Int. J. Bio-Inorg. Hybr. Nanomater., 8(3): 125-133, Autumn 2019

# Activation Strategies for Enhancement the Catalytic Activity of Gold Nanocatalysts

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Received: 2 Jun 2019; Accepted: 5 August 2019

**ABSTRACT:** Recent advances in nanoscience have led to the development of numerous methodologies for controlled synthesis of mono dispersed nanoparticles and/or nanoclusters via surface stabilization by organic capping ligands. The application of these nanoparticles in catalysis and other fields often requires the removal of organic ligands. It is known that the removal of organic capping agents or organic residues on gold nanoparticles is necessary for achieving high activity of the catalyst and should ensure the particle remains isolated on the surface without agglomeration. The nanoparticles are deposited on a support and the stabilizing ligands-capped metal particles are then removed to activate the catalyst because in the surface chemistry, clean metal surfaces are more active than “dirty” surfaces, which are passivated by organic fragments. There are many ways to activated supported noble metals particles or clusters like gold including washing procedure, heat treatment, combination of washing procedure and thermal treatment, plasma, ozonolysis and permanganate or even potassium manganite. The gold nanocatalysts activation helps to determine both the physical and chemical nature of the active species and can play an important role in controlling the activity and the selectivity of supported noble metals nanoparticles and nanoclusters.

**Keywords:** *Heat treatment, Ozonolysis, Permanganate-potassium manganite, Plasma, Washing procedure.*

## INTRODUCTION

Ligands are commonly used to protect metal nanoparticles during synthesis, but their presence can be detrimental to catalytic activity [1] because they shield the gold cores from the reactants [2, 3]. However, recent researchers have found that the presence of ligands is essential for the catalytic activity of some metal particle systems. Jin *et al*. demonstrated that the core/shell nature of the thiolated gold clusters is primarily responsible for their catalytic activity and that thermal treatment should be avoided because it can decompose the gold catalyst structure [4]. As-made clusters and colloids could, in principle, be used as homogeneous catalysts even without ligand removal; such systems would suffer from problems with aggregation due to exposed active sites and recyclability. Immobilization of chemically made nanoparticle precursors onto truly heterogeneous supports opens pathways toward fabrication of better catalysts. Many factors affect the

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catalytic activity of gold nanocatalysts, and several key studies have demonstrated the importance of better understanding the effects of the catalyst activation treatment conditions [5]. Although activations can be used to remove organic residues from gold particles, they can also cause an increase in particle sizes [6, 7]. Key problems that may emerge from the removal of the stabilizing ligand include the loss of stability and sintering of the particles on the support. Lopez-Sanchez *et al.* improved the catalytic activity for benzyl alcohol oxidation of gold catalysts by removing polyvinyl alcohol (PVA) ligands. However, TEM images showed that the gold particles aggregated after the catalysts' activation, increasing size from 3.0 to 4.8 nm diameter [1]. Catalytic enhancement of gold catalysts arises from the interplay of several factors: a) removal of the stabilizing ligands, permitting access of reagents to the active sites at the surface of supported gold particles; b) establishment of a direct interaction between metal nanoparticles and support; and c) changes in size of the particles following ligand removal [1, 8-10]. In this paper the impact of different types of activations including washed with a solvent (i.e., toluene or NaOH in MilliQ water) and/or heated in different atmospheres (i.e., $O_2$, $H_2$, vacuum, $O_2$-$H_2$ and static air), ozonolysis procedure, permanganate or potassium permanganate and plasma are disused on the catalytic activity of gold catalysts.

## ACTIVATION METHODS

It is generally assumed that ligand removal is relatively crucial for good control of the particles size of supported gold nanoparticles [11]. Consequently, the activity of gold nanocatalysts is likely to depend on the type of treatment [12]. Here, some methods reported for activation of supported gold particles/clusters in the following sections:

