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Design of Novel Structured Gold Nanocatalysts

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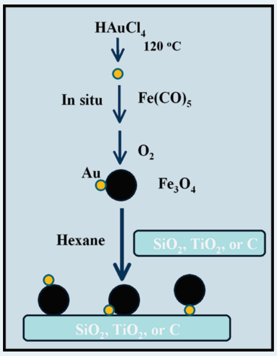
ABSTRACT: Small gold nanoparticles dispersed on certain oxide supports exhibit unprecedented catalytic activities in low-temperature CO oxidation, and gold catalysts show a great potential for selective oxidation or hydrogenation of organic substrates. Nevertheless, most gold catalysts (e.g., Au/TiO_2, Au/Al_2O_3, Au/Fe_2O_3, Au/SiO_2, Au/CeO_2) have been prepared by loading gold on unmodified or modified solid supports through traditional synthesis methodologies (e.g., deposition precipitation, wet impregnation), therefore having simple metal-on-support structures and metal−support interactions. The current Perspective highlights some recent progress in the design of novel structured gold nanocatalysts, including unsupported or supported core−shell or yolk−shell structures, gold nanoparticles encapsulated in an inorganic matrix, postmodified gold catalysts, gold-based alloy catalysts, and gold catalysts with additional interfacial sites (or metal oxide components) carried to supports or formed in situ on supports. The objective of most of these studies was to demonstrate synthetic protocols by testing the catalytic performance of the prepared catalysts in simple probe reactions, and the focus was more on materials synthesis than on catalytic reactions or reaction mechanisms. These novel structured gold catalysts will certainly bring new opportunities for studying their performance in various catalytic reactions, the nature of active sites, reaction mechanisms, and correlations between structure and catalytic properties.



KEYWORDS: gold nanoparticles, catalyst design, gold catalysis, CO oxidation, core−shell structure

1. INTRODUCTION

Gold is often regarded as chemically inert, since bulk gold cannot be oxidized in air and it does not react with most chemical reagents. It was previously deemed useless in catalysis due to the low catalytic activity observed. However, low catalytic activity may not be intrinsic to gold catalysts, because previous gold catalysts prepared by impregnation had large gold particle sizes. In the 1980s, Haruta and co-workers found that certain metal oxide-supported gold catalysts prepared via coprecipitation or deposition−precipitation methods showed high activity in CO oxidation below room temperature.[1−3] The resulting catalysts were portrayed by gold nanoparticles finely dispersed on metal oxide supports, often with redox properties (e.g., TiO_2, Fe_2O_3). Later, Goodman and co-workers prepared model Au/TiO_2 catalysts by physical evaporation of gold atoms onto a TiO_2 (110)-(1 × 2) surface.[4] The activity in CO oxidation was found to be dependent critically on the size of the gold nanoparticles, being the highest when the size of the gold nanoparticles was ∼3 nm. Because gold is cheaper than platinum, palladium, and most other noble metals used as catalyst components, and nanosized gold possesses unique catalytic properties, gold catalysis has been a hot topic recently.[5−16]

Thousands of relevant reports have delved into the following topics:[5−16] (1) effects of various preparation methods (e.g., coprecipitation, deposition−precipitation, colloidal deposition) on the physicochemical and catalytic properties of the resulting gold catalysts; (2) effects of various preparation details (e.g., preparation temperature, pH value of the synthesis mixture, pretreatment conditions) on the activity of the resulting catalysts; (3) development of novel structured gold catalysts from a perspective of delicate inorganic materials synthesis; (4) environmental catalysis, such as CO oxidation, water−gas shift, de-NO_x, and catalytic combustion of organic pollutants; (5) organic catalysis, such as liquid-phase oxidation, hydrogenation, and carbon−carbon coupling reactions; (6) investigation of the nature of active sites and reaction mechanisms employing X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy, infrared spectroscopy, etc.; and (7) surface chemistry studies and theoretical calculations based on model catalyst systems. These studies, with a few being exceedingly interesting,[4,17−29] have expanded the scope of gold catalysis research pioneered by Haruta and co-workers. The reader who is interested is referred to a classic book, *Catalysis by Gold*, and the references cited therein for more background information.[9]

Although publications in the field are many, much effort continues to be expended on CO oxidation on gold catalysts for the following reasons: (1) CO oxidation has practical applications in face masks, car emission control, and fuel cells. (2) CO oxidation is a sensitive probe reaction, and the temperature regions in which different catalysts work are wide. The catalytic activity in CO oxidation can often be correlated to the size of the supported gold nanoparticles. If the preparation method is not optimized and large gold particles dominate, the resulting catalysts either show low CO conversions at room

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temperature or can work only at high reaction temperatures. On the other hand, if the catalyst preparation is optimized and small gold nanoparticles dominate, the resulting catalysts may likely show high CO conversions at or below room temperature. However, small gold nanoparticles dispersed on supports do not necessarily lead to high CO conversions; other parameters, such as the support effect and pretreatment method, may also influence catalytic activity. (3) CO oxidation is a simple reaction involving two gaseous reactants and one gaseous product, and the apparatus for catalyst screening is easy to construct. (4) Although CO oxidation seems to be simple, many fundamental questions, such as the nature of active sites and reaction mechanisms, are quite interesting and under hot debate.

The catalysts most frequently used in gold catalysis are Au/TiO_2, Au/ZrO_2, Au/Al_2O_3, Au/Fe_2O_3, and Au/CeO_2. Based on a metal (gold) and a simple support, they are usually prepared by deposition−precipitation in the presence of an aqueous base. Alternatively, they may be prepared by coprecipitation, colloidal deposition, impregnation, and other methods.[9] Simple metal oxide supports can be acquired commercially or prepared easily in the laboratory. The use of simple metal oxide supports to make gold catalysts allows structure−function correlations to be made in a relatively straightforward manner. In only limited cases are gold catalysts prepared using supports with complicated structures/morphologies or prepared via delicate inorganic synthesis.[30−37]

In recent years, advances have been made toward the design of novel structured gold nanocatalysts. The development in this direction is motivated by the fact that synthesis protocols for making catalytic materials with controlled sizes and isolated sites are being sought, and better catalysts with enhanced catalytic activity, selectivity, and stability are always welcome. Although the size of gold nanoparticles is important for achieving high activity, the types,[38−41] crystal phases,[42−45] sizes,[46−49] and shapes[50−52] of supports, together with the structures of the gold catalysts,[31,37,53] are also important factors for improving catalytic performance. To improve catalytic performance, gold nanoparticles need to be finely dispersed and stabilized on supports, the gold particle size should be well controlled, and the catalytic structure should be better defined.

