

New Advances in Gold Catalysis Part II*

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Some of the unique features of gold catalysis were described in Part 1. Further examples of reactions catalysed by supported transition metal oxides are given in this second part. These include both selective and complete oxidation of hydrocarbons and a number of hydrogenation reactions. In fact, gold has now been demonstrated to be the element of choice for some catalytic reactions. As a result, both chemical processing and environmental applications are foreseen for supported gold catalyst systems. In this, the second of two articles, the overall current state of knowledge on gold catalysis is reviewed and some early examples of homogeneous gold catalysis, in solution, assessed.

HETEROGENEOUS CATALYSIS

We have seen from the work described in Part I (1) that gold species supported on activated carbon are the most active for the hydrochlorination of acetylene (ethyne), and that Au/ α -Fe₂O₃ is the best catalyst found to date for the oxidation of carbon monoxide at low temperatures. The control of gold particle size to *ca* 2-5 nm is important and this can be achieved using deposition precipitation or co-precipitation preparative procedures for the catalysts.

In Part II of this pair of articles we will consider other heterogeneous reactions catalysed by gold, including catalytic combustion of hydrocarbons, selective oxidation, hydrogenation of carbon oxides, the reduction of nitrogen oxides with propene, carbon monoxide or hydrogen, and the oxidative decomposition of halogen compounds.

Catalytic Combustion of Hydrocarbons

Waters *et al* (2) have evaluated co-precipitated gold on transition metal oxide catalysts for their activity towards methane oxidation to carbon dioxide and water. Activities were found to fall in the following order:



5% Au/Co₃O₄ is active at below 523 K. A dual site mechanism was proposed to explain the results since the catalyst systems are also active at higher temperatures. The activities increased with increased oxidation state of gold.

Haruta (3) has shown (Figure 1) that catalytic activity, as expressed by temperature at 50% conversion, for the oxidation of methane (CH₄)

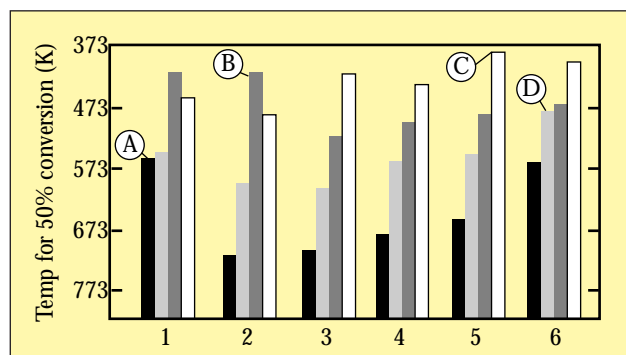
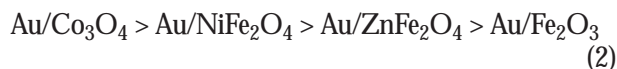


Figure 1 Temperature for 50% conversion in the catalytic combustion of hydrocarbons and trimethylamine. 1wt%Pd/Al₂O₃ and Pt/Al₂O₃ were prepared by impregnation. 1:19 Au/support catalysts were prepared by co-precipitation and calcined in air at 673 K. 1 1wt%Pd/Al₂O₃; 2 1wt%Pt/Al₂O₃; 3 10wt%Au/Fe₂O₃; 4 10wt%Au/ZnFe₂O₄; 5 10wt%Au/NiFe₂O₄; 6 10wt%Au/Co₃O₄. A: methane; B: propene; C: trimethylamine; D: propane. The concentrations of reactant gases in air were: CH₄: 0.25 vol%; C₃H₈ and C₃H₆: 0.1 vol%; (CH₃)₃N: 0.05 vol%; balanced with air to 1 atm.; SV 2 x 10⁴ ml (g cat)⁻¹ h⁻¹. (Based on reference 3)

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propane (C₃H₈), and propene (C₃H₆) decreases in the order:



In the oxidation of methane and propane the supported gold catalysts are more active than the Pt/Al₂O₃ catalyst. The most highly active gold catalyst, *ie* Au/Co₃O₄ gives approximately the same level of activity as a commercial Pd/Al₂O₃ catalyst. Gold should therefore be considered along with palladium and platinum for the complete oxidation of saturated hydrocarbons. For the complete oxidation of unsaturated hydrocarbons, such as propene, platinum and palladium are more active than supported gold catalysts. Figure 1 also includes conversions for trimethylamine, an indicator for the removal of odours from gas streams.

