Industrial applications of gold catalysis

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Gold catalysis has recently found its first large-scale applications in the chemical industry. In this mini review, we provide a critical analysis of the success factors and of the main obstacles that had to be overcome on the long way from discovery to commercialization. The insights should be useful to researchers in both academia and industry working on the development of tomorrow's gold catalysts to tackle significant environmental and economic issues.

Keywords: gold nanoparticle; gold catalysis; industrial applications; heterogeneous

The image displays also a carbide-based PVC plant in China. We thank the United Nations Environment Programme and its Global Mercury Partnership for providing the picture.

Introduction

The discovery of the very first heterogeneous catalyst containing gold, a catalyst for the oxidative acetoxylation of ethylene to vinyl acetate, goes back almost exactly half a century. The patent claiming it was filed in June 1965 by the German company Knapsack.[1] Four decades have passed since the discovery of Bond and Sermon that the activity of Au/SiO_2 catalysts prepared by mild thermal treatment of impregnated $HAuCl_4$ for the hydrogenation of 1-pentene at 373 K increased by a factor of 7000 as gold content was decreased from 1% to 0.01%.[2] And three decades have gone by since the almost simultaneous discoveries of Hutchings[3] and Haruta[4] that nanoscale gold supported on activated carbon or on 'reducible' supports such as titania (the reducibility of a catalyst support is its ability to generate oxygen vacancies and to transfer the oxygen onto the metal particle) are exceptionally effective redox catalyst for acetylene hydrochlorination and CO oxidation. Now the time has finally arrived when heterogeneous catalysts containing gold start to appear in large-scale applications in the chemical industry.

According to the noble nature of the metal, extended gold surfaces do not chemisorb oxygen, nor do they corrode. It came thus as a surprise for the chemical community when the scientists above first showed that gold, when prepared as supported nanoparticles, can be an excellent catalyst. This marked the starting point for heterogeneous gold catalysis. Only a few years later a further breakthrough also came with the discovery that gold can also be a very active homogeneous catalyst,[5] including remarkable quasi-homogeneous catalysis for which subnanoparticle gold clusters (3 to 10 atoms) formed in solution give reaction turnover numbers of 10^7 at room temperature.[6]

All these discoveries contributed to the emergence of gold catalysis, both homogeneous and heterogeneous, as a major research topic.[7,8]

The history of the discovery, development, and commercialization of gold catalysts for acetylene hydrochlorination as a replacement for the $HgCl_2$ has been recently recounted.[9] To the best of our knowledge, to date two other Au containing solid catalysts are commercially employed in the chemical industry: the Au-doped Pd catalyst for the vinyl acetate synthesis, which has been in use for almost half a century,[10] and the core-shell $AuNiO_x$ catalyst for the oxidative esterification of methacrolein to methyl methacrylate.[11]

A first analysis on the commercial aspects of heterogeneous gold catalysis published in 2005 concluded that the two limiting factors to address prior to industrial applications were the catalyst durability under operating conditions, and viable methods of catalyst preparation.[12] Another analysis by one of the authors also pointed out that new catalysts have to be seen in the context of the chemical process they are embedded in.[13] For a new catalyst to come into use one of two options have to be fulfilled. One option is that the new catalyst enables the development of an entirely new process with different raw materials and breakthrough economics. This was the case for the vinyl acetate catalyst, which allowed the replacement of acetylene by the much cheaper ethylene as raw material. In such a case the new catalyst will lead to the construction of many new plants and to a step change in technology.

Another option is that the catalyst uses the same raw materials as conventional catalysts but offers a moderate economic hub, for instance because it is more selective than conventional catalyst. In this case a new catalyst will only find application if it can be developed as a drop-in for existing plants. This was the case with both the catalyst for hydrochlorination of acetylene and for the oxidative esterification of methacrolein. They could only be successfully introduced, because they could replace old catalysts in existing plants.

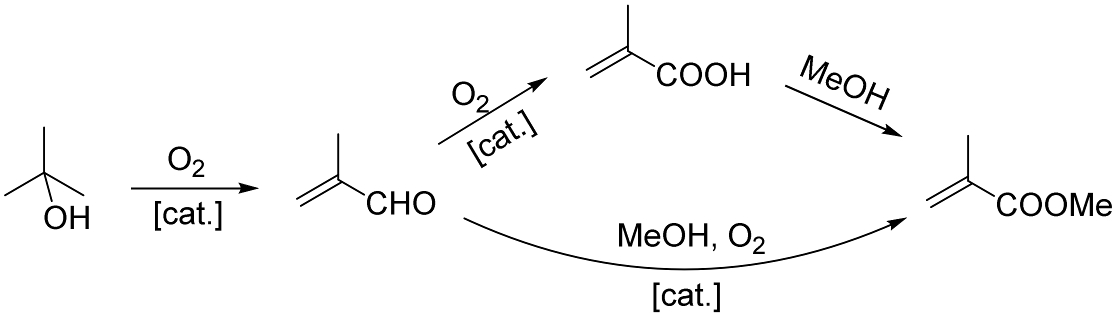
For specific reactions gold can show significantly higher activity and selectivity when compared with other metal catalysts, including platinum-group metals (PGMs), often under milder reaction conditions and this can pave the way to new applications.[14]

Catalysts based on similarly expensive, supported PGMs are widely employed in the chemical industry due to their ability to activate industrially and economically important molecules (H_2 and O_2, as ideally suited redox catalysts, but also CO, olefins etc.). The fact that gold is more abundant than other PGMs is certainly a positive aspect. In 2015, global gold production from mining was estimated at 3,000 tonnes.[15] In the same year the overall production of Pt was only 178 tonnes and that of Pd only 207.5 tonnes.

