMFCA. Gold nanoparticles were substantially more stable on HSAG supports with lower concentration of surface oxygen groups, while Au nanoparticles on HSAG and HSAG-ox with oxygen-rich surfaces showed severe particle growth during the reaction.
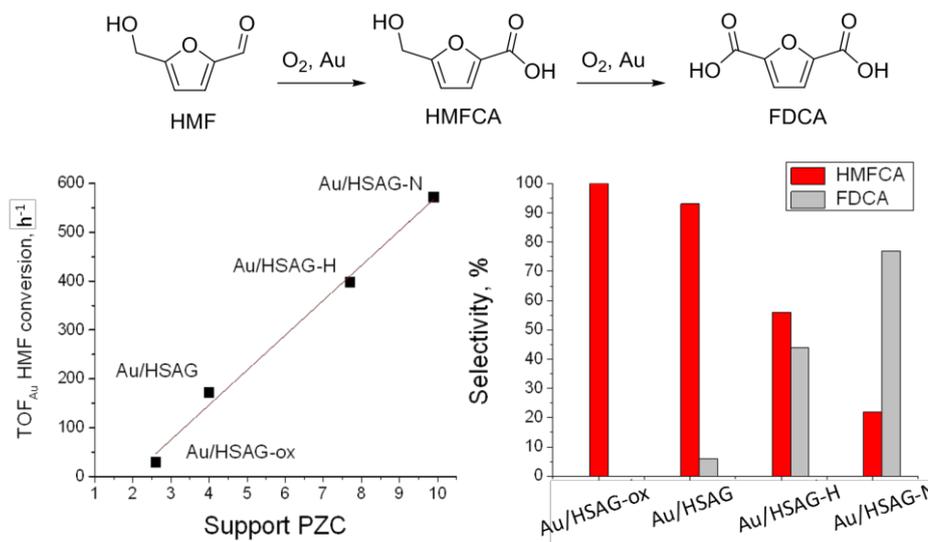

Figure 1. Activity and selectivity of Au/HSAG-x in the oxidation of HMF.

The observed strong differences in activity and selectivity between catalysts immobilized on the modified HSAG supports primarily originate from the differences in the reactant and intermediate adsorption on the surface of the catalysts, as will be discussed in more detail in the conference contribution. Furthermore, a comparison of a catalyst behavior as a function of carbon surface properties in a gas-phase reaction (hydrogenation of butadiene), as well as the guidelines for the rational design/choice of optimal carbon supports for highly active, selective and stable Au catalysts will be also given in the conference contribution.

References

1- J. L. Figueiredo, J. Mater. Chem. A, **1**, 9351 (2013).
2- T. J. Bandosz, In Carbon Materials for Catalysis; P. Serp, J. L. Figueiredo, Eds.; Wiley: Hoboken, NJ, 45 (2009).
3- B. Donoeva, N. Masoud, P.E. de Jongh, ACS Catal., **7**, 4581 (2017).

Corresponding author email: b.donoeva@uu.nl

Selective oxidation of methane to methanol with molecular oxygen using aqueous Au-Pd colloids at low temperature

N. Agarwal[1], S. Freakley[1], Sultan M. Althahban[2], C.J. Kiely[2], G.J. Hutchings[1]

(1) *Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, CF103AT, UK*
(2) *Department of Materials Science and Engineering, Lehigh University, PA 18015, USA*

In industry, CH_4 is used as a feedstock by first indirectly converting it to methanol (CH_3OH) via the production of synthesis gas ($CO + H_2$) at high temperatures and pressures, an expensive and energy intensive process. The direct oxidation of CH_4 to CH_3OH, which is challenging as over oxidation must be avoided, has been the subject of intensive study for many decades. CH_4 oxidation using supported AuPd nanoparticles (NPs) under mild aqueous conditions using H_2O_2 as oxidant at 50°C has been reported (1). The reaction proceeded through a radical mechanism. However, the relatively high cost of H_2O_2 for even stoichiometric oxidation of CH_4 makes it difficult to be economically viable. Incorporation of O_2 into the primary oxidation products would represent substantial progress toward a feasible CH_4 to CH_3OH process. Thus, this reaction has been performed here under mild conditions using colloidal AuPd NPs in the presence of both H_2O_2 and O_2, with the selectivity to primary products reaching >90% with minimal CO_2 produced.

