



Account/Revue

## Evolution in the chemical making of gold oxidation catalysts



### *Evolution des méthodes chimiques de préparation des catalyseurs d'oxydation à l'or*

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## ABSTRACT

Despite the inertia of bulk gold and of extended gold surfaces towards oxygen, gold-oxide nanocomposites were found, at the end of the 20th Century, to display exceptional low temperature catalytic activity in oxidation reactions, based on a concerted mechanism involving support-mediated oxygen activation. Since then, both experimental and theoretical studies have converged in showing that further decreasing the size of gold nanoparticles (Au NPs) would lead to non-assisted gold catalysis. This opens up new perspectives in the choice of the gold dispersant and in the development of more efficient, sustainable, viable gold catalysis. However, given the low melting point of gold, stabilizing such small Au NPs remains challenging. This article reviews the way in which gold catalyst preparation, i.e., synthetic strategies to tackle and address the size challenge in bottom-up chemical methods, has evolved as the understanding of the mechanism of the gold-catalyzed oxidation of CO has progressed.

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## 1. Introduction

Gold has been known for centuries as a precious, non-oxidizable metal. Indeed, bulk gold is resistant against air oxidation, which makes it quite different from, e.g., copper and silver, the two metals sharing the same column of the Mendeleev periodic table of elements. While the surface of copper and silver objects is easily altered in air/moisture environments, due to the formation of copper and silver oxides respectively, gold retains its shiny aspect over time because gold oxides are not stable. The first usage of bulk gold in decoration, ornamentation and jewelry that is intended to last is directly related to the inalterability of its surface. In the 20th Century, the near perfect corrosion

resistance of gold, combined with high ductility and high electrical conductivity, started to be exploited in electronics. The inertia of the gold surface also led to applications in biomedicine, where sub-micrometric gold particles serve as biocompatible carriers for imaging molecules and as drug delivery agents. For a long time, the only functional properties of gold particles that were used were their optical properties, i.e., their size-dependent color. Still in 1995 gold was coined “the noblest metal of all” and the “least reactive metal towards atoms or molecules at the interface with a gas or a liquid” [1]. However, at the same period it was discovered that, when the dimension of the gold surface was reduced to a few nanometers, the surface was not inert anymore; indeed, despite the non-reactivity of an extended gold surface towards oxygen, gold-based nanocomposites were found to display exceptional catalytic activity at low temperatures especially in oxidation reactions [2,3].

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## 2. Evolution in the understanding of the catalytic oxidation activity of gold-based nanocomposites: from a gold-support concerted mechanism to gold-only catalyzed CO oxidation

### 2.1. Reducible oxide-supported Au NPs: redox-type, support-mediated oxygen activation at the metal-support interface

In 1987, Prof. Haruta [4] and his team reported for the first time that gold particles, about 5 nm in diameter, associated with iron oxide, catalyzed the oxidation of CO at sub-ambient temperatures [2]. This has never been equaled by any other metals until now (except recently by some morphology-controlled  $\text{Co}_3\text{O}_4$  cobalt oxides [5]). The years following this discovery were devoted to the determination of the reaction mechanism. The surface of gold had been considered as inert for so long that it was difficult for the catalysis community to accept the fact that it could activate both  $\text{O}_2$  and CO. In particular,  $\text{O}_2$  chemisorption over gold surfaces had exhibited such high energy barriers that its occurrence was considered impossible at the temperatures at which the composite was found active. Hence, according to the first models, oxygen activation had to be ensured by the oxide component of the catalyst: oxygen would thus be activated at the support surface, or at the gold–support interface, and react, via a Langmuir–Hinshelwood-type mechanism, at the gold–support interface, with pre-activated carbon monoxide, i.e., CO physisorbed over gold [6]. In agreement with this model, reducible oxides were initially found to be more “active” than non-reducible oxides and an “active” (e.g., titania, zirconia, etc.) vs. “inert” (alumina and silica) classification of supports for Au NPs was established [7]. CO oxidation activity was found to be directly related to the number of perimeter sites [8], i.e., the number of bifunctional gold–support sites at the Au NP periphery. Alumina-based gold catalysts could be made active by placing reducible nanooxides (such as NiO,  $\text{TiO}_x$ , and  $\text{FeO}_x$ ) in close proximity/vicinity to Au NPs [9]. The importance of the sites at the perimeter/periphery of Au NPs in ensuring low temperature CO oxidation was recently re-emphasized [10].

