Development of Novel Supported Gold Catalysts: A Materials Perspective

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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-NOₓ, catalytic combustion.
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, Fe₃O₄, 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 (CH3)2Si(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, and CoO, 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 
avactive for CO oxidation. Alternatively, gold particles 
capped with alkanethiol and alkoxysilane 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 = 
ethylene diamine) 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)₂Cl₂-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.
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 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 crystallizes 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,
60, and 700 °C). The surface area of the TiO$_2$ 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 Fe$_3$O$_4$) 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 $\alpha$-Fe$_2$O$_3$, with decreasing surface areas (35, 30, and 14 m$^2$/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 $\gamma$-Al$_2$O$_3$ nanofibers were much more active than those supported on commercial $\gamma$-Al$_2$O$_3$ in CO oxidation [109]. The authors proposed, based on diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) data, that the OH groups bonding to $\gamma$-Al$_2$O$_3$ nanofibers may facilitate CO oxidation. Zhong and co-workers dispersed gold colloids onto porous $\alpha$-Fe$_2$O$_3$ nanorods, and found that the resulting catalyst was more active than gold nanoparticles dispersed on commercial $\alpha$-Fe$_2$O$_3$ [45]. Cao and co-workers found that the activity of Au/$\beta$-MnO$_2$ nanorods was higher than that of Au/commercial $\beta$-MnO$_2$ particulates in the solvent-free aerobic oxidation of alcohol [111]. The authors ascribed the high activity of Au/$\beta$-MnO$_2$ 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 MnO$_2$ nanorods.

Flytzani-Stephanopoulos and co-workers synthesized CeO$_2$ nanorods, nanocubes, and nanopolyhedra via hydrothermal synthesis, and subsequently loaded gold via deposition–precipitation [110]. As shown in Fig. 5, the width of the CeO$_2$ 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 CeO$_2$ nanocubes was 29.5 nm ± 10.6 nm, and the diameter of the CeO$_2$ 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/CeO$_2$ nanorods > Au/CeO$_2$ nanopolyhedra > Au/CeO$_2$ nanocubes. The lowest activity of the Au/CeO$_2$ 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 (H$_2$-TPR) [110]. Subsequently, Yuan and co-workers found that the activity in the preferential CO oxidation in H$_2$-rich gas followed the same trend mentioned above [112, 114]. Cao and co-workers demonstrated that the activity of Au/CeO$_2$ nanorods in CO oxidation was much higher than that of Au/CeO$_2$ nanoparticles [113].
Li and co-workers synthesized spindle-shaped $\text{Fe}_2\text{O}_3$ nanoparticles using acidic amino acid additives, and they also prepared rhombohedral $\text{Fe}_2\text{O}_3$ nanoparticles using basic amino acids [108]. The particle size of the $\text{Fe}_2\text{O}_3$ 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/$\text{Fe}_2\text{O}_3$ showed higher activity than the rhombohedral Au/$\text{Fe}_2\text{O}_3$, 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 $\text{Fe}_2\text{O}_3$ 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 TiO$_2$ (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 SiO$_2$ supports

SiO$_2$ is not suitable for loading gold nanoparticles via deposition–precipitation because SiO$_2$ has a low isoelectric point (IEP ~2), so the Au(OH)$_4^-$ species cannot effectively adsorb onto the negatively charged SiO$_2$ surface under basic conditions. One way to overcome this obstacle is to introduce a high-isoelectric-point metal oxide onto the SiO$_2$ surface. As a result, Au(OH)$_4^-$ species may adsorb more efficiently onto the functionalized support.

