BOOK REVIEW

# Surface Chemistry and Catalysis

**Edited by Albert F. Carley, Philip R. Davies, Graham J. Hutchings and Michael S. Spencer**

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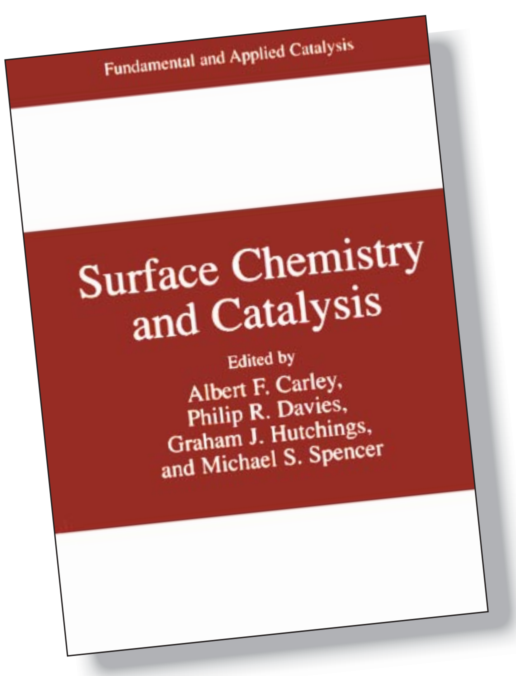


This book is dedicated to Professor Wyn Roberts of Cardiff University, UK, who in 2001 celebrated his 70th birthday and 50 years of working in surface science and catalysis. His notable scientific achievements are referred to in the chapters by Sir Ronald Mason and Sir John Meurig Thomas. The list of 247 publications by Wyn (M.W.) Roberts given in the Appendix contains seven titles on gold surface science and catalysis, (1971, 1972, 1973(2), 1976(2), 1991), most of them from the 1970s when gold was still regarded as a poor catalyst. These papers reported use of gold for the catalytic decomposition of methanol, the adsorption of mercury and water on gold, the development of stepped surface regions on polycrystalline gold, the decomposition of formic acid, and the activation of carbon dioxide on gold surfaces.

It is therefore appropriate that two of the twelve chapters in this book describe catalysis by gold : *ie* 'Surface Chemistry of Model Oxide-Supported Metal Catalysts: an Overview of Gold on Titania' by Douglas C. Meier, Xiaofeng Lai and D. Wayne Goodman of the Department of Chemistry, Texas A&M University, College Station, USA, and 'Nanoscale Catalysis by Gold' by G.U. Kulkarni, C.P. Vinod and C.N.R. Rao from the Chemical and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore, India. In a further chapter on 'Selectivity in Metal-Catalysed Hydrogenation' by Peter B. Wells, Cardiff, the special role of gold's high electronegativity in producing the highest yield of but-1-ene in the hydrogenation of buta-1,3-diene is apparent.

In the chapter by Douglas C. Meier, Xiaofeng Lai and D. Wayne Goodman, the importance of having an insight into the atomic-level surface chemistry of metals on oxide surfaces is emphasized. In the work described, scanning tunnelling microscopy was used in conjunction with traditional surface science techniques to study gold metal clusters on a planar titania support. When gold is vapour deposited onto $TiO_2$(110) under ultra-high vacuum conditions, it grows as three-dimensional hemispherical clusters on $TiO_2$(110). Annealing studies reveal that gold clusters form large microcrystals with well-defined hexagonal shapes above 1000 K. Furthermore, an oxygen-induced cluster ripening is observed after Au/$TiO_2$(110) is exposed to 10 Torr $O_2$ in an elevated pressure reactor. The morphological change of gold clusters induced by $O_2$ exposure suggests that $O_2$ chemisorption takes place on both the gold clusters and the $TiO_2$ substrate at room temperature. Gold clusters exhibit a clear bimodal size distribution after oxygen exposure due to Ostwald ripening: some clusters increase in size while others shrink. Deposition of gold onto titania provides a convenient way to model important aspects of a supported metal catalyst and represents a promising method of simulating a 'real world' catalyst in an experimentally tractable manner.