### 2.2. Oxide-supported Au NPs: metal-support interaction (electronic effects) and OH-mediated oxygen activation

However, it appeared that raw  $\text{Au}/\text{Al}_2\text{O}_3$  catalysts could be as active as  $\text{Au}/\text{TiO}_2$  catalysts [11]. Hence, oxygen activation did not need to proceed via a redox-type mechanism. It was shown that the so-called “metal–support interaction”, i.e., the nature of the interface, was key in gold oxidation catalysis, not only because it determined the number of bifunctional gold–support sites at the Au NP periphery, but also because it determined the shape of Au NPs and electronic state of Au surface atoms. For example, the morphology of Au NPs over the support turned out to be important; in particular, a bilayer was found to be a highly active structure [12] and round-shaped Au NPs were found to “flatten” on alumina upon CO exposure [13]. This may account for the CO oxidation activity of  $\text{Au}/\text{Al}_2\text{O}_3$  catalysts and for the activation, upon heating under reaction

conditions, of some gold catalysts containing initially hemispherical Au NPs [14].

Besides, it was proposed that –OH terminations, e.g., those of a titania or alumina support located at the gold–support interface [15,16] or those introduced into a  $\text{Au}/\text{SiO}_2$  catalyst [17], were active in promoting CO oxidation, accounting in particular for the promoting role of water/moisture often observed [18–23].

At the same time, it was established that gold-catalyzed CO oxidation was structure-sensitive [24]. Below 5 nm, the turnover frequencies in CO oxidation indeed exponentially increase with decreasing Au NP size, whatever the support [25], so that a slight variation of Au NP size distribution could account for the differences observed between different catalysts. It thus became evident that further understanding of the reaction mechanism would require dissociating Au NP size and support effects; producing the same gold dispersions/morphologies over various supports thus became essential.

### 2.3. Au NP size effect

The higher intrinsic activity of the smaller Au NPs was attributed to the higher population of the low-coordinated atoms of cubooctahedral Au NPs (corner sites). The population of such sites indeed increases exponentially with decreasing Au NP size [26]. These sites have not only been proposed as sites for CO adsorption/activation, but theoretical studies also suggested that these sites could activate molecular oxygen at low temperatures, without any involvement of the support [27–29]. One particular study clearly emphasized that the size effect largely dominated gold oxidation catalysis, and that support or dopant effects were only minor compared to the size effect [25]. Hence, stabilizing sub-nanometric Au NPs would not only enhance the catalytic activity of gold, but also make it (quasi-)independent of the support. Au NPs of such size would allow considering other supports than those used so far, in particular those presenting a surface that is more suited to the catalysis (e.g., more resistant against reaction conditions). This could make gold catalysts more stable to reaction conditions, more durable and thus viable. As a matter of fact, unsupported Au NPs have indeed proven active for CO oxidation [30].

## 3. Initial challenges in the preparation of gold catalysts

### 3.1. Discovery by serendipity

The synthesis of the first reported active gold catalyst is a clear example of serendipity. In the eighties, the dominating method for preparing noble metal catalysts (Pd and Pt) was the impregnation of an alumina support with a metal salt, followed by drying, calcination and reduction to produce a high dispersion of metal nanoparticles at the alumina surface. The gold catalysts prepared by this method always appeared inactive, so that gold was disregarded for a long time as a potential catalyst. However, in the mid-eighties, Prof. Haruta and his team mixed  $\text{HAuCl}_4$ ,  $\text{Fe}(\text{NO}_3)_3$  and a base (sodium carbonate), which led to a

