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Silica-Supported Gold Nanocatalyst for CO Oxidation

Ziyouddin S. Qureshi and EA Jaseer

Abstract

Even though gold is inert in its bulk practice, greatly disseminated gold nanoparticles (Au NPs) with dimensions less than 5 nm have been found to be active for a number of oxygen transfer reactions, particularly for low-temperature CO oxidation. The catalytic activity not only be subject to the particle size of Au but also on the nature of the support and the synthesis method of the catalyst. These factors are frequently inter-related such that their separate contributions cannot be easily unraveled. Also, the activity of a supported Au catalyst is ruled by a complex combination of contributions of the particle morphology, metal dispersion, and electronic properties of the gold. Higher catalytic activity is being observed for Au NPs supported on reducible metal oxides such as TiO_2 , Co_3O_4 , CeO_2 , and Fe_2O_3 . However, silica is an inert, inexpensive, and convenient support that can be shaped into a host of attractive and varied morphologies. In this chapter, the study of CO oxidation catalyzed by mono- and bimetallic Au NPs over various silica supports is discussed in detail.

Keywords: gold nanoparticles, silica supports, mono-/bimetallic gold nanoparticles, CO oxidation, heterogeneous catalysis

1. Introduction

Since the revelation of the earliest inspiring studies [1], catalysis by Au NPs has been in the limelight of chemical research and it has been recognized as a vital tool for a wide range of transformations such as selective oxidations and hydrogenations of organic substrates [2–6], water-gas shift reaction [7–9], acetylene hydrochlorination [10, 11], direct synthesis of hydrogen peroxide [12], reduction of NO to N_2 [13, 14], and the addition of nucleophiles to acetylenes [15]. Particularly, the aerobic oxidation of CO by gold [16] has been a subject of constant exploration, where it plays a crucial role for industry and the environment [17].

Carbon monoxide is a colorless and odorless gas [18]. Due to its high affinity with hemoglobin, it is enormously toxic for humans and animals. Its long-term exposure should not exceed 25 ppm in 8 h, where more and more obvious harmful effects are observed above this limit up to the lethal concentration of around 650–700 ppm. Massive amount of CO is continuously being emitted (1.09 billion tons in 2000), frequently from transportation, power plants, and industrial and domestic doings [19]. CO is also an originator of ground-level ozone, which can cause several severe respiratory problems. Also, it is not well soluble in water ($23 \text{ mL}_{\text{CO(g)}} \text{ L}^{-1}_{\text{H}_2\text{O(l)}}$), which also limits its removal from air by means of aqueous treatments. So its oxidation into CO_2 is a key solution for CO reduction in air

depollution managements. To achieve CO elimination, it is necessary to design catalysts, which permits the oxidation reaction with a sufficient rate.

Au NPs supported over metal oxides demonstrate high catalytic activity for CO oxidation under mild conditions and even below room temperature [20]. Concerning the structure-activity relationship, Au NPs size has been witnessed to play a key role in this transformation, with a finest activity observed for gold clusters in the size range of 2–5 nm [21]. The nature of the support and the way the Au NPs is being prepared and interacted are significant [22]. Till the beginning of the twentieth century, scarce oxides such as hopcalite have been identified to oxidize CO at ambient temperature. Hopcalite is composed of a binary amorphous Mn–Cu oxide, whose texture will get stabilized by the addition of CaO, Al₂O₃, or bentonite clay [23]. Later, several oxides have been investigated and higher catalytic activity are being observed for Au NPs supported on various reducible metal oxides such as TiO₂, [24] Co₃O₄, [25] CeO₂, [26], and Fe₂O₃ [27]. However, silica is an inert, inexpensive, and convenient support that can be shaped into a host of attractive and varied morphologies [28]. Silica-based mesoporous supports have been acclaimed in precise for high surface area, high accessibility of the catalytically active center, and reduced particle sintering [29]. However, it is still challenging to make properly sized, well-dispersed, and uniform Au NPs placed within the nanopores of the material without conceding mass transfer and morphological properties [30]. Gold alloy (bimetallic nanocatalysts) along with other metals such as Pd, Cu, and Ag, also found to exhibit high and exceptional catalytic activity compared to Au alone.

There are few reviews on different facets of gold catalysis [31–37]. This chapter will offer an overview of the different possible methodologies available for the synthesis of silica supported especially mono and bimetallic gold nanocatalyst for CO oxidation. The key advantages or limits for the proposed methods are shortly discussed; in some cases, the most important features of the presented methodologies are highlighted from an industrial point of view.

1.1 Methods to synthesize gold nanocatalyst supported on silica for CO oxidation

1.1.1 Post-synthetic treatment of silica before gold loading

Schuth et al. reported the method for the preparation of an active gold catalyst for CO oxidation, supported on silica, made by a novel solution technique [38]. The surface of SBA-15 was functionalized by treating with positively charged groups, and [AuCl₄][−] species into the channel structure through ion exchange. Later on reduction with NaBH₄, resulted a highly dispersed Au NPs in the channels system of the mesoporous host. This composite material showed a reaction rate of $2.7 \times 10^{-4} \text{ mmol g}^{-1} \text{ cats}^{-1}$ for CO oxidation. The Au NPs to some extent get stabilized by the pore system of SBA-15. Still, the interaction is relatively weak and sintering was observed around 100°C, which was confirmed from TEM images of Au/SBA-15. The authors conclude that a specific interaction between gold and the support is not compulsory for the generation of very active gold-based catalysts.

Datye et al. demonstrated a novel silica geometry, which allows to trap nanoparticles and limit the mobility of species that lead to thermal sintering [39]. Mesoporous silica was prepared by two different methods, spontaneous self-assembly of amphiphilic molecules (batch synthesis) and evaporation-induced self-assembly (aerosol synthesis). To deposit gold inside the pores of mesoporous silica, firstly silica surface was functionalized with organic amine then treated with Au precursor. These reduced catalysts were tested for CO oxidation with 20% CO and 10% O₂ from room temperature up to 400°C. Results showed that the hexagonal structure inside aerosol silica shells support to contain the Au NPs within the pore

structure and protect the active part from gas phase poisons, allowing facile access to gas phase species as related to straight pores in MCM-41.

Datye et al. further investigated the role of pore size and structure in controlling the thermal sintering of Au NPs on mesoporous silica [40]. The phenomenon of sintering of Au NPs is dependent on pore size, pore wall thickness (strength of pores), and pore connectivity. Au was placed on mesoporous silica samples with a varied range of pore sizes and pore arrangements (2-D hexagonal, 3-D hexagonal, and cubic) (**Figure 1**). Later, all catalysts were reduced at 200°C in flow of H₂ and then used for CO oxidation at temperatures ranging from 25 to 400°C. Among all samples, SBA-15 with the thickest pore walls was found most active at regulatory growth of the Au particles.

Mou et al. have prepared the Au NPs embedded within the mesoporous silica's and used as catalysts for CO oxidation [41]. The silane APTS (H₂N(CH₂)₃-Si(OMe)₃) was used for the surface-functionalization of mesoporous silica such as MCM-41, MCM-48, and SBA-15. The catalysts were activated by calcinations and later reduced with H₂ reduction at 600°C. The catalysts were found to be active for CO oxidation, reaching a very high activity values as $7.0 \times 10^{-3} \text{ mmolg}^{-1} \text{ cats}^{-1}$ at

