

Industrial Applications of Gold Catalysis

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Dedicated to Professor Graham
Hutchings

Gold catalysis has recently found its first large-scale applications in the chemical industry. This Minireview provides a critical analysis of the success factors and of the main obstacles that had to be overcome on the long way from the discovery to the commercialization of gold catalysts. 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.

1. 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 describing the catalyst was filed in June 1965 by the German company Knapsack.^[1] Four decades have passed since the discovery by Bond and Sermon that the activity of Au/SiO₂ catalysts (prepared by mild thermal treatment of impregnated HAuCl₄) for the hydrogenation of 1-pentene at 373 K increased by a factor of 7000 as the gold content was decreased from 1% to 0.01%.^[2] Three decades have gone by since the almost simultaneous discoveries by Hutchings and co-workers^[3] and Haruta et al.^[4] that nano-scale gold supported on activated carbon or on “reducible” supports such as titania are exceptionally effective redox catalysts for the hydrochlorination of acetylene and oxidation of CO. The reducibility of a catalyst support is its ability to generate oxygen vacancies and to transfer the oxygen to the metal particle. The time has now finally arrived when heterogeneous catalysts containing gold are starting 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 it was first shown 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 came with the discovery that gold can also be a very active homogeneous catalyst.^[5] This culminated in the remarkable discovery that quasi-homogeneous gold clusters (with 3–10 atoms) formed in solution give reaction turnover numbers of up to 10⁷ 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 the hydrochlorination of acetylene as a replacement for the then used HgCl₂ catalyst has recently been recounted.^[9] To the best of our knowledge, two other Au-containing solid catalysts are commercially employed to date in the chemical industry: the Au-doped Pd catalyst for the synthesis of vinyl acetate, 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 of the commercial aspects of heterogeneous gold catalysis published in 2005 concluded that the two limiting factors to address prior to industrial application were the catalyst durability under operating conditions, and viable methods of catalyst preparation.^[12] Furthermore, new catalysts have to be seen in the context of the chemical process they are to be employed 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 catalyst of the vinyl acetate synthesis, which allowed the replacement of acetylene by the much cheaper ethylene as a 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.

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Another option is that the catalyst uses the same raw materials as the conventional catalysts but offers a moderate economic improvement, for example, because it is more selective than the 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 the hydrochlorination of acetylene and the catalyst 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 than other metal catalysts, including platinum-group metals (PGMs), often under milder reaction conditions, and this can pave the way to new applications.^[14]



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Catalysts based on similarly expensive, supported PGMs are widely employed in the chemical industry because of their ability to activate industrially and economically important molecules (H_2 and O_2 , as ideal 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 to be 3000 tonnes.^[15] In the same year, the overall production of Pt was only 178 tonnes and that of Pd only 208 tonnes.

In the following sections, 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. Examples of such applications are 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]

2. 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



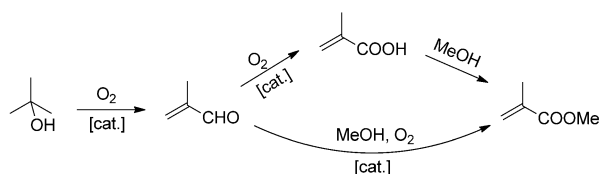
Joaquim Henrique Teles studied chemistry and chemical engineering at the Technical University of Lisbon (Portugal) and obtained his PhD in 1988 from the University of Giessen (Germany) under the supervision of Prof. G. Maier. He was a postdoctoral fellow with Prof. W. von E. Doering at Harvard University and later a Humboldt fellow at the University of Giessen, before joining BASF in 1991 as a research chemist. Since 2001 he has led a research group at the Process Research and Chemical Engineering laboratory of BASF in Ludwigshafen. His research focuses mainly on oxidation (e.g. the production of propylene oxide using H_2O_2 and of cyclododecanone using N_2O) and phosgene chemistry.



Mario Pagliaro studied Chemistry (Diploma 1993) at the University of Palermo and completed his PhD in 1998 in Bologna with a thesis on carbohydrate oxidation catalysis, for work primarily conducted in the group of Prof. D. Avnir at the Hebrew University of Jerusalem. He then moved to the Netherlands where he worked first at Leiden University and then at Zeist's TNO Institute of Food Sciences with Dr. A. de Nooy. In late 2000, he became a full-time researcher at Italy's CNR chemistry Institute in Palermo. His research focuses on green and organic chemistry, materials and nanochemistry, solar energy, and bioeconomy.

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.

