

Development of Novel Supported Gold Catalysts: A Materials Perspective

Zhen Ma¹ (✉) and Sheng Dai² (✉)

¹ Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, China

² Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

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ABSTRACT

Since Haruta et al. discovered that small gold nanoparticles finely dispersed on certain metal oxide supports can exhibit surprisingly high activity in CO oxidation below room temperature, heterogeneous catalysis by supported gold nanoparticles has attracted tremendous attention. The majority of publications deal with the preparation and characterization of conventional gold catalysts (e.g., Au/TiO₂), the use of gold catalysts in various catalytic reactions, as well as elucidation of the nature of the active sites and reaction mechanisms. In this overview, we highlight the development of novel supported gold catalysts from a materials perspective. Examples, mostly from those reported by our group, are given concerning the development of simple gold catalysts with single metal-support interfaces and heterostructured gold catalysts with complicated interfacial structures. Catalysts in the first category include active Au/SiO₂ and Au/metal phosphate catalysts, and those in the second category include catalysts prepared by pre-modification of supports before loading gold, by post-modification of supported gold catalysts, or by simultaneous dispersion of gold and an inorganic component onto a support. CO oxidation has generally been employed as a probe reaction to screen the activities of these catalysts. These novel gold catalysts not only provide possibilities for applied catalysis, but also furnish grounds for fundamental research.

KEYWORDS

Gold, nanoparticles, catalyst design, catalyst support, functionalization, promotion, CO oxidation

1. Introduction

Nanoscience and nanotechnology play an important role in the design of novel heterogeneous catalysts [1–8]. When the sizes of supported or unsupported metal particles are decreased down to a few nanometers, these nanoparticles may exhibit unprecedented physicochemical and catalytic properties [9–14]. This is the case for supported gold nanoparticles. One of the most

important discoveries in catalysis research is that finely divided gold nanoparticles on certain metal oxide supports can be very active for CO oxidation below room temperature [15–17]. This discovery has changed the traditional impression that gold is neither active nor useful in catalysis, and has pinpointed “gold mines” in catalysis research. Supported gold catalysts have ample applications in environmental catalysis (CO oxidation, de-NO_x, catalytic combustion

Address correspondence to Zhen Ma, zhenma@fudan.edu.cn; Sheng Dai, dais@ornl.gov



of volatile organic compounds (VOCs), photocatalysis), energy processing (the water–gas shift reaction, selective CO oxidation in excess H₂), and chemical synthesis (selective hydrogenation, selective oxidation, carbon–carbon coupling, oxidation of H₂ to form H₂O₂), with tangible commercial prospects [18–25].

The recent decade has witnessed an explosion of publications in the field of gold catalysis. The bulk of publications deal with the preparation and characterization of conventional gold catalysts (e.g., Au/TiO₂), the applications of gold catalysts in different reactions, as well as elucidation of the nature of the active sites and reaction mechanisms [26–33]. Many papers have elaborated on the effects of different preparation methods (e.g., deposition–precipitation, coprecipitation, colloidal deposition) and synthesis details (e.g., pH value and temperature of the synthesis mixture, duration of aging, gold loading, calcination temperature) on catalyst properties and catalytic performance [34–40], and have furnished firm grounds for a scientific understanding of catalyst preparation. Nevertheless, further development calls for the innovative design of novel gold catalysts with more complex structures or with the input from materials synthesis techniques [41–63]. Such design, interesting for both materials researchers and catalysis workers, is not only important for the development of better catalysts with tailored structures and catalytic properties, but also useful for understanding structure–property correlations from a fundamental perspective.

Our group at Oak Ridge National Laboratory embarked on the development of nanostructured gold catalysts in the early 2000s, and published our first relevant paper on the synthesis of mesoporous SiO₂-supported gold catalysts in 2003 [64]. Since then, advances have been made centering around the synthesis of novel supported gold catalysts from a materials perspective [64–95], i.e., adopting a materials-driven research strategy. Gold has been loaded onto various commercial or functionalized inorganic solid supports via deposition–precipitation or colloidal deposition, and the catalytic performance of the resulting catalysts, often with complicated interfacial structures, has been evaluated using CO oxidation and other reactions as probe reactions. Structure–property correlations have been established with the

aid of conventional characterization tools.

Herein, we review some advanced ways of designing gold-based nanocatalysts. In Section 2 we highlight the synthesis of gold catalysts with single metal–support interfaces. In Section 3 we review the engineering of interfacial structures of gold catalysts via pre-modification of supports, post-modification of supported gold catalysts, and simultaneous deposition of both gold and an inorganic component onto the support. We end in Section 4 by furnishing our assessment and perspectives. Overall, the focus of our review is not intended to be on catalytic reactions or reaction mechanisms, but on novel gold catalysts with interesting structures and/or delicate synthesis procedures. Furthermore, this review is not intended to be comprehensive. Rather, the examples highlighted are mostly from those reported by our group. Although there are a number of reviews on various aspects of gold catalysis [18–33], few have specifically focused on the development of novel gold catalysts from a materials perspective [89].

2. Gold catalysts with single metal-support interfaces

2.1 General considerations

Supported gold catalysts are often prepared by loading gold onto pristine supports, such as TiO₂, CeO₂, Fe₂O₃, ZrO₂, Al₂O₃, SiO₂, and C via deposition–precipitation, coprecipitation, or colloidal dispersion. Pristine supports are often used, because these supports are commercially available, and it is relatively easy to establish the structure–property correlation if a supported catalyst is composed of only a metal and a pristine support. Plus, in the initial publications of Haruta and co-workers [15–17], they used pristine supports, so most subsequent researchers have continued to use such supports to load gold.

In general, solid supports can disperse and stabilize gold nanoparticles, provide active sites at the metal–support boundary, and influence the oxidation state of gold. Efforts have been made to improve the structural properties and catalytic activity of existing gold catalysts by adjusting the synthesis details [34–40]. It would be interesting to ask: (1) can we

make materials traditionally viewed as inactive (e.g., Au/SiO₂) into active catalysts for CO oxidation by applying new synthesis methods or unconventional synthesis techniques? (2) can we find active gold catalysts based on previously overlooked supports (e.g., metal phosphates)? In addition, the effects of the crystal phase [65, 82, 96–100], size [99, 101–108], and shape [45, 108–114] of solid supports on the catalytic performance are also of interest. Below we first present the development of Au/SiO₂ and Au/metal phosphate catalysts in our group, and then highlight recent findings on the effects of the particle size and shape of solid supports.

2.2 Au/SiO₂

SiO₂ has been widely used as a support to prepare supported metal catalysts (e.g., Pt/SiO₂) owing to its high surface area, thermal stability, mechanical strength, and non-reducibility, but it is challenging to make Au/SiO₂ active for CO oxidation. Au/SiO₂ catalysts prepared by the impregnation of SiO₂ with HAuCl₄ or AuCl₃ have relatively large gold particles because the residual chloride ions facilitate the sintering of gold nanoparticles on calcination [115]. Au/SiO₂ prepared by deposition–precipitation has a low gold loading because, under the basic conditions used to hydrolyze HAuCl₄ to Au(OH)₄⁻, the SiO₂ surface is also negatively charged due to the low isoelectric point of SiO₂ (IEP ~2). The negatively charged Au(OH)₄⁻ species is difficult to adsorb onto the negatively charged SiO₂, so the catalytic activity of the resulting Au/SiO₂ in CO oxidation is often quite low [66].

To tackle these issues, our group employed the regular template-mediated synthesis of mesoporous SiO₂ in the presence of both Au³⁺ as the gold source and (CH₃O)₃Si(CH₂)₃NH(CH₂)₂NH₂ as a bifunctional ligand to interact with both Au³⁺ and the SiO₂ matrix [64]. The as-synthesized Au/MCM-41 was ion-exchanged with NH₄Cl, and then reduced in H₂. Although small gold particles were confined in the pore channels, the catalyst was not active for CO oxidation when the reaction temperature was below 100 °C [116]. In contrast, Au/mesoporous TiO₂ exhibited complete CO conversion at room temperature [116].

The failure to obtain high activity may lead one to

generalize that SiO₂ is inherently a bad support for making active gold catalysts for CO oxidation [116]. Indeed, Fe₂O₃, TiO₂, NiO_x, and CoO_x have been classified as “active” supports because they are reducible and can activate and store oxygen, whereas Al₂O₃ and SiO₂ were classified as “inert” supports because they may not be able to supply reactive oxygen for CO oxidation [117]. Nevertheless, Au/Al₂O₃ [82, 109, 118, 119] and Au/SiO₂ [93, 95, 120–125] can be active for CO oxidation. For example, Au/SiO₂ prepared via gas-phase grafting of dimethyl gold acetylacetonate exhibited high activity in CO oxidation [120–122]. The grafting of alkylammonium ions [123] or aminosilane [124] onto mesoporous SiO₂ could facilitate the uptake of a gold precursor on the grafted SiO₂ surface, and the resulting catalysts were active for CO oxidation. Alternatively, gold particles capped with alkanethiol and alkoxy silane groups can undergo polymerization with tetraethyl orthosilicate to form an Au/SiO₂ material active for CO oxidation after calcination [125]. These interesting findings concerning the high activities of Au/Al₂O₃ and Au/SiO₂ catalysts lead to the conclusion that a rigid classification into “active supports” and “inactive supports” cannot be the whole story.

Our group prepared Au/mesoporous SiO₂ (Au/SBA-15 and Au/MCM-41) catalysts using Au(en)₂Cl₃ (en = ethylenediamine) as the precursor (Fig. 1) [75, 83]. The same precursor has also been used by others to prepare Au/NaHY [126], Au/TiO₂ [35], Au/C [127], and Au/clay mineral [128] catalysts. The Au/SBA-15 and Au/MCM-41 catalysts prepared at pH > 8.0 were found to be very active for low-temperature CO oxidation [75, 83]. These catalysts are among the most active Au/SiO₂ catalysts reported; normally Au/SiO₂ catalysts reported in the literature do not show CO conversion when the reaction temperature is below 0 °C. A similar preparation method was used by Zanella and coworkers to prepare gold nanoparticles supported on Aerosil fumed SiO₂, but no reaction data were reported [129].