Selective Oxidation

Haruta (4) found that for the oxidation of propene to propene oxide, greater than 99% selectivities could be obtained at low conversions (1%) using 1wt% Au/TiO₂ at 323 K. The feed gas was hydrogen / oxygen / propene / argon in the ratio 10 : 10 : 10 : 70 vol% at a flow rate of 2 x 10³ ml h⁻¹, using 0.5 g catalyst. The catalyst was prepared by deposition precipitation. Similar palladium and platinum catalysts produced no propene oxide under similar conditions. As with gold catalyst systems used in complete oxidation reactions, the method of preparation was again found to be important and best results were obtained when the gold particles had a mean particle diameter of 2.4 nm and a narrow size distribution. More research is now required regarding means for achieving high selectivity at higher conversions, although a recycle process using a low conversion situation could also be considered.

Hydrogenation of Carbon Oxides

If gold supported on zinc oxide is prepared by co-precipitation, it gives methanol from the hydrogenation of carbon monoxide and carbon dioxide (4), while other noble metal catalysts give methane as the principal product. The selectivity and activity differ only a little amongst the Group 11 metals; basic metal oxides such as ZnO are the best for production of methanol, whilst acidic metal oxide supports, *eg* TiO₂, give carbon monoxide *via* reverse water gas shift at much higher rates. In Figure 2 the methanol yield is given as a function of the reaction temperature in the hydrogenation of carbon dioxide, for a number of supported gold catalysts. The

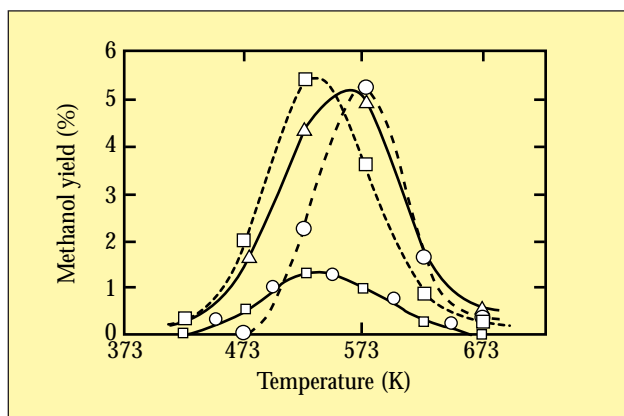


Figure 2 Methanol yield as a function of reaction temperature in the hydrogenation of carbon dioxide over supported gold catalysts. Au/α-Fe₂O₃ (□); Cu/ZnO (△); Au/ZnO (○); Au/TiO₂ (◻); Au/M (M = Fe, Zn, Ti) = 1:19. CO₂:H₂:Ar = 23:67:10; 50 atm pressure; SV = 3000 ml (g cat)⁻¹ h⁻¹. (Based on reference 4)

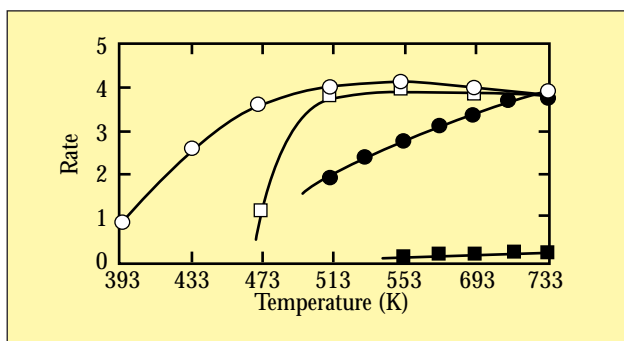


Figure 3 Temperature dependence of the catalytic activity of supported gold and base metal oxide catalysts in the Water Gas Shift. Starting reaction gas mixture was 4.88 vol% carbon monoxide in argon; water vapour partial pressure 223 Torr; SV 4000 h⁻¹; 1atm. Au/α-Fe₂O₃ (○); CuO/ZnO/Al₂O₃ (□); α-Fe₂O₃ (●); Au/Al₂O₃ (■). Rates are expressed in mol m⁻² h⁻¹ x 10⁻². (Based on reference 6)

activity per unit surface area increases with decreasing particle diameter of the gold (5).