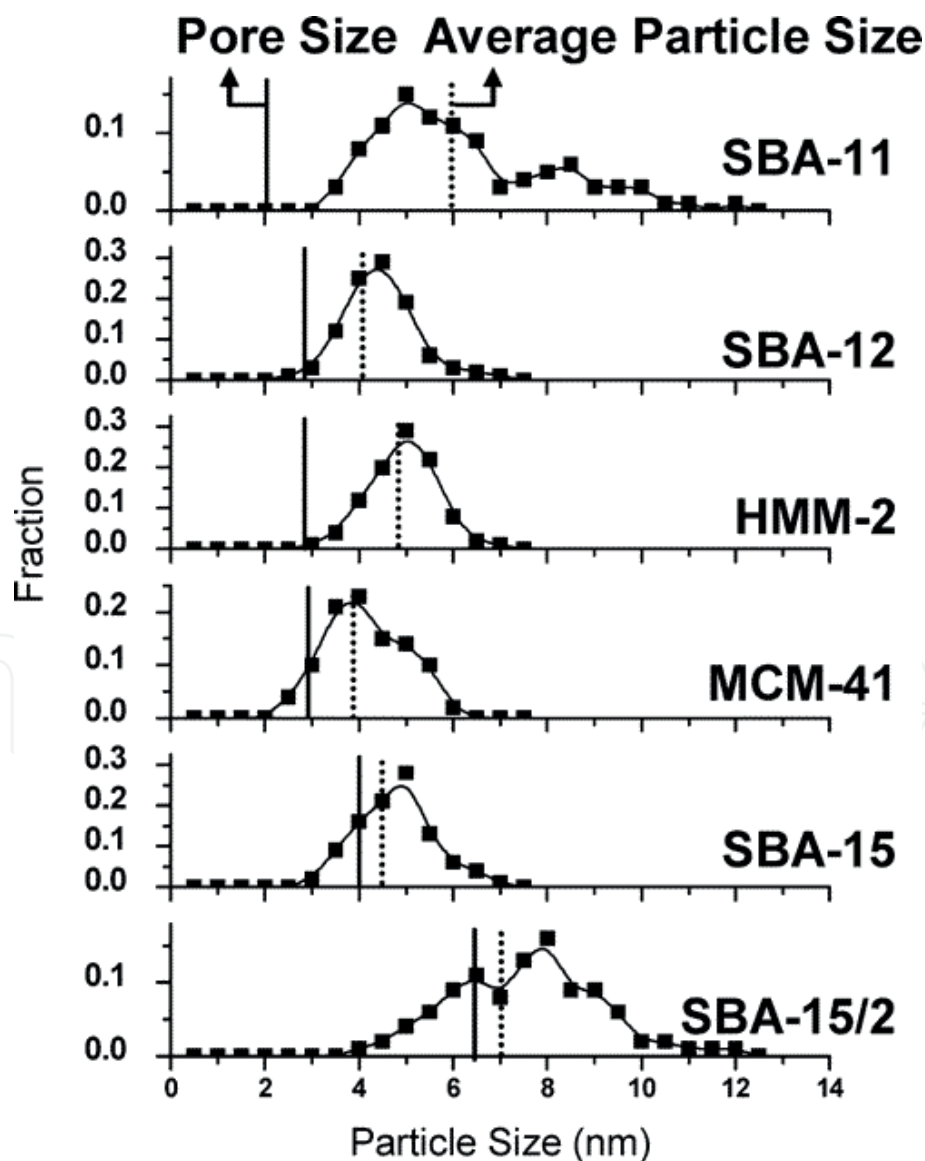


Figure 1. Au particle size distributions after reduction at 200°C for 2 h in flowing hydrogen. Pore sizes of the samples are calculated using BJH theory. Average Au particle sizes are number averages. Reproduced with permission, copyright 2018, American Chemical Society.

80°C as compared to the results from catalysts made with the standard precipitation-deposition method. Studies also recommend that the CO conversion increases with decreasing size of Au NPs.

Rombi et al. [42] have functionalized SBA-15 with new mercaptopropyltrimethoxysilane (MPS) and used for the preparation of supported gold nanocatalyst for the low-temperature CO oxidation reaction. It has been observed that, the presence of organic residues and the size of the Au NPs intensely affect catalytic activity. High temperature calcination (300–560°C) in air followed by treatment (600°C) under H₂ atmosphere only leads to the formation of homogeneously small size Au spherical nanocrystals dispersed inside the SBA-15 channels with average crystal sizes of about 6.5 nm. The catalysts were first calcined at 560°C and then reduced under H₂/He 600°C. Though, regardless of their large particle size, remarkable catalytic activity for CO oxidation was observed, while the as-made catalysts were found to be inactive for CO oxidation at low temperatures. Gold was found mostly in metallic Au(0) state, due to the strong interaction between the mercapto functional groups and Au, positively charged Au^{δ+} species also exist.

SBA-15 functionalization with 3-MPS has been used by Ferino et al. to make a supported gold catalyst for the low-temperature CO oxidation [43]. Catalytic runs were studied by varying different reaction parameters such as atmospheric pressure, temperature 40–150°C, and different thermal treatments of the sample prior to reaction. The catalyst was pretreated toward different thermal treatments, that is, calcination in air, treatment in H₂ atmosphere, and calcination followed by H₂ treatment. It has been observed that, the pre-treatment conditions sturdily affect not only the gold particle size but also the nature of the Au surface species. A substantial catalytic activity for CO oxidation was observed for the catalysts treated at 600°C in H₂/He atmosphere, only after the removal of functionalizing agent by an earlier high-temperature calcination (**Table 1**).

Rombi et al. further slightly modified the procedure for the preparation of silica-supported gold catalyst for CO oxidation by functionalizing the silica surface with 3-MPS, anchoring gold using HAuCl₄ solution, and later reducing it with sodium citrate [44]. Before the catalytic runs, the Au/SiO₂–SH catalyst was submitted to different thermal treatments. It has been achieved a notable CO conversion when the catalyst was calcined in air at 560°C and afterward treated in H₂/He at 600°C or directly treated in H₂/He at 600°C.

1.1.2 Direct synthesis

Lin et al. have studied CO oxidation over Au/SiO₂ and Au/TiO₂ catalysts [45]. It has been found that, after a high-temperature reduction (HTR) at 500°C, TiO₂-supported Au became very active for CO oxidation at 40°C, an order of magnitude

Thermal treatment	Conversion (mol%)		TOF (s-1)	
	40 °C	80 °C	40 °C	80 °C
Air 560 °C	1.85	1.96	1.11. 10 ⁻²	1.17. 10 ⁻²
H ₂ /He 600 °C	0.55	0.87	1.57. 10 ⁻³	2.46. 10 ⁻³
Air 560 °C–H ₂ /He 600 °C	11.60	22.74	7.80. 10 ⁻²	1.53. 10 ⁻¹
H ₂ /He 600 °C –air 560 °C –H ₂ /He 600 °C	21.13	31.47	8.21. 10 ⁻²	1.22. 10 ⁻¹

Table 1.
Catalytic performance of the Au/SBA-15-SH sample for the low-temperature CO oxidation reaction.

more active than Au/SiO₂. However a low-temperature reduction (LTR) at 200°C made an Au/TiO₂ catalyst with very low activity. It has been observed that, a HTR step followed by calcination at 400°C and a LTR step (HTR/C/LTR) provided the most active Au/TiO₂ catalyst of all, which at 40°C 100-fold more active than a typical 2% Pd/Al₂O₃ catalyst and also found to be stable above temperature 127°C, while a sharp reduction in activity was observed with the other Au/TiO₂ (HTR) sample. Besides, the activity of the Au/SiO₂ catalyst was ten-fold higher than the Au/TiO₂ (LTR) sample but ten-fold lower than the Au/TiO₂ (HTR/C/LTR) catalyst. Later, Cl analysis disclosed that the Au/TiO₂ (LTR) sample retained around 50% of the Cl from the Au precursor, while the other three catalysts retained only 16%, which gave a final Cl/Au ratio of 0.5; subsequently, the low activity of the Au/TiO₂ (LTR) sample may be due to its high chloride content. However, the inhibitive role of Cl impurity has not yet been established.

Au catalysts supported over mesoporous silica and titania supports were made by Overbury et al. and tested for the oxidation of CO [46]. Two methods were used for the preparation of silica-supported catalysts using triamine as complexing ligands, which lead to mesoporous silica with wormhole and hexagonal structures. The use of triamine ligands is the essential for the synthesis of uniformly sized 2–3 nm Au MPs in the silica pores. While over mesoporous titania, high gold dispersions were obtained without using functional ligand. It was noticed that, Au supported on titania showed a much higher activity for CO oxidation, even the Au particle sizes were essentially equal on the titania and the wormhole silica support. The results advise that the presence of small size Au NPs (2–3 nm) alone is not very satisfactory to achieve high activity in CO oxidation (**Figure 2**). Instead, the support also impacts the activity through other possible ways such as stabilization of active sub-nanometer particles, formation of active oxygen-containing reactant intermediates (such as hydroxyls or O₂), or stabilization of optimal Au structures.

Effect of moisture on the catalytic activity for CO oxidation over three gold catalysts prepared over TiO₂, Al₂O₃, and SiO₂ supports were investigated by Date et al. [47]. A varied range of concentrations was studied, from about 0.1 to 6000 ppm H₂O.