Our group also loaded gold onto Cab-O-Sil fumed SiO₂ using Au(en)₂Cl₃ as the precursor [76]. Figure 2 shows the CO conversion as a function of reaction temperature and a TEM image of the catalyst. The catalyst had to be pretreated in O₂–He at 500 °C to



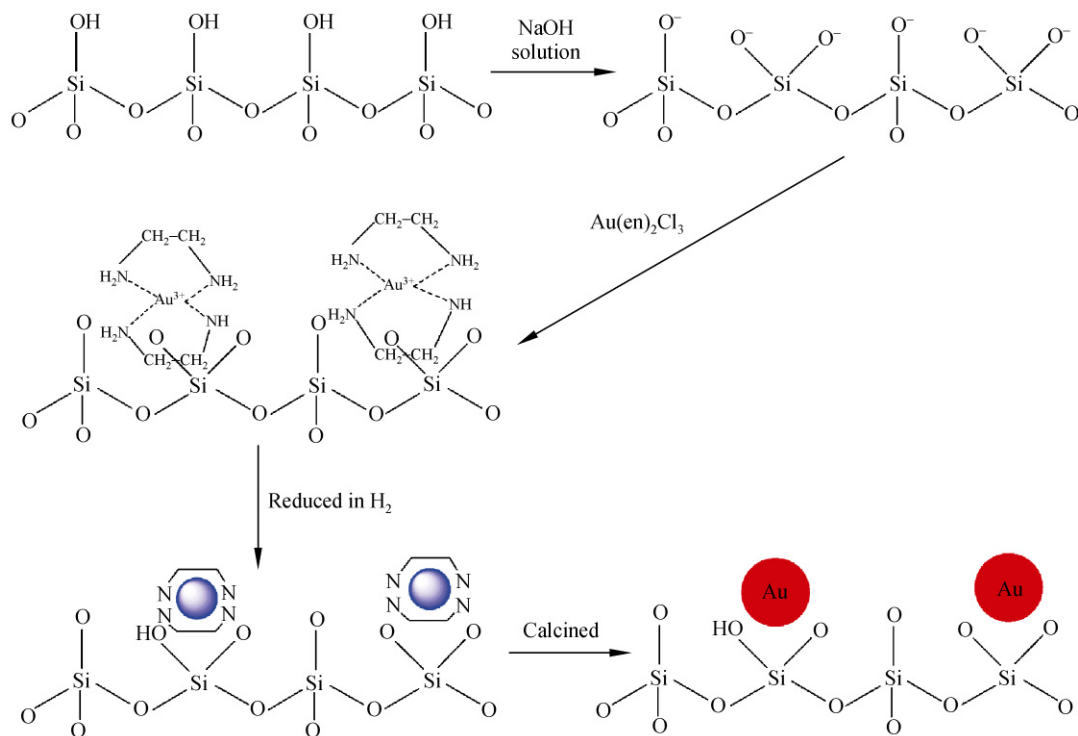


Figure 1 The preparation of Au/SiO₂ catalysts using Au(en)₂Cl₂ as the precursor in basic media. Reproduced by permission of Elsevier from Ref. [76]

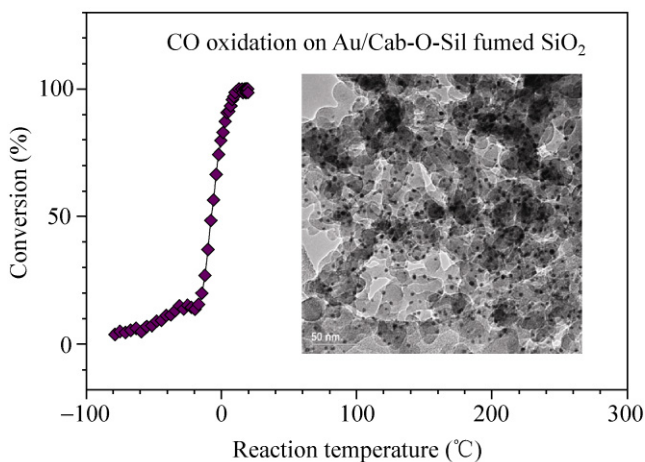


Figure 2 A conversion curve showing the performance of an Au/fumed SiO₂ catalyst in CO oxidation. The inset shows a TEM image of the catalyst. Reproduced by permission of Elsevier from Ref. [76]

burn off residual organic species in order to obtain high activity, since the catalyst obtained without such a pretreatment was not active when the reaction temperature was below 300 °C [76]. The high activity

of Au/fumed SiO₂ below room temperature shows that highly active Au/SiO₂ catalysts can be obtained without employing the ordered pore channels of mesoporous SiO₂ to stabilize small gold particles. Apparently, SiO₂ is not inherently a bad support for gold catalysts, and many conventional methods have masked the real value of SiO₂ as a support for the synthesis of active gold catalysts.

The development of Au(en)₂Cl₃-derived Au/SiO₂ catalysts has facilitated subsequent fundamental research. Wu et al. conducted a detailed FTIR study of CO oxidation on Au/fumed SiO₂ [130, 131]. They found that the thermal treatment of Au/SiO₂ in O₂ resulted in the formation of gold nanoparticles on the SiO₂ support, as demonstrated by TEM. However, the predominant gold species on the gold surface is cationic gold, as probed by CO adsorption experiments and FTIR spectroscopy. Treatment with H₂ or CO can reduce the cationic gold species and enhance the catalytic activity. They concluded that metallic gold species are responsible for the high catalytic activity of Au/SiO₂. They also found that the presence of

water or hydroxyl groups can activate oxygen and facilitate the reduction of cationic gold species [130, 131]. This work is relevant, because it is based on very active, rather than not-so-active, Au/SiO₂ catalysts.

In other work, our group studied the thermal behavior of Au/SBA-15 after pretreatment at various temperatures, focusing on the structural aspects of both gold and the support [132]. It was found that Au/SBA-15 pretreated in N₂ at 500 °C was active for CO oxidation below room temperature. In contrast, the catalyst pretreated at 900 °C was not active when the reaction temperature was below 100 °C. This was not because there were no small gold nanoparticles present, but rather because these small gold nanoparticles were unexpectedly encapsulated by the restructured and crystallized SiO₂ matrix, and such restructuring was facilitated by the exposure to NaOH used to adjust the pH value of aqueous Au(en)₂Cl₃ [132]. Strategic aqua regia leaching and SEM/TEM experiments were coupled to demonstrate the encapsulation of gold nanoparticles by the restructured SiO₂ matrix. Gold nanoparticles could also be encapsulated in the restructured SiO₂ matrix when using Cab-O-Sil fumed silica as the precursor, but that process only took place under much higher temperatures [132]. These findings provide a new explanation for the deactivation of supported Au/SiO₂ catalysts under high-temperature conditions; it should be noted, however, that the treatment temperature was much higher than those encountered in applied catalysis.

2.3 Au/metal phosphates

The majority of supported gold catalysts have been prepared by loading gold on metal oxide supports. However, metal salts have been seldom used as supports for making gold catalysts [73, 133–144]. This is so, not only because the bulk of gold catalysis papers have been following the classic work of Haruta and co-workers who used metal oxide supports [15–17], but also because compared with metal salts, metal oxides are more frequently encountered in heterogeneous catalysis. Among examples of metal salt-based gold catalysts, Lian et al. found that Au/BaCO₃ was active for CO oxidation at room temperature [134]. In addition, Au/Ca₁₀(PO₄)₆(OH)₂ catalysts were

found to be active for the water–gas shift reaction [133], CO oxidation [135], wet oxidation of organic compounds [136], deoxygenation of epoxides to give alkenes [144], and direct tandem synthesis of imines and oximes [138]. Li and coworkers found that an Au/LaVO₄ nanocomposite was active for CO oxidation when the reaction temperature was below 50 °C [137]. Our group found that gold nanoparticles supported on nanosized LaPO₄ (6–8 nm) were active for low-temperature CO oxidation [73]. The LaPO₄ nanoparticles were obtained through delicate ultrasonic synthesis.

If LaPO₄ can be used as a support for loading gold, then it is tempting to enquire whether other metal phosphates can be used for that purpose. This idea is similar to the development of superconductors where a metal component (e.g., La) of a superconductor is often replaced by another metal to see what happens. We systematically prepared an array of Au/M–P–O catalysts via deposition–precipitation [86]. Apart from Zr–P–O which was prepared by precipitation, the other M–P–O supports were purchased from a commercial supplier. We found that Au/M–P–O (M = Ca, Fe, Co, Y, La, Pr, Nd, Sm, Eu, Ho, Er) showed high CO conversions when the reaction temperature was below 50 °C, whereas Au/M–P–O (M = Mg, Al, Zn, Zr) were not active (Fig. 3). Gold particles supported on Zr–P–O were quite large, whereas small gold nanoparticles could be well dispersed on some metal phosphate supports (Fig. 4). However, the size of the gold particles was not the only factor determining the catalytic activity, because Au/Mg–P–O, Au/Al–P–O, and Au/Zn–P–O all had small gold nanoparticles, but they were not particularly active for CO oxidation [86]. Therefore, the so-called “support effect” is also important. The “support effect” is merely a vague term that describes the observed phenomenon, however, and it is still not clear why Au/Mg–P–O, Au/Al–P–O, and Au/Zn–P–O were not active for CO oxidation.

In subsequent work, we prepared Au/M–P–O (M = Al, Ca, Fe, Zn, La, Eu, Ho) catalysts using dodecanethiol-capped gold nanoparticles as the precursor. These catalysts were pretreated in O₂–He at 300 or 500 °C because we found that as-synthesized Au/La–P–O (without any thermal pretreatment) was not active