The objective of the current Perspective is to highlight some recent progress in the design of novel structured gold catalysts. These catalysts are different from the traditional catalysts made by simply loading gold nanoparticles or gold precursors on unmodified or modified supports (and therefore having simple metal-on-support structures). Rather, they are often heterostructured or undergo structural changes upon appropriate treatments, and they often entail delicate inorganic synthesis. The presence of an oxide or another component near gold nanoparticles or atoms may tune the physicochemical properties and provide additional functionality to the catalyst systems, thereby leading to high-performance catalysts. The Perspective does not intend to be comprehensive. Instead, selected examples in the literature are highlighted. Finally, we analyze the importance and limitations in the field and suggest new directions for future research.

2. CORE−SHELL AND YOLK−SHELL STRUCTURES

2.1. General Considerations. Traditional metal catalysts are prepared by impregnating a solid support with a soluble metal salt, followed by drying and reduction. The sintering of metal nanoparticles at elevated temperatures, due to the low melting points of metal nanoparticles and insufficient metal−support interactions, often constitutes a problem for practical applications. In addition, it is difficult to isolate metal nanoparticles and catalytic sites in a controlled manner. Attempts have been made to support metal nanoparticles inside the pore channels of mesoporous materials, such as mesoporous SiO_2[54−56] and TiO_2.[57,58] The ordered nanopores confine the metal nanoparticles and allow for the diffusion of reactants and products, but the sintering of metal nanoparticles still cannot be avoided because the nanopores are open. It is therefore tempting to encapsulate metal nanoparticles inside inorganic shells.[59−65]

Inorganic shells can serve as physical barriers or cages that separate the metal nanoparticles from each other and hinder their escape from the shells. In addition, the presence of oxide shells surrounding metal nanoparticles may create interfacial sites. The creation of micropores or mesopores in shells is crucial for achieving high activity; otherwise, the totally encapsulated metal nanoparticles will not be accessible to the reactants. On the other hand, the pores in shells should not be too large; otherwise, the escape of the metal nanoparticles inside will become facilitated. The core−shell structures can be used in (1) catalysis after appropriate activation to burn off residual organic species or (2) making novel supported catalysts by dispersing core−shell structures on solid supports. Examples of core−shell catalysts include Pt@CeO_2,[66−69] Rh@SiO_2,[70] Ni@SiO_2,[71] Pt@SiO_2,[72−75] and Pd@SiO_2;[76−78] examples of supported core−shell catalysts include Pt@SiO_2/Al_2O_3,[72,79] Ag−Pt@SiO_2/Al_2O_3,[80] and Pt@CeO_2/Al_2O_3.[69] These catalysts generally exhibit enhanced thermal stability against sintering due to the protection of inorganic shells.

The core−shell arrangement enhances the interaction between the metal core and the oxide shell, thus creating more boundary sites, but it is tempting to inquire why the shell has to be in close contact with the core. This question is valid, because one may incorporate additional functional groups or organometallic catalysts inside the shells. Therefore, yolk−shell structures, which have empty space between the encapsulated nanoparticle (yolk) and the hollow shell, have been developed. This can be achieved by partially etching the metal core while keeping the shell intact, by etching a portion of material between the metal core and the outer shell, by enlarging the space between the metal core and the shell through the Kirkendall effect, or by using a water-in-oil microemulsion as a template. Examples of yolk−shell catalysts include Pt@hollow CoO,[81] Ni@hollow SiO_2,[65] Co@hollow SiO_2,[82] Fe@hollow SiO_2,[82] NiPt@hollow SiO_2,[83] Pt@hollow C,[84,85] and Rh@hollow C.[86] Below, we highlight some examples of work on the synthesis and application of gold-based core−shell and yolk−shell catalysts. The examples are organized according to the chemical composition of the shells.

2.2. Au@SiO_2. There is much interest in the preparation of Au@SiO_2 core−shell structures from a colloidal chemistry perspective,[87−89] but the catalytic applications of these materials were often not reported. Yin and co-workers reported a surface-protected etching strategy for the preparation of Au@SiO_2 core−shell structures with porous shells (Figure 1).[90] To begin with, Au@SiO_2 core−shell particles prepared by a modified sol−gel procedure were coated by poly(vinyl pyrrolidone) (PVP) as the protecting ligand, and an aqueous NaOH was used as a leaching agent to diffuse through the SiO_2 shells and create pores. The PVP-protected SiO_2 shells were not dissolved, whereas the pores created by controlled NaOH leaching made

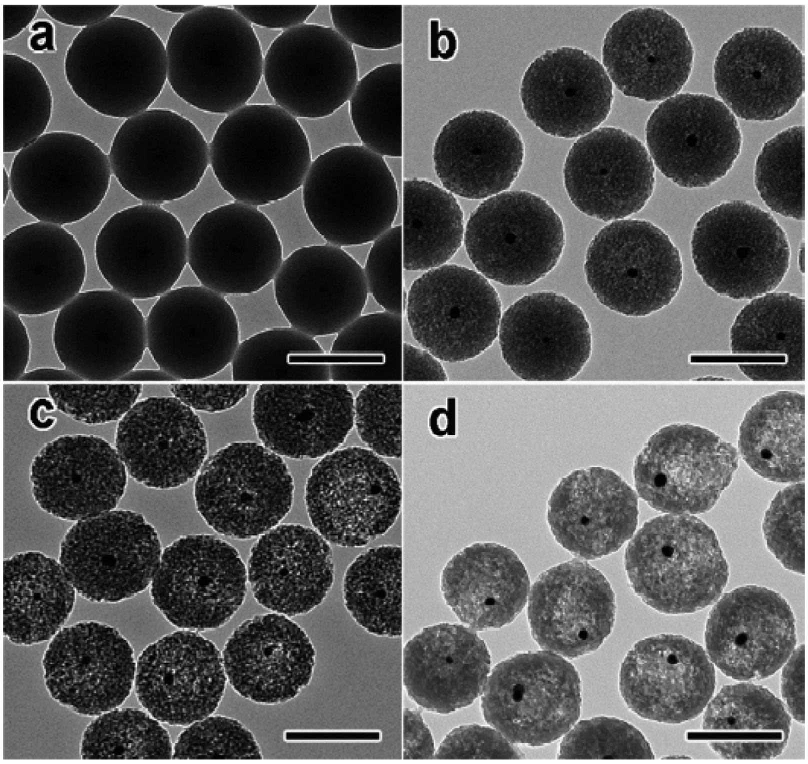

Figure 1. TEM images showing the structure evolution of Au@SiO_2 core−shell structures: (a) the original particles without NaOH etching, and the sample etched by NaOH for (b) 2 h, (c) 2 h 45 min, and (d) 3 h.[90] The scale bars represent 200 nm. Reproduced with permission of the American Chemical Society from Zhang, Q.; Zhang, T. R.; Ge, J. P.; Yin, Y. D. *Nano Lett.* **2008**, *8*, 2867.

the gold cores accessible to the reactants. Such catalysts showed good activity and recyclability in the catalytic reduction of 4-nitrophenol using $NaBH_4$ as a reducing agent. In contrast, gold nanoparticles without any SiO_2 coating aggregated easily during the reaction.[90] The authors nicely showed that the openings in the SiO_2 shells increased with the duration of etching (Figure 1), and hence, the catalytic activity increased, but the pores were not arranged in an ordered manner, and the sizes and volumes of the created pores as a function of etching time were not reported.