The use of Au/α-Fe₂O₃ in the catalysis of the water gas shift has been reported by Andreeva *et al* (6, 7) (Figure 3). The gold particles had an average size of 3.5nm and were situated in close proximity to the iron oxide crystallites. The gold on iron oxide catalyst was active at low temperatures, and its performance overall compares favourably with the CuO/ZnO/Al₂O₃ catalyst which is commercially well established for this reaction. Haruta *et al* (8) have also reported catalysts active at low temperatures: gold supported on titania,

prepared by deposition precipitation of gold hydroxide from chloroauric acid and titanium dioxide powder, was shown to be active for both the forward and the backward water gas shift.

Reduction of Nitric Oxide with Carbon Monoxide, Hydrogen or Propene

The reduction of nitric oxide with carbon monoxide in the absence of oxygen occurs at temperatures below 373 K over gold supported on α -Fe₂O₃ or NiFe₂O₄, yielding nitrogen as the main product, while the product over unsupported gold is N₂O (4). Au(I)/ZSM-5 is also active for this reaction at low temperatures (9). Platinum Group Metals require higher temperatures and produce more nitrous oxide (4). The reaction between nitric oxide and carbon monoxide is deactivated by the presence of oxygen, but not by water (over Au/ α -Fe₂O₃).

Salama *et al* (10 - 13) have studied the reduction of nitric oxide by carbon monoxide and hydrogen:



Freshly reduced Au/NaY zeolite catalyst was used at 673 K and some of the results are illustrated in Figure 4.

The reduction of nitric oxide to nitrogen with propene takes place over several supported gold catalysts and is accelerated by the presence of oxygen and water (14): Figure 5 indicates that gold on zinc oxide, magnesia, titania, or alumina is active between 473 and 773 K. Au/Al₂O₃ gives the highest conversion of nitric oxide to nitrogen. Over the Au/Al₂O₃ catalyst nitric oxide is oxidized to nitrogen dioxide which then reacts with propene to give nitrogen. The addition of

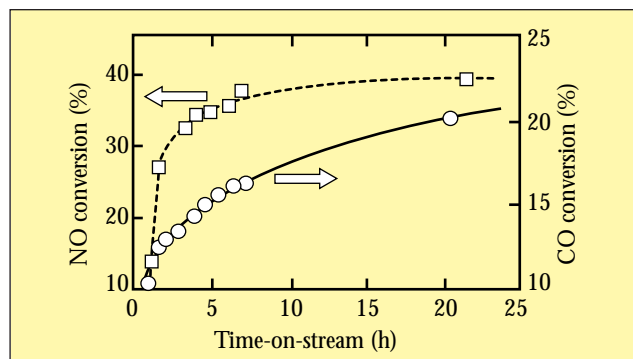


Figure 4 Conversion of nitric oxide and carbon monoxide to nitrogen and carbon dioxide respectively as functions of time on stream in the NO/CO/H₂ reaction over Au/NaY zeolite at 673 K. The inlet composition was [NO] = 4810 ppm, [CO] = [H₂] = 1%. (Based on reference 10)

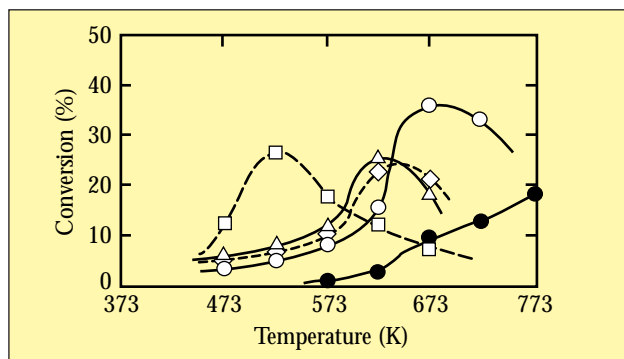


Figure 5 Temperature dependence of nitric oxide conversion to nitrogen using propene for Au/ZnO (\square); Au/TiO₂ (\triangle); Au/MgO (\diamond); Au/Al₂O₃ (\circ); and Al₂O₃ (\bullet). Gold loading is 1.0wt%; reaction gas is nitric oxide 1000 ppm, propene 500 ppm, 5.0 vol% oxygen, 1.8vol% H₂O, He balance; space velocity $2 \times 10^4 \text{ ml (g cat)}^{-1} \text{ h}^{-1}$. (Based on reference 4)