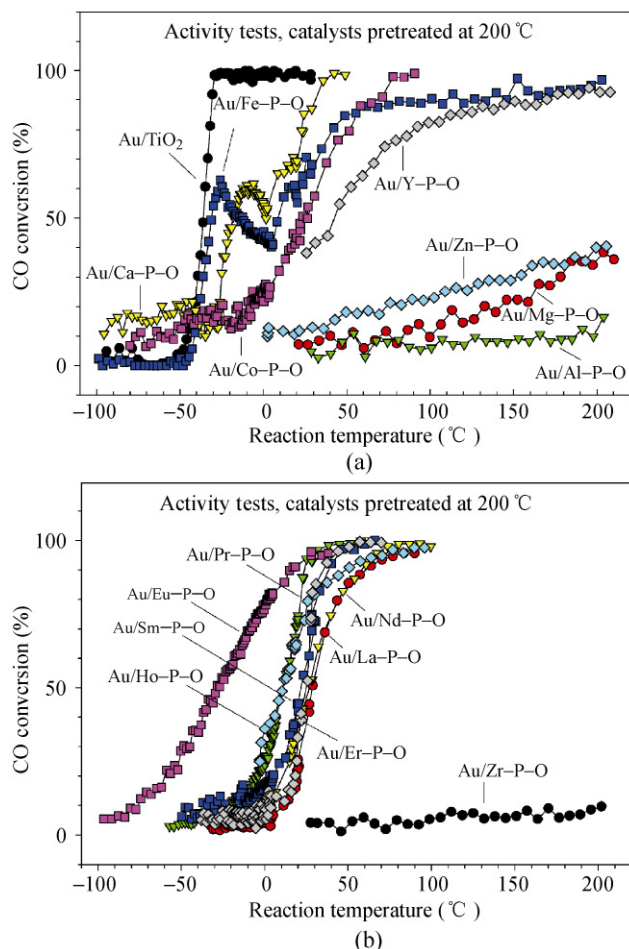


Figure 3 CO conversion curves of Au/TiO₂ and Au/M-P-O catalysts pretreated at 200 °C. Reproduced by permission of Springer from Ref. [86]

when the reaction temperature was below 200 °C, due to the influence of the capping agents, whereas the pretreatment at 300–500 °C was sufficient to activate the Au/La-P-O catalyst. After testing all of these Au/M-P-O samples, we found that only Au/La-P-O was active for CO oxidation below room temperature [94]. Therefore, the activities of supported gold nanoparticles are not only related to the size of gold nanoparticles, but also influenced by the support and the preparation method. The presumed different levels of residual sulfur may also subtly influence the catalytic performance, although the residual sulfur contents were not measured. Considering the multiple functionalities of these catalysts (i.e., gold has its own catalytic function, and metal phosphates have acid-base properties [145]), we believe that

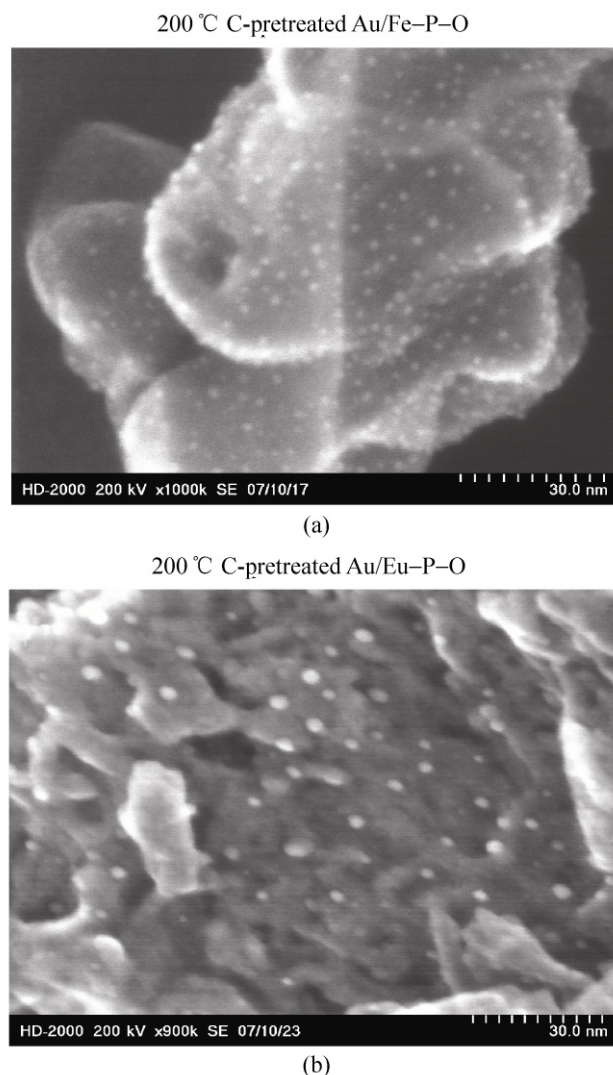


Figure 4 SEM images of Au/Fe-P-O (A) and Au/Eu-P-O (B) catalysts collected after pretreatment at 200 °C and subsequent reaction testing. Reproduced by permission of Springer from Ref. [86]

these catalysts may find applications in organic catalysis.

The development of Au/M-P-O catalysts has provided new possibilities for fundamental research. Overbury and co-workers studied CO adsorption and oxidation on deposition-precipitation-derived Au/Fe-P-O using FTIR spectroscopy [146]. They found that the catalyst pretreated in O₂ at 200 °C contained both metallic and cationic gold species on the gold nanoparticle surfaces, and the subsequent exposure of the catalyst to CO at room temperature could reduce some, but not all, of the cationic gold species. The authors proved that metallic gold

species on Au/Fe–P–O were important for CO oxidation, and they identified two reaction channels: (1) a redox channel where the FePO₄ support supplied active oxygen; (2) a direct channel involving either a Langmuir–Hinshelwood or Rideal–Eley mechanism [146]. It should be mentioned that the Au/Fe–P–O catalyst made by deposition–precipitation contained a significant amount of residual K (9 wt%), and it is not clear whether the conclusion would still be valid if no K was present. The relative contributions of each channel are not clear, either. Even for the direct channel defined by the authors, it is still not clear whether a Langmuir–Hinshelwood mechanism or Rideal–Eley mechanism is dominant. In addition, the fact that two reaction channels (a redox channel and a direct channel) coexist on Au/Fe–P–O does not necessarily mean that a catalyst requires two reaction channels to work properly, and it does not guarantee that the same result would be observed on other phosphate-based gold catalysts. Further systematic experiments are still needed to address these issues.

2.4 Effect of the particle size of the support

So far, we have described the development of active Au/SiO₂ and Au/metal phosphate catalysts by our group, mostly using commercial supports, but the effects of particle size and shape of the supports were often not addressed in our studies. Although Au/support catalysts have simple metal–support interfaces, the size and shape of support particles may have a profound influence on the performance of supported gold catalysts, and these parameters may be controlled with the help of materials synthesis techniques.

Rolison and co-workers fabricated Au–TiO₂ composite aerogels by adding gold colloids (~2 nm) to a TiO₂ sol before gelation [101, 102]. The size of the gold nanoparticles increased to ~6 nm after calcination to remove the organic capping agents, and the size of the anatase crystallites was about 10–12 nm, comparable to that of the gold nanoparticles. The resulting catalyst was very active in CO oxidation. The authors proposed that gold nanoparticles can make contact with multiple domains of small sized TiO₂ particles, leading to the creation of more interfacial active sites

[101, 102]. The amount of active sites is expected to be much less when the size of the support is much larger than that of gold nanoparticles.

To take advantage of the size effect of supports, Corma and co-workers used nanocrystalline CeO₂ (~4 nm, surface area 180 m²/g) as a support for gold, and demonstrated that the activity of the resulting gold catalyst in CO oxidation was two orders of magnitude higher than that of a gold catalyst prepared by loading gold on a conventional CeO₂ support (surface area 70 m²/g) [103]. They also found that nanocrystalline and mesostructured Y₂O₃ could be used as supports for making active gold catalysts [104]. In subsequent work, Corma and co-workers characterized Au/nanocrystalline CeO₂ and Au/nanocrystalline Y₂O₃ in detail, and concluded that the existence of reactive peroxides at the gold–support interfaces was beneficial for enhancing the activity in CO oxidation [147, 148].

Xu and co-workers explored the size effect of zirconia in Au/ZrO₂ catalysts for CO oxidation [105]. They found that nanocomposite Au/ZrO₂ catalysts with comparably sized gold particles (4–5 nm) and ZrO₂ nanoparticles (5–15 nm) were much more active in CO oxidation than those containing similarly sized gold particle but larger ZrO₂ particles (40–200 nm). They authors proposed that the reduction in the particle size of the support may not only create more contact between the metal and support, but also create more oxygen vacancies so that oxygen can be activated and migrate more easily [105]. Similarly, Shen and co-workers prepared several gold catalysts with similar gold particle sizes on ZrO₂ supports with different particle sizes, and found that the activity in the water–gas shift reaction decreased when the size of ZrO₂ support particles was increased [107].

In the above papers, the authors varied the particle size of the metal oxide supports, assuming that the sizes of gold nanoparticles on the different supports were not drastically different or at least not a major concern. Some TEM experiments were carried out to demonstrate that this assumption was valid. In contrast, Bokhimi and co-workers provided another perspective on the particle size effect of supports [106]. They prepared nanosized rutile TiO₂, divided the sample into five parts, and heated each sample of the support at different temperatures (300, 400, 500,



600, and 700 °C). The surface area of the TiO₂ support decreased with increasing treatment temperature, whereas the crystallite size of the support increased from 10 to 76 nm. Gold was loaded onto these supports using deposition–precipitation with urea, and the gold particle size was analyzed by XRD. It was found that the size of gold nanoparticles increased with increasing treatment temperature of the support. Therefore, larger rutile support particles with lower surface area may lead to higher local concentrations of gold species and fewer pinning centers on the support surface, resulting in more obvious sintering of the gold nanoparticles and lower activity in CO oxidation.

A similar observation was made by Dai and co-workers [99]. They prepared nanosized FeO_x (shown by XRD to be Fe₃O₄) by a hydrothermal method, and then calcined the material at different temperatures. The samples calcined at 550, 600, and 700 °C were found to be mainly α-Fe₂O₃, with decreasing surface areas (35, 30, and 14 m²/g, respectively) and increasing particle sizes (as shown by XRD data). The gold nanoparticles on these supports also had increasing particle sizes (5.1, 7.1, and 7.6 nm, respectively), thus leading to decreasing turnover frequency (TOF) in the oxidative dehydrogenation of 1,4-butanediol (250, 79, and 21 h⁻¹, respectively) [99]. The effect of the particle size of the supports is difficult to assess in these cases where both particle size of the support and the size of gold nanoparticles are varied.

2.5 Effect of the particle morphology of the support

The particle shape or morphology of the support has been found to influence the catalytic activity of the resulting gold catalysts. That is intriguing, considering that Au/support catalysts with differently shaped support particles have gold-support interfaces with similar chemical components. Although some earlier studies employed supports with exotic morphologies (e.g., nanotubes) to load gold, either no comparison with regular gold catalysts was made, or the catalytic activities of both the exotic gold catalysts and regular gold catalysts were low. Essentially, sometimes one is comparing a bad catalyst with a worse one, so we refrain from reviewing these inconclusive data.