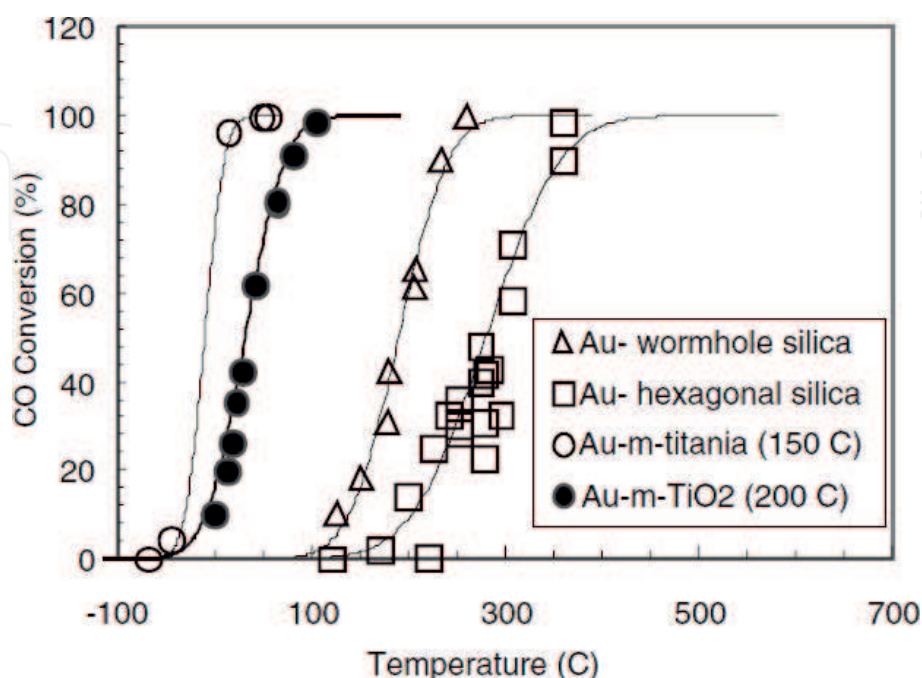


Figure 2. CO conversion (points) is shown as function of temperature for different supported Au catalysts. Reproduced with permission, copyright 2018, Springer.

It has been observed that, the degree of rate of improvement rest on the type of support used: high for insulating Al_2O_3 and SiO_2 and moderate for semiconducting TiO_2 . The effect of moisture becomes notable only above about 200 ppm H_2O for $\text{Au}/\text{Al}_2\text{O}_3$, while the activity for Au/SiO_2 decreases significantly with a decrease in moisture to about 0.3 ppm. While the catalytic activity of Au/TiO_2 at about 3000 ppm H_2O is very high and reaches full CO conversion (100%). The authors also proposed as a mechanism model that moisture improves the catalytic activities for no less than two orders of magnitude and the effect of moisture depends over the type of metal oxides used. Moisture plays dual role in the reaction: one is the activation of oxygen and other is the decomposition of carbonate.

Dai et al. demonstrated the surface sol-gel process (SSP) for the modification of silica mesopores surfaces and the tuning of mesopore diameters [48]. The procedure involves the preparation of one or multilayers of titanium oxide over SBA-15 [49]. This layer-by-layer approach controls the mesopore diameters with monolayer precision (**Figure 3**). Ultra-small Au NPs were effectively prepared on surface-modified SBA-15 via a deposition-precipitation method without the restriction of surface isoelectric point (**Figure 3**). These developed materials are found very active catalysts for CO oxidation.

Corma et al. presented a modified sol-gel approach for the preparation of Au NPs embedded in silica, and Au NPs are capped with two different thiol molecules, 1-dodecanethiol (DT) and 3-mercaptopropyltrimethoxysilane (MPMS), which lead to high-surface area Au/SiO_2 catalysts [50]. The synthesis comprises the formation of a three-component metal-organic-inorganic structure collected of Au NPs capped with alkanethiols and partly functionalized with alkoxysilane groups, and polymerized with tetraethyl orthosilicate (TEOS). Upon calcination, the material becomes highly active catalyst for the CO oxidation at low temperatures, the same as that obtained with gold on TiO_2 . This clearly specifies that it is possible to attain highly active gold-silica catalysts by a liquid-based method, as long as accessible small gold particles and strong metal-support interactions exist.

The structure and oxidation state of gold clusters of different sizes supported over various metal oxides (Al_2O_3 , TiO_2 , and SiO_2) were studied to different CO oxidation conditions that were investigated by Bokhoven et al. using in situ X-ray absorption spectroscopy at the Au L3 edge [51]. During catalysis, only phase detected in all catalysts was Au0 with no other oxidation states. For the most active catalyst with small size gold particles ($\text{Au}/\text{Al}_2\text{O}_3$), difference in the electronic structure of the gold clusters in changing reaction conditions was observed by XANES spectroscopy and attributed to the adsorption of CO on the metallic gold clusters.

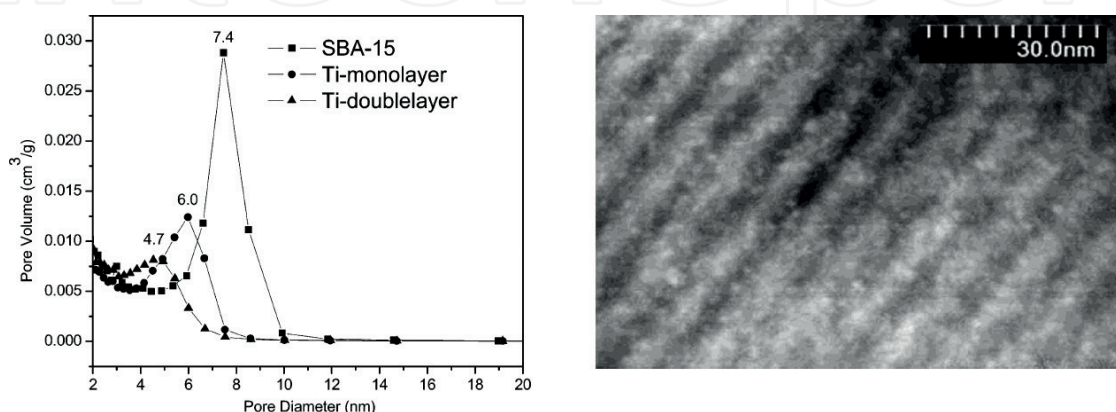


Figure 3. Pore-size distribution as function of the number of TiO_2 layers (left), Z-contrast TEM image of ultra-small Au NPs on ordered mesoporous materials (right). The bright spots (0.8–1.0 nm) correspond to Au NPs. Reproduced with permission, copyright 2018, American Chemical Society.

Further FEFF8 calculations confirmed that the changes in the XANES signature of Au/Al₂O₃ could be due to the back donation of d-electrons into the π^* orbitals of CO. For Au/Al₂O₃, Au-O backscattering was also seen in the EXAFS, suggesting weak cluster-support interactions. Nevertheless for Au/SiO₂ and Au/TiO₂, the structure of the gold clusters remained unaffected throughout all experiments.

It is well recognized that several-supported metal particles are subjected to the geometric/electronic variations when treated in oxidizing atmosphere at high temperatures [52–53]. Recently, Huang et al. examined the effect of oxygen treatment on the catalytic performance of Au/SiO₂ catalysts toward CO oxidation [54]. The Au/SiO₂ catalysts were synthesized using deposition-precipitation practice. It was observed that, the as-prepared Au/SiO₂ catalyst executes a poor catalytic activity, which is because of the relatively large size of Au particles. After treating the catalyst in O₂ at temperatures higher than 800°C efficiently enhances the catalytic activity with the agglomeration of Au particles. However, TEM results reveal the co-existence of uniformly well-dispersed ultrafine Au particles over the surface. XPS results disclose that after the oxygen pretreatment at temperatures above 800°C, the Au 4f binding energy moves to higher binding energy. Remarkably, dealing of the Au/SiO₂ catalyst in He at 800°C also displays the similar geometric and electronic structure changes of Au particles. Therefore, the enhancement effect as that in O₂, indicates that the Au-O₂ interactions at high temperatures do not contribute greatly to the progress of catalytic activity. The authors proposed that evaporation-deposition mechanism of gold particles treated at high temperatures, which accounts for the formation of ultrafine Au particles, is responsible for the improvement of the catalytic activity (**Figure 4**).