Au–Fe<sub>2</sub>O<sub>3</sub> composite powder [2]. This composite appeared to display unprecedented catalytic activity for CO (and hydrogen) oxidation. The first report of this activity mentioned that the co-precipitation method used by the inventors produced much smaller Au NPs (2–8 nm) than those produced by impregnation (>10 nm). The team had indeed discovered the first method to make gold catalytically active. This was a major discovery since Au NPs did not just mimic platinum group metal (PGM) catalysts; the catalytic properties of Au NPs could be obtained at much lower temperatures than those considered/required by PGM catalysts. Gold catalysts turned out to be active at sub-ambient temperatures, a range of temperatures never reached before for this reaction, because, unlike the typical PGM catalysts, Au NPs exhibit low affinity for CO. Hence they do not get poisoned by low temperature (<200 °C) CO adsorption, which is known to block oxygen activation in PGM catalysts.

### 3.2. Challenge of Au NP size control

Co-precipitation thus allowed the production of the right size of gold in association with a suitable oxide. This method provides conditions for controlling and limiting the growth of Au NPs during the synthesis. What had been overlooked before is the much lower melting point of gold (1064 °C), as compared with that of PGM (>1600 °C). This essential/major difference implies that gold atoms/particles are much more mobile than, e.g., Pt atoms on an inorganic surface. Hence gold particles are much more prone to coalescence and sintering than PGM. The rough application of impregnation to gold thus leads to a very different material than the one obtained with Pt. In particular, heat treatments cause much larger sintering in the case of Au due to the lower Tammann temperature (the temperature at which a nanoparticle of a given size melts). Hence, in this case, the same preparation method does not lead to the same catalytic metallic dispersion. It has thus appeared essential to adapt the method of preparation to the desired product, more specifically to design new methods which take into account the specific reactivities and affinities with the surface of gold and its precursors.

### 3.3. Rationalizing Au catalyst design

Several bottom-up chemical methods have thus been designed to produce gold catalysts in a more rational way. They are performed in the liquid phase and all involve the chemical or thermal reduction of a gold precursor (mostly chloroauric acid) before or after addition of the support (O- and OH-terminated inorganic supports). These methods all target a particle size below 5 nm, which is the *sine qua non* condition for activity. Most of them are designed to deposit and/or form such Au NPs over pre-formed oxide supports [3]. Amongst them, deposition-precipitation (DP) was developed in 1991 [31]. In this method, the pH of an aqueous HAuCl<sub>4</sub> solution is first adjusted to 9 before it is added to a suspension of the TiO<sub>2</sub> powder support at ambient temperature. The idea is to avoid the presence of chloride on the catalyst surface, by

transforming the heavily chlorinated precursor into a gold hydroxide anion before it reacts with titania [32,33]. Chlorine is indeed suspected to facilitate the migration/mobility/diffusion of gold atoms on an oxide surface, during the subsequent heat treatment required to reduce the chlorinated Au<sup>III</sup> grafted complex into supported Au<sup>0</sup> NPs, and to favor the coalescence of particles into larger, inactive ones [34]. On the other hand, thermal reduction of the grafted Au<sup>III</sup>(OH)<sub>4</sub> species leads to catalytically active Au NPs. Besides, the grafted Au<sup>III</sup>(OH)<sub>4</sub> complex spontaneously decomposes into Au<sup>0</sup> in air at ambient temperature, so that the post-synthesis heat treatment can be avoided. Overcoming the sintering issue in that way is however achieved at the expense of the gold loading in the final material. Indeed, the iso-electric point of titania (IEP) being close to 5, the surface is negatively charged at pH 9 and it thus only weakly reacts with the soluble Au(OH)<sub>4</sub><sup>-</sup> anion. Hence, only loadings of less than 1.5wt.% can be obtained by the DP method. Furthermore, HAuCl<sub>4</sub> being a strong Bronsted acid, the pH of a HAuCl<sub>4</sub> solution is a function of its concentration and, in order to reach a pH of 9 with a limited amount of base (NaOH, KOH, NaCO<sub>3</sub>...), the initial concentration of HAuCl<sub>4</sub> should typically be lower than 10<sup>-2</sup> M (pH 1.5–3). This prevents any scale-up as these highly diluted environments are not industrially viable. Besides, such basification of the synthesis medium provides only limited control over the amount (and nature) of heteroelements introduced on the catalyst surface significantly impacting the activity of Au NPs, which has been suggested as a major cause for the occurrence of lack of reproducibility.