Among conclusive and typical examples, Han and

co-workers found that gold nanoparticles supported on γ-Al₂O₃ nanofibers were much more active than those supported on commercial γ-Al₂O₃ in CO oxidation [109]. The authors proposed, based on diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) data, that the OH groups bonding to γ-Al₂O₃ nanofibers may facilitate CO oxidation. Zhong and co-workers dispersed gold colloids onto porous α-Fe₂O₃ nanorods, and found that the resulting catalyst was more active than gold nanoparticles dispersed on commercial α-Fe₂O₃ [45]. Cao and co-workers found that the activity of Au/β-MnO₂ nanorods was higher than that of Au/commercial β-MnO₂ particulates in the solvent-free aerobic oxidation of alcohol [111]. The authors ascribed the high activity of Au/β-MnO₂ nanorods to the beneficial presence of more cationic gold species and surface oxygen vacancies resulting from the strong interaction between gold and the reactive surface of the MnO₂ nanorods.

Flytzani-Stephanopoulos and co-workers synthesized CeO₂ nanorods, nanocubes, and nanopolyhedra via hydrothermal synthesis, and subsequently loaded gold via deposition–precipitation [110]. As shown in Fig. 5, the width of the CeO₂ nanorods was 10.1 nm ± 2.8 nm, and their length was in the range 50–200 nm. The length of the sides of the CeO₂ nanocubes was 29.5 nm ± 10.6 nm, and the diameter of the CeO₂ nanopolyhedra was 11.0 nm ± 2.1 nm. The nanorods had exposed (110) and (100) crystal planes, the nanocubes had exposed (100) crystal planes, and the nanopolyhedra had exposed (111) and (100) crystal planes. Interestingly, the authors found that the activity in the water–gas shift reaction followed the sequence Au/CeO₂ nanorods > Au/CeO₂ nanopolyhedra > Au/CeO₂ nanocubes. The lowest activity of the Au/CeO₂ nanocubes was explained by the predominance of metallic gold species on the support surface and the negligible metal–support interaction, as demonstrated by X-ray photoelectron spectroscopy (XPS) and hydrogen-temperature programmed reduction (H₂-TPR) [110]. Subsequently, Yuan and co-workers found that the activity in the preferential CO oxidation in H₂-rich gas followed the same trend mentioned above [112, 114]. Cao and co-workers demonstrated that the activity of Au/CeO₂ nanorods in CO oxidation was much higher than that of Au/CeO₂ nanoparticles [113].

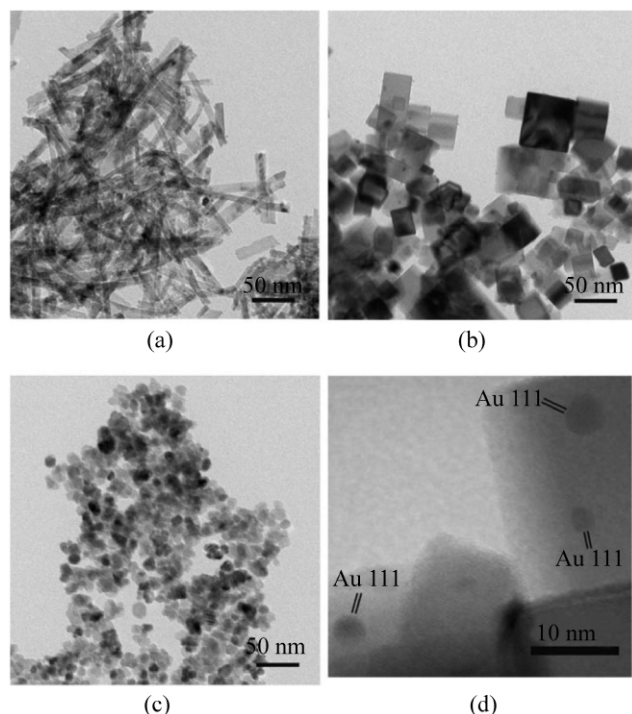


Figure 5 TEM (a)–(c) and HRTEM (d) images of 1% Au on CeO₂ nanorods (a), CeO₂ nanocubes ((b), (d)), and CeO₂ nanopolyhedra (c). Reproduced by permission of Wiley-VCH from Ref. [110]

Li and co-workers synthesized spindle-shaped Fe₂O₃ nanoparticles using acidic amino acid additives, and they also prepared rhombohedral Fe₂O₃ nanoparticles using basic amino acids [108]. The particle size of the Fe₂O₃ supports could also be controlled by changing the concentration of the amino acids. They loaded gold nanoparticles on these supports by colloidal deposition, and concluded that the spindle-shaped Au/Fe₂O₃ showed higher activity than the rhombohedral Au/Fe₂O₃, although the sizes of gold nanoparticles on the two supports were comparable (3–4 nm) and the particle sizes of the supports were also very similar (about 80 and 77 nm, respectively). The authors suggested that the rough surfaces or edges or defects of the spindle-shaped Fe₂O₃ may lead to the higher catalytic activity.

Although variations in catalytic activity are clearly observed in the above-mentioned studies, the fundamental reasons for the observed shape effect are still not clear. Theoretical studies are still needed to determine why the shape of support particles exerts such a dramatic influence on the catalytic

performance of the resulting gold catalysts. Besides, the preparation of solid supports with different particle shapes often involves different preparation methods, different synthesis details, and different levels of residual organic or inorganic species on support surfaces. It is difficult to exclude the possibility that these differences influence the catalytic activity. The same critical concerns are also valid when seeing the claim that different crystal phases of TiO₂ (anatase, rutile, brookite) influence the activity of supported gold catalysts [65]. Although the difference in catalytic activity is real, one should question whether the difference in catalytic activity as a function of the crystal phase of support is intrinsic, i.e., whether the catalytic activities of Au/brookite (or Au/anatase, Au/rutile) catalysts themselves would be the same, if several brookite (or anatase, rutile) supports prepared by different methods were used to load gold. There may be an interplay between size effects, shape effects, crystal phase effects, impurity effects, and other unknown factors such as different synthesis procedures or synthesis details, and it is dangerous to attribute the difference in catalytic activity to one single factor.

3. Interfacial structure engineering

3.1 General considerations

The majority of reported gold catalysts have been prepared by loading gold nanoparticles on commercially available supports. To enhance the diversity of available catalysts, tune the catalytic properties, and establish structure-property correlations, it is desirable to build up more complex catalytic architectures by incorporating additional components (e.g., modifiers, additives). The promotion of heterogeneous catalysts in this way is standard practice in the field of heterogeneous catalysis [149].

Three strategies have been adopted to make such heterostructured gold catalysts, depending on the sequence of introducing gold and the modifier or additive. In the pre-modification strategy, a catalyst support is first treated by a modifier, and gold is subsequently deposited onto the pre-modified support. In the post-modification strategy, gold is loaded onto

a support, and a modifier is subsequently introduced. In the co-addition strategy, gold and an inorganic component are simultaneously deposited onto the support. Therefore, metal-support, metal-modifier, and modifier-support interfaces are all constructed. As a result, new active sites may be created, and gold nanoparticles may be stabilized at these relatively complex interfaces.

3.2 Pre-modification of supports

3.2.1 Pre-modification of SiO₂ supports

SiO₂ is not suitable for loading gold nanoparticles via deposition–precipitation because SiO₂ has a low isoelectric point (IEP ~2), so the Au(OH)₄[−] species cannot effectively adsorb onto the negatively charged SiO₂ surface under basic conditions. One way to overcome this obstacle is to introduce a high-isoelectric-point metal oxide onto the SiO₂ surface. As a result, Au(OH)₄[−] species may adsorb more efficiently onto the functionalized support.

Our group modified mesoporous and fumed SiO₂ surfaces with amorphous TiO₂ via a surface–sol–gel technique under non-aqueous conditions (Fig. 6) [66, 72]. Ti(OC₄H₉)₄ was used as the precursor to load surface TiO₂, and methanol and toluene were used as the solvents. Gold nanoparticles were loaded onto TiO₂/SiO₂, and the activity of Au/TiO₂/SiO₂ in CO oxidation was found to be much higher than that of Au/SiO₂. The enhanced activity is not only due to the higher gold loading of Au/TiO₂/SiO₂ compared to that of Au/SiO₂, but also due to the presence of an active Au–TiO₂ interface. The resulting Au/TiO₂/SiO₂ catalysts should not be classified as “SiO₂ supported gold catalysts”, and may be more appropriately described as “SiO₂-based gold catalysts”. Since the presence of TiO₂ increases the catalytic activity and the Au/TiO₂/SiO₂ catalyst is merely an Au/TiO₂ catalyst supported on SiO₂, one may question why Au/TiO₂ was not used for CO oxidation in the first place and why we need Au/TiO₂/SiO₂. To respond to these questions, we comment here that this work demonstrates a new way to make functionalized mesostructured catalysts, and these catalysts with their nanosized pores may be useful for shape-selective organic catalysis.

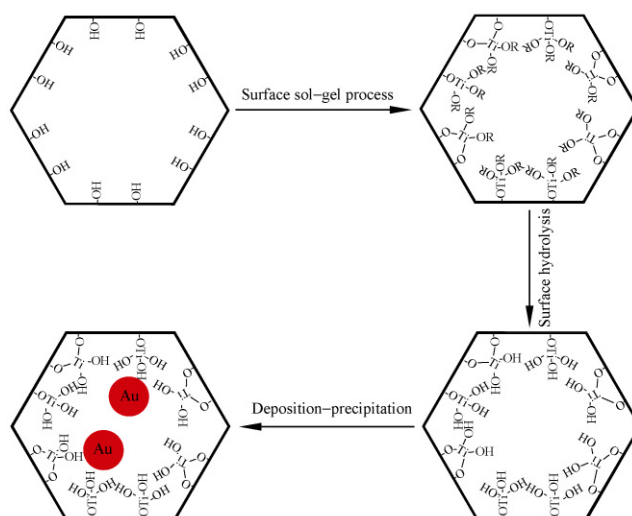


Figure 6 The modification of mesoporous SiO₂ by TiO₂ using a surface–sol–gel approach for loading gold nanoparticles. Reproduced by permission of the American Chemical Society from Ref. [66]

The pre-modification strategy has also been used by others to prepare SiO₂-based gold catalysts, such as Au/Al₂O₃/SiO₂ [72, 150], Au/TiO₂/SiO₂ [151–165], Au/FeO_x/SiO₂ [150, 166, 167], Au/CoO_x/SiO₂ [150, 168–171], Au/ZnO/SiO₂ [172], Au/LaO_x/SiO₂ [168], and Au/CeO₂/SiO₂ [159, 173–175]. Even though the addition of certain promoters can enhance the catalytic activity, most of the resulting catalysts were not particularly active in CO oxidation, presumably because the deposition–precipitation method does not work well for making active Au/SiO₂ catalysts. Therefore, the development of catalysts based on a better starting point (such as highly active Au/SiO₂ [75, 76]) should be considered.