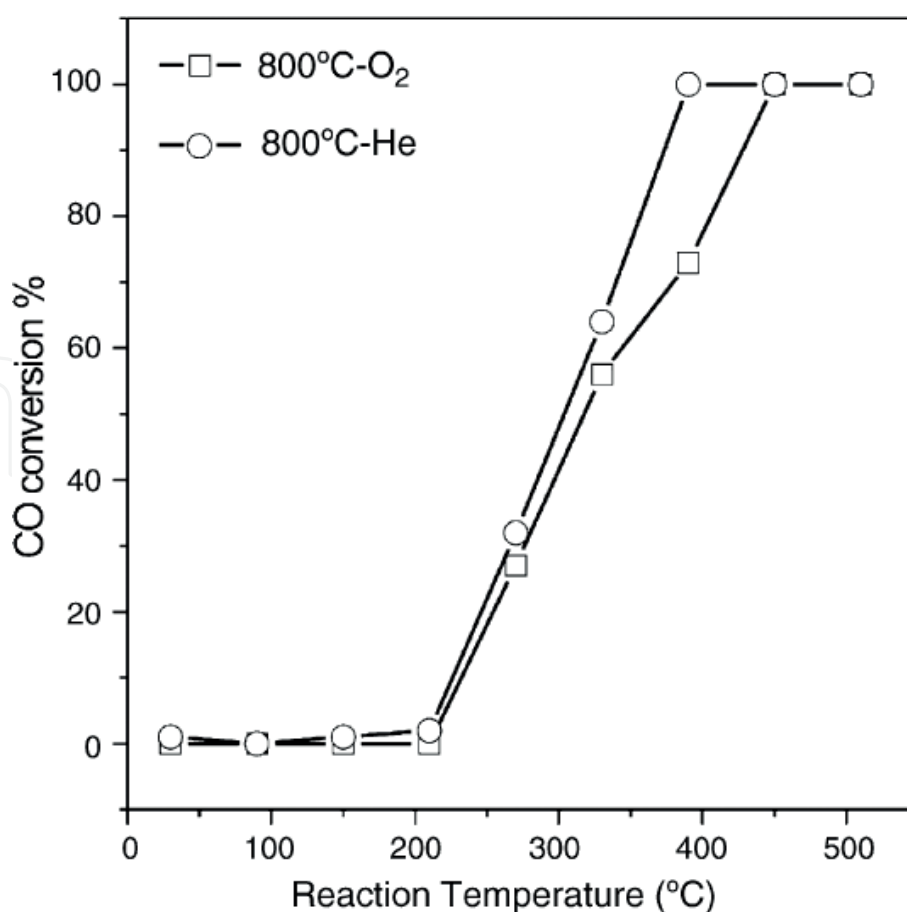


Figure 4.
 The CO conversion of Au/SiO₂-O₂-800 and Au/SiO₂-He-800 catalysts. Reproduced with permission, copyright 2018, Elsevier.

MCM-41 was fused with Au NPs by Mokhonoana et al. [55] using ethylenediamine through a modified deposition-precipitation method, where ethylenediamine operated as both base and complexing agent for the Au(III) species. Synthesis involves the mixing aqueous solution of HAuCl_4 separately with both the as-synthesized MCM-41 (still containing CTABr) and the calcined MCM-41 for 1 h. pH was adjusted to 10 using 1 M ethylenediamine solution. Resulting slurry was agitated at room temperature for 13 h, and the recovered solids were filtered, washed with warm water to eliminate the chloride ions, dried and calcined at 500°C for 12 h (for the as-synthesized MCM-41) or 400°C for 4 h (for the calcined MCM-41).

It has been observed that, subsequent catalysts with (4 and 5% nominal Au loading, respectively), having average Au NPs of 12 and 10 nm, respectively, holds the ordered structure and high surface area of the MCM-41 material. Nevertheless, calcination at 500°C results in aggregation and migration of Au NPs to the surface. Still, both catalysts show good activity in the CO oxidation at $T > 250^\circ\text{C}$.

Huang et al. investigated that, NaOH additive to Au/ SiO_2 catalyst considerably improves the catalytic activity of inert in catalyzing CO oxidation at temperatures below 150°C , while Au/NaOH/ SiO_2 catalyst with a NaOH:Au atomic ratio of 6 is active at room temperature [56]. It has been witnessed that both particle size distribution and the electronic structure of Au NPs remain equal in Au/ SiO_2 and Au/NaOH/ SiO_2 catalysts, where hydroxyls excite the activation of O_2 on “inert” Au NPs, which benefits to catalyze CO oxidation even at room temperature. Further, density functional theory (DFT) calculation results also proves the defining role of COOH in hydroxyls-induced activation of O_2 on the Au(111) surface.

The impact of pretreatments effect for gold supported over hexagonal mesoporous silica (HMS) with He, O_2 , and H_2 on the physicochemical and catalytic properties has been studied by Pestryakov et al. [57]. It has been investigated that, gold supported on mesoporous silica forms different states such as Au^{3+} and Au^+ ions, neutral, partly charged gold clusters, and metal NPs of varied sizes. It is noted that as-prepared catalyst with Au^{3+} ions does not show any catalytic activity in CO oxidation. While reduced pretreated catalysts increases the catalytic activity and its oxidative treatments deactivate the catalyst. Catalytic tests demonstrate that, reduced samples contain several regions with various catalytic behaviors at $20\text{--}200^\circ\text{C}$, $200\text{--}400^\circ\text{C}$, and $>400^\circ\text{C}$; this is because of the co-existence of gold active sites of varied forms. Further, a comparative analysis using XPS, UV-visible spectroscopy, FTIR and catalytic data shows that $\text{Au}^{\delta+}_n$ clusters or/and Au^+ ions are responsible for the activity in the low-temperature region (i.e. $<200^\circ\text{C}$); while neutral Au_n clusters are found to be active in the temperature range $200\text{--}400^\circ\text{C}$; and Au NPs catalyze the high-temperature CO oxidation.

Vinod et al. have proposed and confirmed the theory of active sites. They have examined the role of interfaces for the CO oxidation reaction for trisoctahedral (TOH) Au NPs adorned with nano oxides of CeO_2 and TiO_2 encapsulated in porous silica system [58]. The TEM images display that size of TOH morphology of the Au NPs is ~ 70 nm, which shows the high index facets with unvarying defect sites. Its atomic model shows the existence of $\{221\}$ and $\{331\}$ high index planes, which carries $\{111\}$ terrace and mono atomic $\{110\}$ step atoms as reported earlier [59]. Further, line profile analysis of HRTEM image from the surface of the TOH particle reveals the existence of step-terrace geometry. These oxides adorned and silica-encapsulated system were found to display substantial activity and stability for CO oxidation at room temperature; nevertheless, the Au particle size was above the optimum range. This is due to the conservation of morphology and thereby the active centers due to encapsulation.

1.1.3 Synthesis of Au/SiO₂ using cationic gold complex [Au(en)₂]Cl₃ (en = ethylenediamine)

Dai et al. reported a unique deposition-precipitation (DP) method for the preparation of highly active Au catalysts supported over mesoporous silica (SBA-15) using a gold cationic complex precursor [Au(en)₂]³⁺ via a wet chemical process [60] (**Figure 5**). This new DP procedure comprises the use a cationic gold precursor instead of anionic AuCl₄⁻, which is facilitated by ion-exchange route. The subsequent mesoporous catalyst is found to be extremely active for CO oxidation reaction at room temperature and even below 0°C. Its catalytic activity is found to be much greater than that of silica-supported Au catalysts formerly prepared through solution techniques.

In addition, pH of the gold precursor solution founds to play a key role in determining the catalytic activity through the regulation of [Au(en)₂]³⁺ deprotonation reaction and the surface interaction of silica with the gold precursor (**Figure 6**). It is also observed that these mesoporous gold silica catalyst are highly resistant toward sintering because of the stabilization of Au NPs within mesopores. The authors projected that this synthesis strategy of silica-supported gold catalysts is entirely solution-based and can be applied to prepare gold catalysts supported over different kinds of silica materials (e.g., silica particles and microporous zeolites).