Our group modified meso porous and fumed SiO$_2$ surfaces with amorphous TiO$_2$ via a surface–sol–gel technique under non-aqueous conditions (Fig. 6) [66, 72]. Ti(OC$_4$H$_9$)$_4$ was used as the precursor to load surface TiO$_2$, and methanol and toluene were used as the solvents. Gold nanoparticles were loaded onto TiO$_2$/SiO$_2$ and the activity of Au/TiO$_2$/SiO$_2$ in CO oxidation was found to be much higher than that of Au/SiO$_2$. The enhanced activity is not only due to the higher gold loading of Au/TiO$_2$/SiO$_2$ compared to that of Au/SiO$_2$, but also due to the presence of an active Au–TiO$_2$ interface. The resulting Au/TiO$_2$/SiO$_2$ catalysts should not be classified as “SiO$_2$ supported gold catalysts”, and may be more appropriately described as “SiO$_2$-based gold catalysts”. Since the presence of TiO$_2$ increases the catalytic activity and the Au/TiO$_2$/SiO$_2$ catalyst is merely an Au/TiO$_2$ catalyst supported on SiO$_2$, one may question why Au/TiO$_2$ was not used for CO oxidation in the first place and why we need Au/TiO$_2$/SiO$_2$. 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 SiO$_2$ by TiO$_2$ 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 SiO$_2$-based gold catalysts, such as Au/Al$_2$O$_3$/SiO$_2$ [72, 150], Au/TiO$_2$/SiO$_2$ [151–165], Au/FeO$_x$/SiO$_2$ [150, 166, 167], Au/CoO$_x$/SiO$_2$ [150, 168–171], Au/ZnO/SiO$_2$ [172], Au/FeO$_x$/SiO$_2$ [168], and Au/CeO$_2$/SiO$_2$ [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/SiO$_2$ catalysts. Therefore, the development of catalysts based on a better starting point (such as highly active Au/SiO$_2$ [75, 76]) should be considered.

Our group prepared a series of M$_x$O$_y$/SiO$_2$ (M = Mg, Al, Fe, Ni, Zn, Ba, La, Ce) supports either by impregnation or by using NaOH as the precipitating agent [76]. A TiO$_2$/SiO$_2$ support was prepared by grafting a Ti$_{16}$O$_{16}$(OEt)$_{32}$ precursor onto SiO$_2$. Gold was loaded onto these functionalized supports using Au(en)$_2$Cl$_3$ as the precursor. It was found that Au/FeO$_x$/SiO$_2$, Au/TiO$_2$/SiO$_2$, and Au/BaO/SiO$_2$ were more active in low-temperature CO oxidation than Au/SiO$_2$ 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 TiO₂ supports

Au/TiO₂ is very active for CO oxidation below room temperature, but gold nanoparticles on TiO₂ can sinter easily at high temperature, even more easily than those on SiO₂ [176]. Our group found that modification of the TiO₂ support by amorphous Al₂O₃ followed by loading of gold could alleviate the sintering problem [71]. The Al₂O₃/TiO₂ support was synthesized by surface–sol–gel processing of Al(sec-O₅C₄H₉)₃ on TiO₂ followed by controlled hydrolysis. Whereas Au/TiO₂ underwent significant thermal deactivation at 500 °C, ascribed to the agglomeration of gold particles, Au/Al₂O₃/TiO₂ underwent minimal thermal deactivation at the same temperature. This can be ascribed to the stabilization of gold nanoparticles by the amorphous Al₂O₃ coating, as clearly shown by TEM images.

Since Au/Al₂O₃/TiO₂ is a successful catalyst, it is interesting to know whether other metal oxide additives can play a role similar to Al₂O₃. In subsequent work, we loaded various metal oxide additives onto the TiO₂ support via excess-solution impregnation of soluble precursors followed by calcination, and established that Au/MₓOᵧ/TiO₂ (M = Ca, Ni, Zn, Ga, Y, Zr, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, 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/TiO₂ collected after pretreatment at 500 °C and subsequent use in the water–gas shift reaction contained mostly large gold particles, whereas Au/ZnO/TiO₂ 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 TiO₂-based gold catalysts, such as Au/MgO/TiO₂ [177], Au/MnO₂/TiO₂ [178], Au/FeOₓ/TiO₂ [179, 180], Au/CuOₓ/TiO₂ [181], Au/ZnO/TiO₂ [182], and Au/CeOₓ/TiO₂ [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 Al₂O₃ support by La₂O₃ could stabilize metallic nickel particles for CO methanation [185].