In the following, we will discuss the main obstacles that had to be overcome on the long way from discovery to commercialization. This critical analysis is intended to provide guidance and inspiration to researchers in both academia and industry working on new gold-catalysts and gold-catalyzed processes for potentially industrially important problems as for example, the direct synthesis of hydrogen peroxide,[16] the direct oxidation of hydrocarbons,[17] and the selective oxidation of renewable substrates of primary importance in the emerging biorefinery field.[18]

Oxidative esterification of methacrolein to methyl methacrylate

Since 1976 Asahi Kasei (the former Asahi Chemical) has been producing methyl methacrylate at its facility in Kawasaki, Japan. The plant used a three-step process from *tert*-butyl alcohol, which was first oxidized to methacrolein and subsequently to methacrylic acid, both processes taking place in the gas phase using two different Mo catalysts. Finally, the methacrylic acid was esterified with methanol to give the desired methyl methacrylate. However, this process was hampered by high specific investment costs and particularly by the low lifetime of the catalyst in the second oxidation step.



Scheme 1. The old Asahi process (upper route) and the new Direct-Metha Process (lower route) to methyl methacrylate.

In order to overcome these problems, Asahi developed a process where methacrolein was oxidatively esterified with methanol in the liquid phase to give directly the desired methyl methacrylate, the so-called “Direct-Metha Process” (Scheme 1).[19]

Originally, the oxidative esterification of MA with methanol in the presence of molecular oxygen was carried out in the liquid phase over a catalyst containing the intermetallic phase Pd_3Pb as the active phase supported on alumina.[20] The introduction of the catalytic oxidative esterification was a very important development, because it allowed reducing the number of steps from three to two, thus addressing the major drawback of the original Asahi process, which was the high specific investment. However, the new Direct-Metha process, which was in use after 1982, still had drawbacks. The selectivity to methyl methacrylate based on methacrolein was quite good but, unfortunately, the catalyst also oxidized methanol to methyl formate to a considerable extent. Thus, using the Pd_3Pb catalyst 0.2 moles of methyl formate were produced per mole of methyl methacrylate. Additionally the Pd_3Pb catalyst was difficult to produce because any Pd not bound in the Pd_3Pb phase leads to selectivity losses due to decarbonylation of methacrolein. Yet, the most pressing problem was to reduce the losses of methanol and the formation of methyl formate as by-product. The research team at Asahi led by Ken Suzuki, succeeded in discovering a new catalyst to replace the original Pd_3Pb catalyst, which had a much lower rate of formation of methyl formate.

Since the pioneering work of Hayashi and his group at Nippon Shokubai between 2002 and 2006 on the oxidative esterification of ethylene glycol in the presence of methanol to methyl glycolate, it was known that gold was a competent metal to catalyze oxidative esterifications.[21] The preferred catalyst was gold, sometimes with Pb as dopant, supported on alumina. Although the selectivity based on ethylene glycol was quite good, these catalysts still produced considerable amounts of methyl formate as by-product (between 0.15 and 0.36 moles of methyl formate per mol of methyl glycolate, depending on the molar ratio of methanol to ethylene glycol used in the reaction). The work at Nippon Shokubai never went beyond the pilot plant scale, but it surely served as an inspiration for the group at Asahi Kasei.

The best catalyst identified was a $Au\text{-}NiO/SiO_2\text{-}Al_2O_3\text{-}MgO$ catalyst which produced methyl methacrylate with a selectivity based on methacrolein of 98% at a methacrolein conversion of 58%. However, the most important finding was that now the oxidation of methanol to methyl formate was negligible (only 0.007 moles of methyl formate were formed per mol of methyl methacrylate). This catalyst, though, was not commercially usable because of insufficient mechanical stability.

To overcome this problem the team at Asahi Kasei developed a core-shell catalyst containing gold-nickel oxide ($AuNiO_x$) nanoparticles supported on a silica-based carrier where the Au nanoparticles are not exposed directly at the surface but just below it in order to protect the Au particles from mechanical abrasion. The stability of this catalyst was verified in long running pilot plant experiments and finally the catalyst was used in the existing commercial MMA production plant in 2008.[22]

The Au-NiO_x nanoparticles (optimal composition, 20 mol.-% of Au) have a core-shell structure, with Au nanoparticles at the core and the surface covered by highly oxidized NiO_x. These core-shell nanoparticles showed the desired activity and selectivity, but the catalyst was still not technically useful. The oxidative esterification of methacrolein is performed in suspension and this implies that the catalyst is subject to a high mechanical stress. The abrasion caused by the mechanical stress led to a loss of the catalytically active nanoparticles and to a deactivation of the catalyst.