Mn₂O₃ to the Au/alumina in order to enhance nitrogen dioxide formation, markedly improves the conversion of nitric oxide to nitrogen over a wide range of temperatures (15). This composite gold catalyst offers one of the best performances in nitric oxide conversion amongst the catalysts so far developed (see also A. Ueda and M. Haruta, *Gold Bull.*, 1999, **32**, 3 -this issue).

Reactions with Halogenated Compounds

Gold supported on cobalt oxide or alumina are claimed to be as active as platinum catalysts for the oxidative decomposition of dichlorodifluoromethane and methyl chloride (16). For example, 5wt% Au/Co₃O₄ can be used to completely decompose methyl chloride at around 600 K.

Gas purification

In addition to the removal of carbon monoxide from air and other gas mixtures, other gas cleaning roles can be envisaged for supported gold catalysts, *eg* hydrogen has been removed from carbon dioxide feed gas, used in the production of urea, using gold supported on iron oxide prepared using a co-precipitation technique (17).

PREPARATION AND CHARACTERIZATION OF SUPPORTED GOLD CATALYSTS

It has gradually emerged over the years that careful preparation of gold and gold alloy catalysts is a key to obtaining repeatability in their performance. In describing

the activity of bimetallic catalysts in 1985, Schwank (18) concluded that "The nature of the support and the preparative conditions play a decisive role in determining the microstructural characteristics of the active catalyst surface. In many cases gold seems to act more or less as an inert diluent, and ensemble or cluster effects seem to dominate the catalytic behaviour. These ensemble effects can be used to manipulate catalytic activity".

The importance of careful preparation has been emphasized much more recently by two of the leaders of research in heterogeneous gold catalysis, Haruta (4) and Hutchings (19). Haruta has described the adsorption properties and reactivities of gold in terms of their size dependency from bulk to fine particles.

The catalytic performance of gold markedly depends on dispersion, supports and preparation methods. When gold is deposited on selected metal oxides as hemispherical ultrafine particles with diameters smaller than 5nm, it exhibits surprisingly high activities and/or selectivities in the combustion of carbon monoxide and saturated hydrocarbons, the oxidation/decomposition of amines and organic halogen compounds, the partial oxidation of hydrocarbons, the hydrogenation of carbon oxides, unsaturated carbonyl compounds, alkynes and alkadienes, and the reduction of nitrogen oxides. In both the selective oxidation of propene and the complete oxidation of carbon monoxide, gold particle sizes in the range 2 - 5 nm give the highest turnover frequencies and product yields (4).

Hutchings (19) emphasized the importance of Haruta's work, confirming that for low temperature carbon monoxide oxidation the method used for catalyst preparation was crucial. Co-precipitation and deposition precipitation have been shown to be the best preparative methods, producing hemispherical particles strongly attached to the oxide support. Haruta showed that gold catalysts prepared using a conventional impregnation procedure are considerably less active than platinum group metals catalysts prepared in a similar way, but if a co-precipitation procedure was utilized, high activity catalysts were obtained with gold. The catalysts were prepared from addition of an aqueous solution of chloroauric acid and a metal nitrate to an aqueous sodium carbonate solution. The precipitate was then washed, vacuum dried and calcined at 673 K. In addition, Haruta (20) has also shown that catalysts can be prepared using deposition precipitation. A uniform dispersion of small gold particles on the support is a necessary characteristic for good performance. The best results

are obtained when reaction temperatures are >328 K (4). Direct comparison with other precious metals is not necessarily available because impregnation is the most commonly used technique for these metals.

The influence of preparation methods on the catalytic activity for carbon monoxide oxidation was found to be very large for Au/TiO₂ and negligible for Pt/TiO₂ catalysts (21). Platinum and gold were deposited on titania by deposition precipitation, photodecomposition and impregnation. The deposition precipitation method gave the most active catalysts for both platinum and gold. Gold catalysts prepared by deposition precipitation were active at temperatures below 273 K and showed a much greater activity than platinum catalysts.