Bimetallic Au-Pd nanoparticles were formed by standard colloidal method by using polyvinylpyrrolidone (PVP) as the stabilizing agent and $NaBH_4$ as the reducing agent. In the methane oxidation experiments we first used H_2O_2 as an oxidant at 50°C and we found that when the unsupported AuPd colloid was used as a catalyst the level of decomposition of H_2O_2 was much lower than when the AuPd colloid was supported on TiO_2. In view of this the products observed with the unsupported catalyst were substantial (Fig. 1). However, when molecular oxygen was added to the reaction gases the amount of products observed increased markedly. Use of isotopically labelled $^{18}O_2$ showed that up to 70% of the methanol contained oxygen from the molecular oxygen. In this reaction the H_2O_2 acts as an initiator but more oxygenated products were formed than H_2O_2 consumed, suggesting that the controlled breakdown of H_2O_2 activates methane which subsequently incorporates molecular oxygen through a radical process as shown in scheme.
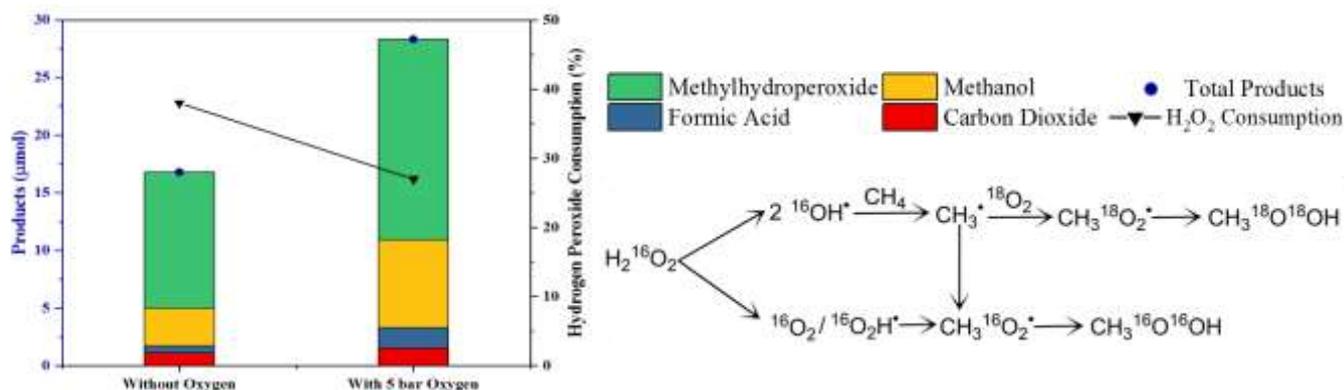

Figure 1. Conversion of methane using unsupported AuPd colloid with oxygen. And proposed reaction mechanism. Test conditions: 0.5 h, 50°C, H_2O_2 amount: 1000 µmol, 1500 rpm, $P(CH_4)$ = 30 bar, $P(O_2)$ = 5 bar, 6.6 µmol metal per reaction

Fresh and used catalyst were characterized using electron microscopy and XPS. Particles were found to be alloyed with icosahedral structure with no size dependent composition variation and no single atoms or clusters were detected in fresh and used catalyst. The catalyst was found to be stable for longer reactions and reuse.

The reaction proceeded with same efficiency at room temperature and the activation energy for the reaction was found to be 39 kJ/mol. Using unsupported AuPd colloids with H_2O_2 as an initiator together with O_2, methane can be oxidized to methanol where the oxygen in the methanol is derived from O_2.