Our group prepared a series of M_xO_y/SiO₂ (M = Mg, Al, Fe, Ni, Zn, Ba, La, Ce) supports either by impregnation or by using NaOH as the precipitating agent [76]. A TiO₂/SiO₂ support was prepared by grafting a Ti₁₆O₁₆(OEt)₃₂ precursor onto SiO₂. Gold was loaded onto these functionalized supports using Au(en)₂Cl₃ as the precursor. It was found that Au/FeO_x/SiO₂, Au/TiO₂/SiO₂, and Au/BaO/SiO₂ were more active in low-temperature CO oxidation than Au/SiO₂ with a comparable gold loading [76]. However, the local interfacial structures were not characterized, and the reasons for the activity enhancement were not clarified. It is not clear whether the promotional effect is due to

the modification of the oxidation state of gold, the size of gold nanoparticles, or the creation of new gold–modifier interfaces.

3.2.2 Pre-modification of TiO_2 supports

Au/TiO_2 is very active for CO oxidation below room temperature, but gold nanoparticles on TiO_2 can sinter easily at high temperature, even more easily than those on SiO_2 [176]. Our group found that modification of the TiO_2 support by amorphous Al_2O_3 followed by loading of gold could alleviate the sintering problem [71]. The $\text{Al}_2\text{O}_3/\text{TiO}_2$ support was synthesized by surface–sol–gel processing of $\text{Al}(\text{sec-OC}_4\text{H}_9)_3$ on TiO_2 followed by controlled hydrolysis. Whereas Au/TiO_2 underwent significant thermal deactivation at 500 °C, ascribed to the agglomeration of gold particles, $\text{Au}/\text{Al}_2\text{O}_3/\text{TiO}_2$ underwent minimal thermal deactivation at the same temperature. This can be ascribed to the stabilization of gold nanoparticles by the amorphous Al_2O_3 coating, as clearly shown by TEM images.

Since $\text{Au}/\text{Al}_2\text{O}_3/\text{TiO}_2$ is a successful catalyst, it is interesting to know whether other metal oxide additives can play a role similar to Al_2O_3 . In subsequent work, we loaded various metal oxide additives onto the TiO_2 support via excess-solution impregnation of soluble precursors followed by calcination, and established that $\text{Au}/\text{M}_x\text{O}_y/\text{TiO}_2$ ($\text{M} = \text{Ca}, \text{Ni}, \text{Zn}, \text{Ga}, \text{Y}, \text{Zr}, \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Er}, \text{or Yb}$) all retained significant activity in CO oxidation at ambient temperature even after pretreatment at 500 °C [78]. The stabilizing effect of these metal oxide additives was demonstrated by XRD and TEM. As shown in Fig. 7, Au/TiO_2 collected after pretreatment at 500 °C and subsequent use in the water–gas shift reaction contained mostly large gold particles, whereas $\text{Au}/\text{ZnO}/\text{TiO}_2$ retained small gold nanoparticles after pretreatment at 500 °C [92]. Although we ascribed the difference in catalytic activity to the size of the gold nanoparticles in our publications [78, 92], we now believe that different metal oxide additives may also have different redox properties, and may even change the oxidation states of gold and create new active sites. The pre-modification strategy has also been used by others to prepare TiO_2 -based gold catalysts, such as $\text{Au}/\text{MgO}/\text{TiO}_2$ [177], $\text{Au}/\text{MnO}_2/\text{TiO}_2$ [178],

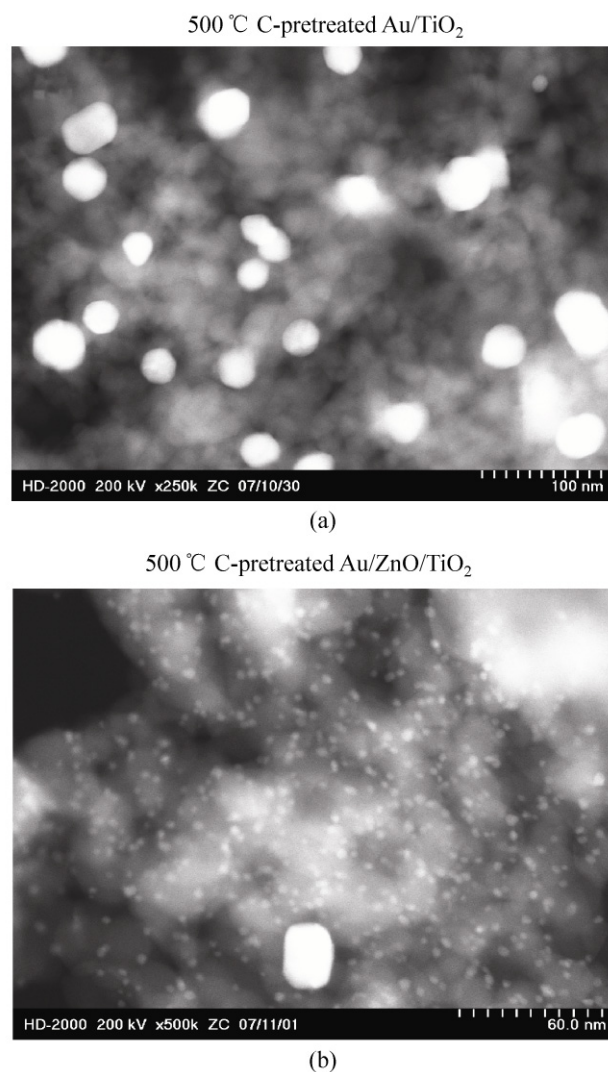


Figure 7 Dark-field TEM images of Au/TiO_2 and $\text{Au}/\text{ZnO}/\text{TiO}_2$ catalysts collected after pretreatment at 500 °C followed by use in the water-gas shift reaction. Reproduced by permission of Springer from Ref. [92]

$\text{Au}/\text{FeO}_x/\text{TiO}_2$ [179, 180], $\text{Au}/\text{CuO}_x/\text{TiO}_2$ [181], $\text{Au}/\text{ZnO}/\text{TiO}_2$ [182], and $\text{Au}/\text{CeO}_x/\text{TiO}_2$ [183, 184]. However, the local interfacial structures were often not characterized sufficiently. In addition, we need to point out that the stabilization of metal nanoparticles by adding a suitable modifier on a support is a general phenomenon. In 1990, Xie and Tang mentioned in a review that the modification of an Al_2O_3 support by La_2O_3 could stabilize metallic nickel particles for CO methanation [185].

The development of $\text{Au}/\text{M}_x\text{O}_y/\text{TiO}_2$ catalysts has led to some subsequent fundamental research. By means of density functional theory (DFT) calculations,



Liu and co-workers found that the binding of gold on $\text{Al}_2\text{O}_3/\text{TiO}_2$ was much stronger than that of gold on TiO_2 [186]. Although they assumed that Al_2O_3 was dispersed homogeneously on TiO_2 support when calculating the binding energy, and the conclusions at that point were consistent with the proposed anti-sintering behavior of $\text{Au}/\text{Al}_2\text{O}_3/\text{TiO}_2$ catalysts, their calculations also showed that the activity of CO oxidation on $\text{Au}/\text{Al}_2\text{O}_3/\text{TiO}_2$ was low if TiO_2 was fully coated by Al_2O_3 . Therefore, they concluded that the TiO_2 should not be fully coated by Al_2O_3 , so that gold nanoparticles are in contact with both the TiO_2 support and Al_2O_3 patches [186]. Although we think that the coating of Al_2O_3 on TiO_2 support may not be homogeneous and several $\text{Au}/\text{Al}_2\text{O}_3/\text{TiO}_2$ catalysts with a range of Al_2O_3 contents are all active catalysts [78], we need to point out that the assumption in the calculations that the $\text{Au}-\text{Al}_2\text{O}_3$ interface is not active for CO oxidation [186] should be treated with caution, because experimentally, $\text{Au}/\text{Al}_2\text{O}_3$ catalysts were found to be active for CO oxidation [82, 109, 118, 119]. Indeed, Liu and co-workers recently found that the presence of moisture could assist the activation of oxygen, thus promoting CO oxidation on $\text{Au}/\text{Al}_2\text{O}_3$ [187].

Hagaman and co-workers conducted a solid-state ^{27}Al magic angle spinning (MAS) and triple quantum magic angle spinning (3QMAS) NMR investigation of a series of $\text{Al}_2\text{O}_3/\text{TiO}_2$ supports with different Al_2O_3 loadings which were calcined at different temperatures [188]. These supports were used in our previous work [78] to prepare $\text{Au}/\text{Al}_2\text{O}_3/\text{TiO}_2$ catalysts. The highest catalytic activity and the smallest gold particle size reported in our previous paper [78] showed a good correlation with maximum number of monolayer-type octahedral Al_2O_3 species on the TiO_2 support. It was also found that there was no difference between the dispersed Al_2O_3 species obtained by excess-solution impregnation or surface-sol-gel methods [188].

3.2.3 Pre-modification of Al_2O_3 supports

The pre-modification of Al_2O_3 supports by metal oxides followed by assembly of gold nanoparticles has also been studied. Gold catalysts based on oxide-modified Al_2O_3 supports include $\text{Au}/\text{MgO}/\text{Al}_2\text{O}_3$

[189–191], $\text{Au}/\text{MnO}_x/\text{Al}_2\text{O}_3$ [192–194], $\text{Au}/\text{FeO}_x/\text{Al}_2\text{O}_3$ [192–196], $\text{Au}/\text{CoO}_x/\text{Al}_2\text{O}_3$ [192, 194], $\text{Au}/\text{ZnO}/\text{Al}_2\text{O}_3$ [192, 197], $\text{Au}/\text{SnO}_x/\text{Al}_2\text{O}_3$ [198], $\text{Au}/\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ [199], and $\text{Au}/\text{CeO}_2/\text{Al}_2\text{O}_3$ [200–203]. In particular, Nieuwenhuys and coworkers tested the performance of Al_2O_3 -based gold catalysts in a number of reactions, and established that $\text{MgO}/\text{Al}_2\text{O}_3$ [189], $\text{BaO}/\text{Al}_2\text{O}_3$ [204, 205], $\text{ZnO}/\text{Al}_2\text{O}_3$ [197], and $\text{ZrO}_x/\text{Al}_2\text{O}_3$ [197] could all stabilize gold nanoparticles against thermal sintering.