Gies et al. and coworkers have deposited Au NPs around 3 nm particles inside the channels of mesoporous silica-TiO₂-MCM-48 using deposition techniques [61]. It

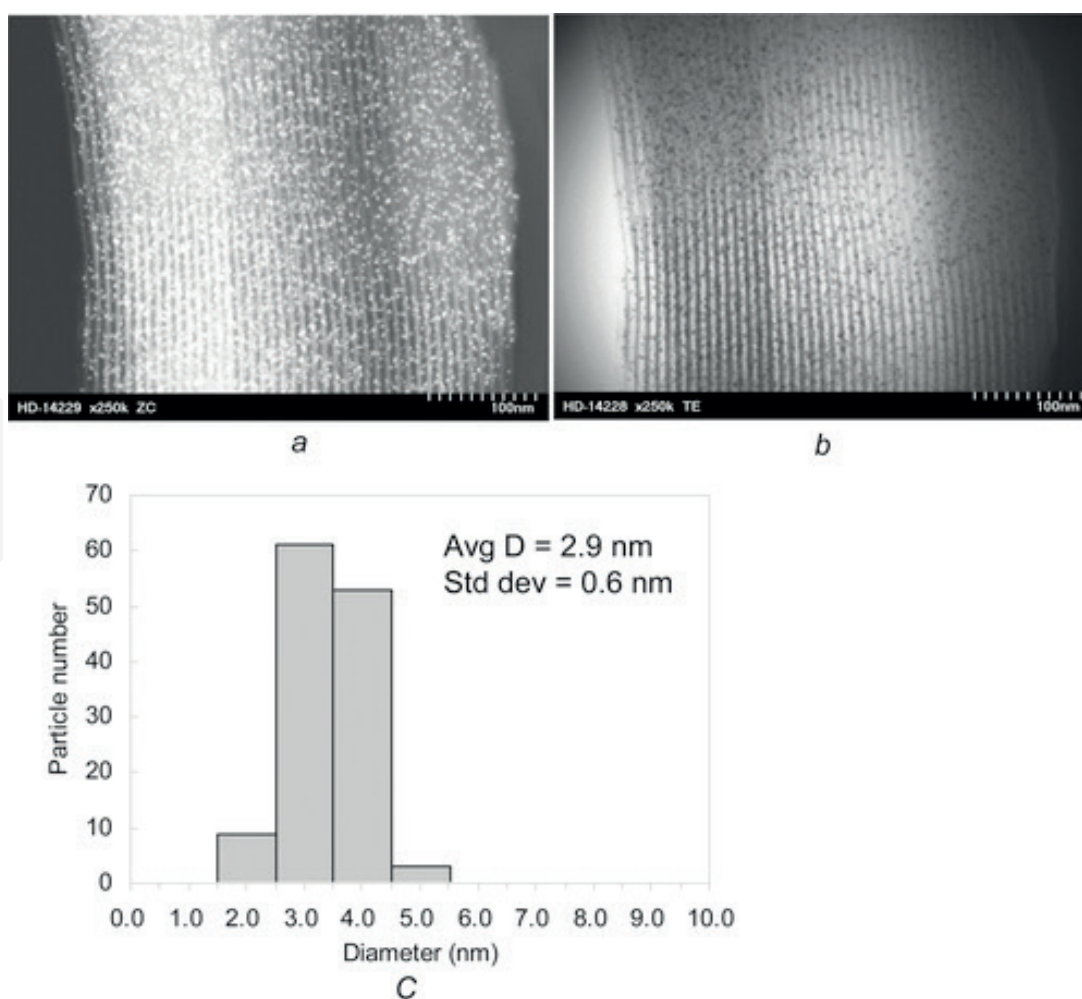


Figure 5. TEM images [(a) dark field, (b) bright field and (c) size distribution histogram] of the Au catalyst supported on SBA-15 (synthesized at pH of 9.6 and reduced at 150 °C).

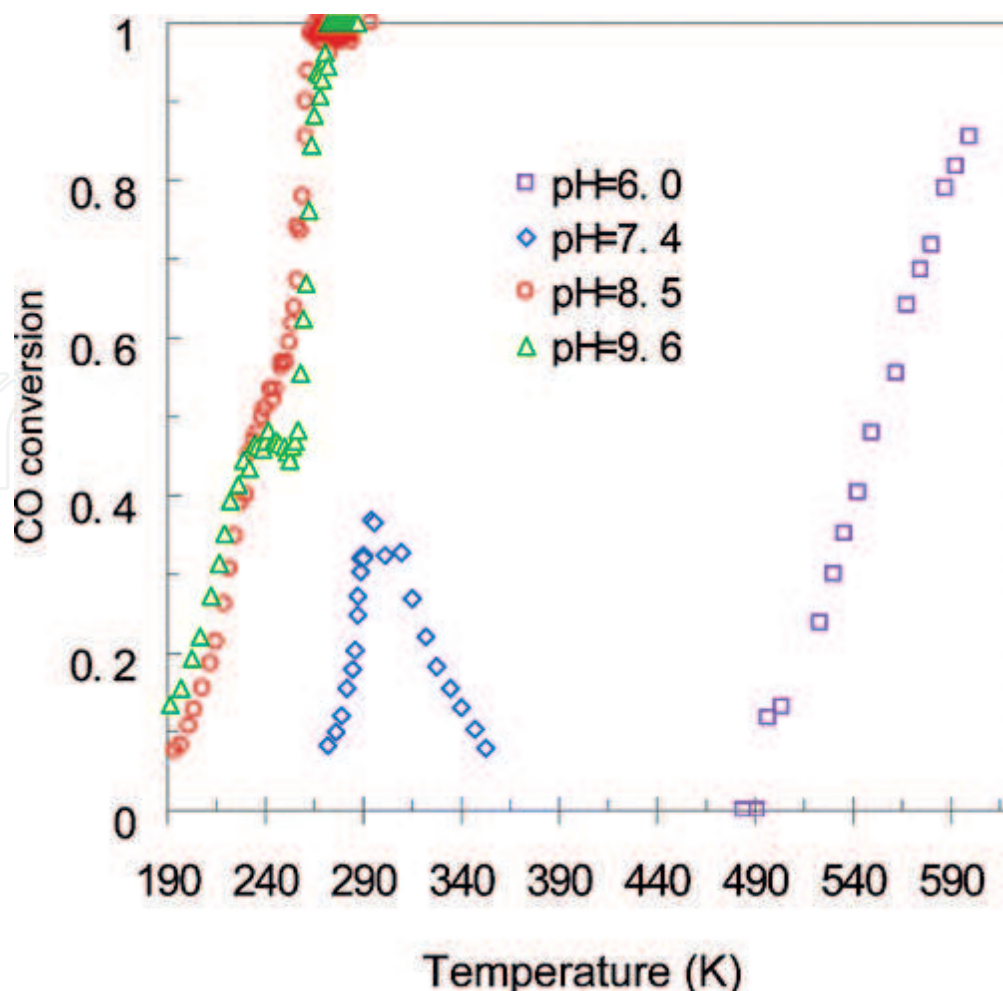


Figure 6.

Light-off curves of the Au catalysts supported on SBA-15, synthesized in the solutions of $\text{Au}(\text{en})_2\text{Cl}_3$ with different pH values. Reproduced with permission, copyright 2018, American Chemical Society.

has been revealed that, Au NPs catalyst over mesoporous silica not only converts CO to CO_2 at 50% level at -20°C but also stable against sintering up to at least 200°C .

Dai et al. [62] described a novel method for the synthesis, characterization, and catalytic behavior of small and well-dispersed Au NPs on Au/Cab-O-Sil fumed SiO_2 and Au/ MOx/SiO_2 catalysts using $\text{Au}(\text{en})_2\text{Cl}_3$ (en = ethylenediamine) as the precursor. It has been found that, these Au/ SiO_2 catalysts are extremely active for CO oxidation below 0°C . Pretreating of as-synthesized Au/ SiO_2 in H_2 -Ar at 150°C and in O_2 -He at 500°C is found to be very cooperative for high activity with optimum gold loading of 1.1 and 2.5 wt%. Furthermore, the post-treatment of calcined (and activated) Au/ SiO_2 in different media motivates the activity in CO oxidation. Moreover, the addition of metal oxide dopants also has been used to tune the catalytic activity.

Wu et al. investigated the nature of Au species over Au/ SiO_2 catalyst after oxidative and reductive pretreatments and also their role in room temperature CO oxidation using operando diffuse reflectance infrared spectroscopy (DRIFT) coupled with quadruple mass spectrometry (QMS) [63]. It has been observed that, the oxidative pretreatment of catalyst leads to a cationic Au species, which is inactive for CO oxidation at rt. However, in situ reduction of the cationic Au during CO oxidation leads to the formation of Au(0) species, which is active for CO oxidation. It is recognized that the reductive pretreatment results in a Au(0) species, which have sturdier interaction with the support and thus are more active for CO oxidation than those on oxidatively treated catalyst. It is also shown that, water has two positive effects in CO oxidation reaction on Au/ SiO_2 : activating O_2 species and supporting the reduction of Au species.