## 4. Evolution in the methods of preparation of gold catalysts: from overcoming limitations of the initial methods to exploring new strategies

The first improvements were intended to overcome some of the limitations of the initial methods of preparation, namely the low gold loading of the final material and the limited number of oxides over which suitably sized Au NPs can be prepared. Some modifications were also induced by the need for establishing clear structure-activity relationships and gaining insight into the reaction mechanisms, while others focused on enhancing at least one aspect of the catalytic function, mostly activity. In 2007, stability/durability of gold catalysts was identified by the World Gold Council as the main hurdle towards their commercialization [35], which led to the design of a few new catalytic structures with improved durability, which is so far obtained at the expense of activity. This Section will highlight the main bottom-up chemical strategies developed to tackle these challenges.

### 4.1. Improving the initial DP-NaOH method

Both methods described below are based on the concept/strategy of the DP method, i.e., on the reduction of a chloride-free grafted gold species, in order to limit Au NP growth. They differ in the base used to hydrolyze the [AuCl<sub>4</sub>]<sup>-</sup> anion, before or after the reaction with the surface, and possibly on the nature of the grafted species.

#### 4.1.1. Increasing gold loading and deposition efficiency

C. Louis et al. proposed in 2002 a method called DP-urea [36] or homogeneous deposition-precipitation (HDP, which can also stand for high-yield deposition-precipitation). In this method, urea ( $(\text{NH}_2)_2\text{C}=\text{O}$ ) is used as the base to bring the pH of an aqueous  $\text{HAuCl}_4$  solution to 9. The synthesis is carried out at  $>70^\circ\text{C}$  in order to allow gradual and homogeneous release of hydroxide ions upon decomposition of urea ( $(\text{NH}_2)_2\text{C}=\text{O} + 3\text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{NH}_4^+ + 2\text{OH}^-$ ). Inspired by the Geus method, which was developed for Ni catalysts in 1977 [37] to solve the dispersion and loading issues of impregnation [38], HDP was specifically designed for combining high dispersion and high loadings [39,40] but successfully applied and adapted to gold catalysts only in 2002. It yields materials which combine the small Au NP size of the DP-NaOH method with a much higher gold loading, of up to 8wt.% on titania, associated with a 100% deposition yield. Calcination at  $300^\circ\text{C}$  seems however necessary to reduce the surface species into  $\text{Au}^0$  NPs, which suggests that the species initially formed at the surface might differ from the hydroxide gold species obtained by DP-NaOH and similar to the species obtained by the DAE method described below. In particular, it is not clear how ammonium ions react with the surface and how they might contribute to the high intrinsic activity of these catalysts.