The development of Au/MₓOᵧ/TiO₂ 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 Al2O3/TiO2 was much stronger than that of gold on TiO2 [186]. Although they assumed that Al2O3 was dispersed homogeneously on TiO2 support when calculating the binding energy, and the conclusions at that point were consistent with the proposed anti-sintering behavior of Au/Al2O3/TiO2 catalysts, their calculations also showed that the activity of CO oxidation on Au/Al2O3/TiO2 was low if TiO2 was fully coated by Al2O3. Therefore, they concluded that the TiO2 should not be fully coated by Al2O3, so that gold nanoparticles are in contact with both the TiO2 support and Al2O3 patches [186]. Although we think that the coating of Al2O3 on TiO2 support may not be homogeneous and several Au/Al2O3/TiO2 catalysts with a range of Al2O3 contents are all active catalysts [78], we need to point out that the assumption in the calculations that the Au–Al2O3 interface is not active for CO oxidation [186] should be treated with caution, because experimentally, Au/Al2O3 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 Au/Al2O3 [187].

Hagaman and co-workers conducted a solid-state 27Al magic angle spinning (MAS) and triple quantum magic angle spinning (3QMAS) NMR investigation of a series of Al2O3/TiO2 supports with different Al2O3 loadings which were calcined at different temperatures [188]. These supports were used in our previous work [78] to prepare Au/Al2O3/TiO2 catalysts. The highest catalytic activity and the smallest gold particle size reported in our previous paper [78], we need to point out that the assumption in the calculations that the Au–Al2O3 interface is not active for CO oxidation [186] should be treated with caution, because experimentally, Au/Al2O3 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 Au/Al2O3 [187].

3.2.3 Pre-modification of Al2O3 supports

The pre-modification of Al2O3 supports by metal oxides followed by assembly of gold nanoparticles has also been studied. Gold catalysts based on oxide-modified Al2O3 supports include Au/MgO/Al2O3 [189–191], Au/MnO/Al2O3 [192–194], Au/Fe2O3/Al2O3 [192–196], Au/Co2O4/Al2O3 [192, 194], Au/ZnO/Al2O3 [192, 197], Au/SnO2/Al2O3 [198], Au/La2O3/Al2O3 [199], and Au/TeO2/Al2O3 [200–203]. In particular, Niewenhuys and coworkers tested the performance of Al2O3-based gold catalysts in a number of reactions, and established that MgO/Al2O3 [189], BaO/Al2O3 [204, 205], ZnO/Al2O3 [197], and ZrO2/Al2O3 [197] could all stabilize gold nanoparticles against thermal sintering.

Our group modified various Al2O3 supports (boehmite AlOOH, amorphous Al(OH)3, and highly crystalline γ-Al2O3) by amorphous TiO2 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 Au/TiO2/Al2O3 catalysts at high temperature. The role of the dispersed amorphous TiO2 is not to stabilize gold nanoparticles, because the gold nanoparticles on pristine Al2O3 supports were also small after high-temperature pretreatment. Rather, we propose that its role is to create an Au–TiO2 interface which is more active than Au–Al2O3 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 Au3+ 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 KMnO₄. In this case, carbon is a sacrificial reductant, and undergoes a self-limiting reaction with aqueous KMnO₄ to form a decoration of MnOₓ on the surface (i.e., 4KMnO₄ + 3C + 2H₂O → 4MnO₂ + 3CO₂ + 4KOH) [208]. We then loaded gold onto the MnOₓ/C support via deposition–precipitation [80]. The resulting Au/MnOₓ/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 Au/TiO₂/C [209–211], Au/FeOₓ/C [212], and Au/ZnO/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/TiO₂

Au/TiO₂ 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 TiO₂, and then soaked the Au/TiO₂ in an aqueous H₃PO₄, followed by extensive washing [79]. The resulting H₃PO₄/Au/TiO₂ prepared under optimal conditions was still active for CO oxidation after high-temperature treatment indicating that the gold nanoparticles were effectively stabilized. In contrast, Au/TiO₂ sintered significantly after pretreatment at 500 °C, and its activity in CO oxidation decreased dramatically. Nevertheless, the catalytic activity of H₃PO₄/Au/TiO₂, either before or after thermal treatment, was not particularly high. It is also not clear why the H₃PO₄ 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 NaNO₃ (0.00625 and 0.0125 wt% Na) to Au/TiO₂ led to significant enhancement in CO oxidation activity, whereas excess NaNO₃ (0.0375 wt% Na) deactivated the catalyst [214].

