What restricts gold clusters reactivity in catalysis and gas sensing effects: A focused review

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ABSTRACT

The conditions under which the gold nanoclusters may exhibit enhanced reactivity when used in gas sensors and catalysts were analyzed. The methods used for the formation of gold nanoclusters and shortcomings of these methods were also shortly considered.

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1. Introduction

Considerable interest to the study of gold clusters appeared after works of Haruta et al. [1–3], who showed their enhanced catalytic activity. However, it should be noted that the first mention of the unusual catalytic activity of the gold nanoparticles (AuNPs) have been made in the work performed by Parravano's group [4–6]. Studies carried out by Parravano's and Haruta's groups showed that the nanoparticles of noble metals such as Au, deposited on the surface of the metal oxides become very reactive and catalytically active in the reactions such as CO and H_2 oxidation. For example, in this case a reaction of the CO oxidation occurs at an increased rate at significantly lower temperatures than when using the conventional catalysts [7]. In several experiments the CO conversion was observed even at such extremely low temperature as $-70\ °C$ [1,8]. As a result, at present one can find a lot of published papers describing both the formation of gold nanoclusters on the surfaces of various metal oxides such as TiO_2, SnO_2, WO_3, In_2O_3, ZnO, Fe_2O_3, NiO, CO_3O_4, CeO_2, ZrO_2, and the possibility of AuNPs use for improving the performance of the catalysts designed for processes such as water–gas shift reaction, alcohol oxidation, the reduction of nitrogen oxides, organic synthesis, low-temperature epoxidation of olefin, propylene and propene, complete oxidation of hydrocarbons, etc. [9–15], various biomedical applications [16–18], and gas sensors design [19–25].

However, the same experiments have shown that even the use of gold nanoclusters is no guarantee of achieving extraordinary parameters of Au-based catalysts and gas sensors. It turned out that the achievement of enhanced low-temperature catalytic activity of gold nanoparticles is possible only if several specific conditions, related to the size of AuNPs, the state of gold in the cluster, and the properties of metal oxide support used for Au-based catalyst design, are fulfilled.

2. Parameters controlling reactivity of gold clusters

Detailed analysis of results obtained in the field of designing Au-based catalysts and gas sensors allowed us to formulate and summarize the most important parameters controlling reactivity of gold clusters. From our point of view, they are as follows:

Firstly, for forming Au-based catalysts, active at low temperatures, gold clusters should have size 2.5–3.0 nm [2,7] or smaller [26]. For example, Fu et al. [27], studying Au/CeO_2 catalysts for water–gas-shift reaction, have supposed that high reactivity of the Au/MeO_x system could rather be due to the presence of adsorbed single Au atoms than metallic AuNPs. Molina et al. [28] have also found that the Au atoms on the TiO_2 surface can be very active for the CO oxidation. In addition, these particles or atoms should be uniformly dispersed on high surface area oxide supports without aggregation.

Secondly, for activation of the MeO_x/Au system it should be annealed at a temperature of 100–200 °C. At lower and higher temperatures, the activity drops sharply [29]. For samples prepared using a

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co-precipitation method, the permissible temperature range can be increased up to 300–400 °C [2].

Thirdly, a number of studies have shown that gold in the cluster should be present in both ionic and metallic states [30]. Just such a situation is realized in the Au/MeO$_x$ samples after calcination at 200 °C [31], including Au/SnO$_2$ system [29]. This T_{cal} corresponds to maximal activity of Au/MeO$_x$-based catalysts. XPS study of the samples with low catalytic activity (T_{cal} > 300–400 °C, d_{Au} > 6 nm) has shown that Au was only in a metallic state (Au^0). Wagner et al. [32] have also found that Au$^+$ species were more active than Au^0 particles.

Fourthly, the selection of appropriate support oxides is also required. It was found that gold becomes active only on a suitable substrate. For example, Haruta et al. [2] have established that for the Au/Al$_2$O$_3$ catalysts prepared by the co-precipitation, the $T_{1/2}$ value for the CO oxidation is much higher than those for Au/α-Fe$_2$O$_3$, Au/Co$_3$O$_4$, Au/NiO, and Au/SnO$_2$ even though the crystallite size of Au is similar in all cases, i.e. Au clusters are more active on conductive support. The same effect was also observed for other reducible and nonreducible metal oxides [33–35]. This means that a synergistic mechanism occurs at the AuNP–metal oxide interface, which with the conductive oxide support becomes part of the catalytic process. In other words, such behavior of the Au/MeO$_x$ catalysts suggests that the catalytic reactions involving gold occur on the surface of the substrate or at the interface of Au/MeO$_x$ structures. Apparently, conductive metal oxides such as Fe$_2$O$_3$, CeO$_2$, TiO$_2$ or SnO$_2$ are "active" supports in reactions due to their high oxygen storage capacity and well known catalytic and redox properties.

