Catalysis by Gold/Platinum Group Metals

MIXED METAL SYSTEMS DISPLAYING INCREASED ACTIVITY

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The recent surge of new interest in catalysis by gold (1–3) has led researchers to investigate the effects of adding other metals to the gold. As a result, there are a number of reactions with potential for industrial application where combinations of gold with a platinum group metal (pgm) have been shown to have advantages over either gold or the pgm alone. These findings are expected to lead to applications in chemical processing, pollution control and fuel cell applications. Here, a number of catalytic processes that have benefited from the synergy between a pgm and gold are described, and some interesting reports from recent conferences are highlighted.

One of the major uses of gold/platinum group metals catalysis is for vinyl acetate monomer (VAM) production. It is interesting to reflect that VAM has been produced industrially for some time from acetic acid, ethene and oxygen using palladium-gold (Pd-Au) catalysts in fixed bed processes. The reaction proceeds with selectivities as high as 95% (4):

$$C_2H_4 + CH_3COOH + \tfrac{1}{2}O_2 \rightarrow C_2H_3OOCCH_3 + H_2O$$
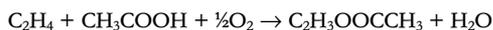
Work at DuPont by Provine *et al.* (4) utilising Pd-Au silica-supported catalysts promoted with potassium acetate showed that the addition of gold to palladium can significantly improve the rate of production for VAM, see Table I. Around 80% of VAM plants worldwide are more than 20 years old and use fixed bed processes (5). However, the first fluidised bed process for VAM has now been commissioned by BP, for a new plant in Hull, U.K. (5). The fluidised bed process has been developed by BP Chemicals as a more cost effective route, and allows process simplification and intensification. Compared with the two reactors usually needed in the fixed bed process, the fluidised process requires only a single reactor. A new catalyst was required for the fluidised operation, and the VAM catalyst that was selected is a Au/Pd mix developed in collaboration with Johnson Matthey in the form of spheres so fine that they almost appear to flow as a liquid. Thus, a Au/pgm catalyst is finding use on an industrial scale in this process.

Hydrogen Peroxide Production

About 1.9×10^6 tonnes of the oxidising agent hydrogen peroxide (H_2O_2) are manufactured each year – a very large market (6). There is a need for the hydrogen peroxide to be synthesised where it is to be used to avoid the heavy transport costs of this hazardous material. It is currently only economic to produce H_2O_2 on a large scale (4–6×10^4 tonnes/annum) using the sequential hydrogenation and oxidation of alkyl anthraquinone, but H_2O_2 is often required on a much smaller scale (6). Both theoretical calculations (7) and experimental results (6) have shown that the formation of H_2O_2 from hydrogen and oxygen is favoured over gold catalysts. Hutchings *et al.* (6) have shown that H_2O_2

Table I		
Yields of Vinyl Acetate Monomer as Reported by DuPont (4)		
Catalyst	Space time yield g/l-h	Selectivity, %
Au/Pd/KOAc	764	93.6
Pd/KOAc	100	95.4
Au/Pd	594	91.6
Pd	124	94.7

Fixed bed performance of Au/Pd/KOAc catalysts after 40 h on stream. Test conditions: 165°C, 115 psig, with feed consisting of ethene, acetic acid, oxygen and nitrogen

Formation of Hydrogen Peroxide from the Reaction between Hydrogen and Oxygen over Au and Pd Catalysts in Methanol under 3.7 MPa Pressure (6)

Catalyst	Temperature, K	O_2/H_2 mol ratio	H_2O_2[a], mmol g cat^{-1} h^{-1}
Au/Al_2O_3	275	1.2	1530
Au:Pd (1:1)/Al_2O_3	275	1.2	4460
Pd/Al_2O_3	275	1.2	370

[a] *Rate of H_2O_2 formation averaged over 30 min experiments*

can be formed at a high rate using a supported gold catalyst at 275 K, with selectivity for H_2O_2 over a Au/Al_2O_3 catalyst of 53%. This supported Au catalyst produced more H_2O_2 than the supported Pd catalyst used to-date in industry. However, more interestingly, a supported Au/Pd (1:1 by wt.) catalyst produces even more H_2O_2 than the pure Au catalyst. This indicates there is a synergistic effect with Pd acting as a promoter for the Au catalyst, see Table II. Furthermore, they showed that the metal nanoparticles are in fact Au-Pd alloys.

Further Synergistic PGM-Au Reactions

The addition of gold to palladium by simultaneous deposition-precipitation on cerium oxide has been reported to increase the catalytic activity for methanol decomposition to carbon monoxide and hydrogen at 180°C (8). No significant promotional effect was observed by the addition of rhodium or iridium to palladium.