References

1- N. Agarwal et al. *Science* **2017**, 358, 223.
2- M. H. Ab Rahim et al. *Angew. Chem. Intl. Ed.* **2013**, 52, 1280.

*Corresponding author email: agarwaln12@cardiff.ac.uk*

Supported gold catalysts for the low temperature solvent-free oxidation of cyclohexene to cyclohexanediol using molecular oxygen as oxidant

O. Rogers,[1] S. Pattisson,[1] J. Macginley,[1] K. Whiston,[2] G. J. Hutchings[1] and S. H. Taylor[1]

(1) *Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, United Kingdom.*
(2) *INVISTA Performance Technologies. The Wilton Centre, Wilton, Redcar, United Kingdom*

The industrial production of adipic acid historically relies on the aerobic oxidation of cyclohexane. However, the possibility of using cyclohexene as a feedstock has lately become an option due to the recent improvements in the partial hydrogenation of benzene in the Asahi process.[1] The higher reactivity of cyclohexene allows it to be oxidised at lower temperatures by O_2 and hydrogen peroxide, avoiding N_2O formation. Routes to adipic acid based on aerobic oxidation with air as the terminal oxidant are therefore of continuing research interest. Previous work by Ovoshchnikov et al.[2] has shown the selective formation of the epoxide utilising diatomic oxygen as oxidant. Tungsten oxide was found to be efficient in the activation of oxygen and selective epoxidation of cyclohexene. In this work, we demonstrate the modification of this system for production of cyclohexane diol. The use of highly active supported gold nanoparticles leads to the formation cyclohexanediol, an intermediate to producing adipic acid. These catalysts were prepared via impregnation and sol immobilisation and tested using solvent-less, initiator-free conditions using O_2 as oxidant. In addition, WO_3 was used as a co-catalyst to improve selectivity towards the epoxide which could then be completely converted to the diol through the addition of water with minimal effect of activity achieving a selectivity of 30% in comparison to 4% without WO_3. The addition of water to WO_3 only systems led to complete quenching of the reaction due to residence of WO_3 in the aqueous phase. Impregnation catalysts suffered from low reproducibility and a low activity of ~40 % in contrast to the sol immobilisation catalysts which were highly reproducible and showed a high activity of ~75%. However, yield of the epoxide and therefore cyclohexane diol is ultimately limited to 50 % by the formation of equimolar amounts of the allylic alcohol. The high activity of the sol immobilisation catalysts were explained by their particle size distribution as obtained through TEM imaging and some of these images are shown in figure 1. The Au graphite catalyst had a mean particle size diameter of 4.2 nm with the Au graphene having a similar mean particle size of 4.5 nm and a standard deviations 1.1 and 1.2 nm for the graphite and graphene supported catalysts respectively. The BSE images of the impregnation catalyst show a much wider dispersion and distribution of particles. These particles had a mean diameter of 19.3 nm and a standard deviation of 6.6 nm. The narrow size distribution and wide dispersion of particles leads to an unprecedented activity for cyclohexene oxidation which has not been observed in previous studies. However, the activity of these catalysts is offset with a low selectivity to the desired products. This will be the subject of further investigation for the implementation of a more selective co-catalyst to the diol.
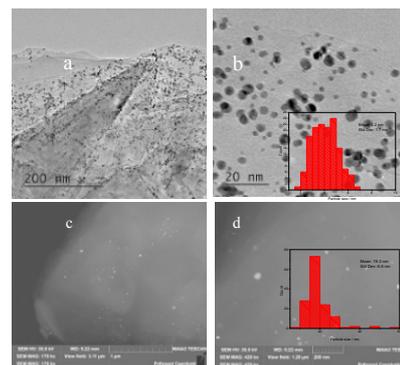
Figure 1 (a-b) Bright field TEM images of 1% Au/Graphite *via* sol immobilisation show mean particle diameter of 4.2 nm, standard deviation of 1.1 nm. BSE images (c-d) of 1% Au/Graphite prepared by impregnation show mean particle size of 19.3 nm and a standard deviation of 6.6 nm.