Fifthly, metal oxide support should be fine dispersed with large surface area and good crystallinity. However, at that metal oxide must have a sufficient concentration of oxygen vacancies. It was established that gold atoms prefer binding to oxygen vacancies [11,36,37]. In addition, it was suggested that for reducible oxides, the presence of oxygen vacancy defects either improves O$_2$ trapping by the support [38,39], or provides the change of the charge state of the Au nanoparticles [40]. Apparently, the grain size in metal oxide support should also be in the nanometer range. In experiments demonstrating maximal activity of Au clusters on the metal oxide the size of metal oxide crystallites did not exceed 5 – 6 nm [29]. The latter assumption is justified, because oxides with such small crystallite size perform chemistry that does not take place on a more coarse material with the same chemical composition. For example, the smaller metal oxide nanoparticles may supply more active sites and contribute to the strong interaction between gold and nanocrystalline metal oxide.

Sixthly, the substrate must be resistant to sintering, should promote the activity conservation of AuNPs located at the right places, and to prevent their agglomeration.

Seventh, the conditions of gold clusters forming should provide strong interaction of AuNPs with substrate [2]. For example, there is an assumption that Au/TiO$_2$ to become active for the CO oxidation, the Au atoms should replace Ti atom on the surface of TiO$_2$ [41]. To achieve high activity, electron transfer on the gold cluster is also desirable. Many works indicate that the activity of gold clusters in this case is much higher. Moreover, in the literature it has been proposed that exactly the transfer of electrons from oxygen vacancies on the Au clusters makes them active as oxidation catalysts.

Naturally, the realization of all these conditions is challenging enough. Gold has very low melting temperature, poor sublimation energy, and very low Tammann temperature [42]. Therefore, gold clusters are characterized by high mobility; the preparation method and pretreatment conditions strongly influence their properties, and the gold cluster reactivity strongly depends on the variety of factors, including ensemble effects, metal nanoparticles functionality, etc., which can easily be changed during the reaction [2,43]. For example, Kemper et al. [44] have shown that the mobility of the Au atoms strongly depends on the surface

hydroxylation and parameters of previous substrate's thermal treatment.

In addition, it was found that high active state is not stable. Frequently, the activity is of only short duration. Even at near ambient temperature the Au/SnO$_2$ catalyst loses activity after several hours of use [45]. It has been suggested that the observed changes are associated with the growth of the gold clusters size occurring even at such low temperatures [46,47], and with formation on the surface of gold clusters and metal oxide support of unreactive stable species such as carbonate and bicarbonate ions [48], which somehow inhibit the reaction via blocking sites at the surface of support essential for achievement high activity. There is an assumption that a virtually complete reduction of the gold to Au^0, i.e. the reduction of cationic to zero-valent metal could be also responsible for the lost of the activity of Au-based catalysts [45].

3. Approaches to Au nanoclusters forming and their limitations

The experiment showed that for the forming of gold nanoclusters on the metal oxide surface can be used a variety of methods. For example, AuNPs can be prepared using various physical deposition methods such as evaporation, sputtering, laser ablation, discharge plasma synthesis [19]. Methods of deposition from gas phase such as chemical vapor deposition (CVD) can be also used for Au nanoclusters forming [49]. However, physical methods as well as CVD method are rather expensive. In addition, they have significant limitations in the formation of clusters on the developed surfaces. This limitation is especially important for applications in gas sensor design, where the use of materials with high porosity and high surface area is a prerequisite [50]. Wet chemical methods have no such constraints and therefore recently they began to attract a lot of attention. The Turkevich–Frens method [51], the Brust–Schiffrin method [52] and some other methods based on the reduction of gold (III) derivatives one can find in the literature [19]. However, analysis of the literature showed that as a rule, wet chemical methods are being used for synthesizing the gold colloidal nanoparticles with size usually varied in the range from 10 to 150 nm. Reduction of their size as well as the transport of these particles on the surface of the metal oxide requires special approaches [53–55], which sometimes creates difficulties.

Impregnation, conducted by the synthesized powders dipping in metal salt solution with following reduction, simplifies the manufacturing technology of the Au/MeO$_x$-based catalysts and gas sensors. However, conventional impregnation methods hardly allow taking full advantage of the enormous surface areas of mesoporous supports. Moreover, impregnation methods do not provide the level of control over the nanoparticle properties required to optimize their catalytic performance [2,56]. In particular, due to agglomeration, gold in the Au/MeO$_x$ catalysts was obtained only as large particles, usually above 10 nm in diameter. It was found that the reduction of the AuNPs size can be achieved by the addition into a solution of surface-active additives, various ligand molecules, which form self-assembled monolayers on the AuNP surface and thus stabilize the nanoparticles size [57,58]. Typical ligand molecules for AuNPs are phosphines, amines, thiolates and other sulfur-containing organic reagents. However, it was found that additives used for the AuNPs size stabilization are toxic and are the source of sulfur and other impurities, which together with chlorine ions from common precursor HAuCl$_4$ may be incorporated in the synthesized AuNPs and adversely affect their functional properties. Another problem with the AuNPs synthesis, when mentioned above approaches are being used, is the removal of organic molecules of surfactants from the layer of gold nanoparticles. As a result, there are difficulties with controlling both the cluster size, and the adhesion of coatings formed. In addition, capping agents can also hinder the