### *Washing procedure*

Washing procedures are used to remove organic ligands (e.g., $PPh_3$ and PVA) or impurities from supported metal nanocatalysts [1,10,13]. Solvents can be used to remove ligands establishing equilibrium between free (solvated) and coordinated ligands. The most effective washing procedures appear to depend on the type of the solvent. Previous researchers have studied the effects of the activation temperature and the type of solvent used in ligand-removing washing procedures on the catalytic activity of gold particles [1, 13-15]. For instance, Lopez-Sanchez *et al.* investigated the efficiency of water, tetrahydrofuran (THF) and ethanol (as solvent) in removing PVA from supported gold catalysts by washing procedures at 90 °C for 60 min. They used Raman spectroscopy to demonstrate the removal of PVA and TEM images to monitor changes in the particle sizes [16]. Washing treatment with water changed the average particle diameters from 3.0 to 4.8 nm and led to the formation of an active gold catalyst that demonstrated high conversion (100%) in CO oxidation. However, no conversion was observed when the gold catalyst was washed in THF or ethanol [1]. Additionally, Qi *et al.* investigated the effect of washing procedure on the stability of gold particles deposited on Ti-doped nonporous silica. The non-washed catalyst was less stable and more inclined to particle coagulation than the washed catalyst. In addition, the activity and selectivity of the washed catalysts after storage in air at room temperature for 4–6 months was comparable with that of a freshly the washed catalyst [17]. Later, Anderson *et al.* used toluene as a solvent (at 100 °C for 2 h) to wash supported gold particles/clusters. They removed $PPh_3$ ligands to improve gold particles/clusters interaction with $TiO_2$ support [10].

### *Thermal treatments*

Thermal treatments of gold nanocatalysts can result in better interaction between the gold species and the support, and so change the catalytic activity of gold catalysts [18]. Thermal treatment processes in the presence of a specific chemical atmosphere have also been applied to remove impurities or ligands from supported metal nanoparticles like gold and rhtinum nanocatalysts [1,7,13,16,19] and to improve the strength of the contact often deemed necessary between the gold nanoparticles and underlying support [15,20]. Variations in heat temperature permit a range of conditions for removal of the ligands from the catalyst surfaces [17,13,21,22], and may have a pronounced effect on the properties of the final material [7]. High-temperature heat treatment has been widely used to remove organic ligands, but its main drawback is the facile sintering of metal particles. Yin *et al.* showed that the size of gold particles supported on silica ($Au/SiO_2$) increased from 2.1 nm (as-synthesized) to 3.3, 4.5 and 4.8 nm after the calcination in $H_2$ reducing atmosphere at 300, 500 and 600 °C, respectively. The gold catalysts heated at 300 °C showed CO oxidation with 100% conversion [23]. Hence, a significant decrease in the gold catalyst activity can be related to the gold particles sintering at high calcination temperature [24]. Chang *et al.* reported a detailed investigation into the effect of thermal treatment at temperatures from 100 to 475 °C on 2.0 wt% gold catalysts supported on $Mg_2AlO$, made by a co-precipitation method. They showed that the gold catalysts heated at 100 °C are the most active in CO oxidation [25].

Thermal treatment at mild temperature is preferred for fabrication of structure-sensitive gold catalysts because higher temperatures generally lead to more particle agglomeration [13,16,26-30]. The improvement in catalytic activity of gold catalysts demonstrates that low-temperature heat treatment is beneficial for gold particles immobilized on a support. Wang *et al.* studied the effect of heat treatment temperature on the catalytic activity of supported Au particles for benzyl alcohol oxidation. They showed that the mean particle diameters increased from 2.5±0.7 to 2.6±0.7, 2.7±0.8, 3.9±1.2 and 7.9±2.7 nm when the gold catalysts were heated at 100, 200, 300, 400 and 500 °C; the corresponding benzyl alcohol conversions were 92%, 92%, 94%, 84% and 54%, respectively [31]. Pritchard *et al.* studied the effect of (air) thermal treatment temperature on the catalytic activity of carbon-immobilized Pd-Au particles in benzyl alcohol oxidation. The mean particle diameters increased from 2.7 (as-synthesized) to 5.3, 9.4 and 27 nm when the catalysts were heated at 200, 300 and 400 °C, respectively. Heat treatment at 200 °C significantly improved the catalytic activity, but further increases in the calcination temperature, especially over 300 °C, led to a very significant decrease in the catalytic activity of gold catalysts [32]. The challenge remains in selecting an effective thermal treatment temperature for good contact between the gold particles and the support, without inducing significant sintering.