Our group modified various Al_2O_3 supports (boehmite AlOOH , amorphous $\text{Al}(\text{OH})_3$, and highly crystalline $\gamma\text{-Al}_2\text{O}_3$) by amorphous TiO_2 via a surface-sol-gel method, and then loaded gold nanoparticles via deposition-precipitation [82]. The activity in CO oxidation was significantly enhanced after pretreating the $\text{Au}/\text{TiO}_2/\text{Al}_2\text{O}_3$ catalysts at high temperature. The role of the dispersed amorphous TiO_2 is not to stabilize gold nanoparticles, because the gold nanoparticles on pristine Al_2O_3 supports were also small after high-temperature pretreatment. Rather, we propose that its role is to create an $\text{Au}-\text{TiO}_2$ interface which is more active than $\text{Au}-\text{Al}_2\text{O}_3$ for CO oxidation.

3.2.4 Pre-modification of carbon supports

Although Au/C catalysts are useful for certain liquid-phase oxidation reactions [206, 207], they are generally not active for gas-phase CO oxidation. Carbon surfaces are acidic, and they have low isoelectric points. In addition, carbon materials are reducing agents, and they can react with Au^{3+} to form large gold particles during synthesis [206]. We loaded gold onto graphite via deposition-precipitation, and found that the catalyst was not active for CO oxidation [80]. The XRD pattern of the spent catalyst showed sharp peaks corresponding to metallic gold, implying that the supported gold particles were large. However, the XRD results were misleading, because our TEM data showed that there were predominantly small gold nanoparticles on the support surfaces, together with a much smaller number of large gold chunks. Therefore, the fact that Au/C catalysts are not active for CO oxidation cannot be solely explained by the absence of small gold nanoparticles.

To promote the catalytic activity, we first modified

carbon supports by immersing them in aqueous KMnO_4 . In this case, carbon is a sacrificial reductant, and undergoes a self-limiting reaction with aqueous KMnO_4 to form a decoration of MnO_x on the surface (i.e., $4\text{KMnO}_4 + 3\text{C} + 2\text{H}_2\text{O} \rightarrow 4\text{MnO}_2 + 3\text{CO}_2 + 4\text{KOH}$) [208]. We then loaded gold onto the MnO_x/C support via deposition–precipitation [80]. The resulting $\text{Au}/\text{MnO}_x/\text{C}$ catalysts were both active and stable for CO oxidation when the reaction temperature was below 100°C (Fig. 8) [80]. Gold catalysts based on metal oxide-modified carbon supports include $\text{Au}/\text{TiO}_2/\text{C}$ [209–211], $\text{Au}/\text{FeO}_x/\text{C}$ [212], and $\text{Au}/\text{ZnO}/\text{C}$ [213]. Although these catalysts showed improved catalytic performance, they should not be classified as “carbon-supported gold catalysts”, but may be more appropriately described as “carbon-based gold catalysts”. In addition, the local contact structures of these catalysts are not clear.

3.3 Post-modification of supported catalysts

3.3.1 Post-modification of Au/TiO_2

Au/TiO_2 is the most studied gold catalyst, but it often suffers from sintering of the gold nanoparticles at high temperatures. Our group loaded gold nanoparticles on TiO_2 , and then soaked the Au/TiO_2 in an aqueous H_3PO_4 , followed by extensive washing [79]. The resulting $\text{H}_3\text{PO}_4/\text{Au}/\text{TiO}_2$ prepared under optimal conditions was still active for CO oxidation after

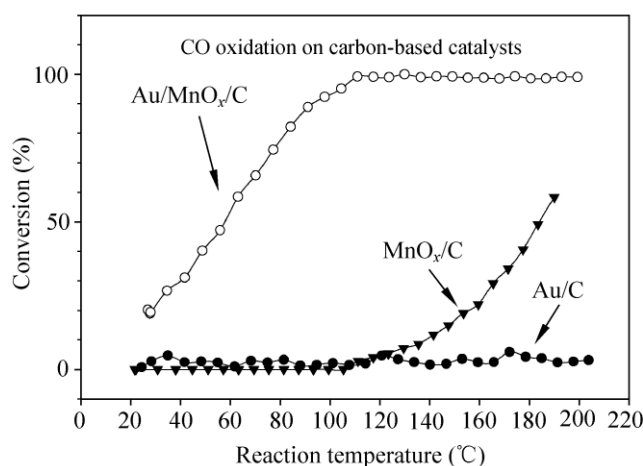


Figure 8 Conversion curves comparing the performance of an $\text{Au}/\text{MnO}_x/\text{C}$ catalyst with that of Au/C , and MnO_x/C catalysts for CO oxidation. Reproduced by permission of Elsevier from Ref. [80]

high-temperature treatment indicating that the gold nanoparticles were effectively stabilized. In contrast, Au/TiO_2 sintered significantly after pretreatment at 500°C , and its activity in CO oxidation decreased dramatically. Nevertheless, the catalytic activity of $\text{H}_3\text{PO}_4/\text{Au}/\text{TiO}_2$, either before or after thermal treatment, was not particularly high. It is also not clear why the H_3PO_4 treatment can stabilize gold nanoparticles. It was established that the presence of an excess of phosphate species may lead to catalyst deactivation. Interestingly, Hutchings and co-workers found that the addition of small amounts of NaNO_3 (0.00625 and 0.0125 wt% Na) to Au/TiO_2 led to significant enhancement in CO oxidation activity, whereas excess NaNO_3 (0.0375 wt% Na) deactivated the catalyst [214].

Our group prepared $\text{SiO}_2/\text{Au}/\text{TiO}_2$ catalysts by a solution-phase chemical grafting of $\text{Si}(\text{OCH}_3)_4$, $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$, or $((\text{CH}_3)_3\text{CO})_3\text{SiOH}$ onto Au/TiO_2 [77]. The as-synthesized $\text{SiO}_2/\text{Au}/\text{TiO}_2$ samples, containing organic fragments, were much less active than Au/TiO_2 . But once these organic moieties were burned off, the $\text{SiO}_2/\text{Au}/\text{TiO}_2$ samples retained small gold particle sizes and significant CO oxidation activity even after thermal treatment at 700°C . However, the post-modification of Au/TiO_2 by amorphous SiO_2 did not result in more active catalysts. The role of SiO_2 is limited to the mitigation of the sintering of gold nanoparticles at elevated temperatures. In later work, we modified Au/TiO_2 by amorphous SiO_2 via a gas-phase atomic layer deposition (ALD) method (Fig. 9), and found that the catalytic activity was not particularly high although gold nanoparticles were still small after high-temperature pretreatment [84]. This difference was explained in terms of the SiO_2 matrix formed via solution-phase chemical grafting being porous, whereas the SiO_2 matrix fabricated via atomic layer deposition is denser. Similar procedures have also been used by others to prepare sintering-resistant $\text{SiO}_2/\text{Pt}/\text{MFI}$ zeolite [215], $\text{SiO}_2/\text{Pt}/\text{C}$ [216–218], and $\text{SiO}_2/\text{Pt}/\text{Fe}_2\text{O}_3$ [219] catalysts.

The stabilization of gold nanoparticles by coating Au/TiO_2 with SiO_2 is understandable because the gold nanoparticles are physically encapsulated. But in some cases the loading of SiO_2 was below monolayer



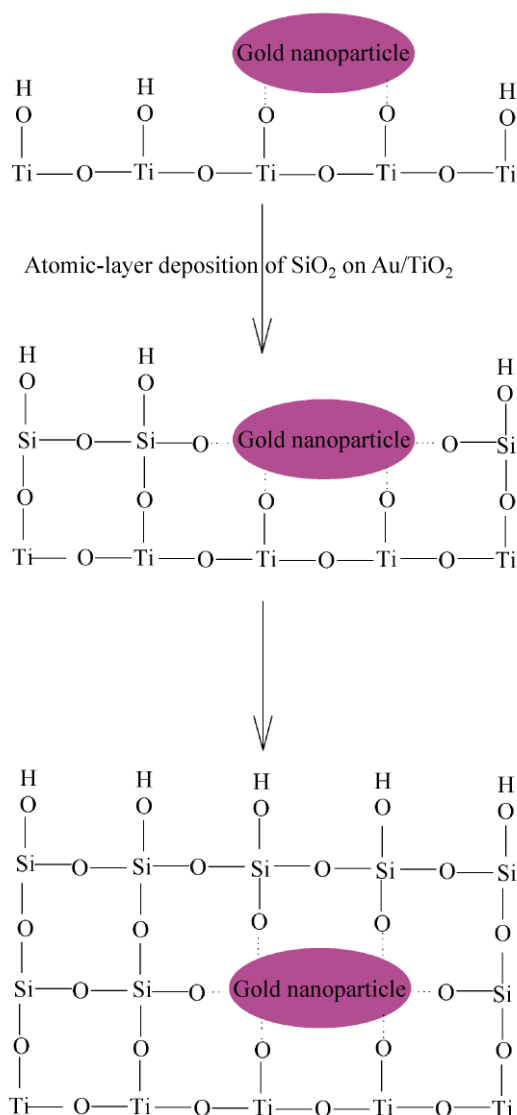


Figure 9 Schematic representation of the ALD of amorphous SiO₂ onto Au/TiO₂. Reproduced by permission of the American Chemical Society from Ref. [84]

coverage [77]. Rashkev and co-workers conducted a first-principles DFT study, and established that the deposition of SiO₂ on a TiO₂ support may cause lattice-mismatch instabilities and lead to the formation of strong anchoring sites for gold nanoparticles, even when the coverage of SiO₂ is below monolayer [220].

3.3.2 Post-modification of Au/SiO₂

The post-modification of Au/SiO₂ catalysts has been rarely studied. Au/SiO₂ is not particularly active for CO oxidation, and the addition of a metal oxide

modifier that creates active gold-modifier interfaces may promote the activity. Horváth and co-workers prepared TiO₂/Au/SiO₂ by depositing gold colloids on an SiO₂ support followed by adsorption of Ti(IV) bis(ammoniumlactato)-dihydroxide (TALH) onto the resulting Au/SiO₂ and a final calcination to remove the organic moieties [41]. The activity of TiO₂/Au/SiO₂ in CO oxidation was significantly higher than that of Au/SiO₂, due to the presence of the Au–TiO₂ interface. Similarly, Guzzi and co-workers deposited FeO_x layers onto Au/SiO₂/Si(100) by pulsed laser deposition, and found that the catalytic activity of the FeO_x/Au/SiO₂/Si(100) model catalyst was higher than those of Au/SiO₂/Si(100) and FeO_x/SiO₂/Si(100) due to the creation of an active Au–FeO_x interface [221, 222].