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



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

Originally, the oxidative esterification of methacrolein with methanol in the presence of molecular oxygen was carried out in the liquid phase over an alumina-supported catalyst containing the intermetallic phase Pd_3Pb as the active phase.^[20] The introduction of the catalytic oxidative esterification was a very important development, because it allowed the number of steps to be reduced 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 for methyl methacrylate from methacrolein was quite good but, unfortunately, the catalyst also oxidized methanol to methyl formate to a considerable extent (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 as a result of decarbonylation of methacrolein. However, the most pressing problem was to reduce the methanol loss and the formation of methyl formate as a by-product. The research team at Asahi, led by Suzuki, succeeded in discovering a new catalyst to replace the original Pd_3Pb catalyst and 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 to methyl glycolate in the presence of methanol, it has been known that gold is a competent metal to catalyze oxidative esterifications.^[21] The preferred catalyst was gold, sometimes with Pb as a 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 mole 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 an $\text{Au-NiO/SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ 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 the oxidation of methanol to methyl formate was now negligible (only 0.007 moles of methyl formate were formed per mole of methyl methacrylate). This catalyst, though, could not be used commercially 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 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, since the oxidative esterification of methacrolein is performed in suspension and 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 deactivation of the catalyst.

To solve this problem, the team at Asahi used a mechanically robust $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ support in the form of 60 μm spheres and controlled the deposition process in such a way that the gold nanoparticles were preferentially located just below the surface but only down to a depth of less than 10 μm (Figure 1). In this way, the gold nanoparticles remain highly 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 without loss of catalytic activity. During this period, MMA was obtained with high selectivity (96–97 %) and constant yield (ca. 60 %), and negligible gold and nickel

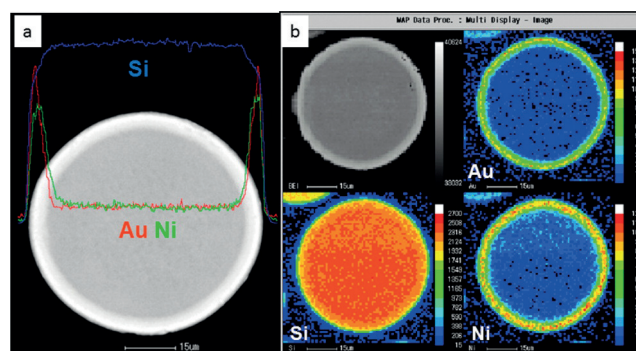


Figure 1. Electron-probe microanalysis of a single particle of $\text{AuNiO}_x/\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$. a) Secondary electron image and line analysis. b) Color mapping (Ni in green, Au in red) display corresponding to the concentration of the element distribution [reproduced from Ref. [11], with kind permission].

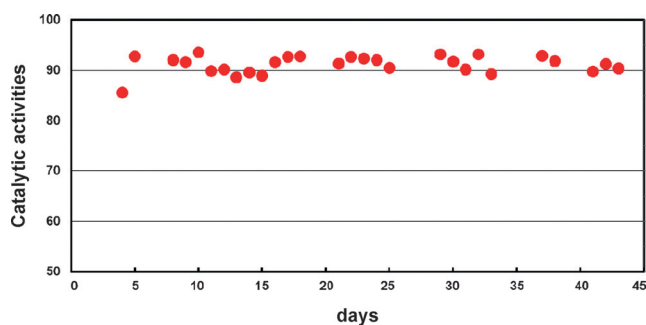


Figure 2. Catalytic activity of $\text{AuNiO}_x/\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ over time in a continuous-flow reaction apparatus [Reproduced from Ref. [11], with kind permission].

leaching (Au and Ni in the reaction mixture < 2.5 ppb). An examination of the catalyst after the long-running test showed no sintering of the AuNiO_x nanoparticles, with the macroscopic core-shell structure remaining intact.

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 that of the original catalyst. These are the essential requirements for a drop-in catalyst. Additionally, the new catalyst provides a lower rate of by-product formation (by-products are still formed, although in smaller amounts, while the amount of waste water remains essentially unchanged) and a lower catalyst cost because of the lower amount of precious metal required for a similar productivity.

3. Hydrochlorination of Acetylene

In 2015, catalyst manufacturer Johnson Matthey officially announced the introduction its newly developed gold catalyst with the brand name Pricat MFC 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, which 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 six months and the mercury losses 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 in 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 those with the catalyst being replaced.