Thermal treatment often improves the activity of gold catalysts that demonstrate low activity in their untreated form [16]. By heating procedure, the stabilizer ligands are removed from the gold clusters/particles and are deposited on supports surface, while the gold clusters/particles cores are either partially or fully [9,13,16]. Strong contact between gold and the underlying support may sometimes be achieved via thermal treatment, normally at temperatures below the melting point of the reactants and products [15,20]. It has been reported that the chemical nature of the atmosphere used during heat treatment can exert an influence on the final structure and catalytic activity of the supported gold particles [30,33,34]. Overall, thermal treatment of the gold catalysts under different atmospheres (i.e., in $H_2$, $O_2$, $O_2$–$H_2$ or air) can significantly affect the catalytic activity. Therefore, the type of thermal treatment (i.e., in static air, O2, H2, inert gas, $O_2$–$H_2$ or under vacuum) will be discussed for supported gold particles as following:

### *Thermal treatment in static air*

Thermal treatments in oxidative atmospheres, such as air can remarkably improve the catalytic activity of gold catalysts [16,18,35]. Yuan *et al.* heated supported $[Au(PPh_3)(NO_3)]$ and $[Au_9(PPh_3)_8]_3$ in air flow and tested the resultant materials as catalysts for low-temperature CO oxidation, with $PPh_3$ ligand removal confirmed by a Fourier-transform extended X-ray absorption fine structure (EXAFS) oscillations technique [35]. Based on X-ray diffraction (XRD) and TEM images, they proposed that better contact was established between the gold catalysts and reactants. However, the air treatment invariably led to substantial particle growth, from ~1 to 25 nm diameter, following ligand removal [36]. Additionally, Haruta *et al.* demonstrated enhanced activity, after high-temperatures air heat treatment, for a mixture of colloidal gold particles with $TiO_2$ powder as a support, which they attributed to a stronger metal-support interaction [37]. Air thermal treatment can also rid the surface of contaminant from the support or precursor materials [7]. However, it invariably leads to the substantial particle size growth following ligand removal [6,16].

### *Thermal treatment in oxygen gas*

Thermal treatment performed in an oxygen-rich atmosphere facilitates ligand removal by partial or complete oxidation [9,13]. Overall, it can be substantially more effective at removing ligands than reductive or inert processes even at high temperatures [38]. However, it can also improve the catalytic activity by surface restructuring and formation of subsurface oxygen species providing an oxygen-enriched interface with an enhanced metal-support synergy [39,40]. Reaction steps involving oxygen can be more effective on gold sites present on larger and smoother gold particles [41]. This proposal agrees well with the observed higher initial activity of oxidatively activated gold nanocatalysts with fewer surface-stabilizing ligands due to ligand decomposition [26].

### *Thermal treatment in hydrogen gas*

Hydrogen gas treatment can reductively detach stabilizer ligands from the gold particles/clusters with subsequent re-deposition onto the support surface [13,39]. However, it can lead to the formation of metallic gold [40]. For this type of heat treatment, the temperature is crucial to the catalytic performance in organic compounds oxidation [42] because of its influence on the size and structure of resulting metal particles [39]. Lopez-Sanchez *et al.* investigated the effect of heat treatment in hydrogen gas at 200 °C on the catalytic activity of supported gold nanoparticles for CO oxidation. The result confirmed very low activity of the heated gold catalysts [1], because the reductive treatment processing led to large particles sizes in comparison with the oxidative treatment [26]. However, Bulushev *et al.* found that the supported gold nanoparticles can be active catalysts for CO oxidation if the hydrogen calcination is performed at high temperatures in the range 400–500 °C [7]. Additionally, untreated Au/$TiO_2$ demonstrated no conversion in benzyl alcohol oxidation; but conversion increased to 43% when the catalysts were heated in hydrogen gas at 300 °C for 3 h [33]. It was proposed that better contact was established with partial removal of PVC ligands, an idea that was supported by laser Raman spectroscopy and TEM images. The TEM images also showed an increase of gold particle diameters from 3.0 to 6.1 nm after this procedure [1].