Table 1. *Performance of catalysts in cyclohexene oxidation*

Catalyst	Prep method	Conv / %	Selectivity / %				
			Cy-oxide	Cy-ol	Cy-one	CyOOH	Cy-diol
1% Au/G +WO₃	Impreg	53.6	32.3	21.7	15.4	11.3	7.6
	SI	78.4	1.5	12.5	36.4	2.4	15.6

Cyclohexene (10 mL), n-decane (1 mL) catalyst (0.1 g) + WO_3 (0.1g), O2 (3 atm), 60 °C, 24 h

References

1- H. Nagahara, M. Ono, M. Konishi and Y. Fukuoka, Appl. Surf. Sci., 1997, 121, 448–451.
2- D. S. Ovoshchnikov, B. G. Donoeva, B. E. Williamson and V. B. Golovko, Catal. Sci. Technol., 2014, 4, 752

Corresponding author email: Pattissonsd@Cardiff.ac.uk

Oxidative Esterification of Aliphatic Aldehydes by Gold Nanoparticle Catalysts in a Continuous Flow Reactor

A. Taketoshi[1,2*], T. Ishida[1,2], T. Murayama[1,2], M. Haruta[1,2]

(1) *Research Center for Gold Chemistry, Tokyo Metropolitan University, Tokyo, Japan*
(2) *Department of Applied Chemistry for Environment, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, Tokyo, Japan*

Aliphatic esters are important compounds as flavors and fragrance. In industry, esters are produced by two steps, oxidation of aldehyde to carboxylic acid followed by acid-catalyzed esterification. From the point of view of green chemistry, oxidative esterification by single step has been attracting attention. Recently, several groups reported the synthesis of methyl esters from aldehydes by one step using gold catalysts[1-3]. In this work, we chose oxidative esterification of octanal with ethanol as a model reaction to give ethyl octanoate, because they are less reactive than aromatic aldehydes and methanol.

As catalysts, Au/ZnO and Au/Al$_2$O$_3$ were purchased from Haruta Gold Inc., and Au/SiO$_2$ was prepared by solid grinding (SG). In a batch, to an autoclave was charged octanal (1.00 mmol), ethanol (2 mL), 1 wt% gold catalyst (100 mg, Au 0.5 mol%), and tridecane as an internal standard. The autoclave was purged and filled with O$_2$ until the gage pressure reached 0.5 MPa. The reaction mixture was stirred at 100 °C for 5 h. The mixture was filtered and analyzed by GC.

In a flow reactor (EYELA, FFX-1000G), catalyst (200 mg) was packed into a stainless column (ϕ5 x 50 mm bed reactor) that was attached to a heat block. The solution of octanal (0.5 M) in ethanol and tridecane was fed at a flow rate of 0.08 or 0.02 mL min^{-1}. The oxygen pressure at the inlet of the reactor and the flow rate of oxygen were set at 0.35 MPa and 3.6 mL min^{-1}, respectively. The reaction mixture was collected every 20 min and analyzed by GC.

Table 1 *Oxidative esterification of octanal over Au catalysts in batch and flow reactors.*
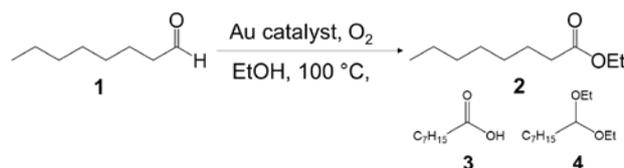
Support	Method	Conv. / %	Selectivity / %		
			2	**3**	**4**
ZnO	batch	100	86	5	2
	flow[a]	83[c]	95	4	0.1
	flow[b]	97[c]	94	5	0.6
Al$_2$O$_3$	batch	100	81	9	0.4
	flow[a]	66[c]	91	4	0.1
	flow[b]	98[c]	94	0	1
SiO$_2$	batch	100	80	3	1
	flow[a]	70[c]	97	1	2
	flow[b]	97[c]	88	4	7

a) Substrate flow rate: 0.08 mL min^{-1}, b) Substrate flow rate: 0.02 mL min^{-1}, c) after 1 h.