Corma and co-workers encapsulated gold nanoparticles in mesoporous SiO_2 spheres.[91] Gold nanoparticles with an average size of 15 or 30 nm were modified by 3-aminopropyltrimethoxysilane (APTMS) and then coated by a thin layer of amorous SiO_2. The APTMS adopted could interact with both the gold core and the amorphous SiO_2 coating. Gold−amorphous SiO_2 nanospheres (denoted as GSN) were obtained by controlled growth of the SiO_2 wall in an ethanol/water mixture, and gold−mesoporous SiO_2 nanoparticles (denoted as GMSN) were prepared by stirring GSN in an alkaline solution of cetyltrimethylammonium bromide (CTAB), followed by calcination to remove the CTAB template. The SiO_2 shell had wormhole-like pores and a high surface area of ∼1000 m^2/g, but no catalytic data were reported. Pt@mesoporous SiO_2 with similar mesoporous shells was synthesized, and the catalytic performance in CO oxidation was reported more recently.[75]

Song and co-workers fabricated Au@SiO_2 yolk−shell nanoreactors by coating gold particles (102 ± 8 nm) with porous SiO_2 shells (17 ± 2 nm) with the help of a porogen; that is, octadecyltrimethoxysilane (C_{18}TMS).[92] The porosity of the SiO_2 shell was tuned by adjusting the amount of C_{18}TMS used. On the other hand, the sizes of gold particles decreased by etching using a KCN solution. The resulting Au@SiO_2 yolk−shell nanoreactors exhibited good performance in the reduction of *o*-nitroaniline by $NaBH_4$, and the catalytic activity was further improved by functionalizing gold particle surfaces with 3-mercaptopropionic acid (3-MPA). The authors explained that the thiol group of 3-MPA could bind onto the gold surface, whereas the carboxylate anion might form strong hydrogen bonding with the amine group of *o*-nitroaniline, resulting in a relatively long reactant retention time and large concentration gradients around the active gold surface.[92] The concept of a nanoreactor containing different components was demonstrated therein, but the sizes of gold nanoparticles were still large, and the KCN used for leaching is hazardous. Apparently, a portion of gold was wasted by leaching, and one would question why smaller gold nanoparticles were not used to make core−shell catalysts in the first place.

Shi and co-workers developed a structural difference-based selective etching strategy to prepare Au@hollow mesoporous SiO_2 yolk−shell structures with mesostructured pores.[93] Gold nanoparticles were coated by thick SiO_2 shells, and then the Au@SiO_2 was coated by a mesoporous SiO_2 shell with a much higher degree of condensation than that of the thick SiO_2 shell. The Au@SiO_2@mesoporous SiO_2 was treated in an aqueous Na_2CO_3 to selectively leach the inner thick SiO_2 shell, leaving behind Au@hollow mesoporous SiO_2 with a surface area of 297 m^2/g and an average pore size of 4.6 nm. The authors proposed that the advantage of this catalyst is its resistance to sintering,[93] although there were no data showing that the thermal stability was improved or the catalytic activity was better.

More recently, Mou and co-workers reported the preparation of hollow SiO_2 structures (average diameter 26 nm, wall

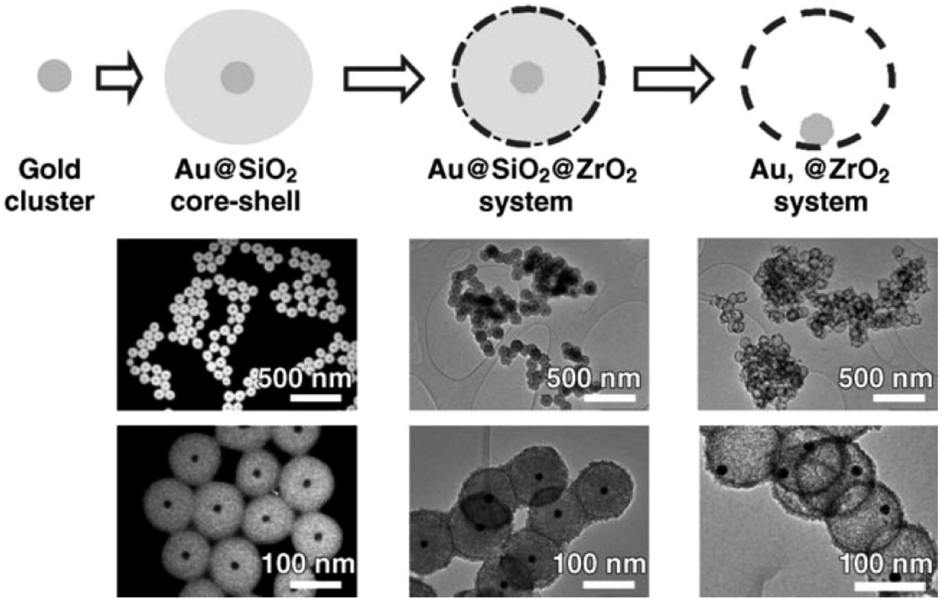

Figure 2. The synthesis procedure and TEM images of the products obtained after each step leading to the encapsulation of gold nanoparticles by ZrO_2 hollow shells.[105] Reproduced with permission of Wiley-VCH from Arnal, P. M.; Comotti, M.; Schüth F. *Angew. Chem. Int. Ed.* **2006**, *45*, 8224.

thickness 6 nm) using a water-in-oil microemulsion as a template.[94] By simply using aqueous $HAuCl_4$ solutions with different concentrations instead of water to conduct the microemulsion templating, Au@hollow SiO_2 samples with varied gold particle sizes (2.8, 3.3, 4.5 nm) were synthesized. The catalyst with the smallest gold particle size showed the highest catalytic activity in the reduction of 4-nitrophenolate to 4-aminophenolate by $NaBH_4$.[94] In another work, Zhang and co-workers fabricated Au@hollow SiO_2 using polystyrene-*co*-poly(4-vinylpyridine) microspheres as a template to create the SiO_2 shell.[95] The resulting catalysts showed size-dependent activity in the reduction of 4-nitrophenol with $NaBH_4$.