1.1.4 Chemical vapor deposition

To elucidate the effect of metal oxide support on the catalytic activity of gold for CO oxidation, Okumura et al. have deposited gold on SiO₂, Al₂O₃, and TiO₂ with high dispersion by chemical vapor deposition (CVD) of an organo-gold complex [64]. The results show that orders of TOF values for CO oxidation at 0°C are similar among Au/Al₂O₃, Au/SiO₂, and Au/TiO₂. Further, it was demonstrated that, the deposition of gold particles on the support with strong interaction is a major key controlling factor for the evolution of catalytic activity for CO oxidation at temperature 0°C (and not at -70°C) and the nature of the support is not a dominant factor.

Similarly, silica-supported Au NPs of size 1.4 nm were prepared by organo-metallic chemical vapor deposition method (Au/SiO₂-CVD) by Claus et al. [65]. Furthermore, the synthesized catalysts show a notable activity for CO oxidation at low temperature.

Okumura et al. have deposited gold on Al₂O₃, SiO₂, MCM-41, TiO₂, SiO₂-Al₂O₃, and active carbon (AC) support by gas-phase grafting (GG) of an organo-gold complex with high dispersion to display the effect of support in CO oxidation [66]. It has been found that, order of TOF values for CO oxidation at 0 °C are similar among Au/Al₂O₃, Au/SiO₂, and Au/TiO₂, this clearly shows the deposition of Au NPs on the supports with strong interaction which play important role in catalytic activity. Whereas semi-conductive or reducible nature of the support is not a presiding factor for CO oxidation at 0 °C. Au/SiO₂-Al₂O₃ and Au/AC shows lower catalytic activities due to acidic and nonmetal-oxide supports respectively.

Veith et al. reported a new way to prepare small size Au NPs (2.5 nm) over a fumed silica support, using the physical vapor deposition technique of magnetron sputtering [67]. These Au/SiO₂ catalysts are found to be structurally stable when heated in air to 500°C for several weeks or during a CO oxidation reaction. However, under these annealing conditions, traditional Au/TiO₂ catalysts rapidly sinter to form large 13.9 nm gold clusters, resulting in a fivefold decrease in activity. The authors witnessed that the stability of Au/SiO₂ is usually accredited to the absence of residual impurities (ensured by the halide-free production method) and a strong bond between gold and defects at the silica surface (about 3 eV per bond) is calculated from density functional theory (DFT) calculations. Properties that make the material worthy of study include the ability to easily reactivate the catalyst, thermal stability, and the unique gold-support interactions.

1.1.5 Synthesis by dispersion of gold colloids or pre-synthesized AuNPs

McFarland et al. examined the reactivity of gold clusters (8–22 nm diameter) supported on different metal oxides TiO₂, ZnO, ZrO₂, and SiO₂ in a continuous flow reactor [68]. Synthesis involves the encapsulation of gold clusters within diblock copolymer [polystyrene_{81,000}-block-poly(2-vinylpyridine)_{14,200}] in toluene solution, impregnated onto the bulk supports, and reduced by calcination at temperature 300°C. TiO₂ > ZrO₂ > ZnO order of support-dependent sintering was observed in air at 300°C. Au nanoclusters on TiO₂ found to exhibit the highest activity for CO oxidation compared to other metal oxide supports.

1.1.6 New methods

Guczi et al. [69] have reported a new method for the preparation of Au NPs sizes of about 50–100 × 20–30 × 2–7 nm along with spheres of 5–10 nm diameter over SiO₂/Si(100) by Ar⁺ ion implantation of a bulk-like Au/SiO₂/Si(100) thin film of 10 nm thickness. Photoemission spectra show that during size reduction, Au 5d

valence band of Au NPs shows a change in the valence band density state, and hence the catalytic activity in the CO oxidation increases. Moreover, it has been observed that, at high-temperature catalytic tests, both size and valence band of the Au NPs get returned to its typical bulk gold, which consequently curbed its catalytic activity.

Margitfalvi et al. reported a novel process for the preparation of silica-supported nanosized gold catalysts using HAuCl_4 gold precursor and ammonia solution. This gold catalyst showed relatively high catalytic activity in CO oxidation in a broad temperature region [70]. It was identified that, uniform well deposition of gold over silica support takes place because of the electrostatic interaction between the silica surface and the positively charged gold amine complexes resulting due to the being of ammonia solution, which avoids the growth of particle during hydrogen treatment at 350°C ; this subsequently results in a highly dispersed gold particles over the silica surface. Margitfalvi et al. also observed that the presence of moisture in reactant mixture increases the catalytic activity of Au/SiO_2 catalysts, while TOS study reveals the unstability of Au/SiO_2 catalysts.

Coperet et al. and coworkers, described a novel route for the direct preparation of Au NP (1.8 nm) on partially dehydroxylated silica at 700°C [$\text{SiO}_{2-(700)}$] by surface organometallic chemistry [71]. Method involves the controlled formation of well-defined and dispersed Au NPs functionalized over passivated silica surface with a AuI complex, $\{\text{Au}[\text{N}(\text{SiMe}_3)_2]\}_4$, followed by mild reduction under H_2 at 300°C (**Figure 7**). This methodology results in a very efficient tailor-made gold

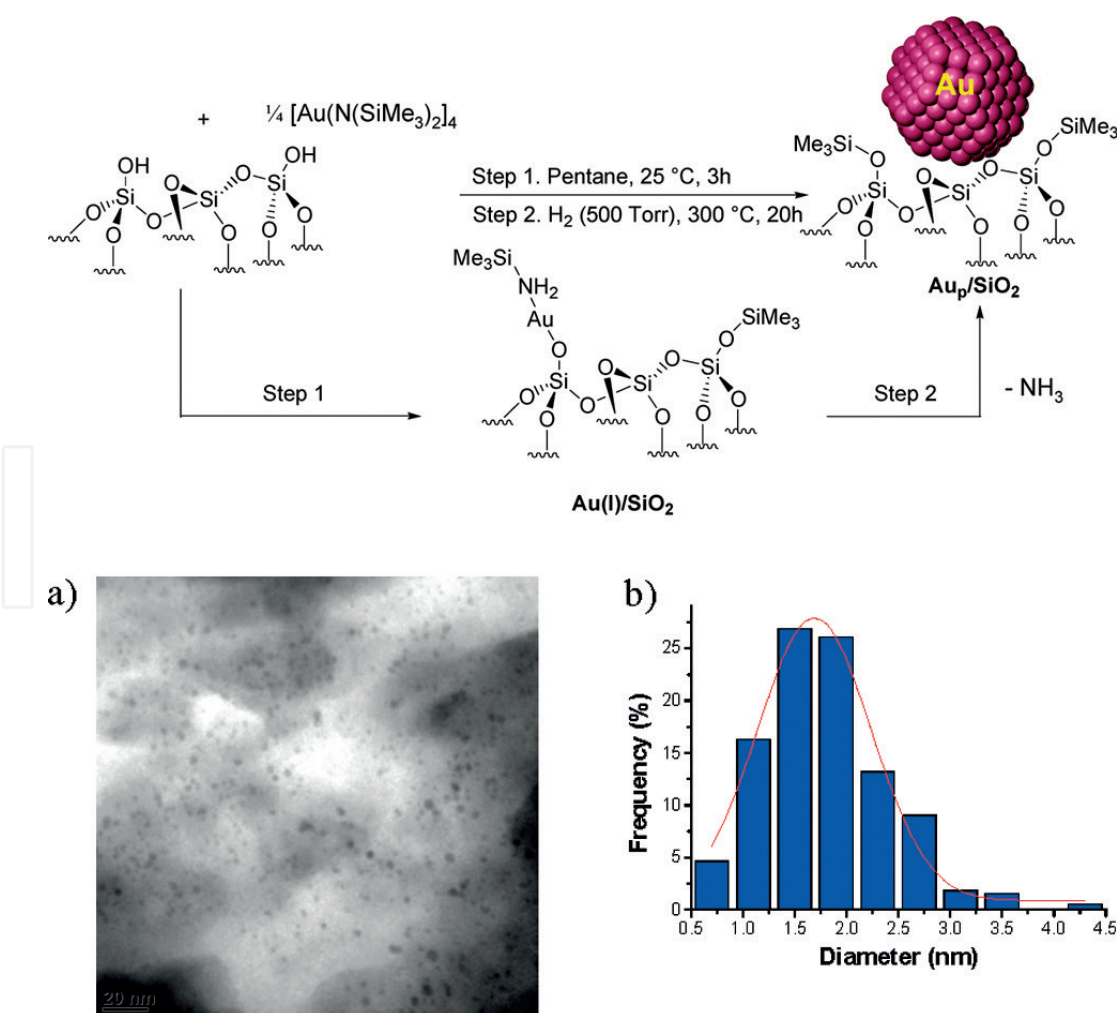


Figure 7. (A) Schematic route for the preparation of AuNP on passivated silica by SOMC (2.79 wt% Au). (B) (a) HR-TEM image and (b) size distribution histogram of AuNPs over passivated silica by SOMC.

catalyst, suitable not only for liquid phase aerobic epoxidation of trans-stilbene but also for oxidation of CO.