#### 4.1.2. Preparing highly active, thermally stable Au NPs on non-reducible alumina support

V. Pitchon et al. developed in 2004 a method called Direct Anionic Exchange (DAE) [41]. In this method, the pH of the starting  $\text{HAuCl}_4$  solution is first increased to 3.5–5 by decreasing the concentration of  $\text{HAuCl}_4$  to  $10^{-4}$ – $10^{-5}$  M. The alumina support is then allowed to react with these highly diluted gold solutions for one hour at  $70^\circ\text{C}$ . Under these conditions, a quantitative deposition yield can be obtained due to the higher IEP of alumina (8–9) allowing strong interactions between the soluble anions and the positively charged surface. A mixture of  $\text{Au}(\text{Cl})_2(\text{OH})_2$  and  $\text{AuCl}(\text{OH})_3$  species has been found at the surface [42]. Calcination at  $300^\circ\text{C}$  allows to get active gold catalysts. However, if an ammonia treatment of the powder is applied at ambient temperature before calcination (4 M, pH 11), complete substitution of the chlorine ligands with  $-\text{OH}$  or  $-\text{NH}_3$  moieties is achieved yielding, upon calcination at  $300^\circ\text{C}$ , highly active, thermally stable [43] 2 nm Au NPs over alumina, which are similar in size and shape to those obtained by DP-NaOH over titania. The loading of the catalyst is however impacted by the ammonia wash, which causes a loss of 25–30% of the gold content. Besides, the possible contribution of nitrogen-containing functions and nitrogen residues to the high activity and stability of these catalysts has never been evaluated, as the nitrogen content has never been quantified.

#### 4.2. Dissociating Au NP size and support effects

An alternative approach to the design of a support-specific method for the preparation of Au NPs of a given size consists in chemically reducing a gold precursor in solution, in the presence of a stabilizing agent, before introduction of the support, as had already been done for

other metals [44]. In this strategy, Au NPs are formed and stabilized in solution and the resulting protected Au sols are subsequently adsorbed on the chosen supports. This method is referred to as colloidal deposition or sol immobilization. It is intended to produce the same gold dispersions over different supports [45]. Initially developed by M. Comotti et al. [46], it has been used essentially for mechanistic studies, to evaluate the extent of the support effect in CO oxidation [47] and liquid phase oxidations [48] catalyzed by oxide-supported Au NPs. In the original method,  $\text{HAuCl}_4$  ( $10^{-4}$  M) is reduced by sodium borohydride in the aqueous phase in the presence of polyvinylalcohol (PVA). After immobilization of the 3 nm gold sol, PVA is removed by calcination at  $250^\circ\text{C}$ . In organic media, Stucky et al. also obtained size-controlled, monodisperse Au NPs by mild reduction of  $\text{AuPPh}_3\text{Cl}$  with amineboranes in the presence of strong stabilizers, namely alkylthiols [49]. Average Au NP sizes of 2–8 nm were produced depending on the conditions (Au/amine-borane ratios). After deposition of the 6 nm Au sol on a series of hydroxyl-terminated oxide supports, various oxide-supported 6 nm Au NPs were obtained and the protecting agent was removed by calcination at  $300^\circ\text{C}$  before catalysis [50]. In these methods, although gold is already chemically reduced before addition to the support, calcination is still required in order to clear the Au NP surface and also to create a gold/support interface. And, as for the methods based on the reduction of a grafted species, neither the possible presence of heteroatoms coming from the reaction of the reducing and protecting agents with the surface, nor the possible impact of these atoms on the catalytic properties of the catalyst has been investigated yet. It is noted that these catalysts are generally less active in CO oxidation than those prepared by reduction of a grafted gold species. This could be attributed to insufficient access to the Au NP surface due to the presence of poisoning residues or to an insufficient gold/support interaction which is engineered after formation of Au NPs and might lack the strong covalent/ionic bonds created in the grafting methods.

#### 4.3. Stabilizing sub-nanometric Au NPs

In 2009, it became clear that to achieve higher levels of activity and maximize intrinsic activities of Au NPs, the size of Au NPs should be further decreased down to the sub-nanometer level ( $<1$  nm). Both strategies were used to that end, i.e., stabilize Au nanoclusters on inorganic supports. Gates et al. first grafted a dimethyl acetylacetonate gold complex ( $\text{Au}^{\text{III}}(\text{CH}_3)_2(\text{acac})$ ) on a partially dehydroxylated magnesium oxide surface before applying a mild reducing treatment. The latter transformed the site-isolated mononuclear Au complex on the  $\text{MgO}$  surface, first into sub-nanometer  $\text{Au}_2$  to  $\text{Au}_6$  clusters, along with some isolated Au atoms ( $\text{He}/45^\circ\text{C}$ ), and then into 0.6–1 nm Au NPs ( $\text{He}$ ,  $100^\circ\text{C}$ ), as evidenced by aberration-corrected high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) [51]. However, the catalytic activity of such objects has not been reported and it is not known how the Au NP size would evolve under reaction conditions. Limited stability under reaction conditions can be expected. On the other hand, Tsukuda et al. reported the synthesis of  $\text{PPh}_3$ -