We may conclude that Au@SiO_2 core−shell or yolk−shell structures can be fabricated by various methods, with different physicochemical properties, such as gold particle size, shell thickness, shell porosity, and additional functional groups. Gold nanoparticles could be presynthesized, treated with a leaching agent, or formed in situ, and therefore, the preparation can be controlled to some extent. The stability of catalysts and the catalytic applications of these materials have been demonstrated in certain cases. Nevertheless, the sizes of gold nanoparticles were often not small enough. In addition, the catalytic applications of these materials in a variety of reactions were not demonstrated. In particular, the creation of porous shells may provide new opportunities for designing shape-selective catalysts, but the shape selectivity in organic catalysis was virtually not demonstrated. Gold nanoparticles supported on SiO_2 are often known to be inactive for CO oxidation, unless the preparation methods are carefully chosen and the synthesis conditions are well controlled.[96−102] The catalytic performance of these Au@SiO_2 structures in the benchmark reaction (CO oxidation) was not reported.

2.3. Au@TiO_2 and Au@ZrO_2. Although the synthesis of Au@SiO_2 is more established than that of core−shell catalysts with metal oxide shells, SiO_2 is generally not a good support for making gold catalysts active for CO oxidation, so it is tempting to use other oxide shells. In particular, Au−TiO_2 interface is known to be active for CO oxidation, so TiO_2 shell should be a good choice. Along this line, Yu and co-workers synthesized Au@TiO_2 core−shell particles with truncated wedge-shaped morphology via a hydrothermal route using TiF_4 as the precursor.[103] The size of the gold core was as large as 37.5 nm, and that parameter could be further tuned by changing the concentration of $HAuCl_4$ and ascorbic acid. The size of the wedgelike TiO_2 shell was ∼110 nm, and the roughness of the shell could be adjusted by changing either the concentration of TiF_4 solution or the reaction time. The resulting Au@TiO_2 core−shell particles were more active than Degussa TiO_2 nanoparticles (∼33 nm) and hollow TiO_2 shells in photocatalytic degradation of acetaldehyde.[103] However, no comparison to the photocatalytic performance of Au/Degussa TiO_2 was made. In addition, the sizes of both gold nanoparticles and TiO_2 shells may be too large for some other catalytic reactions, such as CO oxidation.

Zhang and co-workers prepared Au@TiO_2 nanoparticles by adding tetrabutyl titanate solution diluted in ethanol to as-prepared gold sols, followed by reflux at 200 °C.[104] The size of the gold core was 10−15 nm, and the thickness of the TiO_2 shell was 1−3 nm, as determined by TEM. The T_{50} (temperature required for 50% conversion) value of this catalyst in CO oxidation was 220 °C, whereas Au/TiO_2 with such a large gold particle size was regarded as inactive for this reaction (although the CO conversions on Au/TiO_2 were not shown). The authors proposed that the irregular gold surface induced by thermal treatment of Au@TiO_2 and the maximum degree of metal−support contact might be responsible for the enhanced catalytic activity.[104] However, the activity of Au@TiO_2 in CO oxidation was, indeed, low, and one would question why gold nanoparticles with smaller sizes were not used in the first place.

ZrO_2 is also a good support to make active gold catalysts, so attempts have been made to prepare novel gold catalysts with ZrO_2 shells. Schüth and co-workers designed a novel "Au, @ZrO_2" yolk−shell catalyst portrayed by the encapsulation of a gold nanoparticle in a much larger ZrO_2 shell; that is, there was free space between the gold nanoparticle and the ZrO_2 shell

(Figure 2).[105] To begin with, gold nanoparticles were coated by SiO_2 shells, the $Au@SiO_2$ core−shell particles were coated by ZrO_2 shells, and the SiO_2 shells were leached subsequently. The ZrO_2 shells were composed of nanosized ZrO_2 (∼10 nm), and the pores between ZrO_2 particles were 3−4 nm in size.[105] The advantage was that the gold nanoparticles encapsulated were free from thermal sintering, but the activity in CO oxidation was not particularly high, due to the use of 15 nm gold nanoparticles as the starting material. In view of the report that the size of gold nanoparticles in $Au@SiO_2$ core−shell structures could be decreased by controlled etching with KCN,[106] Schüth and co-workers prepared "Au, @ZrO_2" catalyst with smaller sizes by decreasing the size of gold nanoparticles in $Au@SiO_2$ by NaCN.[107] The authors noted that controlling the leaching process was too difficult to reliably achieve gold particle sizes below 10 nm. In another study, Zheng and co-workers used smaller gold nanoparticles (6 nm) as the cores to make "Au, @ZrO_2" and "Au, @TiO_2" catalysts for 4-nitrophenol reduction and CO oxidation.[108]

We may conclude that although various synthetic protocols have been demonstrated, the sizes of the gold nanoparticles and the physicochemical properties (e.g., thickness, porosity) of the shells have not been well controlled. The interplay between the gold nanoparticles and the inorganic shells and its effect on catalysis has not been studied sufficiently. In particular, it is difficult to quantify the interfacial sites active for CO oxidation. Advantages of the core−shell or yolk structures and the metal oxide shells with redox properties in catalytic reactions have not been demonstrated well, and the so-called nanoreactors have virtually not been modified with organometallic catalysts or inorganic promoters to test their performance in more demanding reactions.

2.4. $Au@SnO_2$ and $Au@Fe_2O_3$. SnO_2 can also be used as a support to make gold catalysts active for CO oxidation; however, examples on $Au@SnO_2$ core−shell catalysts are rare. Xie and co-workers fabricated $Au@SnO_2$ core−shell particles by an intermetallics-based dry oxidation approach in which AuSn alloy particles were subjected to a three-step oxidation process in a furnace.[109] The size of the gold core was 15 nm, and the thickness of the SnO_2 shell was 6−7 nm. The catalyst showed 50% CO conversion at 230 °C (the activity was regarded by the authors to be high, because the catalyst was previously calcined at 850 °C, and the size of gold core was as large as 15 nm), whereas a nonencapsulated Au/SnO_2 catalyst showed 50% CO conversion at 330 °C.[109] The relatively high activity of $Au@SnO_2$ was ascribed to a synergetic confinement effect. This work made an interesting case for the oxidative transformation of AuSn alloy particles to an $Au@SnO_2$ core−shell catalyst, but the size of the gold core was still too large for low-temperature CO oxidation. It would be interesting to develop alternative methods for the preparation of $Au@SnO_2$ catalysts with controlled gold particle sizes and SnO_2 shell thicknesses.