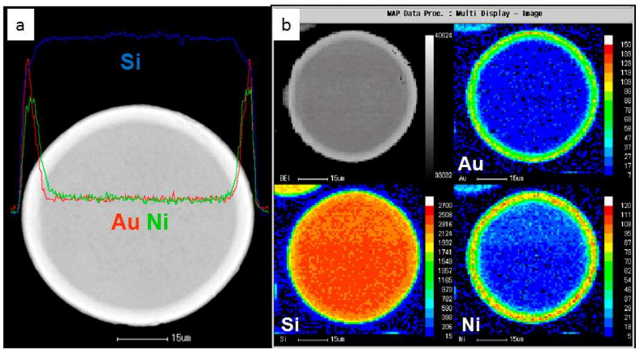


Figure 1. Electron-probe microanalysis spectra of a single particle of $AuNiO_x/SiO_2–Al_2O_3–MgO$. (a) Secondary electron image and line analysis. (b) Color mapping (Ni in green, Au in red) display corresponding to the concentration of the element distribution. [Reproduced from Ref.11, with kind permission].

In order to solve this problem, the team at Asahi used a mechanically robust SiO_2-Al_2O_3-MgO support as 60 µm spheres and controlled the deposition process in such a way that the gold nanoparticles are preferentially located just below the surface but only down to a depth of less than 10 µm (see Figure 1). In this way the gold nanoparticles remain well accessible but are protected from losses through abrasion. Only through this improved deposition procedure was it possible to obtain a robust, long-lived catalyst. As shown in Figure 2, this catalyst was operated in a continuous manner for 40 days with stable catalytic activity. During this period MMA was obtained with high selectivity (96-97%) and constant yield (ca. 60%), and negligible gold and nickel leaching (Au and Ni in the reaction mixture <2.5 ppb). An examination of the catalyst after the long time run showed no sintering of the $AuNiO_x$ nanoparticles with the macroscopic core-shell structure remaining intact.

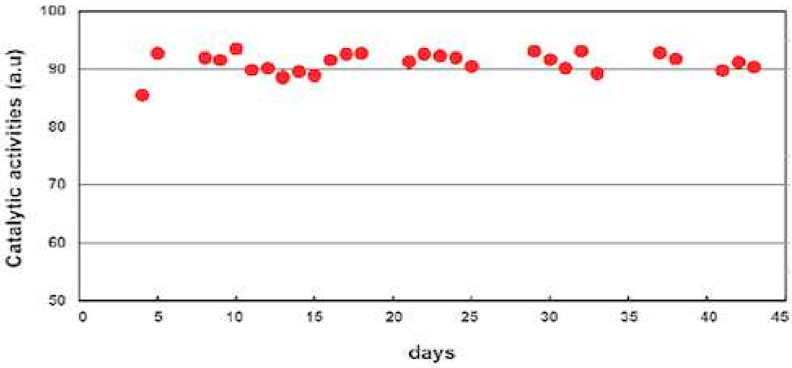


Figure 2. Catalytic activity of $AuNiO_x/SiO_2–Al_2O_3–MgO$ over time in a continuous-flow reaction apparatus [Reproduced from Ref.11, with kind permission].

In summary, several factors were decisive for the success of this new catalyst. First of all the reaction conditions for the new catalyst are very similar to the ones of the original catalyst, and the new catalyst has a deactivation rate (both chemical and mechanical) which is not faster than the one of the original catalyst. These are the *sine qua non* requirements for a drop-in catalyst. Additionally, the new catalyst provides a lower rate of by-product formation (by-products are still formed, albeit in reduced amounts, while the amount of waste water remains essentially unchanged), and a lower catalyst cost due to the lower amount of precious metal required for a similar productivity.

Hydrochlorination of acetylene

In 2015, catalyst manufacturer Johnson Matthey officially announced the introduction of Pricat MFC as the brand for its newly developed gold catalyst for the manufacture of vinyl chloride monomer (VCM), the monomer for polyvinyl chloride (PVC, the world's third largest polymer).[23] About one third of the approximately 50 million tons per year of VCM capacity worldwide uses the acetylene hydrochlorination technology but the plants using it are almost exclusively located in China. These plants, that still use $HgCl_2$ supported on carbon as the catalyst, have come under pressure because the Minamata Convention on Mercury requires that before 2022 all VCM plants have to switch to a mercury-free catalyst, providing there is an economically viable alternative. The mercury catalyst has a limited lifetime of just 6 months and the losses of mercury during operation and catalyst recovery for all the existing plants amounts to 600 tons per year, which is roundabout 50% of the world consumption of mercury.

There is thus a big incentive from both a regulatory and an environmental point of view to replace these mercury catalysts. However, the new catalyst has to be a drop-in catalyst for existing plants, because the economical hub will be only modest: the plants will still use the same starting materials and only small improvements on selectivity can be expected. The replacement catalyst must thus work under similar reaction conditions, must have a similar catalytic activity, at least equal selectivity and the overall catalyst costs have to be in the same range as with the catalyst being replaced.

The catalytic activity of tetrachloroauric acid, both in homogeneous and heterogeneous form, is actually known since 1977, when the Japanese company Denki Kagaku Kogyo, known today as Denka, filed two patents on the production of vinyl chloride from acetylene and HCl.[24] Although the patents mainly claim mixtures of gold with platinum or palladium, they also contain experiments where gold alone shows good catalytic activity and selectivity. But these patents fell into oblivion and it took another 10 years before this subject was picked up again, by Hutchings and his team who showed that tributylammonium tetrachloroaurate in isopropanol/decane was a competent homogeneous catalyst for the addition of HCl to acetylene,[25] although the catalytic activity was only moderate.

The first heterogeneous catalysts were simply prepared by simple adsorption of $HAuCl_4$ from aqueous solution onto an activated carbon.[3,26] These catalysts were almost as active and as selective as the mercury catalyst, but they deactivated rather quickly. Although activity could be recovered by treating with HCl, the deactivation after regeneration was at least as fast as with a fresh catalyst and it was clear that such a catalyst would not be technically usable.

