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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A B S T R A C T

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].

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 Co_3O_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 O_2 and CO. In particular, 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, TiO_x, and 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 Au/Al_2O_3 catalysts could be as active as Au/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 Au/Al_2O_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 Au/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 $HAuCl_4$, $Fe(NO_3)_3$ and a base (sodium carbonate), which led to a