Our group developed MnO_x/Au/SiO₂ catalysts by soaking Au(en)₂Cl₃-derived Au/SiO₂ in an aqueous KMnO₄ solution followed by treatment in O₂–He at 300–600 °C (Fig. 10) [85]. This study was motivated by previous observations that aqueous KMnO₄ could partially oxidize the organic templates in as-synthesized mesoporous SiO₂ to yield MnO_x-containing mesoporous SiO₂ upon calcination [223, 224]. In our case, the KMnO₄ solution partially oxidized residual organic species on Au(en)₂Cl₃-derived Au/SiO₂, leaving behind MnO_x in close contact with gold nanoparticles on the SiO₂ support. The presence of MnO_x species facilitated the removal of residual organic fragments at lower temperatures and stabilized gold nanoparticles against thermal sintering. The presence of an Au–MnO_x

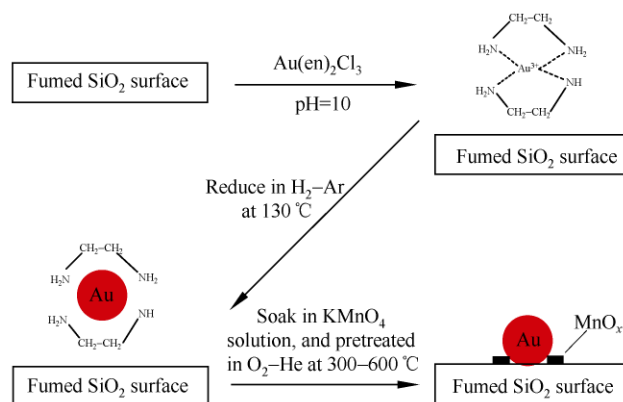


Figure 10 Schematic representation of the preparation of MnO_x-loaded Au/SiO₂ by treating Au(en)₂Cl₃-derived Au/SiO₂ with KMnO₄ solution followed by thermal activation. Reproduced by permission of the American Chemical Society from Ref. [85]

interface is responsible for the enhanced activity in CO oxidation at low reaction temperatures (below $-10\text{ }^{\circ}\text{C}$) [85].

Later, our group designed another catalyst by depositing dodecanethiol-protected gold nanoparticles onto a Cab-O-Sil SiO_2 support followed by treating the sample with an aqueous solution of KMnO_4 or K_2MnO_4 (Fig. 11) [93]. The activity of the catalyst in low-temperature CO oxidation was significantly improved due to the creation of active Au-MnO_x interfaces [93]. One astonishing finding in that work was the formation of a composite structure composed of numerous gold nanoparticles connected by amorphous MnO_x . To the best of our knowledge, such a feature had not been reported in previous publications dealing with supported gold catalysts.

3.3.3 Post-modification of more complicated gold catalysts

In Sections 3.3.1 and 3.3.2, respectively, we summarized the post-modification of Au/TiO_2 and Au/SiO_2 catalysts. The supports in these studies are conventional (i.e., TiO_2 , SiO_2), and the modification is relatively straightforward. Some recent papers in the literature have reported the fabrication of more complicated catalysts with magnetic core-shell supports and post-installed porous shells, as summarized below.

Yin and co-workers developed novel gold catalysts by using an “encapsulation and etching” strategy (Fig. 12) [50]. In this strategy, gold nanoparticles were immobilized onto $\text{SiO}_2\text{@Fe}_2\text{O}_3$ core-shell particles to form core-satellite structures, and the composite was then coated by another layer of silica followed by surface-protected etching using aqueous NaOH as the etching agent. The etching process transformed

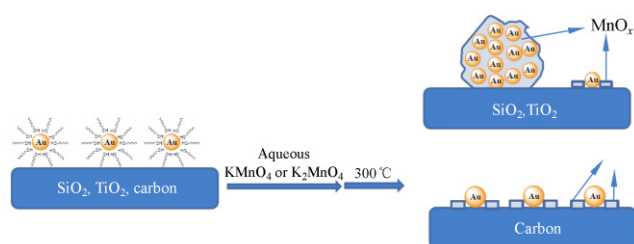


Figure 11 Formation of Au-MnO_x composites and MnO_x -modified gold nanoparticles by treatment of supported gold catalysts with aqueous KMnO_4 or K_2MnO_4 . Reproduced by permission of Springer from Ref. [93]

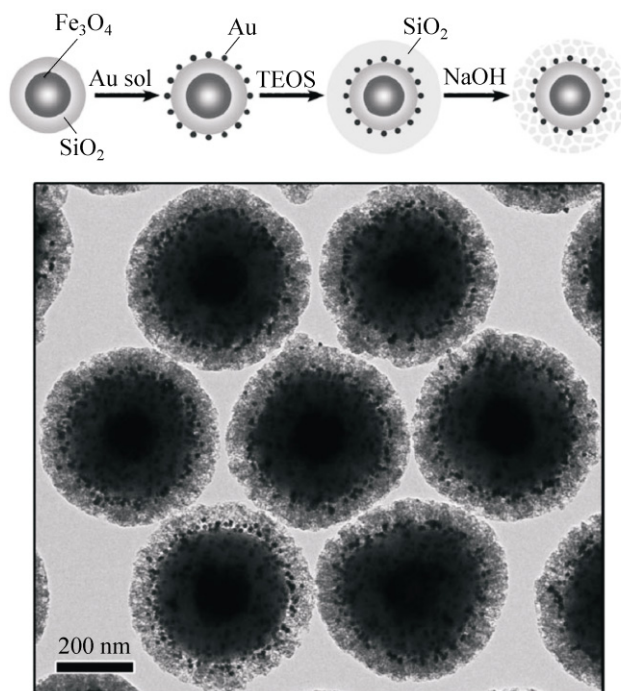


Figure 12 Schematic illustration of the synthesis procedure and a TEM image of a porous silica-protected $\text{Au/SiO}_2/\text{Fe}_3\text{O}_4$ composite structure. Reproduced with permission of Wiley-VCH from Ref. [50]

the dense silica coating to porous silica shells possessing mesopores, as demonstrated by N_2 adsorption-desorption measurements. The resulting catalysts showed high activities in the reduction of 4-nitrophenol by NaBH_4 , and the activity increased with the extent of etching, i.e., with the pore size of the SiO_2 shell. The catalysts showed good recyclability, whereas the detachment and agglomeration of supported gold nanoparticles was a problem for an $\text{Au/SiO}_2/\text{Fe}_3\text{O}_4$ catalyst. The authors proposed that the “encapsulation and etching strategy” is a versatile way of making new catalysts with various sizes, shapes, and compositions, and is superior to simply supporting metal nanoparticles in mesoporous silica, because the migration and sintering of metal nanoparticles is still possible in mesoporous silica [50].

Zhao and co-workers fabricated multifunctional mesoporous composite microspheres as a highly integrated catalyst system [60]. In their synthesis, $\text{Fe}_3\text{O}_4\text{@SiO}_2$ microspheres were modified with 3-aminopropyl triethylsilane (APTS), and gold nanoparticles prepared by citrate reduction of HAuCl_4 were immobilized onto the support. The

gold loading could be tuned by varying the grafting density of APTS molecules. The resulting $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Au}$ microspheres were coated by mesoporous SiO_2 layers using TEOS as the silica source and cetyltrimethylammonium bromide (CTAB) as the structure-directing agent, and the CTAB surfactant was then removed by extensive acetone extraction. The resulting catalyst showed high efficiency for the reduction of 4-nitrophenol by NaBH_4 and for epoxidation of styrene. Nevertheless, the gold nanoparticles prepared were as large as ~ 12 nm, and further improvement in these systems can be expected.

3.4 Simultaneous dispersion of gold and an inorganic component on a support

3.4.1 Dispersion of Au- Fe_3O_4 dumbbells on a support

Gold nanoparticles may sinter easily on pristine supports. Our group prepared Au- $\text{Fe}_3\text{O}_4/\text{SiO}_2$, Au- $\text{Fe}_3\text{O}_4/\text{TiO}_2$, and Au- $\text{Fe}_3\text{O}_4/\text{C}$ catalysts by dispersing dumbbell-like Au- Fe_3O_4 nanocomposites onto SiO_2 , TiO_2 , and C supports (Fig. 13) [87]. This process relies on the facts that the synthesis of dumbbell-like Au- Fe_3O_4 is well-established [225–227], and Au- Fe_3O_4 itself is active for CO oxidation. Because each dumbbell consists of a strongly interacting heterostructure with a gold nanoparticle at one end and a Fe_3O_4 nanoparticle at the other end, the relative positions of each component can be fixed, and sintering can thus be minimized. The resulting catalysts were found to be highly active for CO oxidation [57, 87]. In addition to the active Au- Fe_3O_4 interface, the interface between exposed gold surfaces

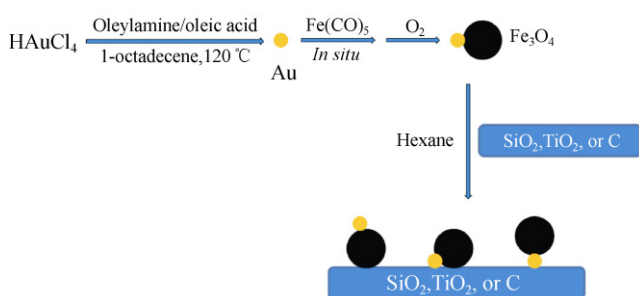


Figure 13 Synthesis of Au- Fe_3O_4 dumbbell nanoparticle catalysts deposited on selected solid supports. Reproduced by permission of the Royal Society of Chemistry from Ref. [87]

and the support may also contribute to the catalytic activity. Nevertheless, it is still not clear how these dumbbells interact with the support surface, i.e., whether only gold nanoparticles are in contact with the support, only the Fe_3O_4 nanoparticles are in contact with the support, or both components are in contact with the support. In later work, Zheng and co-workers found that the activity of Au (6.7 nm)- $\text{Fe}_3\text{O}_4/\text{TiO}_2$ in CO oxidation increased with decreasing size of the Fe_3O_4 nanoparticles [52], consistent with the previous finding that the catalytic activity of Au/ ZrO_2 in CO oxidation increased when the particle size of the ZrO_2 support decreased [105].