stabilized 0.8 nm Au clusters from  $\text{NaBH}_4$  reduction of  $\text{AuPPh}_3\text{Cl}$  and the subsequent immobilization of these sols inside mesoporous silica [52]. These materials catalyze the microwave-assisted oxidation of benzyl alcohol with  $\text{H}_2\text{O}_2$  at ambient temperature. Highly stable  $<1$  nm Au NPs were also obtained in SBA-15 from the chemical reduction of  $\text{AuCl}_4^-$  moieties in strong interactions with  $\text{MPTMS}$  (mercaptopropyl trimethoxysilane)-functionalized SBA-15 [53], which proved more efficient than TPTAC (trimethoxysilylpropyl-*N,N,N*-trimethylammonium chloride) functionalization [54]. Activity in the aerobic oxidations of cyclohexene and stilbene was evidenced. However, the catalytic properties for CO oxidation are documented for none of these systems. Only one report of interestingly high CO oxidation activity has been made, concerning somewhat larger Au NPs of 1.8 nm on silica, obtained by hydrogen reduction at  $300^\circ\text{C}$  of  $\{\text{Au}[\text{N}(\text{SiMe}_3)_2]_4\}$  grafted on partially dehydroxylated silica. It turns out that, in this material, the silica is passivated by the reaction between the silanol groups and the decomposition products of the complex ( $-\text{SiMe}_3$ ), yielding  $\text{CH}_3$ -terminated silica [55].

#### 4.4. Increasing durability and selectivity

When seeking to improve the durability of gold catalysts, most studies have aimed at preventing Au NP mobility and sintering under reaction conditions, which results in a loss of the active gold surface and thus of catalytic activity. In order to do so, enhancing the gold-support interaction, both electronically and geometrically, was the priority target. For example, studies by Dai et al. [56–59] and Schüth et al. [60,61] have focused on tuning the O and OH composition of the surface, by e.g., changing the crystalline structure of the oxide and the exposed surface, and on tuning the morphology of the oxide and the gold-oxide interface, by e.g., confining Au NPs into oxide capsules [62–64] or adding silica at a Au/ $\text{TiO}_2$  interface [65].

However, other factors are responsible for the low durability of gold catalysts under CO oxidation conditions. In particular, the high reactivity of hydroxyl-terminated surfaces towards  $\text{CO}_2$  results in the formation of carbonate-type species which poison the gold-support interface, block the doping effect of OH groups in oxygen activation and thus also result in loss of activity [66]. We have recently considered stabilizing Au NPs on OH-free surfaces and on commercially available  $\text{CH}_3$ -terminated silicas in particular. Since all methods developed so far for the preparation of gold catalysts had been exclusively designed for O- and OH-terminated supports, we proposed in 2012 a novel approach inspired by the studies on sub-nanometric Au NPs. In this straight-forward, one-pot method,  $\text{AuPPh}_3\text{Cl}$  is chemically reduced by  $\text{NaBH}_4$  in the presence of the hydrophobic support [67]. This approach is intermediate between sol immobilization (reduction in the absence of the support) and grafting (reduction of a grafted species); it allows both species, those free in solution and those somehow interacting with the surface, to be reduced and to react at any stage of the reduction with the methyl-terminated surface. It yields 3 nm Au NPs with highly durable activity in CO oxidation [68]. This catalyst is also more selective than reference gold catalysts when the oxidation of CO is performed in the presence of hydrogen [68].