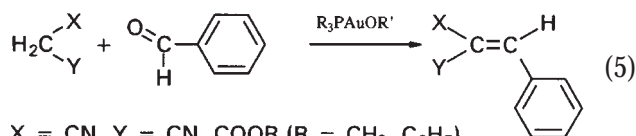
It is clear that gold dispersed on transition metal oxide has an intimate interaction with the support. Gold alone is less active as a catalyst than supported gold. Until recently much of the literature on the topic has assumed that metallic gold is the active species, but the present reviewer would like to highlight the possibility of a monolayer of gold oxide being present on the surface of the gold during oxidation reactions (22). The interface between the gold and the support and the interaction between the gold and the support also appear to be important (21). The activities are affected by the pretreatment procedures and recent work indicates that higher activities are obtained if the supported gold is not calcined (23 - 25).

HOMOGENEOUS CATALYSIS

Involvement of gold complexes of any type in homogeneous catalysis is very rare, and there are only a limited number of known examples. The rarity of examples is in marked contrast to those for the platinum group metals, many of which readily undergo catalytic oxidative-addition / reductive-elimination cycles (26). This has been rationalized by saying that this type of catalysis requires a very delicate balance between the stabilities of the two oxidation states involved, and this has not often been achieved for gold. An additional factor is thought to be the reluctance of gold to form hydride complexes, so that the oxidation of gold(I) by dihydrogen, or the formation of alkene complexes by β -elimination in gold(III)-alkyl complexes are virtually unknown (there is one case recorded of a *tert*-butyl *iso*-butyl isomerization, thought to occur by β -elimination (27)). Although gold(I) complexes readily undergo oxidative addition, *eg* with alkyl halides, the resulting

A chemical description of a gold carbonyl catalyst is given in Figure 6 (29). Gold(III) oxide (Au_2O_3) in concentrated sulfuric acid is reduced by carbon monoxide to form $[\text{Au}(\text{CO})_n]$ in one step. The gold monocarbonyl (1) and the gold dicarbonyl (2) coexist in this solution. This non-classical gold(I) carbonyl solution has proved to be an effective catalyst for the formation of *t*-carboxylic acids from olefins at room temperature and atmospheric pressure but the turnover numbers are very small. The proposed mechanism is given in Figure 7. This is an example of a Koch reaction, also known to be catalysed by copper and silver.

Gold(I) and gold(III) alkoxides have been shown to catalyse the condensation of benzaldehyde with compounds containing an active methylene group, $\text{CH}_2(\text{X})\text{Y}$, again with very low turnover numbers (26, 30):



$\text{X} = \text{CN}, \text{Y} = \text{CN}, \text{COOR} (\text{R} = \text{CH}_3, \text{C}_2\text{H}_5)$

$\text{X} = \text{H}, \text{Y} = \text{COC}_6\text{H}_5$

Best results were obtained with gold(I) catalysts of the more electron-withdrawing alkoxides: $\text{R}_3\text{PAu}(\text{OR}')$, $\text{R} = \text{Ph}, \text{C}_6\text{H}_{11}$; $\text{R}' = \text{OCH}_2(\text{CF}_3)_2$. The proposed mechanism is shown in Figure 8: the alkoxide **IV** initially reacts with $\text{CH}_2(\text{X})\text{Y}$ from which it abstracts a proton to form the corresponding alcohol and an $\text{Au}-\text{CH}(\text{X})\text{Y}$ species **V** (such compounds themselves catalyse the reaction, but less efficiently). The carbonyl group of benzaldehyde inserts into the $\text{Au}-\text{C}$ bond of **V** and the resulting complex deprotonates either $\text{CH}_2(\text{X})\text{Y}$ or the alcohol, to reform **IV** or **V**; the initially formed alcohol (**VI**) loses water spontaneously.