The catalytic activity of tetrachloroauric acid, both in homogeneous and heterogeneous form, has actually been 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. Unfortunately, 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 2-propanol/*n*-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 deactivation mechanisms 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, despite 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 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 with disposing of waste streams containing aqua regia. The targeted loading is significantly lower than typical 0.5–1 % Au loadings of conventional Au/C catalysts, 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 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 than the mercury catalyst) on a pilot-plant scale.^[29] The catalyst, however, was never commercialized because the company's

internal project was terminated. In 2006, the company started to cooperate with Johnson Matthey and with the group of 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 to build a pilot plant by a VCM manufacturer in western China that replicated 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 from mid-2011, with six different catalysts tested to fine-tune the catalyst formulation. Eventually, the team was able to prepare a highly active catalyst with 0.1 % loading by supporting $\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2$ on carbon extrudates.^[32] Seemingly, the presence of the sulfur-containing anions helped stabilize the cationic gold and generated a catalyst less prone to deactivation, and at the same time allowing 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 six 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.

The reactor was operated under conditions equivalent to those of the process using the HgCl_2/C catalyst for more than 4500 h on stream (Figure 3). At a productivity level of 1000 kg VCM per kg catalyst, the performance of the catalyst (and reactor) was identical to the performance on the 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 overall improved economics while eliminating the mercury emissions altogether.

4. Production of Industrial Gold Catalysts

A few companies already manufacture and sell supported gold catalysts.^[33] In 2009, South Africa's AuTEK (a joint venture between the 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 under the trade-names AUOLite (Au/TiO₂, Au/ZnO, Au/Al₂O₃) and AUROLith (Au/Al₂O₃/cordierite), obtained by a deposition/precipitation method patented in 2005.^[34] These catalysts were marketed as ideally suited to catalyze oxidation reactions (in both the gas and liquid phase).

A catalyst developed by 3M for CO oxidation, especially for escape masks, is NanAucat, which is formed by chemical vapor deposition of Au nanoparticles 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 happens with the currently used Hopcalite. Thus, the catalyst does not require 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, were nanoparticle size and reproducibility of the synthetic method.^[12] Recent innovations in catalyst preparation routes have solved many of these issues, thereby allowing the production of highly active, robust, and selective catalysts with low levels of gold loading.

For example, 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 later developed by Johnston and co-workers established a new method for the preparation of stable supported cationic gold catalysts with a Au loading in the 0.15–0.6 % range which, being based on sulfur-containing gold-containing complexes, exploits the well-known stability of gold–sulfur bonds. Remarkably from a “green chemistry” viewpoint, furthermore, the preparation of these gold catalysts takes place in the aqueous phase.

In the case of the Asahi catalyst, Au and NiO were supported on the mixed oxide SiO₂-Al₂O₃-MgO obtained by an aqueous sol-gel route. The support had a specific surface area of 149 m² g⁻¹, an average pore diameter of 8 nm, and an average particle size of 60 μm. The catalyst was prepared by

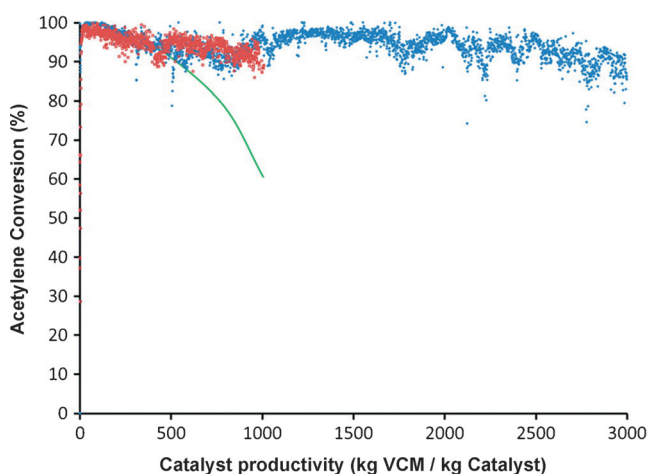


Figure 3. Comparison of catalyst performance in a primary reactor for a 10 % HgCl_2/C catalyst (green), pilot-plant operation for 0.1 % Au/C to a yield of 1000 kg VCM per kg catalyst (red), and full-scale commercial reactor for 0.1 % Au/C to a yield of 3000 kg VCM/kg catalyst (blue). Catalyst = 0.1 % Au/C prepared by supporting $\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2$ on carbon extrudates [reproduced from Ref. [9], with kind permission].

co-precipitation through heating an aqueous solution containing $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and HAuCl_4 (12 mL, 1.3 mol L^{-1}) 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.

5. Heterogeneous Versus Homogeneous Catalysis

Remarkably, the first industrial applications of gold catalysis concern the production of bulk chemicals, and not 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 concentration of palladium or platinum (both classified as “Metals of significant safety concern”) in APIs is below 10 ppm if orally administered, and <1 ppm if administered parenterally, has not changed the situation.^[36]

The high cost of gold, the need to recover it by 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 an industrial scale.

