A golden future

Catalysis using gold has fast become a major research field with great potential, and many new discoveries are being made. **Graham Hutchings** reflects on how this has come about.

Gold is the most noble of the elements and by virtue of this holds a central place in the world of finance, art and jewellery. It is associated with great historical objects — for example the mask of Tutankhamun's mummy — that remain as beautiful today as the day they were first made several thousand years ago. Gold is also synonymous with great wealth, and for centuries alchemists tried in vain to make gold from base elements — one sect of alchemists, known as the Mercurialists, considered gold to be made from mercury and sulfur.

Gold is considered to be a timeless element — it is immutable — so one would not expect to associate it with any chemical reactivity. Indeed, chemistry textbooks always devote the fewest pages to gold — often regarded as a rather boring element from a chemical perspective. However, since the 1980s, it has been found that this is no longer the case. Divided into very tiny nanosized pieces that comprise just a few atoms, gold becomes exceptionally effective as a catalyst, and catalysis lies at the heart of the manufacture of most goods we use today. It has taken so long for the wonders of gold catalysis to be unravelled because of our preconceptions of this element — it was thought to be chemically uninteresting and relatively unreactive, no one thought to investigate further.

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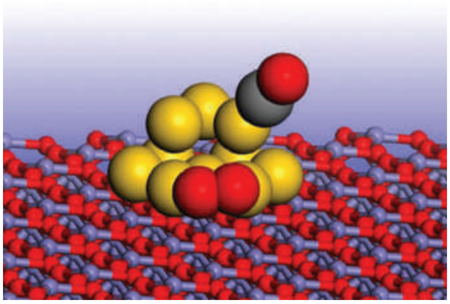
It was two discoveries made at similar times in the 1980s that made chemists start to look at gold in a new light. Masatake Haruta, then working at the Government Industrial Research Institute in Osaka, Japan, tried to make mixed oxides containing gold, and discovered that these materials were remarkably active catalysts for the oxidation of carbon monoxide. He subsequently found that they comprised nanoparticles of gold supported on the oxide. This combination showed activity at temperatures as low as –76 °C — this is close to the coldest ambient temperature on this planet (–89.2 °C at Vostok in Antartica) — and gold can therefore be used widely for the oxidation of carbon monoxide at ambient temperature.



DAVID WILLOCK

Small clusters of gold atoms, such as Au_{10} schematically shown here on iron oxide, may be associated with high catalytic reactivity for the oxidation of carbon monoxide.

The discovery that gold was so active as a catalyst led to an explosion of interest in this element; the chemical world was eager to understand why gold is so effective. Initially, researchers thought that gold nanoparticles approximately 2–5 nm in diameter were the active species. However, this conclusion was based on the extent of the resolution of electron microscopy. With the advent of aberration-corrected instrumentation, single gold atoms can be resolved and we now know that catalytic activity can be associated with very small gold clusters, containing as few as 7–10 atoms.

At the time that Haruta made his discovery in Japan, I was working in industry in South Africa, trying to discover a catalyst for acetylene hydrochlorination, which is central to PVC manufacture. The industrial catalyst for this process has been the environmentally non-friendly mercuric chloride. So, on a wet Saturday afternoon in Johannesburg in September 1982, I was analysing some published data that showed great variations in catalytic activity were possible with a broad range of over 30 metal chlorides. The data could not be used predictively. Replotting the activity data against the standard electrode potential, however, immediately showed a correlation. To me this was the 'eureka' moment: I could predict that gold would be the best catalyst for this reaction, and subsequently verified this experimentally — my first wonderful involvement with using gold as a catalyst.

Gold now lies at the heart of many discoveries in both heterogeneous and homogeneous catalysis. It is providing new inroads into advances in green and sustainable chemistry. Apart from carbon monoxide oxidation and acetylene hydrochlorination — the initial two reactions for which gold was discovered to be by far the best catalyst — gold is effective for other oxidation reactions. In particular it catalyses alkene epoxidation and alcohol oxidation, including the oxidation of biorenewable feedstocks such as glycerol and sugars. Gold is also a highly selective hydrogenation catalyst. Furthermore, combined with palladium, it is an excellent catalyst for the production of hydrogen peroxide from its constituent elements, which may offer a greener route to the manufacture of this commodity chemical.

At times it is now tempting to think that gold will be the best catalyst for every reaction, and although clearly this is not the case, it is true that gold has been transformed from the Cinderella of the elements and has finally got to go the chemical reactivity ball. ❐

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