Recently, we have described a facile route for the synthesis of Au NPs of different average sizes (ranging from 1 to 2, 3 to 5, and 11 to 13 nm) on to the fibrous silica nano-spheres (KCC-1) either by immobilizing pre-made Au NPs on amine-functionalized KCC-1 (Au/KCC-1-NH₂) or by grafting HAuCl₄ on Au/KCC-1-NH₂ followed by reduction by NaBH₄, CO, and citrate [72]. It's been important to note that size and the location of the Au NPs over the support were found to influence by the preparation method (**Figure 8**). These catalysts were then tested for the oxidation of CO. The catalytic activity of the Au NPs over KCC-1 was proved to be size dependent (**Figure 9**).

Recently, Fan et al. have prepared an exceptional pollen-structured hierarchically meso-/macroporous silica spheres (PHMSs) created from unique rape pollen grains and a triblock copolymer poly(ethylene oxide-block-propylene oxide-block-ethylene oxide) (P123) as templates [73]. The PHMSs are enclosed of mesoporous walls, which create a macroporous structure repeating the net-like morphology of the pollen grain exine. This newly structured catalyst found to exhibit a high BET surface area of 626 m² g⁻¹ and uniform mesopores of average pore size less than 5 nm. Au NPs supported on PHMSs (Au 6.8 wt%) show a higher CO conversion at an ambient temperature (30°C), compared to those supported on typical mesoporous silica SBA-15. Furthermore, the effects of silica support on the catalytic activity have been discovered from the calculation of diffusion coefficients and simulation of gas diffusion in both PHMSs and SBA-15. Catalytic performance for CO oxidation proves that the hierarchical PHMSs facilitate better gas diffusion than the nonhierarchical SBA-15.

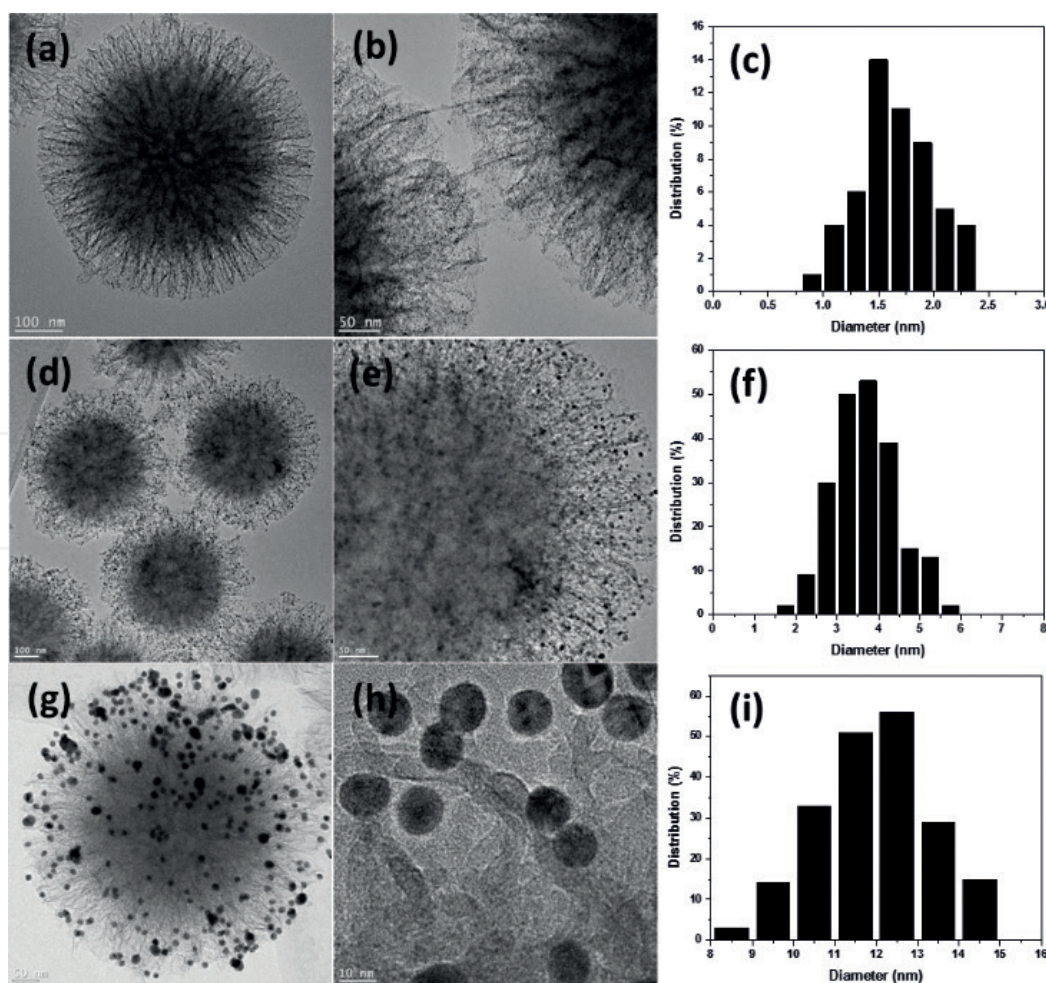


Figure 8. HR-TEM images and size histogram of Au/KCC-1-NH₂-a1 (a-c), Au/KCC-1-NH₂-a2 (d-f), and Au/KCC-1-NH₂-b1 (g-i). Reproduced with permission, copyright 2018, Wiley.

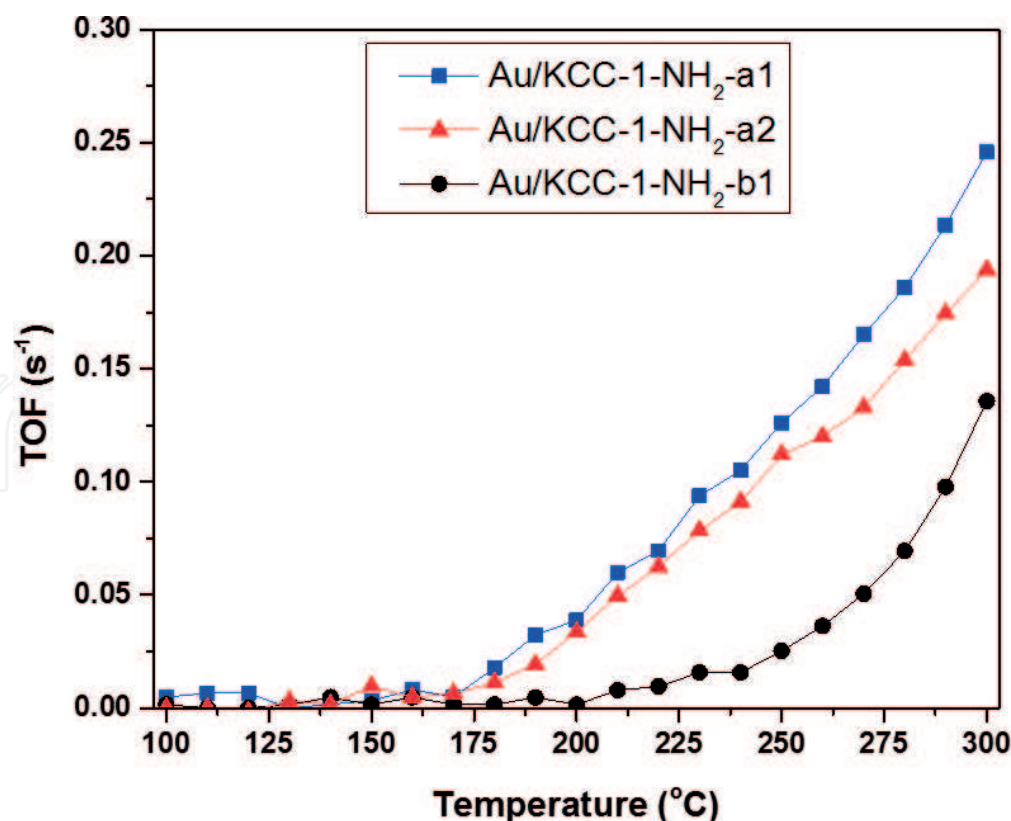


Figure 9.