3.4.2 In situ transformation of NiAu/ SiO_2 into Au-NiO

Above, we have summarized ways of fabricating gold catalysts with either simple or complex structures, and gold nanoparticles were involved in all these studies. It is interesting to tune the catalytic performance by using supported alloy catalysts [228–234]. For instance, Crooks and co-workers synthesized PdAu/ TiO_2 using dendrimer-encapsulated alloy nanoparticles as the precursor, and found that the activities of the catalysts in CO oxidation followed the sequence PdAu/ $\text{TiO}_2 > \text{Pd}/\text{TiO}_2 > \text{Au}/\text{TiO}_2$ [235]. Mou and co-workers synthesized AuAg/Al-MCM-41 catalysts via both a one-step approach [236–239] and a two step method [55], and demonstrated enhanced catalytic activity in CO oxidation associated with the alloyed silver. Zhang and co-workers used a similar two-step approach to prepare AuAg/ SiO_2 [53], AuAg/ Al_2O_3 [53], AuCu/SBA-15 [240], and AuCu/silica gel [63] catalysts, and demonstrated their good performance in CO oxidation. Sun and co-workers prepared AuAg/ SiO_2 catalysts using oleylamine-coated AuAg alloy nanoparticles as the precursor, and found that the one with an Au/Ag ratio of 1/1 showed highest CO conversion [54]. In most of these studies, the oxidation state of the alloyed metal after undergoing CO oxidation was not studied, and the authors generally assumed that the alloy species was metallic. Furthermore, the deposition of gold and another metal on support surfaces may not be simultaneous.

Our group synthesized NiAu nanoparticles via a co-reduction method employing butyllithium as the reducing agent and trioctylphosphine as the protecting

agent [88, 90]. These nanoparticles were loaded onto an amorphous SiO_2 support to obtain NiAu/SiO_2 . This sample was transformed into Au-NiO/SiO_2 after low-temperature reduction and subsequent high-temperature oxidation pretreatment (Fig. 14) [88]. Interestingly, the size of the gold nanoparticles was quite small due to the protection afforded by the surrounding NiO , whereas Au/SiO_2 underwent significant sintering on calcination. The success of the new catalyst relies on the *in situ* transformation of a bimetallic NiAu alloy into an Au-NiO composite structure. The presence of NiO in close contact with gold nanoparticles can stabilize the latter on support surfaces.

It should be mentioned that the *in situ* transformation of bimetallic alloys to metal-metal oxide composite structures has been found in other systems. For instance, Baiker and co-workers prepared Pd/ZrO_2 catalysts from an amorphous Pd-Zr alloy [241, 242] and gold-zirconia-iron oxide and gold-silver-zirconia catalysts from amorphous $\text{Au}_5\text{FeZr}_{14}$ and $\text{Au}_5\text{AgZr}_{14}$ alloys [243]. Schaak and co-workers obtained a $\text{Bi}_2\text{O}_3/\text{Pd}$ nanocomposite by oxidation of Bi_2Pd nanocubes [244]. More recently, Albonetti and co-workers prepared $\text{Au-FeO}_x/\text{TiO}_2$ catalysts using bimetallic carbonyl cluster salts, e.g., $[\text{NET}_4]_4[\text{Au}_4\text{Fe}_4(\text{CO})_{16}]$ and $[\text{NET}_4][\text{AuFe}_4(\text{CO})_{16}]$ [245, 246].

3.4.3 Dispersion of Au@oxide core-shell structures on a support

Great efforts have been made to design metal@oxide core-shell structures [49, 247–253]. However, only limited attention has been paid to the use of such core-shell structures [252, 254–261] or their supported versions [262–264] in the fabrication of new catalysts [265, 266]. Some researchers have developed new

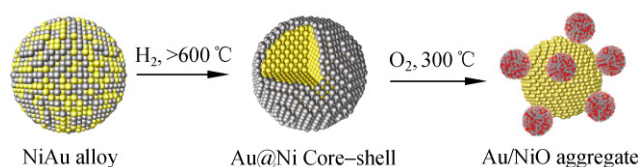


Figure 14 Schematic representation of the phase transformation from a NiAu alloy to a Au/NiO hetero-aggregate [88]. The SiO_2 support is omitted for simplicity. Reproduced by permission of Wiley-VCH from Ref. [88]

catalysts featuring the strategic location of small gold nanoparticles in much bigger hollow ZrO_2 or SiO_2 shells to form yolk-shell structures [43, 267–271], or the entrapment of a number of gold nanoparticles in an amorphous SiO_2 matrix [125]. Au@TiO_2 core-shell structures were prepared and tested in photooxidation [272, 273], but the gold cores were too large for other catalytically interesting reactions, and the TiO_2 shells were thick and rough. Zhang and co-workers prepared Au@TiO_2 with gold particle sizes of 10–15 nm and a TiO_2 thickness of 1–3 nm, and tested its activity in CO oxidation [274]. However, the CO conversion was very low when the reaction temperature was below 100 °C. Xie and coworkers synthesized Au@SnO_2 core-shell structures by an intermetallics-based dry-oxidation approach [46]. Gold nanoparticles with a mean size of 15 nm were encapsulated by a SnO_2 shell having a thickness of 6–7 nm. The core-shell structured catalyst still showed 50% CO conversion when the reaction temperature was 230 °C, even though the catalyst was pretreated at 850 °C prior to reaction [46]. Xu and co-workers synthesized bimetallic Au-Ni nanoparticles embedded in SiO_2 spheres, and demonstrated that the resulting Au-Ni@SiO_2 showed higher catalytic activity and better durability than monometallic Au@SiO_2 or Ni@SiO_2 in the hydrolysis of ammonia-borane [56]. Alivisatos and co-workers prepared $\text{Au@Fe}_2\text{O}_3$ core-shell structures by depositing an iron shell around gold nanoparticles stabilized by oleylamine, hexadecylamine, or dodecanethiol, followed by oxidation of the iron shell to form an Fe_2O_3 shell [251]. The magnetic properties of the resulting materials were characterized, but no catalytic data were reported.

Our group recently designed $\text{Au@Fe}_2\text{O}_3/\text{SiO}_2$ catalysts by dispersing $\text{Au@Fe}_2\text{O}_3$ core-shell structures on a SiO_2 support (Fig. 15) [95]. It was necessary to pretreat the catalysts at elevated temperatures to remove residual organic species and create pores in the Fe_2O_3 shell. However, collapse of the core-shell structure and sintering of gold nanoparticles were still observed when the catalysts were treated at 700 °C. The catalytic activity in CO oxidation generally decreased with increasing thickness of the SiO_2 shell, but was still higher than that of $\text{Au/Fe}_2\text{O}_3$

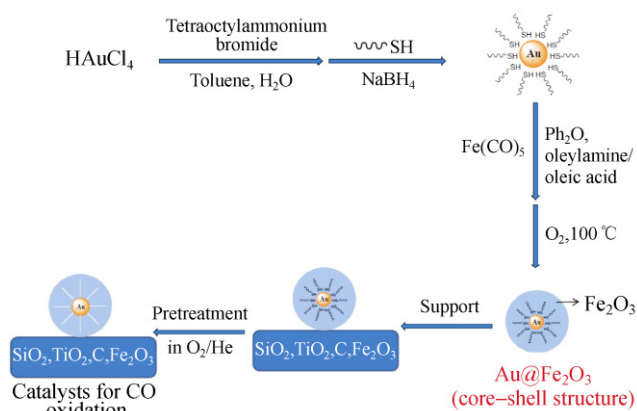


Figure 15 Preparation and catalytic reaction of supported Au@Fe₂O₃ nanoparticles. Reproduced by permission of Elsevier from Ref. [95]

or Au/SiO₂ with comparable gold loadings prepared by colloidal deposition. Other catalysts, such as Au@Fe₂O₃/TiO₂, Au@Fe₂O₃/C, and Au@Fe₂O₃/Fe₂O₃, were also developed in the same way. Although we used CO oxidation as a probe reaction for these catalysts, we believe that these catalysts may also be useful in other reactions.

4. Concluding remarks

In this review we have provided a survey of the development of novel supported gold catalysts from a materials perspective. Examples have been highlighted of the synthesis of novel gold catalysts with relatively simple metal–support interfaces, the pre-modification of supports before loading gold nanoparticles, the post-modification of supported gold catalysts, and the simultaneous dispersion of gold and an inorganic component on supports. Although most of the examples were taken from our own work, references to the wider literature were made when appropriate. We need to emphasize here again that most of the reviews in this field deal with new preparation methods, synthesis details, catalytic reactions, and the nature of the active sites and reaction mechanisms [18–33], with a very limited number written from a materials perspective [89]. From the references cited herein, one can see that the use of a materials perspective to develop new gold catalysts has resulted in rapid progress in recent years.

The importance of our work in relation to catalyst development lies in several points. First, we have developed new gold catalysts not previously reported, thus enriching the pool of gold catalysts. Most of our newly developed catalysts were not covered in a classic book “Catalysis by Gold” published in 2006 [28]. Second, we have improved the diversity of the morphology, built up complex metal-support interfaces, enhanced the thermal stability of gold catalysts, and added more functionality to the catalyst system. This is novel, because most of the papers in the literature have dealt with Au/TiO₂ with relatively simple metal-support interfaces and poor thermal stability. Third, we have established some correlations between structure and function by means of systematic characterization, although these correlations have not been summarized in detail here. Last but not least, the development of these gold catalysts has provided new opportunities for further fundamental and applied research [130, 131, 146, 186, 188, 220, 275–278]. For instance, the development of Au/SiO₂ [75, 76] and Au/FePO₄ [86] catalysts makes it possible to study the nature of active sites and reaction mechanisms [130, 131, 146], and the development of Au/Al₂O₃/TiO₂ [71] and SiO₂/Au/TiO₂ [77, 84] catalysts prompted the subsequent DFT studies [186, 220].

We propose several ideas for further research. First, most of the previous experiments were carried out by studying the catalysts before and after thermal treatment and reaction testing, but the details of any physical changes in the catalysts are not clear. Therefore, the sintering process should be observed by direct TEM imaging [279–281]. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging should also be helpful to obtain images with higher resolution [282–284]. Second, although we observed the phenomenon in many systems, the physical reasons for the anti-sintering behavior are not clear. Detailed and systematic first-principles calculations on these catalyst systems should lead to interesting results [186, 220]. For instance, the binding energies of gold with various supports and functionalized supports should be compared. Third, considering that these modified catalysts have complex interfaces, the ways in which these interfaces may influence the nature of

active sites and the reaction mechanisms in CO oxidation should be studied. These can be done by using XPS, X-ray absorption near edge structure (XANES), and FTIR measurements, and theoretical calculations can also be carried out. Finally, most of the catalysts have only been used in CO oxidation. This is not only because CO oxidation is useful in environmental protection, but also because it is a sensitive probe reaction and easy to carry out. It would be worthwhile to explore applications of these catalysts in other reactions, such as liquid-phase oxidation, hydrogenation, de-NO_x reactions, and combustions of VOCs. We think that the effort put into these aspects to date is insufficient and ample opportunities exist for future study in these directions.

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