Fe_2O_3 is an important oxide to be considered as shells because Au−Fe_2O_3 interface is known to be active for CO oxidation. Alivisatos and co-workers developed $Au@Fe_2O_3$ core−shell particles by depositing an iron shell around gold nanoparticles stabilized by oleyamine, hexadecylamine, or dodecanethiol, followed by the oxidation of the iron shell to form an Fe_2O_3 shell.[110] The magnetic properties of the materials were studied, but no catalysis data was reported. Our group prepared Au@-Fe_2O_3 core−shell particles with controlled core size (2.1 nm) and shell thicknesses (1, 2, 3, 4 nm) and loaded these core−shell particles onto different supports (SiO_2, TiO_2, C) via colloidal deposition.[111] In particular, extensive work was done with $Au@Fe_2O_3/SiO_2$ catalysts. As shown in Figure 3,[111] the as-synthesized $Au@Fe_2O_3/SiO_2$ was not active for CO oxidation due to the presence of residual organic species. Once the organic species were removed by an oxidative treatment at 300−500 °C, the $Au@Fe_2O_3/SiO_2$ catalyst showed high CO conversions when the reaction temperature was below 0 °C. However, an oxidative treatment at 700 °C led to the crystallization of the amorphous Fe_2O_3 shell and growth of gold nanoparticles, thus resulting in decreased catalytic activity. The catalytic activity generally decreased with an increase in shell thickness, perhaps due to the more obvious crystallization of the Fe_2O_3 shell and enhanced blockage of active sites. The $Au@Fe_2O_3/SiO_2$ was more active than Au/Fe_2O_3 and Au/SiO_2 with comparable gold loadings prepared by depositing gold nanoparticles on commercial Fe_2O_3 and SiO_2 supports via colloidal deposition,[111] indicating the role of interfacial core−shell structures in catalytic CO oxidation. Unsupported $Au@Fe_2O_3$ was also active for low-temperature CO oxidation, given that the catalyst was thoroughly washed at the later stage of preparation and properly pretreated to remove residual organic species. Therefore, the role of supports in determining the activity of supported $Au@Fe_2O_3$ catalysts was not distinguished clearly.

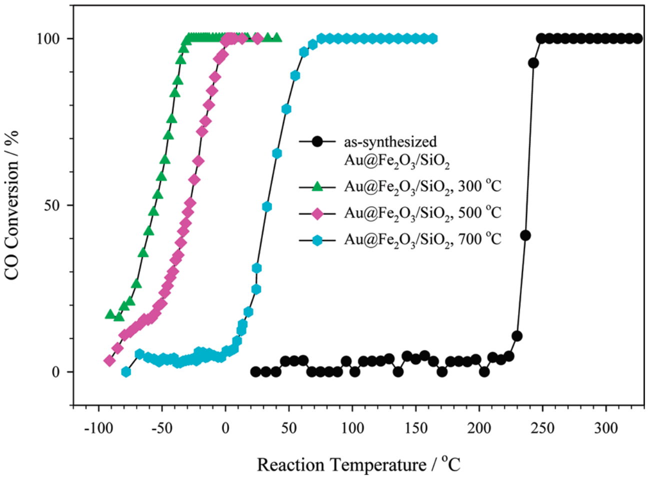

Figure 3. CO conversions on $Au@Fe_2O_3/SiO_2$ either not pretreated or pretreated at different temperatures (300, 500, or 700 °C).[111] Reproduced with permission of Elsevier from Yin, H. F.; Ma, Z.; Chi, M. F.; Dai, S. *Catal. Today* **2011**, *160*, 87.

Some challenges remain and should be addressed on the basis of the findings of our work. First, it seems that the core−shell design is not as bulletproof as initially imagined. There may be structural changes (e.g., shrinkage, crystallization) of the shell at elevated temperatures, so the sintering of the core metal is still possible. In principle, the thermal stability and crystallization temperatures of different oxide shells are different, and there may be possible interactions between the shell and the support. There has been virtually no comparative study elaborating the thermal stability of core−shell catalysts as a function of different shells and supports. In addition, the porosity of the shell is imperfect, and thick shells may influence diffusion of the reactants, thus decreasing catalytic activity. At present, few works have been done to understand the details of these issues.

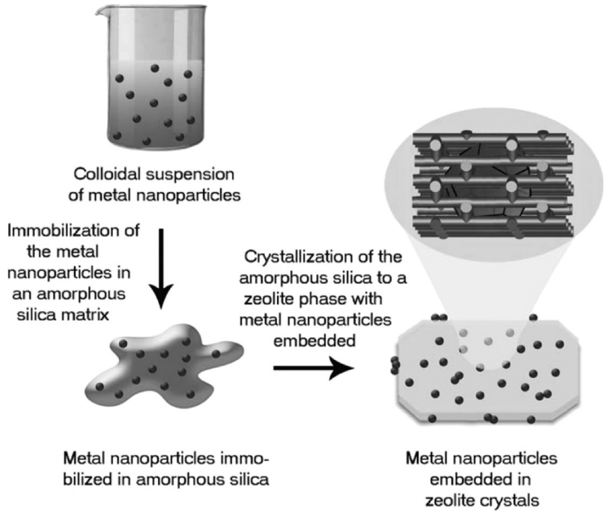

Figure 4. Schematic illustration of the encapsulation of gold nanoparticles in zeolite silicalite-1 crystals.[126] Reproduced with permission of Wiley-VCH from Laursen, A. B.; Højholt, K. T.; Lundegaard, L. F.; Simonsen, S. B.; Helveg, S.; Schüth, F.; Paul, M.; Grunwaldt, J.-D.; Kegnæs, S.; Christensen, C. H.; Egeblad, K. *Angew. Chem. Int. Ed.* **2010**, *49*, 3504.