Our group prepared SiO₂/Au/TiO₂ catalysts by a solution-phase chemical grafting of Si(OCH₃)₄, (C₂H₅O)₃Si(CH₂)₃NH₂, or ((CH₃)₃CO)₃SiOH onto Au/TiO₂ [77]. The as-synthesized SiO₂/Au/TiO₂ samples, containing organic fragments, were much less active than Au/TiO₂. But once these organic moieties were burned off, the SiO₂/Au/TiO₂ samples retained small gold particle sizes and significant CO oxidation activity even after thermal treatment at 700 °C. However, the post-modification of Au/TiO₂ by amorphous SiO₂ did not result in more active catalysts. The role of SiO₂ is limited to the mitigation of the sintering of gold nanoparticles at elevated temperatures. In later work, we modified Au/TiO₂ by amorphous SiO₂ 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 SiO₂ matrix formed via solution-phase chemical grafting being porous, whereas the SiO₂ matrix fabricated via atomic layer deposition is denser. Similar procedures have also been used by others to prepare sintering-resistant SiO₂/Pt/MFI zeolite [215], SiO₂/Pt/C [216–218], and SiO₂/Pt/Fe₂O₃ [219] catalysts.

The stabilization of gold nanoparticles by coating Au/TiO₂ with SiO₂ is understandable because the gold nanoparticles are physically encapsulated. But in some cases the loading of SiO₂ was below monolayer...
coverage [77]. Rashkeev 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, Guczi and co-workers deposited FeOx layers onto Au/SiO2/Si(100) by pulsed laser deposition, and found that the catalytic activity of the FeOx/Au/SiO2/Si(100) model catalyst was higher than those of Au/SiO2/Si(100) and FeOx/SiO2/Si(100) due to the creation of an active Au–FeOx interface [221, 222].

Our group developed MnOx/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 MnOx-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 MnOx in close contact with gold nanoparticles on the SiO2 support. The presence of MnOx species facilitated the removal of residual organic fragments at lower temperatures and stabilized gold nanoparticles against thermal sintering.

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

Figure 10  Schematic representation of the preparation of MnOx-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 °C) [85].

Later, our group designed another catalyst by depositing dodecanethiol-protected gold nanoparticles onto a Cab-O-Sil SiO2 support followed by treating the sample with an aqueous solution of KMnO4 or K2MnO4 (Fig. 11) [93]. The activity of the catalyst in low-temperature CO oxidation was significantly improved due to the creation of active Au–MnOx interfaces [93]. One astonishing finding in that work was the formation of a composite structure composed of numerous gold nanoparticles connected by amorphous MnOx. 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/TiO2 and Au/SiO2 catalysts. The supports in these studies are conventional (i.e., TiO2, SiO2), 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 SiO2@Fe2O3 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 the dense silica coating to porous silica shells possessing mesopores, as demonstrated by N2 adsorption–desorption measurements. The resulting catalysts showed high activities in the reduction of 4-nitrophenol by NaBH4, and the activity increased with the extent of etching, i.e., with the pore size of the SiO2 shell. The catalysts showed good recyclability, whereas the detachment and agglomeration of supported gold nanoparticles was a problem for an Au/SiO2/Fe3O4 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 [50].

Zhao and co-workers fabricated multifunctional mesoporous composite microspheres as a highly integrated catalyst system [60]. In their synthesis, Fe3O4@SiO2 microspheres were modified with 3-aminopropyl triethyilsilane (APTS), and gold nanoparticles prepared by citrate reduction of HAuCl4 were immobilized onto the support. The
gold loading could be tuned by varying the grafting density of APTS molecules. The resulting Fe3O4@SiO2–Au microspheres were coated by mesoporous SiO2 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 NaBH4 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–Fe3O4 dumbbells on a support