The chapter by G.U. Kulkarni C.P. Vined and C.N.R.Rao addresses the important issue of how the nobility of gold breaks down at the nanoscale when it is in contact with oxide supports. The high reactivity of gold catalysts in comparison with other metal catalysts is illustrated by reactions such as oxidation of carbon monoxide and reduction of NO under ambient conditions, as well as the epoxidation and hydrochlorination of ethyne to give vinyl chloride. The observation of maximum reactivity at a cluster size of 2 – 3 nm, coincident with the size-induced metal to non-metal transition in gold forms the central theme of this article. The overall conclusion is that in nanoscale catalysis gold does not remain noble. Nanoscale gold particles dispersed on oxide supports such as titania, magnesia, alumina and zirconia exhibit high activity at ambient temperatures for CO oxidation and NO reduction, reactions which are very important in automotive emission control. Gold catalysts are also candidates for other industrially important reactions such as the hydrogenation of alkenes, the oxidation of propene and hydrochlorination reactions. It is emphasized that gold could be a welcome alternative for platinum group metals, because of its relative abundance. The authors indicate that gold catalysts are not easily deactivated.

Professor H.-J. Freund's group in the Fritz-Haber Institute in Berlin and Professor Graham Hutchings in Cardiff, who are active in the surface chemistry and catalysis by gold, have contributed chapters on other topics, entitled 'Model Systems for Heterogeneous Catalysis: Quo Vadis Surface Science?' and 'Enantioselective Reactions using Modified Microporous and Mesoporous Materials' respectively. Other contributors to this wide-ranging book include Norman Sheppard, University of East Anglia, Norwich, UK, Gabor Somorjai, University of California, Berkeley: Lawrence Berkeley National Laboratory and Wolfgang M.H. Sachtler of the V.N. Ipatieff Laboratory, Center for Catalysis and Surface Science, Northwestern University, Evanston, USA. They write on '50 Years in Vibrational Spectroscopy at the Gas/Solid Interface', 'High Pressure CO Dissociation and CO Oxidation Studies on Platinum Single Crystal Surfaces using Sum Frequency Generation Surface Vibrational Spectroscopy' and 'Catalysis from Art to Science' respectively. In the chapter on platinum single crystals it is interesting to note the high ignition temperatures for CO oxidation of 620, 640 and 500 K for Pt(111), Pt(557) and Pt(100) respectively: similar studies on gold single crystals would undoubtedly reveal much lower ignition temperatures. All twelve chapters cover areas in which Wyn Roberts has made significant contributions, and his continued interest for years to come will be stimulated by their contents. The appearance in a book of twelve chapters of two devoted to gold catalysis indicates the growing importance of gold to the catalysis community.

David Thompson

**Letter to the Editor**

# Fulminating Gold

Dear Sir,

Following a small incident in our own laboratories, with fortunately no serious consequences, I would like to remind readers of the hazards of **explosive 'fulminating' gold**. J.W.Mellor[1] reports that fulminating gold can be prepared by treatment of gold hydroxide or gold chloride with ammonia or an ammonium salt. Further information on the formation of fulminating gold can also be found in Bretherick[2].

The preparation of gold catalysts has received much attention in the recent literature due to the discovery that small gold particles have significant catalytic activity for amongst other reactions, low temperature CO oxidation and low temperature water gas shift.

Two recent papers[3,4] report the preparation of supported catalysts by, in the first case, a hydrolysis deposition route using $HAuCl_4$ and ammonium carbonate and, in the second, treatment of a support containing adsorbed $HAuCl_4$ with ammonia. This is potentially very dangerous because of the risk of making 'fulminating' gold. Cusumano reported in Nature[5] that 'supported metal catalysts which contain gold should never be prepared by impregnation of a support with solutions which contain both gold salts and $NH_4OH$. The dried catalysts contain extremely shock sensitive gold-nitrogen compounds which may explode with the lightest touch'.


1 J.W.Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, 1941, Vol 3, 582.
2 Bretherick's Handbook of Reactive Chemical Hazards (5th edition), Vol. 1, 59
3 Q.Fu, S.Kudriavtesa, H.Saltsburg and M.Flytzani-Stephanopoulos, Chemical Engineering Journal, 2003, **93**, 41.
4 Q.Xu, K.C.C.Kharas and A.K.Datye, Catalysis Letters, 2003, **85**(3-4), 229
5 J.A.Cusumano, Nature, 1974, **247**, 456



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*Note from the editor: This is a timely warning to catalyst and other researchers. We would like to hear from others who may have relevant experience on such hazards that they are willing to share.*