Various kinds of supported gold catalysts have been screened for oxidative esterification in batch. After reaction for 5 h, ethyl octanoate was obtained in high yields with high selectivities by Au/ZnO, Au/Al$_2$O$_3$, and Au/SiO$_2$ (Table 1). To clarify the role of gold, other noble metals such as Pt and Pd were deposited on ZnO by SG. In the case of Pt and Pd, the desired ester was hardly obtained. The acetal was formed even though ZnO only was used as a catalyst. In contrast, the generation of acetal was suppressed by loading of gold, and the desired ester was obtained.

Next, the reaction was carried out in a continuous flow reactor. The catalytic activity could be maintained for 6 h. By changing the flow rate from 0.08 to 0.02 mL min^{-1}, conversion increased in all cases. In the case of Au/ZnO and Au/Al$_2$O$_3$, the selectivity was maintained at 94%, while the yield of acetal increased by Au on acidic SiO$_2$ because the contact time increased.

In summary, Au/ZnO exhibited the highest catalytic activity in both batch and flow reactors. The selectivities of desired ethyl ester in flow were higher than those in batch.

References
1- F.-Z. Su, J. Ni, H. Sun, Y. Cao, H.-Y. He, K. N. Fan, Chem. Eur. J.*,* **14**, 7131 (2008).
2- O. Casanova, S. Iborra, A. Corma, J. Catal., **265**, 109 (2009); F. Menegazzo, M. Signoretto, F. Pinna, M. Manzoli, V. Aina, G. Cerrato, F. Boccuzzi, J. Catal., **309**, 241 (2014).
3- K. Suzuki, T. Yamaguchi, K. Matsushita, C. Iitsuka, J. Miura, T. Akaogi, H. Ishida, ACS Catal., **3**, 1845 (2013); X. Wan, W. Deng, Q. Zhang, Y. Wang, Catal. Today, **233**, 147 (2014)

Corresponding author email: taketoshi-ayako@tmu.ac.jp

Redox Reaction of NAD$^+$/NADH by Au Cluster Catalysts Related to the Coenzyme Regeneration for Dehydrogenases

J. Nishigaki, T. Ishida, M. Haruta

*Research Center for Gold Chemistry, Graduate School of Urban Environmental Sciences,
Tokyo Metropolitan University, Tokyo, Japan*

Synthesis of organic compounds by biocatalysts such as dehydrogenases is attracting growing interests for green sustainable chemistry. However, the usage of oxidoreductases is very limited because stoichiometric amounts of coenzymes are frequently required, increasing the operation costs. Thus the recycling (re-activation) of NADH or NAD$^+$ is an important theme in biocatalytic organic syntheses. There are many reports concerning electrochemical or enzymatic conversions between NADH and NAD$^+$, but these methods require additional energy or extra-substrates. We studied the utilization of small Au clusters to convert NADH and NAD$^+$ using O$_2$/H$_2$ as redox agents without additional energy or substrate.

Au clusters deposited on metal oxides and nanodiamond (ND) were prepared by solid grinding method using Me$_2$Au(acac) as a precursor,[1] and by simple mixing of colloidal Au:PVP,[2] respectively. The small Au cluster catalysts (< 2nm) were obtained. The other Au nanoparticle (NPs) catalysts supported on metal oxides were purchased from Haruta Gold Inc. and used as received.