We recently extended this approach to stabilize Au NPs over highly graphitized, unfunctionalized few-layer graphene [69]. We managed to obtain smaller Au NPs than those obtained over OH-functionalized carbon surfaces [70], by methods relying on  $-\text{OH}$  functions as anchoring points [71,72]. Hence, while functionalization of the support has been unilaterally used to facilitate grafting of the catalytic or pre-catalytic function, and sometimes directly reduce the gold precursor at the support surface [73], its impact on Au NP growth has been overlooked. Less functionalized supports may open up interesting alternatives in terms of efficient Au NP size-control. Tuning synthesis conditions has already proven powerful in the template-free size-controlled design of other nanomaterials [74].

#### 5. Limitations of the current methods and future developments

Due to the low melting point of gold and the resulting high mobility of gold atoms and particles over a surface, the methods for preparing gold catalysts are highly sensitive to any variation in the conditions, probably more than any other metals [75]. They are clearly support-specific: applying the same conditions to two different supports generally yields different gold dispersions. Differences in size and loading can be observed. Each method has thus to be adjusted to the chemistry of the support surface. Some of them simply fail to yield catalytic dispersions of gold over some supports. Direct anionic exchange for example leads to 2–3 nm Au NPs over alumina, titania, zirconia and ceria, but the parameters of the ammonia wash need to be adjusted in order to achieve such a result and different loadings are thus obtained over the various supports [76]. Besides, DAE fails to produce Au NPs smaller than 4 nm on silica, contributing to the low reactivity of these catalysts [55]. Sol immobilization/colloidal deposition produces Au NPs for which the average particle size depends on the nature of the oxide, doped-oxide or mixed oxide and, for a given oxide, on the nature of the crystallographic phase of the oxide [77,78]. The particle size can vary from 2.3 to 5.2 nm (at maximum loading), while maximum gold loadings vary from 0.3 to 1.7wt.%. This clearly highlights the influence of the surface chemical and structural nature on the deposition mechanism. Although gold sols may be monodisperse in size when in solution [79], the reaction with the support surface often destabilizes the sol and immobilization will subsequently depend on the affinity of the surface with the protecting agent. Hence, at a given reaction time for example, sol immobilization may produce Au NPs of similar sizes over various supports (e.g., activated carbons, titania, zirconia, zinc oxide and alumina), but not at the same loading [80].

Hence, for a given support, one given Au NP size/loading target can often be achieved by only one method. For each given support, the method for the preparation of a gold catalyst has thus to be carefully selected. Although some methods (such as sol immobilization) may be considered applicable to a larger number/variety of substrates/supports than others (e.g., deposition-precipitation which is limited to materials with IEP  $>5$ ), fine differences between

particle size distributions have to be highlighted, as they tremendously impact catalytic activity. There is currently no versatile method for the preparation of gold catalysts and, given the intrinsic/specific properties of gold, the development of such method remains quite illusory.

Innovation in bottom-up gold catalyst preparation can be expected from the further development of support-specific methods, i.e., from the rational design of tailor-made gold catalysts. The new target materials should take into account more factors influencing each aspect of the catalytic function of the material, i.e., activity, durability, and, when applicable, selectivity. For example, durability has been shown to be affected by the growth of Au NPs (and subsequent loss of the active phase) under reaction conditions. Most approaches to more durable gold catalysts have thus focused on stabilizing the gold dispersion, i.e., maintaining Au NP size distribution, throughout the reaction. In most cases however, gold catalysis is highly assisted by the support, in a concerted mechanism, so that the reactivity of the support, i.e., the stability of the support surface, under reaction conditions should not be underestimated. Hence, the support should be carefully selected, not only for its ability to stabilize high dispersions of gold, but also for its resistance against/inertia under the reaction conditions considered. From this perspective, ways of stabilizing catalytically active Au NPs over OH-free supports should continue to be sought. As OH groups are generally used as sites for firmly anchoring gold species prior to their reduction into Au NPs, new interactions between the gold precursor and the surface should be investigated, possibly considering other gold precursors than  $\text{HAuCl}_4$ . Besides, interactions of these chemically different surfaces with the already available preformed, ligand-protected Au NPs will need to be evaluated; nature of the protecting agent might require adjusting.