### *Thermal treatment under vacuum*

Thermal treatment under vacuum can lead to oxidation of the gold clusters/particles, most likely via interaction with the support surface after removal of ligands [13]. The stabilizer ligands are removed from the gold particles/clusters but remain in an oxidized form on the surface and their removal leads slightly to agglomeration of the gold particles/clusters [43]. Supported gold clusters exhibit Au–O bonds, coincident with the loss of phosphine ligands and formation of oxidized phosphorous species [9]. For example, Turner *et al.* reported that the removal of ligands by vacuum heat treatment can significantly increase the activity and selectivity of gold nanoparticles with diameters of around 1.5 nm or smaller. The authors used heating at 200 °C under vacuum for 2 h to remove $PPh_3$ stabilizing ligands from Au particles immobilized on silicon dioxide, carbon or boron nitride. Diminution in the intensity of the phosphorus signal in the EDS was used to confirm the success of ligand removal. In the case of low loadings (0.6 wt%), only minor aggregation occurred, but high loadings (6.0 wt%) resulted in pronounced aggregation to larger (3.0 nm) catalytically inactive particles. These results showed that this type of heat treatment is promising for better exposure of some gold catalysts to reactants [44]. After that, Anderson *et al.* investigated thermal treatment under vacuum at 200 °C, of gold nanoparticles and nanoclusters including $Au_8$, $Au_9$, $Au_{11}$ and $Au_{101}$ immobilized on $TiO_2$ by using a synchrotron-based XPS study. Their result confirmed that $PPh_3$ removed from the nanoparticle and became bonded (possibly in oxidized form) to the support surface, resulting in an increase in the phosphorous high-binding energy peak (P-HBP) signal in the XPS. They confirmed that $PPh_3$ was partially removed from the gold catalysts causing improvement of the catalytic activity because of better interaction of the gold particles with the support [10].

### *Thermal treatment in an inert gas*

Thermal treatment in inert atmospheres, such as dry nitrogen, argon and helium can exert influence on the final structure and activity of the supported gold catalysts because the metal particles do not induce additional growth after thermal treatment [40,45-47]. However, in catalyzed reactions by some supported metal particles, like gold particles immobilized on titanium dioxide, it is necessary to increase slightly the gold particles size to be an active catalyst because of better contact between the metal particles and the support [37]. More recently, researchers have shown that thermal treatment an inert gas cannot improve the catalytic activity of gold nanocatalysts. Negligible or even no conversion for organic compounds using activated gold nanocatalysts by an inert gas has been reported; supported gold nanoparticles heated in dry nitrogen demonstrated low activity for CO oxidation to $CO_2$ [1].

### *Thermal treatments in oxygen gas followed by hydrogen gas*

Combinations of oxygen and hydrogen thermal treatments can integrate the advantages of both treatments [13,18]. Hydrogen reduction following oxygen treatment can induce dispersion of metal particles and form partly reduced oxygen-containing particles, which would be active sites for oxidation of organic compounds. Thermal treatments can reduce metal oxide to metallic particles which then readily disperse into the supports [39]. However, this type of thermal treatment can lead to the complete detachment of the stabilizer ligands from the gold particles/clusters and their redeposition onto the support surface, which causes the gold clusters/particles to fully aggregate [9].

### *Washing procedure and followed by thermal treatments*

The surface exposure and the catalytic activity of gold nanocatalysts can be enhanced by removing weakly adsorbed stabilizer ligands by washing procedure. Follow up thermal treatments are then sometimes used to in order to integrate advantages of different activation treatments [13,16,48]. Lopez-Sanchez *et al.* demonstrated successful removal of polyvinyl alcohol (PVA) as an organic ligand from gold nanoparticles immobilized on $TiO_2$ as a support. They washed the catalyst by hot water (as a solvent) and then heated the supported gold nanoparticles (in static air or 5% $H_2$/Ar at 200 °C for 3 h) to get a high conversion for CO oxidation [1]. Later, Ghadamgahi *et al.* investigated the effect of washing procedure (in hot toluene for 2 h) and followed by heat treatment (in static air at 100 °C for 3 h) on the catalytic activity of derived $Au_{101}$ immobilized on Norit® activated carbon. The result showed that this type of activation can improve the catalytic activity of gold catalysts to full conversion (100%). However, the mean diameter of gold particles increased from 1.64±0.05 (as-synthesized) to 3.05± 0.07 nm after the activation. Additionally, the authors showed that the catalytic activity and selectivity of the activated $Au_{101}$ catalysts after storage in a fridge (approximately -4 °C) for 6 months were comparable with the freshly activated gold catalysts [16].