Gold nanoparticles may sinter easily on pristine supports. Our group prepared Au–Fe3O4/SiO2, Au–Fe3O4/TiO2, and Au–Fe3O4/C catalysts by dispersing dumbbell-like Au–Fe3O4 nanocomposites onto SiO2, TiO2, and C supports (Fig. 13) [87]. This process relies on the facts that the synthesis of dumbbell-like Au–Fe3O4 is well-established [225–227], and Au–Fe3O4 itself is active for CO oxidation. Because each dumbbell consists of a strongly interacting heterostructure with a gold nanoparticle at one end and a Fe3O4 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–Fe3O4 interface, the interface between exposed gold surfaces 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 Fe3O4 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)–Fe3O4/TiO2 in CO oxidation increased with decreasing size of the Fe3O4 nanoparticles [52], consistent with the previous finding that the catalytic activity of Au/ZrO2 in CO oxidation increased when the particle size of the ZrO2 support decreased [105].

3.4.2 In situ transformation of NiAu/SiO2 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/TiO2 using dendrimer-encapsulated alloy nanoparticles as the precursor, and found that the activities of the catalysts in CO oxidation followed the sequence PdAu/TiO2 > Pd/TiO2 > Au/TiO2 [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/SiO2 [53], AuAg/Al2O3 [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/SiO2 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\textsubscript{2} support to obtain NiAu/SiO\textsubscript{2}. This sample was transformed into Au–NiO/SiO\textsubscript{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\textsubscript{2} underwent significant sintering on calcination. The success of the new catalyst relies on the \textit{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 \textit{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\textsubscript{2} catalysts from an amorphous Pd–Zr alloy [241, 242] and gold–zirconia–iron oxide and gold–silver–zirconia catalysts from amorphous Au\textsubscript{5}FeZr\textsubscript{14} and Au\textsubscript{5}AgZr\textsubscript{14} alloys [243]. Schaak and co-workers obtained a Bi\textsubscript{2}O\textsubscript{3}/Pd nanocomposite by oxidation of Bi\textsubscript{2}Pd nanocubes [244]. More recently, Albonetti and co-workers prepared Au–Fe\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2} catalysts using bimetallic carbonyl cluster salts, e.g., [NEt\textsubscript{4}]\textsubscript{4}[Au\textsubscript{4}Fe\textsubscript{4}(CO)\textsubscript{16}] and [NEt\textsubscript{4}][AuFe\textsubscript{4}(CO)\textsubscript{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 catalysts featuring the strategic location of small gold nanoparticles in much bigger hollow ZrO\textsubscript{2} or SiO\textsubscript{2} shells to form yolk–shell structures [43, 267–271], or the entrapment of a number of gold nanoparticles in an amorphous SiO\textsubscript{2} matrix [125]. Au@TiO\textsubscript{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\textsubscript{2} shells were thick and rough. Zhang and co-workers prepared Au@TiO\textsubscript{2} with gold particle sizes of 10–15 nm and a TiO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2} spheres, and demonstrated that the resulting Au–Ni@SiO\textsubscript{2} showed higher catalytic activity and better durability than monometallic Au@SiO\textsubscript{2} or Ni@SiO\textsubscript{2} in the hydrolysis of ammonia–borane [56]. Alivisatos and co-workers prepared Au@Fe\textsubscript{3}O\textsubscript{4} 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\textsubscript{3}O\textsubscript{4} shell [251]. The magnetic properties of the resulting materials were characterized, but no catalytic data were reported.

Our group recently designed Au@Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2} catalysts by dispersing Au@Fe\textsubscript{3}O\textsubscript{4} core–shell structures on a SiO\textsubscript{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\textsubscript{3}O\textsubscript{4} 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\textsubscript{2} shell, but was still higher than that of Au/Fe\textsubscript{3}O\textsubscript{4}.
or Au/SiO$_2$ with comparable gold loadings prepared by colloidal deposition. Other catalysts, such as Au@Fe$_2$O$_3$/TiO$_2$, Au@Fe$_2$O$_3$/C, and Au@Fe$_2$O$_3$/Fe$_2$O$_3$, 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/TiO$_2$ 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/SiO$_2$ [75, 76] and Au/FePO$_4$ [86] catalysts makes it possible to study the nature of active sites and reaction mechanisms [130, 131, 146], and the development of Au/Al$_2$O$_3$/TiO$_2$ [71] and SiO$_2$/Au/TiO$_2$ [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-NOx 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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