The potential of homogeneous gold in catalyzing the selective electrophilic activation of $\text{C}\equiv\text{C}$ bonds under mild conditions was evident as early as 1997, when researchers at BASF first patented and then published the discovery that cationic $[\text{L}-\text{Au}^+]$ 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] This high catalytic activity is orders of magnitude better than the preceding results obtained by Fukuda and Utimoto with simple gold(III) salts.^[39] However, even this impressive 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 synthesis of vitamin E, from a mixture of propyne and allene (propadiene), which is available as a by-product 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 and mainly because of the fact that propyne and allene reacted at approximately equal rates.^[40]

In the case of Pd, Kashin and Ananikov 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, in principle, also be operative in heterogeneous gold catalysts. There is great room for practically relevant improvement by merging heteroge-

neous and homogeneous catalysis through an approach similar to that pursued by Toste and co-workers with dendrimer-encapsulated gold.^[42] The authors 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 attachment of homogeneous gold catalysts with the typical propylamino-siloxy linker, Hashmi and co-workers in 2013 obtained the most active homogeneous gold catalyst reported so far.^[43] In this mononuclear phosphorus-containing gold complex, the steric bulk of the ligand is the crucial factor for ensuring long catalyst lifetimes by slowing down catalyst decomposition.^[44]

Similarly, studying CO oxidation over Au/TiO_2 and $\text{Au}/\text{Fe}_2\text{O}_3$ samples, Klyushin et al. have recently shown that metal-support interactions play a key role in Au activation and can be more important than size reduction. The support overlayer on the Au particles have a strong influence on the electronic structure of gold through charge transfer and stabilization of low-coordinated Au atoms (Figure 4).^[45]

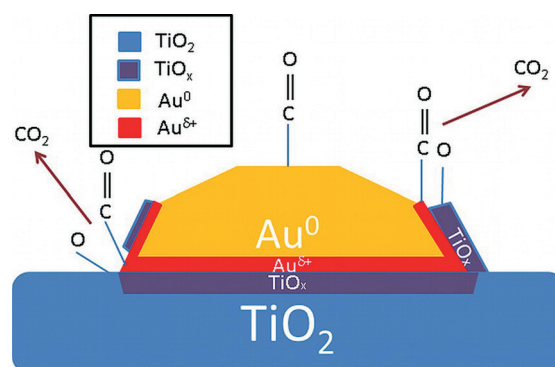


Figure 4. Suggested CO oxidation pathway on titania [reproduced from Ref. [45], with kind permission].

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

6. Conclusions and Perspectives

In 1976, Sermon proclaimed gold to be “an uncommonly good catalyst”.^[46] Almost 40 years later, Asahi Kasei started using a gold catalyst for the production of methyl methacrylate in Kawasaki, Japan, which was 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 developments, 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. The

capacity of the major PVC producers in China for the production of the mercuric chloride catalyst is more than 4000 tons year⁻¹.^[48] Gold, though, is certainly expensive, and currently the most expensive of all the noble metals. Being historically considered a refuge investment vehicle, its value has increased sharply following the global financial crisis since 2008. In early March 2016, the price of gold was \$1245 oz⁻¹^[49] (1 oz = 31.1 g), while palladium was only about half as expensive (\$627 oz⁻¹).^[50] For comparison, in March 2001 the gold price was \$263 oz⁻¹, 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] the price of gold and PGMs can, indeed, vary widely.

Strong fluctuations in price have hampered the application of gold catalysts, for example, in automotive catalytic converters, and caused the first company which had focused its business on this segment of nanoscale gold 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 than platinum and the business proposal became unattractive.^[53] 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 converters^[54] were to be expected.

In the case of the application of heterogeneous gold catalysis to the synthesis of chemicals, gold in the spent solid catalyst is recovered—exactly as 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 0.25 % was the maximum acceptable load for the Au/C catalyst in the manufacture of vinyl chloride. 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 2 % of the 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 become commercially available, with applications including in the fine-chemicals and pharmaceutical industries,^[56] as happens today with palladium catalysis. For example, one might wonder whether the ORMOSIL-encapsulated SiliaCat Au catalyst^[57] or the AUROLite (1 % Au/TiO₂)^[58] will find widespread utilization in flow microreactors, thereby 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.

The availability of methods to make catalysts as well as green catalytic processes are required, but are not a prerequisite. 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 such a case, a catalyst developed specifically for that application (a task that is usually very time consuming) might become available.

Up to now, 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 % AUROLite catalyst for the hydrogenation of CO₂ to formic acid, which was tested but 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 the production of bulk chemicals but also in the biorefinery and in the fine chemical and pharmaceutical industries. Suzuki et al. at Asahi noted that the applicability of the Au-NiO_x catalyst to a broad substrate range has resulted in it being evaluated with the aim of extending 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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