In the following years, two mechanisms of deactivation were identified. At lower reaction temperatures (60-100°C) coke deposition was the major deactivation pathway, but at higher reaction temperatures (120-180°C) reduction of cationic gold species to (inactive) Au(0) was the major deactivation pathway.[27] In the same study the authors also demonstrated that deposition of gold in the presence of the highly oxidizing *aqua regia* leads to considerably more active catalysts, probably because more oxidized gold species are present at the surface of the gold nanoparticles. However, in spite of the high gold loadings and the improved deposition under oxidative conditions, the problem of catalyst deactivation could not be solved.

To establish an economically viable process for VCM producers, the industrial research team at Johnson Matthey led by Peter Johnston set as development targets a maximum gold loading of 0.25%, and a preparation that does not require the use of *aqua regia*, because of the difficulties associated in disposing of *aqua regia* containing waste streams. This loading is significantly lower than typical 0.5-1% Au loadings of conventional Au/C catalyst whose preparation required the use of *aqua regia* as solvent, but above all they had to solve the problem of catalyst deactivation.[28] This was necessary in order to meet the targeted catalyst costs required to compete with the $HgCl_2$ based catalyst.

Reviewing the actual development of this catalyst offers some valuable lessons. In 1995 Aker Solutions, a chemical plant construction company based in Norway later partly acquired by Jacobs, developed a gold catalyst for making VCM and tested it successfully (longer catalyst life *vs* mercury catalyst) on pilot plant scale.[29] The catalyst, however, was never commercialized because the company's internal project was terminated. In 2006 the company started to co-operate with Johnson Matthey and with the group of Graham Hutchings in Cardiff to further develop and commercialize a Au/C catalyst customized for the Chinese VCM process conditions. In 2007, Hutchings and co-workers demonstrated that the activity is maximal for a catalyst containing only gold without any other metals. They also demonstrated that it is essential to maximize the dispersion of gold to ensure the maximum amount of gold can be maintained in the cationic state in the working catalyst.[30] The catalyst preparation then became the key means of improving the catalyst performance and the key challenge.

In 2010 Jacobs was commissioned a pilot plant by a VCM manufacturer in western China replicating a single tube from a commercial reactor (a single 3 m tube with 2 kg catalyst charge).[31] The pilot plant operated continuously for two years since mid-2011, with 6 different catalysts tested in order to fine-tune the catalyst formulation. Eventually, the team was able to prepare an highly active catalyst with 0.1% loading by supporting $Na_3Au(S_2O_3)_2$ on carbon extrudates.[32] Seemingly, the presence of the sulfur containing anions helped stabilize the cationic gold and allowed for a catalyst less prone to deactivation, at the same time allowing for a preparation method that did not require the use of *aqua regia*.

Trials confirmed that the Au/C catalyst family is highly active and highly selective. After the last test showed successful operation over a period of nine months (the test was deemed successful after 6 months stable operation), a full commercial reactor with 790 reactor tubes and 1.6 tons of the gold catalyst was commissioned in 2012, and has been in operation since 2013.

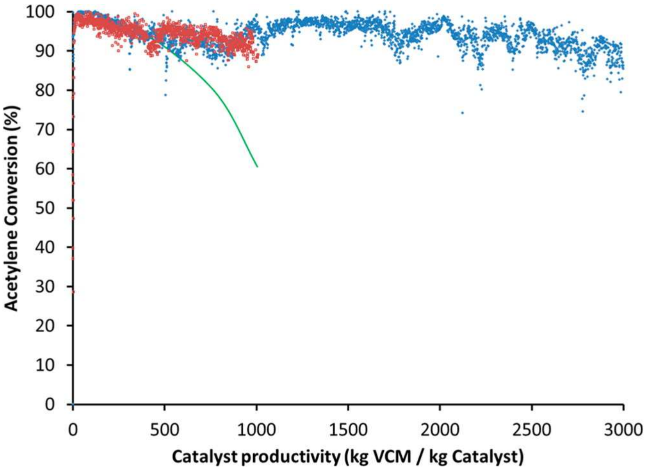


Figure 3. Comparison of catalyst performance in a primary reactor for a 10% $HgCl_2/C$ catalyst (green), pilot plant operation for 0.1% Au/C to a yield of 3000 kg VCM/kg catalyst (blue), full scale commercial reactor for 0.1% Au/C to a yield of 1000 kg VCM/kg catalyst (red). Catalyst = 0.1% Au/C prepared by supporting $Na_3Au(S_2O_3)_2$ on carbon extrudates. [Reproduced from Ref.9, with kind permission].

The reactor was operated under conditions equivalent to those of the process using the $HgCl_2/C$ catalyst for more than 4500 h time on stream (Figure 3). At a productivity level of 1000 kg VCM/kg catalyst, the performance of the catalyst (and reactor) was identical to the performance in pilot plant scale. This is considerably better than the typical yield and productivity that can be achieved with the $HgCl_2/C$ catalyst, with the new catalyst continuing to operate well beyond the point at which the Hg catalyst would have to be removed from the reactor and replaced.

In summary, also in this case, the success of the gold catalyst was due to the fact that it could be used as a drop-in in existing plants without major modifications and of course to the fact that it offered an overall improved economics while eliminating altogether the mercury emissions.