### *Ozonolysis procedure*

The removal of ligands via a reaction using a stronger oxidizer, like ozone, has been used as an effective treatment with less gold particles' aggregation as well as better catalysts' dispersion and thermal stability. This type of treatment was conducted at a mild temperature (i.e., 200 °C) to avoid the risk of catalyst sintering. The ozone-treated gold catalyst showed normal particle size distributions (i.e., the metal particles did not induce additional growth) and high conversion for CO oxidation [34]. Ozone activation may produce partially oxidized states of gold [49], which could reinforce the interactions between the gold nanoparticles and the support. Even higher activity was achieved when ozonolysis was followed by thermal treatment. The exposure of ozone as a gas to activated carbon supports led to deposition on the carbon surface, transforming basic sites into acid sites. New acid sites were also generated by addition of ozone across double bonds of the carbon structure [34].

### *Plasma*

Plasma is an ionized gas consisting of positive ions and free electrons in proportions resulting no overall electric charge, typically at low pressures (as in the upper atmosphere and in fluorescent lamps) or at very high temperatures (as in stars and nuclear fusion reactors) [50]. Plasma treatments, such as corona discharges, spark discharges, and dielectric barrier discharge (DBD) are activation procedures that can be used remove the capping agents or organic ligands to enhance the catalytic activity of supported metal particles even at atmospheric pressure and ambient temperature [51,52]. They can achieve high metal dispersions and enhance metal-support interaction without the exposure of the material to a high temperature environment [52, 53]. They also provide unique ways to enhance metal support interactions while avoiding the formation of large nanoparticles because the temperature is too low overcome the activation energy for aggregation [53,54]. As an example, supported gold particles were activated using $O_2$ plasma procedure for selective hydrogenation of acetylene at ambient temperature [53].

***Permanganate or potassium manganite***

Permanganate or potassium manganite can activate supported gold particles by partially oxidizing residual organic ligands [23], followed by thermal treatment at high temperature (at least 300 °C). $KMnO_4$ or $K_2MnO_4$ treatment can make the gold catalysts more active under certain conditions, regardless of the support chosen and the size of gold nanoparticle [55]. In addition, the treatment with $KMnO_4$ can remove the functional organic ligands with minimal sintering of particles [23]. However, $KMnO_4$ or $K_2MnO_4$ can react with some supports like carbon [56].

## CONCLUSION

Ligands are commonly used to protect gold nanoparticles during synthesis, but their presence can be detrimental to catalytic activity because they shield the gold cores from the reactants. Activation of supported gold particles or clusters proved to be a counterproductive process for the removal of the stabilising ligands from the gold nanocatalysts. Although thermal treatments can be used to remove organic residues from gold particles, they can also cause an increase in particle sizes. Key problems that may emerge from the removal of the stabilizing ligand include the loss of stability and sintering of the particles on the support. The interaction between the gold species and the support has been investigated by measuring change in catalytic activity with different activation methods including washed with a solvent and/or heated in different atmospheres (i.e., $O_2$, $H_2$, vacuum, $O_2$- $H_2$ and static air), ozonolysis procedure, permanganate or potassium permanganate and plasma. The results proved that the activation procedures to be relatively effective on the improvement of the catalytic activity of the gold nanocatalysts. The chemical nature of the atmosphere used during thermal treatment can exert an influence on the final structure and catalytic activity of the supported gold particles. Additionally, a range of heat treatment temperature permits conditions for removal of the ligands from the catalyst surfaces and may have impacted on the properties of the final catalysts because high-temperature of the heat treatment may be caused by the aggregation of gold catalysts. Hence, heat treatment at mild temperatures (100–200 °C) leads to more active catalysts than if the catalysts were heated at higher temperatures because the thermal treatment at high temperature (>200 °C) may cause a severe sintering the gold particles. A combination of thermal treatment methods of removing the ligands (like phosphine) at a lower temperature was discovered allowing more control over this process so that large particle formation may be avoided. The observed enhancement in catalytic activity arose due to removal of the ligands, permitting access to the active metal sites on the supported nanoparticles, and the size of the nanoparticles following ligand removal. Therefore, this review presented in this paper suggests that structural and catalytic properties of gold nanocatalysts depend on the choice of the activation and the temperature.

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