Venezia and colleagues (ISMN-CNR, Palermo, Italy) have found that bimetallic $Au/Pd/SiO_2$ catalysts with a range of Au:Pd ratios are advantageous for the hydrodesulfurisation of dibenzothiophene (9). The Au/Pd alloy particles are resistant to sulfur poisoning compared with a pure palladium catalyst. At 553 K, their 1:1 Au:Pd catalyst produced the highest dibenzothiophene conversion. Results consistent with these have been reported by Pawelec *et al.* (CSIC, Madrid, Spain) (10). They have found that, for the simultaneous hydrogenation of naphthalene and toluene in the presence of dibenzothiophene, a $Au/Pd/Al_2O_3$ catalyst had a higher activity than Pd/Al_2O_3 and the bimetallic catalyst was more resistant to sulfur poisoning.

Mixed metal Au/Pt catalysts were reported by Amiridis, Chandler *et al.* (University of South Carolina, U.S.A.) at the North American Catalysis Society Meeting in Cancun in 2003 (11, 12). Their catalysts were prepared using polyamidoamine (PAMAM) dendrimers. Using these as nanoparticle templates and stabilisers, the stabilised nanoparticles were then adsorbed onto oxide supports (such as SiO_2 or TiO_2) and thermally activated to give supported mixed-metal catalysts. They were investigated for activity in CO oxidation, toluene hydrogenation, and the reduction of NO by propene. Removal of the organic dendrimer by heating at 300°C under an oxygen stream, followed by treatment at 300°C under flowing hydrogen gave intimately mixed Au/Pt catalysts with metal particle sizes of < 4 nm. The resulting $Au_{16}Pt_{16}/SiO_2$ catalyst has a light-off temperature of ~ 30°C, whereas the equivalent Au_{32} catalyst lights off at ~ 130°C and the equivalent Pt_{32} catalyst at ~ 80°C.

Fuel Cells

However, it is perhaps in the area of fuel cells that the biggest potential for using Au/pgms catalysts may lie. C.-J. Zhong *et al.* (13) have prepared Au/Pt/C nanoparticle electrocatalysts using a two-phase protocol and evaluated them for the oxygen reduction reaction at the fuel cell cathode. Their electrochemical results obtained to-date indicate that the bimetallic Au/Pt catalysts have significant-

ly different electrocatalytic properties to either Au or Pt alone. The catalytic activity of Au/Pt is highly dependent on composition and calcination history. Work is continuing on optimising the properties of these catalysts for use in both acid and alkaline fuel cells.

The electrooxidation of hydrogen, carbon monoxide and hydrogen/carbon monoxide (H_2/CO) mixtures over well-characterised Au(111)/Pd and Au(100)/Pd surface alloys has been studied by Ross and colleagues (14). With the Au(111)/Pd surface, the oxidation of 1000 ppm CO in H_2 at potentials below 0.2 V is governed by the slow H_2 oxidation kinetics, but at potentials above 0.2 V the steady state activity of high surface area Au/Pd catalysts can be reached. The investigators claim their results demonstrate that a Pd/Au alloy could be used in principle as a hydrogen electrode catalyst without any loss of performance compared with platinum.

13th ICC

Most of the investigations using Au/pgm alloys are still at a very early stage of development, but at the recent 13th International Congress on Catalysis (15) there were other interesting reports on their catalytic properties. For instance, nano-sized Pd/Au on carbon has been shown to have increased activity over Pd for the selective oxidation of glyoxal to glyoxalic acid, a key intermediate in the synthesis of vanillin (16), and Au/Pd on titania, prepared using a microemulsion technique, was more active for CO oxidation than the component single metal catalysts (17). Alloying gold to palladium has been shown to significantly increase resistance to sulfur poisoning during benzaldehyde hydrogenation (18). Au/Pd was also studied for the selective hydrogenation of buta-1,3-diene (19); and for the formation of H_2O_2 from hydrogen and oxygen (see above), investigators from Kyushu and Oita Universities in Japan reported an optimum Au/Pd ratio of 10:7 (20).

Pt/Au nanoparticles on HY zeolite have been found to have a higher activity for hydrocarbon isomerisation reactions than pure Pt (21).

A possible beneficial effect from the presence of Au/TiO$_2$ on the electrooxidation of methanol using a Pt/Ru catalyst was also described (22). The gold catalyst increased overall catalyst activity and reduced the tendency to CO poisoning. This could find application in fuel cells. However, these were preliminary results based only on a cyclic voltammogram screening test. The 13th ICC website http://www.13icc.jussieu.fr/ carries two-page abstracts of these noted papers.

Other Literature

The surface science of Au/pgm catalysts has been discussed in a recent review paper (23), while Scurrell *et al.* (University of Witwatersrand, South Africa) (24) have studied bimetallic Au/Ru catalysts supported on α-Fe$_2$O$_3$ for the water gas shift reaction. Using atmospheric pressure, the activity of the bimetallic system was found to be higher than for Au/Fe$_2$O$_3$ or Ru/Fe$_2$O$_3$ catalysts over all the reaction temperatures studied (373 to 513 K):

$$CO + H_2O \leftrightarrow H_2 + CO_2$$
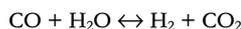
These results have relevance to the supply of hydrogen for fuel cells.

Conclusions

Thus, from these highlights, it is apparent that synergism between a pgm and gold, along with other effects, are providing significant potential for further commercial applications for Au/pgm mixed metal catalysts and alloys.

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