Production of gold industrial catalysts

A few companies already manufacture and sell supported gold catalysts.[33] In 2009, South Africa's AuTEK (a joint venture among minerals research organization Mintek and three gold mining houses) was the first company to establish a plant to reproducibly manufacture significant quantities of 1 wt.-% gold-based catalysts trade named AURO*lite*, (Au/TiO_2, Au/ZnO, Au/Al_2O_3) and AURO*lith* (Au/Al_2O_3/cordierite) obtained via a deposition-precipitation method patented in 2005,[34] marketed as ideally suited to catalyze oxidation reactions (in both gas and liquid phase).

A catalyst developed by 3M for CO oxidation, especially for escape masks, is NanAucat, comprised of Au nanoparticles supported via chemical vapor deposition onto porous amorphous carbon.[35] The catalyst is marketed as the most active and stable one for CO removal. Indeed NanAucat is not susceptible to deactivation by moisture as it happens with the currently used Hopcalite thus not requiring the heavy bed of desiccant used with the latter catalyst, but it is still susceptible to deactivation by amines and sulfur compounds.

In general, as mentioned in the introduction, the main issues in the production of gold supported catalysts identified in 2005 in the discussion on commercial aspects of gold catalysis, were nanoparticle size and reproducibility of the material's synthetic method.[12] Recent innovations in catalyst preparation routes have solved many of these issues, allowing the production of highly active, robust and selective catalysts with low levels of gold loading.

For instance, the key innovation that led to industrialization of the gold-based route to VCM was the ability to synthesize sufficiently active catalysts with just 0.25% gold loading, in place of the typical 1% load of first-generation commercial catalysts. The route lately developed by Johnston and co-workers established a new methodology for the preparation of stable supported cationic gold catalysts with Au loading in 0.15-

0.6% range of Au which, being based on sulphur-containing gold-containing complexes, exploits the well known stability of gold-sulphur bonds. Remarkably from a green chemistry viewpoint, furthermore, the preparation for these gold catalysts takes place in aqueous phase.

In the case of the Asahi catalyst, Au and NiO were supported on a mixed oxide SiO_2–Al_2O_3–MgO obtained via an aqueous sol-gel route (the support having a specific surface area of 149 m^2/g, an average pore diameter of 8 nm, and average particle size of 60 μm) by coprecipitation performed by heating an aqueous solution containing $Ni(NO_3)_2{\cdot}6H_2O$ and $HAuCl_4$ (12 mL, 1.3 mol/L) to 90°C in the presence of the support, followed by drying *in vacuo* and calcination at 450°C for 5 h. The catalyst is obtained as a brown powder containing 0.9 wt.-% Au and 1.1 wt.-% Ni.

Heterogeneous *vs* Homogeneous Catalysis

Remarkably, the first industrial applications of gold catalysis concern the production of bulk chemicals, and *not* to the production of fine chemicals or active pharmaceutical ingredients (APIs), even though the low toxicity of gold when compared to other PGMs should be an important advantage in this application. Even the fact that in this highly regulated sector of the chemical industry the maximum allowed residual concentrations of palladium or platinum (both classified as 'Metals of significant safety concern') in APIs are below 10 ppm if orally administered, and <1 ppm is administered parenterally, has not changed the situation.[36]

The high cost of gold, the need to recover it via scavenging from solution (for example with thiol-functionalized silica gel), and the inevitable loss of the original catalyst may explain why homogeneous gold catalysis for selective organic synthesis, today a well-established field of research with a plethora of reactions being catalyzed by gold complexes,[37] is not yet used on industrial scale.

The potential of homogeneous gold in catalyzing the selective electrophilic activation of multiple bonds under mild conditions was evident as early as 1997, when researchers at BASF first patented and then published the discovery that cationic [L-Au^+] complexes (where L is a phosphine or an arsine) catalyze the addition of alcohols to alkynes under mild conditions (293-323 K) with impressive turnover frequencies of up to 5400 h^{-1},[38] which is orders of magnitude better than the preceding results obtained by Utimoto with simple gold(III) salts.[39] However, even this impressing catalytic activity was not sufficient for commercial success. Back in 1997 the researchers at BASF were looking for catalysts that allowed the synthesis of 2,2-dimethoxypropane, a building block for the vitamin E synthesis, from a mixture of propyne and allene (propadiene), which is available as a by-products from naphtha steam-cracking.

The gold complexes proved to be much more active and long lived than the previously known mercury catalysts, but they had the serious drawback that only propyne reacted at an acceptable rate, while allene remained mostly unconverted. Finally, a simple zinc silicate catalyst proved to be the best option, both because of the low cost of the catalyst but mainly due to the fact that propyne and allene reacted at approximately equal rates.[40]

In the case of Pd, Ananikov and co-workers have shown that *both* heterogeneous and homogeneous catalysis contribute to product formation, with leaching of Pd nanoparticles leading to the formation of metal complexes and clusters in solution.[41] A similar phenomenon should be in principle also operative in gold heterogeneous catalysts. Great room for practically relevant improvement indeed exists by merging heterogeneous and homogeneous catalysis via an approach similar to that pursued by Toste and co-workers with dendrimer-encapsulated gold,[42] who demonstrated in 2012 that changing the dendrimer properties allows the catalytic reactivity to be tuned in a similar fashion to ligand modification. From efforts to mimic the surface-attachement of homogeneous gold catalysts by the typical propylaminosiloxy linker, Hashmi and coworkers in 2013 obtained the most active homogeneous gold catalyst reported so far,[43] namely a mononuclear phosphorus-containing gold complex in which the steric bulkiness of the ligand is the crucial factor ensuring long catalyst lifetimes by slowing down catalyst decomposition.[44]