Another useful example of homogeneous catalysis which appears to involve an organogold intermediate is the cyclization of alkynyl amines such as $\text{R}^1\text{C}\equiv\text{C}(\text{CH}_2)_3\text{CHR}^2\text{NH}_2$ (Figure 9) catalysed by $\text{Na}[\text{AuCl}_4]$ (31). It was suggested that a cyclic intermediate is formed by *exo-dig* addition of Au and N across the triple bond which then undergoes protonolysis and isomerization. The reaction mixture rapidly decolorizes, implying the involvement of gold(I), and the most likely mechanism would be *via* initial formation of a π -alkyne complex. The coordinated triple bond would then be open to nucleophilic attack by the amine group; under sufficient dilution this would occur intramolecularly.

The 'Hyashi' ferrocenyl gold catalyst which is

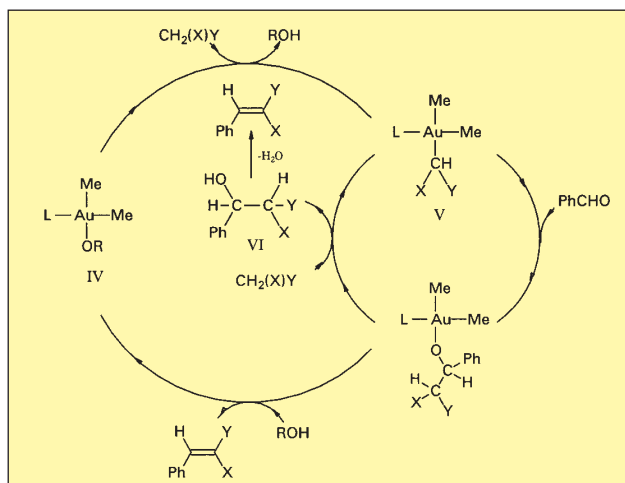


Figure 8 Proposed mechanism for Komiya condensation reaction. (Based on references 26 and 30)

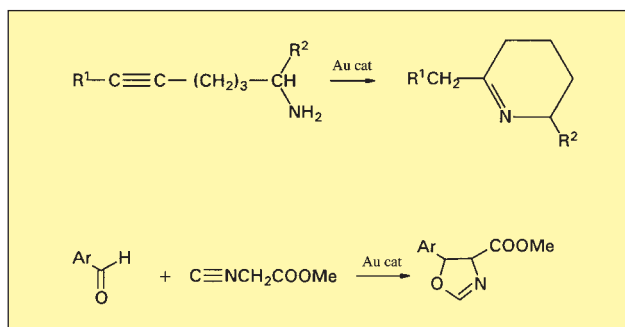


Figure 9 Examples of homogeneous catalysis using gold catalysts. (Based on references 26, 31 and 32)

achieving prominence for the synthesis of asymmetric heterocycles (Figure 9) is also a gold(I) complex, although its mode of action involves formation of an isonitrile complex of gold, rather than an organometallic intermediate (32). There is some evidence that $[\text{AuCl}_4]^-$ catalyses the addition of nucleophiles such as amines and alcohols to isonitriles (33) and that the mechanism involves the formation of carbene complexes (34), but in all cases copper(I) is a far better catalyst.

The possibility of commercial relevance for gold homogeneous catalysis is indicated by the publication of patents by Enichem SPA, Italy naming Calderazzo *et al* as inventors (35). These patents claim a homogeneous catalyst system for the preparation of olefin (ethylene, α -olefin) / carbon monoxide alternating copolymers. The catalysts consist of at least one Group 11 metal salt (Cu, Ag, Au), a P- or N-containing bidentate chelating base, and an oxidizing agent (nitrosium tetrafluoroborate or *p*-benzoquinone)

which is not hydrophilic. The process is used for copolymerizing ethylene and/or other olefinic monomers, either as individuals or as a mixture of two or more, with carbon monoxide. The method simply involves mixing the components together in a solvent. Appropriate mixtures of olefins can be employed to 'tailor-make' polymer properties such as melting point, glass transition temperature and processability.

SUPPORTED HOMOGENEOUS CATALYSIS SYSTEMS

There are some examples of homogeneous catalysts which are known to catalyse reactions after being supported on oxides. For example, Schmid (36) has practical evidence for the importance of 55 atom clusters (particle diameter 1.4 nm) and has described the preparation of $\text{Au}_{55}\text{Cl}_6(\text{PPh}_3)_{12}$. The isomerization of hexanes (2,2-dimethylbutane to *n*-hexane) was studied using 1% Au_{55} on TiO_2 (anatase). Au/Pd colloids, in which the gold is coated with palladium show enhanced catalytic activity for the hydrogenation of 2-hexyne to 2-hexene, and palladium coated with gold is also active, even though pure gold is inactive.