3. ENCAPSULATION OF GOLD NANOPARTICLES

Core−shell catalysts are better defined than conventional catalysts in the sense that, conceptually, each metal core is surrounded by a solid shell. However, because the separation of core−shell catalysts from the liquid-phase reaction mixture is more difficult, one may inquire about the possibility of encapsulating many metal nanoparticles in a solid matrix. That way, these encapsulated metal nanoparticle catalysts not only possess advantages (i.e., site isolation, thermal stability) of their core−shell counterparts but also have potential benefits of easy separation after liquid-phase catalytic reactions. However, experience in this direction is still limited, and successful examples are rare.[112−115]

It is generally known that the encapsulation of metal nanoparticles in a solid matrix would limit the exposure of metal nanoparticles to the reactant, therefore decreasing the catalytic activity. For example, the preparation of supported metal catalysts by coprecipitation or one-step sol−gel method may lead to the partial occlusion of metal nanoparticles and, therefore, a loss of accessible metal surface.[9,116] Our group treated $Au(en)_2Cl_3$-derived Au/SBA-15 at elevated temperatures and found evidence for the encapsulation of gold nanoparticles within the restructured SiO_2 matrix.[117] The residual sodium (an aqueous NaOH was used in catalyst preparation to adjust the pH value) was found to facilitate the structural transformation of SBA-15. Such an encapsulated material was not active for CO oxidation when the reaction temperature was below 100 °C, although there was a significant portion of small gold nanoparticles (<5 nm) within the trapped SiO_2 matrix.

Along this direction, Martino and co-workers encapsulated gold nanoparticles in the pores of SiO_2 xerogels and aerogels by the sequential reduction of $AuCl_3$ by $LiBH_4$, followed by sol−gel processing in an inverse micelle solution.[118] No catalytic data were reported therein. Similar sol−gel-based Pt nanoparticle catalysts were reported later, and their sintering behavior was studied[119] and performance in propane dehydration was reported.[120] Corma and co-workers adopted a modified sol−gel approach for the preparation of gold nanoparticles embedded in SiO_2 accessible for the reactants.[100] The sintering of gold nanoparticles under high-temperature environments was impeded, and the catalyst showed high CO conversions even below room temperature. The authors extended the synthetic approach to the preparation of spongelike porous SiO_2-embedded Pd nanoparticles for the Suzuki−Miyaura reaction.[121] Others have prepared CeO_2-embedded Pd,[122] CeO_2-embedded Au,[123] ZrO_2-embedded Ru,[124] and SiO_2-embedded Pt catalysts.[125] The embedded metal nanoparticles are accessible to the reactants in these cases.

Recently, Laursen et al. encapsulated gold nanoparticles (1−2 nm) in coffin-shaped silicalite-1 crystals by encapsulating gold nanoparticles in an amorphous SiO_2 matrix, followed by hydrothermal crystallization (Figure 4).[126] The shape-selective oxidation ability was demonstrated by the aerobic oxidation of a mixture of benzaldehyde and 3,5-di-*tert*-butylbenzaldehyde in methanol. Only benzaldehyde could be oxidized using gold−silicalite-1 catalyst, whereas both substrates could be oxidized on Au/TiO_2. This is because bulky 3,5-di-*tert*-butylbenzaldehyde cannot get to the internal pores of silicalite-1. This study is interesting because normally it is difficult to put gold nanoparticles in the micropores of zeolites, but the authors thought out of the box and found a way to circumvent the technical challenge.

4. POSTMODIFICATION

The synthesis of supported core−shell structured catalysts is demanding, and the encapsulation of metal nanoparticles in a solid matrix without compromising the catalytic activity is challenging. It is therefore interesting to ask whether it is possible to modify regular supported metal catalysts by adding an inorganic coating after the regular preparation of supported metal catalysts. That way, better catalysts may be prepared more conveniently, that is, by simply postmodifying commercial supported catalysts. Examples of catalysts with such coatings include $SiO_2/Pt/zeolite$,[127] $SiO_2/Pt/C$,[128−130] $SiO_2/Pt/Fe_2O_3$,[131] $SiO_2/Pt/SiO_2$,[132,133] and $Al_2O_3/Pd/Al_2O_3/SiO_2$.[134] The thermal stability of the postmodified catalysts was enhanced significantly.

Our group prepared $SiO_2/Au/TiO_2$ by treating Au/TiO_2 in tetramethyl orthosilane ($Si(OCH_3)_4$), (3-aminopropyl)trimethoxysilane ($H_2N(CH_2)_3Si(OC_2H_5)_3$), or tris(*tert*-butoxy)silanol ($((CH_3)_3C)_3SiOH$) solution followed by calcination in air to form amorphous SiO_2 and to remove residual organic species.[135] Gold nanoparticles could be stabilized against thermal sintering thanks to the protection afforded by SiO_2, whereas gold nanoparticles sintered more dramatically when Au/TiO_2 was not postmodified by SiO_2. As shown in Figure 5,[135] the unmodified Au/TiO_2, calcined at 300 °C, showed high activity in CO oxidation when the reaction temperature was below 0 °C, but the activity went down sharply when Au/TiO_2 was treated at 500 or 700 °C due to the agglomeration of gold nanoparticles. For comparison, as-synthesized $SiO_2/Au/TiO_2$ was not active below 200 °C due to the presence of residual organic species, but once the catalyst was treated at 500 or 700 °C to remove residual organic species, it showed higher CO conversions than Au/TiO_2 treated under the same temperature due to sintering resistance of $SiO_2/Au/TiO_2$ (Figure 5).[135] The sintering resistance property was demonstrated by X-ray diffraction (XRD) and transmission electron microscopy (TEM) data,[36,135] but due to the lack of

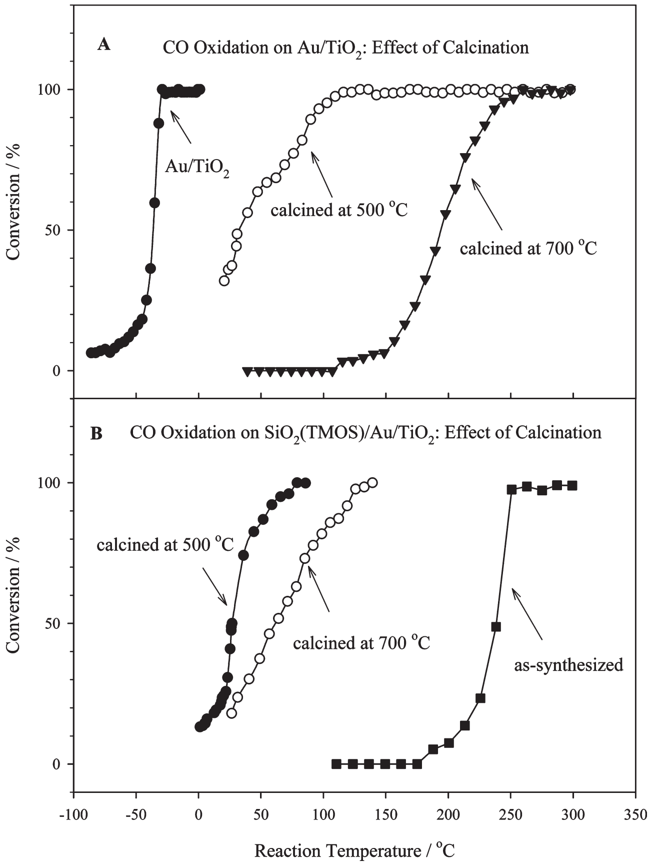

Figure 5. CO conversions on two different catalysts as a function of reaction temperature.[135] (a) Au/TiO$_2$ calcined in a muffle oven at 300 °C and Au/TiO$_2$ further treated in O$_2$—He at 500 or 700 °C. (b) As-synthesized SiO$_2$(TMOS)/Au/TiO$_2$ (prepared by treating Au/TiO$_2$ with tetramethyl orthosilane) and those further treated in O$_2$—He at 500 or 700 °C. Reproduced with permission of Springer from Zhu, H. G.; Ma, Z.; Overbury, S. H.; Dai, S. *Catal. Lett.* **2007**, *116*, 128.