Similarly, studying the CO oxidation over Au/TiO_2 and Au/Fe_2O_3 samples, Klyushin and co-workers have recently shown that metal-support interaction plays a key role in Au activation being *more* important than size reduction, with the support overlayer on Au particles having a strong influence on the electronic structure of gold through charge transfer and stabilization of low coordinated Au atoms.[45]

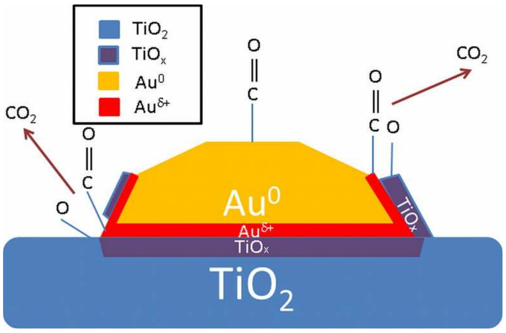


Figure 4. Suggested CO oxidation pathway on titania.
[Reproduced from Ref. 45, with kind permission].

As it happens with metal nanoparticle catalysis, defects (edges, twins, kinks, low-coordinated atoms etc.) in the nanoparticle crystal lattice are beneficial, and any support-metal interaction capable to stabilize such defects on the surface of active samples, will be reflected in enhanced catalytic activity.

Conclusions and Perspectives

In 1976, Sermon proclaimed gold to be *'an uncommonly good catalyst'*.[46] Forty years later, Asahi Kasei started to use a gold catalyst for the methyl methacrylate production in Kawasaki, Japan, followed in 2015 by a large PVC manufacturer near Shanghai switching from a mercury to a gold catalyst for the production of vinyl chloride. Will these large-scale applications be followed by several others so as to fulfil gold's *'potential to save lives, improve health and clean up the planet'*?[47]

To understand the impact of the new gold-catalyzed process, it is enough to consider that China alone accounts for 50% of the world's mercury release in the environment, and PVC production accounts for 60% of China's emissions (installed capacity of the mercuric chloride catalyst by the major PVC producers in China >4000 tons/year).[48] Gold, though, is certainly expensive, and currently the most expensive among all noble metals. Being historically considered a refuge investment vehicle, its value has increased sharply following the global financial crisis after 2008. As of early March 2016, gold price was $1,245/oz[49] (1 oz = 31.1 g) while palladium was only about half as expensive ($627/oz).[50] For comparison, in March 2001 the gold price was $263/oz, with researchers reviewing gold technology applications noting a few months later that the gold price was *'characterized by a remarkably stable value compared to the widely fluctuating prices of the PGMs'*.[51] Prognosticating the price development of precious metals is, and will remain a challenging task. Being the object of financial speculation,[52] indeed, the price of gold and PGMs can vary widely.

Strong fluctuations in price have hampered application of gold catalysts for example in automotive catalytic converters, causing operation of the first company, which had focused its business on this segment of gold nanoscale catalysis, NanoStellar, to cease operations. The company's product was intended to replace half of the platinum-palladium alloy in a diesel oxidation catalyst with palladium-gold, but in

August 2011 gold became more expensive of platinum and business proposal became unattractive.[53] Yet, arguably, this will not be the case for gold-catalysis applied to the synthesis of bulk and eventually also fine chemicals. In the former case, gold losses similar to the ones seen with Pd in automotive catalytic converter[54] were to be expected.

In the case of heterogeneous gold catalysis applied to the synthesis of chemicals, gold in the spent solid catalyst is recovered, exactly as it happens with PGM catalysts which are given back to the catalyst manufacturer for treatment and recovery of the noble metals.[55] In other words, the real problem is not availability, but price.

This explains why in the catalyst cost model used in the manufacture of vinyl chloride 0.25% was the maximum acceptable load for the Au/C. Whereas the costs of the mercury catalyst account for less than 1% of the total PVC production costs (costs to minimize mercury emissions not included), the gold catalyst is at 2% of total PVC production costs. In other words, the impact of the new catalyst on the total PVC production costs is minimal.

One might therefore ask whether industrial gold catalysis will become ubiquitous once highly active and extensively recyclable nanoscale gold catalysts will become commercially available, with applications including the fine chemicals and pharmaceutical industry[56] as it happens today with palladium catalysis. For example, one might wonder whether the ORMOSIL-encapsulated Silia*Cat* Au catalyst[57] or the AURO*lite* (1% Au/TiO_2)[58] will find widespread utilization in flow microreactors allowing dramatically reduced reaction times to selectively oxidize a broad variety of alcohols under base-free aqueous conditions with no by-product formation besides water.

Yet, the availability of methods to make catalysts as well of green catalytic processes is a required but *not* a sufficient condition. Just because a catalyst exists does not mean it will be used (see the case of the homogeneous L-Au^+ catalysts). In the first place the need for an improved catalyst or process has to exist. In other words, an established catalyst producer will only introduce a catalyst in its portfolio if there is an application for it. In that case, a catalyst developed specifically for that application (a task that is usually very time consuming) might become available.