Methods providing control over the type and quantity of heteroelements introduced, or allowing to selectively introduce gold, should be investigated in order to clearly distinguish between gold catalysis and doped catalysis [81], as has been done for Pt catalysis [82,83]. The presence of varying amounts and types of heteroelements has indeed been identified as one likely cause of the recurring issue of reproducibility and of the generalized use of the limited number of reference gold catalysts available (World Gold Council) [84]. Heteroelements such as halides have also been identified as detrimental to the stability of gold dispersions [85]. New synthetic strategies should provide control not only on the initial dispersion of gold over a given surface, but also on the overall chemical composition of the surface (including element interaction and interfacing), in order to, e.g., find more durable dopants for gold than terminal OH groups. That way, a more complete solution to the sustainable preparation of active, selective and durable gold catalysts can be found.

These new methods should take into account the efficiency of transformation of a precious and scarce metal such as gold into a catalytically active phase. It might thus be useful to systematically quantify how much gold is integrated into the catalyst as compared with the amount of gold allowed to react with the support surface, in terms of, e.g., deposition yields. The use of more concentrated starting gold solutions would make the new preparations

viable and scalable. Ultimately, these new methods should offer new catalytic phases in order to overcome existing challenges in a more efficient way, develop the new-born reactions [86–88] as substituents for less green processes [89], and ultimately tackle the new catalytic and energetic challenges facing the 21st century. In this regard, and considering the extensive knowledge gathered/compiled over the years in the structure-sensitive gold-catalyzed oxidation of CO, this reaction is now mature to be used as a probe reaction and to draw structural information on gold materials from their catalytic behavior.

## 6. Conclusion

Evolution in the preparation of gold catalysts has been synchronous with the evolution of the understanding of their catalytic properties in low temperature CO oxidation. After discovery by serendipity of the catalytic activity of Au NP-oxide nanocomposites by serendipity, rationally designed methods of preparation have first targeted low loading oxide-supported Au NPs, in which gold can be seen as a mere dopant of the redox support. Methods have subsequently been designed to prepare more loaded catalysts in which the support can be seen as a dopant of Au NPs. Finally, the now well-documented, well-established Au NP size effect has opened up new opportunities in the design of gold catalysts. New approaches have only started to emerge. Hence, despite the abundant existing literature on gold catalysis, Au NPs might not have revealed their full potential yet. However, revealing this potential might not arise simply from the introduction of existing catalytic phases into new reactions and new reaction conditions. New gold catalysts need to be designed, in particular catalysts containing smaller Au NPs (i.e., higher dispersions of gold), more stable Au NPs and other gold co-catalysts (i.e., other supports and dopants). In this perspective, surface and modeling studies [90] might prove inspiring to define the new targets. New preparation methods should subsequently be developed in order to produce the targeted materials. Inspired by established strategies for catalyst/nanomaterial preparation, they might gain in integrating innovative ways of controlling Au NP growth and Au NP size, engineering new metal-support interactions by tuning the support/matrix morphology, geometry, structuration, nature and by considering other gold precursors and other synthesis conditions (in particular new ways of reduction and activation, via e.g., physical processes such as microwaves, plasma, radiowaves or photons [91]). Low temperature applications should be the priority target, given the intrinsic properties of gold and gold nanoparticles and the energetic challenges facing the 21st century. In particular, the focus on thermal stability might gain to evolve towards stability under reaction conditions. Besides, improving this stability should not be restricted to finding more appropriate reaction conditions; the reasons for low stability must be integrated in the catalyst design in order to produce an intrinsically more stable material. Rational, application-driven catalyst design is required to complete the serendipity approach proposed by the ever growing high through-put techniques and in order to be a source of innovation in the gold catalysis field in the coming years.

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