NADH oxidation was carried out using 15 mg of 1 wt% Au catalysts (1.7 mol%) and 30 mg of NADH under 0.1 MPa O$_2$ at 37 °C. The NADH oxidation activities were dependent on the size of Au particles. Smaller Au cluster catalysts showed higher oxidation activities (82% for 1.8 nm Au/Nb$_2$O$_5$, 79% for 1.4 nm Au/ND), which decreased with increasing Au particle size (Fig.1a). This is due to the fact that the number of active sites (surface Au atoms) in clusters is inversely proportional to the size of Au particles. Similarly, hydrogenation of NAD$^+$ was strongly dependent on the Au particle size. Only < 2nm Au clusters deposited on basic metal oxides could reduce NAD$^+$ by H$_2$ (Fig.1b). These redox reactions were affected by pH value because H$^+$ participated with redox process. Especially, the basicity of reaction site is very important in hydrogenation of NAD$^+$, implying that the interface of Au clusters and supports provides Lewis pair to dissociate H$_2$ heterolytically. Finally, we examined the glucose oxidation in the presence of glucose dehydrogenase (GDH), NADH, and Au/Nb$_2$O$_5$. We found that NAD$^+$ was regenerated by the Au catalyst and used for GDH-catalyzed oxidation.
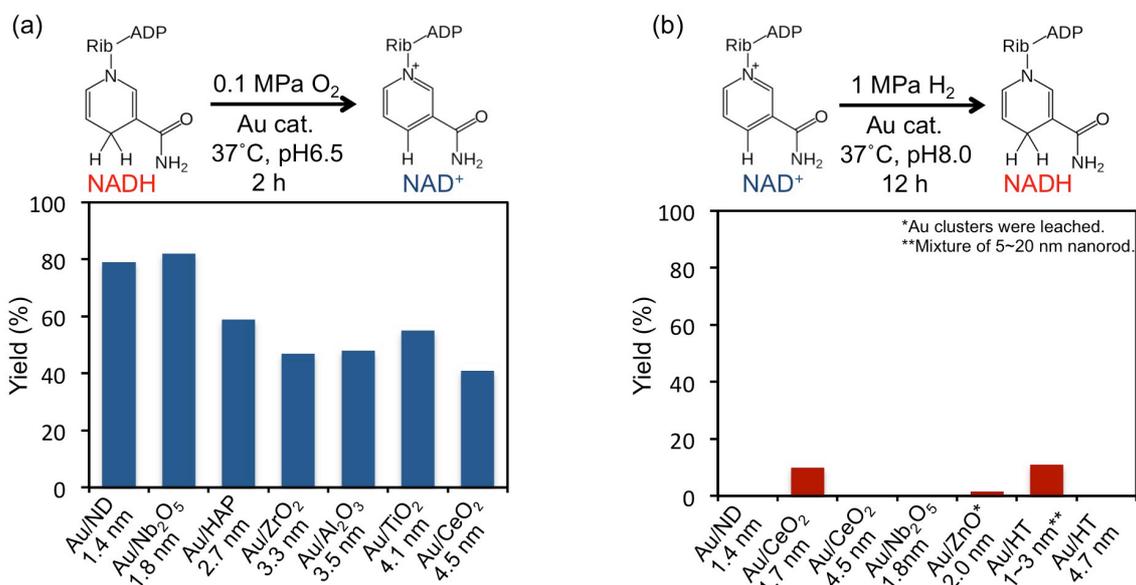

Figure 1. Interconversion of NADH and NAD$^+$ by Au catalysts. (a) Aerobic oxidation of NADH and (b) hydrogenateon of NAD$^+$.

References

1- T. Ishida, M. Nagaoka, T. Akita, M. Haruta, *Chem. Eur. J.*, **14**, 8456 (2008).
2- H. Tsunoyama, T. Tsukuda, *J. Am. Chem. Soc.*, **131**, 18216 (2009).

Corresponding author email: jnishi@tmu.ac.jp