As of today, three gold containing heterogeneous catalysts have found application in commercial plants. Others, which have undergone pilot scale testing were not commercialized, including the 1 wt.-% AURO*lite* catalyst for the hydrogenation of CO_2 to formic acid, which was tested but was not commercialized because of insufficient activity.[59]

It can be expected that in the future the number of Au catalysts actually employed by industry will grow, not only in bulk chemicals but also in biorefinery and in the fine chemical and pharmaceutical industries. Suzuki and co-workers at Asahi noted that due to the broad substrate range applicability of the Au-NiO_x catalyst, it was being evaluated with the aim to extend its application *'to other oxidation reactions'*.[11] An outcome unimaginable in 1985 when Hutchings published his forecast based on the correlation between metal (chloride) catalyst activity and standard electrode potential that, contrary to mainstream theory, gold should be highly active in acetylene hydrochlorination.[60]

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References

1. K. Sennewald, W. Vogt, H. Glaser, Patent DE1244766B, 1967

2. G. C. Bond, P. A. Sermon, *Gold Bull.* **1973**, *6*, 102-105.

3. B. Nkosi, N. J. Coville, G. J. Hutchings, *J. Chem. Soc., Chem. Commun.* **1988**, 71-72.

4. M. Haruta, T. Kobayashi, H. Sano, N. Yamada, *Chem. Lett.* **1987**, *16*, 405-408.

5. J. H. Teles, S. Brode, M. Chabanas, *Angew. Chem. Int. Ed.* **1998**, *37*, 1415-1418.

6. J. Oliver-Meseguer, J. R. Cabrero-Antonino, I. Domínguez, A. Leyva-Pérez, A. Corma, *Science* **2012**, *338*, 1452-1455.

7. (a) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem. Int. Ed.* **2006**, *45*, 7896-7936; (b) A. S. K. Hashmi, *Science* **2012**, *338*, 1434.

8. A. M. Echavarren, A. S. K. Hashmi, F. D. Toste, *Adv. Synth. Catal.* **2016**, *358*, 1347.

9. P. Johnston, N. Carthey, G. J. Hutchings, *J. Am. Chem. Soc.* **2015**, *137*, 14548-14557.

10. F. Gao, D. Wayne Goodman, *Chem. Soc. Rev.* **2012**, *41*, 8009-8020.

11. K. Suzuki, T. Yamaguchi, K. Matsushita, C. Iitsuka, J. Miura, T. Akaogi, H. Ishida, *ACS Catal.* **2013**, *3*, 1845-1849.

12. C. W. Corti, R. J. Holliday, D. T. Thompson, *Appl. Catal., A* **2005**, *291*, 253-261.

13. J. H. Teles, *Gold Bull.* **2008**, *41*, 282.

14. X. Liu, L. He, Y.-M. Liu, Y. Cao, *Acc. Chem. Res.* **2014**, *47*, 793-804.

15. Statista, Global mine production of gold from 2005 to 2015 (in metric tons), New York: 2016. See at the URL: www.statista.com/statistics/238414/global-gold-production-since-2005/

16. J. K. Edwards, B. Solsona, N. B. Ntainjua, A. F. Carley, A. A. Herzing, C. J. Kiely, G. J. Hutchings, *Science* **2009**, *323*, 1037-1041.

17. M. D. Hughes, Y.-J. Xu, P. Jenkins, P. McMorn, P. Landon, D. I. Enache, A. F. Carley, G. A. Attard, G. J. Hutchings, F. King, E. Hugh Stitt, P. Johnston, K. Griffin, C. J. Kiely, *Nature* **2005**, *437*, 1132-1135.

18. C. Della Pina, E. Falletta, M. Rossi, *Chem. Soc. Rev.* **2012**, *41*, 350-369.

19. K. Suzuki, *PETROTECH* **2014**, 37, 642-646.

20. S. Yamamatsu, *Kagaku Kogyo* **2012**, *86*, 17-24.

21. T. Hayashi, T. Inagaki, N. Itayama, H. Baba, *Catal. Today* **2006**, *117*, 210-213.

22. K. Suzuki, T. Yamaguchi, H. Goto, S. Yamane, K. Adachi, Development and commercialization of methyl methacrylate production technology by gold-nickel oxide nanoparticle catalysts with a core-shell structure, *Proceedings of 63rd R&D Symposium of Japan Petroleum Institute*, 27 July 2014.

23. A. Extance, New vinyl catalyst will reduce mercury emissions, *Chemistry World*, 11 January 2016, available online at http://www.rsc.org/chemistryworld/2016/01/gold-catalyst-polyvinyl-chloride-plastic-industry-china-emission, last time accessed June 27, 2016).

24. a) K. Saito, C. Fujii, H. Ito, JP 52136103, **1977**; b) K. Saito, C. Fujii, JP 52136104, **1977**.

25. G. J. Hutchings, R. Joffe, *Appl. Catal.* **1986**, *20*, 215-218.

26. B. Nkosi, N. J. Coville, G. J. Hutchings, *Appl. Catal.* **1988**, *43*, 33-39.

27. B. Nkosi, N. J. Coville, G. J. Hutchings, M. D. Adams, J. Friedl, F. E. Wagner, *J. Catal.* **1991**, *128*, 366-377.

28. N. A. Carthey, P. Johnston, M.L. Smidt, WO2010/055341 A2, **2010**

29. Jacobs and Johnson-Matthey, Working together on a mercury-free VCM catalyst, *Instrument on Mercury (INC3)*, Intergovernmental Negotiating Committee, United Nations Environment Programme, Nairobi, 30 October 2011

30. M. Conte, A. F. Carley, C. Heirene, D. J. Willock, P. Johnston, A. A. Herzing, C. J. Kiely, G. J. Hutchings, *J. Catal.* **2007**, *250*, 231-239.