TEM images with higher resolutions, it is not clear whether the SiO$_2$ actually coated the gold nanoparticles or merely situated near gold nanoparticles.

Supposing that atomic layer deposition (ALD) may be better at controlling the homogeneity and the thickness of the SiO$_2$ coating, we employed this technique to coat Au/TiO$_2$ by amorphous SiO$_2$.[136] Tetramethyl orthosilane vapor was used as the precursor to amorphous SiO$_2$ coatings, and the as-synthesized SiO$_2$/Au/TiO$_2$ sample was again treated at elevated temperatures, cooled down, and tested in CO oxidation as a function of reaction temperature. The amorphous SiO$_2$ coatings were observed by high-resolution TEM, and the film thickness increased with the Si/Ti ratio. Although the SiO$_2$ coatings did stabilize gold nanoparticles against thermal sintering, as clearly seen from XRD and TEM data, the resulting SiO$_2$/Au/TiO$_2$ catalysts did not show high CO conversions, especially when the SiO$_2$ coating was thicker.[136]

Although ALD can make ultrathin films on the metal nanoparticles with controlled thickness, the coating may be too fine to leave pores for diffusion, thus leading to low catalytic activity, although the thermal stability of the metal nanoparticles may be good due to the presence of the protective oxide layer. On the other hand, solution-phase modification is simple and efficient. However, the porosity should be better controlled to obtain advanced catalysts with ordered mesopores. A case in point is the synthesis of mesoporous SiO$_2$/Au/SiO$_2$/Fe$_3$O$_4$ catalysts in which gold nanoparticles were supported onto SiO$_2$-coated Fe$_3$O$_4$ particles, and the whole material was then coated by mesoporous SiO$_2$.[137,138] In addition, the coating types are quite limited. Coating of other oxides (such as CeO$_2$) should be explored, and their catalytic performance assessed, for supported metal catalysts. However, that synthesis is more difficult due to the availability of suitable precursors as well as the reactivity and ease to form homogeneous coatings. The fate of the coatings under elevated temperatures should be studied more carefully with the help of adsorption—desorption techniques and high-resolution TEM.

In the above work, the role of amorphous SiO$_2$ is merely to mitigate the sintering of gold nanoparticles in an attempt to maintain the activity. The next step would be to change the postmodification component to enhance catalytic performance. This may bring additional active sites for catalysis. For example, Horváth and co-workers deposited gold sols onto SiO$_2$ and then used [CH$_3$CH(O—)CO$_2$NH$_4$]$_2$Ti(OH)$_2$ as a precursor to prepare TiO$_2$/Au/SiO$_2$ more active in CO oxidation.[33] The presence of additional Au—TiO$_2$ interfaces may play a key role in the enhancement in activity. The next step would be to prepare supported gold catalysts postmodified by other metal oxides to test the effect of additional gold—oxide interfaces.

The Au—MnO$_x$ interface is active for CO oxidation,[139−141] and KMnO$_4$ solution can be used to treat organic template-containing mesoporous SiO$_2$,[142−144] leading to the formation of MnO$_x$-containing mesoporous SiO$_2$ upon calcination. We therefore prepared MnO$_x$/Au/SiO$_2$ by soaking Au(en)$_2$Cl$_3$-derived Au/SiO$_2$ with KMnO$_4$ solutions, followed by oxidative treatment at 300—600 °C (Figure 6).[145] The KMnO$_4$ treatment can stabilize gold nanoparticles against sintering and facilitate the removal of residual organic species at lower temperatures, but the most important effect is to leave behind amorphous MnO$_x$ near gold nanoparticles, thus creating additional Au—MnO$_x$ interfaces active for low-temperature CO oxidation. In another work, we treated dodecanethiol-capped gold catalysts by an aqueous KMnO$_4$ or K$_2$MnO$_4$ and established a similar promotional effect in CO oxidation.[146] Although MnO$_x$ was supposed to locate near gold nanoparticles and energy-dispersive X-ray spectroscopy (EDX) coupled with TEM demonstrated so, the exact location and distribution were not pinned down due to the lack of EDX and TEM with higher resolutions.

The potential of the posttreatment of gold catalysts by aqueous KMnO$_4$ or K$_2$MnO$_4$ solutions deserves comment. First, this postmodification methodology is limited by the reaction between the reagent and the catalyst. It is difficult to put an element of choice on the catalyst surface. We attempted to use Fenton's reagent to load FeO$_x$ on the surface, only to obtain catalysts with lower activity in CO oxidation due to the agglomeration of gold nanoparticles.[146] The OH radicals generated by Fenton's reagent may facilitate the movement of gold atoms and cause the restructuring of gold surfaces.[147] Second, it is difficult to control precisely the amount of manganese on the surface, and too much manganese would block the active sites. Third, it is expected that the catalyst may be useful in other reactions (e.g., organic catalysis) that need MnO$_x$ as a catalyst or a catalyst promoter, but such a possibility has not been verified to date. Therefore, much work is still ahead to achieve the potential of the postmodification strategy.