Turn over frequency (TOF S⁻¹) for CO oxidation over Au/KCC-1-NH₂-a1, Au/KCC-1-NH₂-a2 and Au/KCC-1-NH₂-b1 after H₂ treatment at 300°C for 1 h. Reproduced with permission, copyright 2018, Wiley.

Yang et al. reported an improved strategy for the preparation of SBA-15-supported metal nanoparticles [74]. Supported Au nanoparticle catalyst Au/SBA-15 exhibited significantly higher activities in the oxidation of CO by molecular oxygen after adding polyvinylpyrrolidone (PVP) to the reaction system. Earlier, it has been reported that, PVP could strongly interact with the soluble Au NPs in water solvent, leading to high activity in oxidation reaction [75–76].

Recently, Behm et al. have developed an improved catalytic system for the stability of metal oxide-supported Au catalysts for low-temperature CO oxidation reaction [77]. Effect of mesoporous silica SBA-15 substrate on the catalytic activity and stability of Au/TiO₂ catalysts has been explored, where the catalyst system composed of a SBA-15 support surface modified by a monolayer of TiO_x and Au NPs on top. Later, TiO_x surface layers were systematically increased without changing the Au loading and particle size. Kinetic measurements were calculated at three different temperatures (30, 80, and 180°C). It was noted that catalyst surface modification with Ti has distinct effect, the performance of these catalysts increases significantly with Ti concentration and also with reaction temperature.

1.2 Au-M bimetallic nanoparticles on various silica support for the CO oxidation reaction

Recent research reveals that bimetallic nanoparticles often exhibit better catalytic performances compared with the monometallic counterparts. This has led to a great interest in both academic and industrial fields. The interaction between the two components of bimetallic catalysts is mostly understood in terms of assemble and ligand effects, where one component may act as a spacer to separate the active sites [78] or as an electronic modifier to the other component [79]. The catalytic performances of bimetallic nanoparticles are subject to depend on several factors,

such as nanostructure, surface composition, particle size, and shape. The most important features which differentiate a bimetallic catalyst from monometallic catalysts are the surface compositions and tunable nanostructures. A bimetallic nanostructure could be a random alloy, a core-shell structure, or just mixed monometallic nanoparticles, which give rise to different catalytic activities.

There are several literature reports in account, for the effect of second metals like Ti [78–88], Cu [89–92], Fe [93–95], Ag [96–98], Ce [99–100], Al [101–102], Co [103], Pd [104], Pt [105], and Sn [106] to the Au NPs for the activity of CO oxidation. It has been established that, synergistic effects of both the metals improve the catalytic performance in CO oxidation reaction. Type of bimetallic catalysts, support, size of the Au NPs, and the gold loading are showing remarkable effects on the activity of the reaction (**Table 2**).

Bimetallic catalyst	Support	Au loading (wt%)	Au size (nm)	Temperature (°C)	Ref.
Au-Ti	Silica aerogel	0.1–20	2.0	–50–70	[80]
	Silica aerogel	3.4–6.7	1.4–6.4	–50–70	[81]
	Silica aerogel	5.0	2.0		[82]
	SBA-15	1.7–3.6	3.0–15	200	[83]
	SBA-15	—	0.8–1.0	–40 (T ₅₀)	[84]
	SBA-15	1	3–4	50	[85]
	MCM-48	3.0–7.5	<1	17–27	[86]
	MCM-48	—	—	<0	[87]
	Silica	1.4–2.0	6.6–7.2	160	[88]
	MCM-41	—	<3	350	[89]
Au-Cu	Silica SBA-15	1.8–2.5	2.9–10.2	120 (T ₅₀)	[90]
	SiO ₂	2 (Au-Cu)	14 (Au-Cu colloidal)	150	[91]
	SiO ₂	2 (Au-Cu)	10	300	[92]
	SiO ₂	4.6 (Au-Cu)	4 (Au-Cu)	25–300	[93]
Au-Fe	SBA-15	6 (Au-Cu)	~3	0	[94]
	SBA-15	0.5–0.8	<4	20	[95]
	Hexagonal mesoporous silica (HMS)	0.4–5.1	3.3–4.5	25 (Au 5.1 wt%)–300 (Au 0.4 wt%)	[96]
	Mesoporous silica	0.4–2.0	>5	–5	[97]
Au-Ag	Silica	4.9–5.6 (Au-Ag)	~3 (Au-Ag)	0	[98]
	MCM	8 (Au-Ag)	6–7	RT	[99]
	MCM	5 (Au-Ag)	4–6 (Au-Ag)	30	[100]
Au-Ce	SBA-15	1.3–2.7	4.4–26	160–170	[101]
	SBA-15	2	3–6	150–350	[102]
Au-Al	SBA-15	3–17	3	80	[103]
	SBA-15	15–20	2.7	80	[104]

Bimetallic catalyst	Support	Au loading (wt%)	Au size (nm)	Temperature (°C)	Ref.
Au-Co	SBA-15	2	<5	0	[105]
Au-Pd	Silica fume	5.9–77.3	4–12	150–250	[106]
Au-Pt	Silica	—	3.5–4.6	280	[107]
Au-Sn	SiO ₂	2.6–3.0	—	200	[108]
Au-Co Au-Fe	MCM-41 Aerosol-silica	5	3–8	>400	[109]
Au-Ti Au-Ce	SBA-15	0.6–2.5	2.9–5.0	Au-Ti 150 Au-Ce 50	[110]
Au-Co Au-Fe Au-Cu	Stober silica	1	5 (Au-M)	300	[111]
Au-Fe Au-Ce Au-Ti	Hexagonal mesoporous silica (HMS)	2.8–3.4	0.5–6	Au-Fe 150 Au-Ce 200 Au-Ti 200	[112]

Table 2.
Au-M bimetallic catalysts with different types of silica supports for the CO oxidation reaction.

2. Conclusions

The synthesis of stable Au NPs and metal oxide support introduces new possibilities for catalysis since their properties are neither those of the bulk materials or of the isolated atoms. Optimum activity for, in particular, CO oxidation is practical for gold clusters in the 2–5 nm range. Furthermore, these gold nanoparticles can have a strong interaction with the support and an electron relocation may happen within either directions. These interactions can result in the formation of stabilized surface charged species, which act as Lewis acids comparable to as of salts in solution or in the corresponding transition metal complexes.

Mono- and bimetallic gold nanocatalysts have been made over a variety of metal oxides supports. In particular, silica is being considered a suitable support for Au NPs using appropriate synthesis methods. Au NPs can be supported over a series of different mesoporous silicas, such as SBA-15, SBA-16, MCM-41, and MCM-48. These silica-supported gold nanocatalysts are found to exhibit exceptional catalytic properties. Most common methods for the modification of silica support is either by direct or post-grafting functionalization with amine or thiol groups, where these groups show dual performances, as ligand for improving the interaction between the metal precursors and the silica surface; and mild reductants under basic conditions for in situ reduction of Au(III).

Several active silica-supported gold nanocatalysts have been prepared by functionalizing the mesoporous silica support by direct or subsequent incorporation of the gold precursor. Major problems related to these processes include particle size, gold loading, uniform dispersion Au NPs, and ligand removal during calcination, which contribute to the aggregation of Au NPs, metal leaching, and low stability.

Finally, it is precise to say that silica-supported gold nanocatalyst has become a hot topic of research for CO oxidation; conversely, there are still many challenges ahead for the improvement of silica-supported gold nanocatalyst filling the main necessities of any catalyst such as easy and low-cost synthesis method, high activity, selectivity, and greater stability at lower temperature. Furthermore, the proof of identity for the active gold species is still a challenging job for CO oxidation reactions catalyzed by gold.

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Conflict of interest


The authors declare that the research was conducted in the absence of any commercial or financial relationship that could be construed as a potential conflict of interest.

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