---

31. Cardiff University, Gold Catalysts for Vinyl Chloride Manufacture, *Research Excellence Framework 2014*, REF3b.

32. P. Bishop, N. A. Carthey, WO 2013/008004, **2013**

33. T. Keel, J. McPherson, “Applications and Future Trends in Gold Catalysis” in *Environmental Catalysis Over Gold-Based Materials,* G. Avgouropoulos, T. Tabakova (Ed.s), RSC Publishing, Cambridge: 2013; Chapter 7.

34. S. J. Roberts, G. Hildegard Steinbach, D. Padayachee, J. Scott Mcpherson, G. Pattrick, E. Van Der Lingen, WO 2005/115612.

35. L. Croll, B. Billingsley, L. Brey, D. Fansler, P. Martinson, Design and Evaluation of Escape and CBRN Respirator Cartridges Using Nano Gold Carbon Monoxide Oxidation Catalysts, *10th International Symposium on Protection against Chemical and Biological Warfare Agents*, Stockholm, 8-11 June 2010.

36. For a thorough discussion on the topic, see: U. Reichert, *Implementing the Guideline on the Specification Limits for Residues of Metal Catalysts or Metal Reagents (EMEA/CHMP/SWP/4446/2000)*, Rheinischen Friedrich-Wilhelms-Universität Bonn, Bonn: 2009.

37. *Gold Catalysis: An Homogeneous Approach*, F. D. Toste, V. Michelet (Ed.s), Imperial College Press, London, **2014**.

38. M. Schulz, J. H. Teles, Patent WO 97/21648, **1997**

39. Y. Fukuda, K. Utimoto, *J. Org. Chem.* **1991**, *56*, 3729-3731.

40. K. Breuer, J. H. Teles, D. Demuth, H. Hibst, A. Schäfer, S. Brode, H. Domgörgen, *Angew. Chem. Int. Ed.* **1999**, *38*, 1401-1405

41. A. S. Kashin, V. P. Ananikov, *J. Org. Chem.* **2013**, *78*, 11117-11125.

42. E. Gross, J. Hung-Chang Liu, F. Dean Toste, G. A. Somorjai, *Nature Chem.* **2012**, *4*, 947-952

43. M. C. Blanco Jaimes, C. R. N. Böhling, J. M. Serrano-Becerra, S. K. Hashmi, *Angew. Chem. Int. Ed.* **2013**, *52*, 7963-7966.

44. M. C. Blanco Jaimes, F. Rominger, M. M. Pereira, R. M. B. Carrilho, S. A. C. Carabineiro, S. K. Hashmi, *Chem. Commun.* **2014**, *50*, 4937-4940.

45. A. Y. Klyushin, M. T. Greiner, X. Huang, T. Lunkenbein, X. Li, O. Timpe, M. Friedrich, M. Hävecker, A. Knop-Gericke, R. Schlögl, *ACS Catal.* **2016**, *6*, 3372–3380

46. P. A. Sermon, *Gold Bull.* **1976**, *9*, 129-131.

47. Prof. G. Hutchings, quoted in: 'A new Gold Rush', 21 July 2015. http://www.cardiff.ac.uk/news/view/124836-a-new-gold-rush

48. China Council for International Cooperation on Environment and Development, *Special Policy Study on Mercury Management in China*, Beijing: 2011. See at the URL: http://www.cciced.net/encciced/policyresearch/report/201205/P020120529368288424164.pdf

49. See data at the URL: http://www.indexmundi.com/commodities/?commodity=gold&months=180 (last time accessed: May 12, 2016).

50. See charts at the URL: www.nasdaq.com/markets/palladium.aspx (last time accessed: May 12, 2016).

51. C. W. Corti, R. J. Holliday, D. T. Thompson, *Gold Bull.* **2002**, *35*, 111-117.

52. R. C. Spurga, “Gold” in *Commodity Fundamentals: How to Trade the Precious Metals, Energy, Grain, and Tropical Commodity Markets*, John Wiley & Sons, Hoboken (NJ): 2012.

53. R. Kozarsky, *Innovation* **2012**, *10* (5), 21-24. See at the URL: http://www.innovation-america.org/how-do-you-move-nano-market

54. K. Boch, M. Schuster, G. Risse, M. Schwarzer, *Anal. Chim. Acta* **2002**, *459*, 257-265.

---

55. P. Grumett, *Platinum Metals Rev.* **2003**, *47*, 163-–166.

56. T. Mallat, A. Baiker, *Annu. Rev. Chem. Biomol. Eng.* **2012**, *3*, 11-28.

57. R. Ciriminna, A. Fidalgo, V. Pandarus, F. Béland, L. M. Ilharco, M. Pagliaro, *ChemCatChem* **2015**, *7*, 254-260.

58. J. Ni, W.-J. Yu, L. He, H. Sun, Y. Cao, H.-Y. He, K. N. Fan, *Green Chem.* **2009**, *11*, 756-759.

59. D. Preti, C. Resta, S. Squarcialupi, G. Fachinetti *Angew. Chem. Int. Ed.* **2011**, *50*, 12551-12554.

60. G. J. Hutchings, *J. Catal.* **1985**, *96*, 292-295.