A phosphine-stabilized mononuclear gold complex, $\text{Au}(\text{PPh}_3)(\text{NO}_3)$, and a phosphine-stabilized gold cluster, $[\text{Au}_9(\text{PPh}_3)_8](\text{NO}_3)_2$, have been used as precursors for supported gold catalysts. Both complexes were inactive for carbon monoxide oxidation if supported on oxides such as $\alpha\text{-Fe}_2\text{O}_3$, titania and silica, whereas the compounds supported on oxides when treated under air or in carbon monoxide or in 5% H_2/Ar atmosphere were found to be active for carbon monoxide oxidation. The catalytic activity depends not only on the conditions of treatment but also on the kind of the precursor and the supports used. The catalysts derived from the first complex showed higher activity than those derived from the second. $\alpha\text{-Fe}_2\text{O}_3$ and titania were much more efficient supports than silica for the gold particles (37, 38).

Pignolet has studied catalytic applications of platinum- and palladium-gold clusters. The H_2/D_2 equilibrium was investigated using $[\text{Pt}(\text{AuPPh}_3)_8](\text{NO}_3)_2$. There was a rate-determining dissociation of PPh_3 . The clusters were then supported on alumina and silica and the H_2/D_2 equilibrium again studied. If activated at moderate temperatures, the cluster could be desorbed after catalysis. It was concluded that partial and reversible ligand desorption

and/or cluster distortion takes place on the support giving rise to significant effects on activation. Treatment under hydrogen increases this effect. Magic Angle Spinning solid state NMR was used to characterize the surface species (39).

CONCLUSIONS

Present knowledge confirms that catalysis by gold is distinctly different from catalysis using other precious metals, both in the techniques required to prepare the catalysts and in the ways that they function during reactions, *ie* some aspects are unique to gold (1). There are a number of areas where gold catalysis has potential for applications, both in the environmental control and chemical processing areas. In depth study of gold catalyst technology is likely to lead to a better understanding of the effects so far recorded and should provide a sound basis for the use of this technology in these fields.

Gold catalysts could have promise for low light off applications, but sintering problems may have to be surmounted at higher temperatures, where for example platinum (m.p. 2042 K) has the advantage of possessing a much higher melting point than gold (m.p. 1337 K). As a result, the Tammann temperature, at which the metal particles begin to sinter is significantly lower for gold. Strong bonding between the gold and its support could, however, overcome this potential disadvantage. For removal of noxious gases such as carbon monoxide and nitrogen oxides supported gold also has potential, and the removal of hydrocarbons is a distinct possibility.

The potential of supported gold catalysts for hydrogenation of carbon oxides and for catalysis of the water gas shift has already been examined and could with benefit be further developed. Homogeneous catalysis has been studied by some industrial research organizations; and the dramatic recent breakthrough using gold catalysts in solution for the addition of methanol to triple bonds could eventually have far reaching consequences. As a result, the hypotheses previously put forward to rationalize the ineffectiveness of gold as a homogeneous catalyst will need to be revised.

As we have seen, gold was previously regarded as an inferior catalyst compared with the other precious metals (1), but the examples given in this pair of articles clearly demonstrate that there are a growing number of reactions where it can be the catalyst of choice. These examples encompass the fields of

heterogeneous, homogeneous and supported homogeneous catalysis.

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David Thompson has participated in and managed upstream, basic and applied research activities in universities (Imperial College, London and University of California, Los Angeles), ICI, and Johnson Matthey. His published papers are concerned with catalysis and materials topics, particularly those involved with precious metals, as well as with organic and inorganic chemistry. He is *Technical Editor of Gold Bulletin* and Consultant to World Gold Council. In his freelance work as a chemical consultant he advises on catalyst system design for chemical processing, pollution control and gas detection. Some of this work is performed in collaboration with universities, and he helps industrial organizations to optimize their contacts with university research. He has contributed to and assisted in the editing of a new book to be published in 1999 entitled 'The Company of the Future'.

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