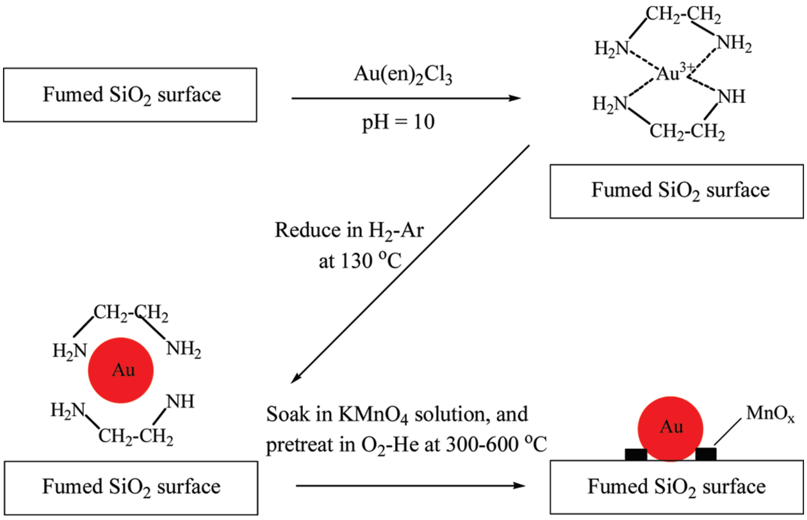

Figure 6. Schematic representation for the preparation of MnO_x-modified Au/SiO_2 by treating $Au(en)_2Cl_3$-derived Au/SiO_2 with $KMnO_4$ solutions, followed by thermal activation.[145] Reproduced with permission of the American Chemical Society from Yin, H. F.; Ma, Z.; Overbury, S. H.; Dai, S. *J. Phys. Chem. C* **2008**, *112*, 8349.

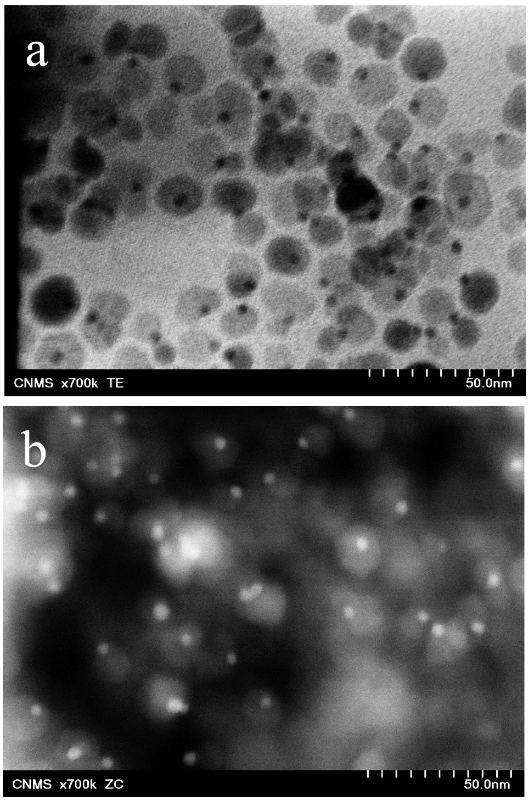

Figure 7. (a) Bright-field TEM image of Au−Fe_3O_4 dispersed in hexane, and (b) dark-field TEM image of Au−Fe_3O_4 dumbbells supported on SiO_2.[154] The scale bars represent 50 nm. Reproduced with permission of the Royal Society of Chemistry from Yin, H. F.; Zhu, H. G.; Wang, C.; Zhu, H. G.; Overbury, S. H.; Sun, S. H.; Dai, S. *Chem. Commun.* **2008**, 4357.

5. DUMBBELL STRUCTURES

We know from the previous discussion that an MnO_x component could be brought near the gold nanoparticles via a postmodification strategy, thereby enhancing catalytic activity. The essence of that work is to create new Au−MnO_x interfaces active for CO oxidation. It is therefore interesting to ask whether inorganic promoters can be attached to gold nanoparticles before landing these heterostructures onto a support. That way, one may be able to control the amount of inorganic promoters and enhance the interaction between inorganic promoters and gold nanoparticles. The synthesis of dumbbell-like or heterodimer nanoparticles can provide such an opportunity.[148−150]

Sun and co-workers recently demonstrated the better performance of Au−Fe_3O_4/C than Au/C and Fe_3O_4/C in electrocatalytic H_2O_2 reduction.[151] Au/C was prepared by leaching Au−Fe_3O_4/C in an aqueous H_2SO_4, and Fe_3O_4 nanoparticles were prepared by a two-step leaching of gold from Au−Fe_3O_4 nanoparticles using KI/I_2 solution. The enhanced performance in catalysis was explained as the polarization effect at the Au−Fe_3O_4 interface, where Fe_3O_4 became more active.[151] The application of dumbbell-like Au−Fe_3O_4 and Pt−Fe_3O_4 nanoparticles in the oxygen reduction reaction was also reported.[152,153]

Our group prepared Au−Fe_3O_4 dumbbell nanoparticles (with gold particle size of 2.5−3.5 nm and Fe_3O_4 particle size of 15−16 nm) via in situ decomposition of $HAuCl_4$ and $Fe(CO)_5$ and then deposited Au−Fe_3O_4 dumbbell nanoparticles onto SiO_2, TiO_2, and carbon.[154] The synthetic protocol is shown in the abstract graphic of the current Perspective, and the TEM images of unsupported Au−Fe_3O_4 and SiO_2-supported Au−Fe_3O_4 are shown in Figure 7. The resulting supported catalysts showed high activity in CO oxidation below room temperature due to the presence of active Au−Fe_3O_4 interfaces (unsupported Au−Fe_3O_4 dumbbell nanoparticles were also active for low-temperature CO oxidation if the catalyst was sufficiently washed at the late stage of preparation and thermally properly pretreated to remove residual organic species prior to reaction testing). In addition, the supported catalysts were stable against thermal sintering because the Fe_3O_4 component interacted strongly with the gold nanoparticles.

Zheng and co-workers did a careful study on the effects of gold particle size, supports, and Fe_3O_4 particle size on catalytic activity in CO oxidation.[155] The gold particle size was chosen to be

6.7 nm rather than the 2.5−3.5 nm in our work to achieve lower activity so that other factors (e.g., support effect) could be examined more easily. When the gold particle size was 6.7 nm and the Fe_3O_4 particle size was 15.2 nm, the catalytic activity of various supported catalysts followed the sequence Au−Fe_3O_4/TiO_2 > Au−Fe_3O_4/SiO_2 > Au/C, although the working temperatures of these catalysts were not low (in the range of 30−190 °C). The result indicated that gold had interaction with the TiO_2 support and that the Au−TiO_2 interface contributed to catalytic activity. The authors found that the catalytic activity decreased when the Au−Fe_3O_4/TiO_2 catalyst was calcined at elevated temperatures, as explained by the higher degree of Au−TiO_2 interface breakage at higher calcination temperature, since the size of the gold nanoparticles did not change.[155] However, it is unclear why this was not due to the change of oxidation state, since no XPS data were furnished. Finally, the authors prepared more active Au−Fe_3O_4/TiO_2 catalysts by introducing TiO_2 via in situ thermal decomposition of titanium isopropoxide and by decreasing the size of Fe_3O_4 nanoparticles to 4.9 nm. Apparently, these two types of modifications created more contact areas between gold−TiO_2 and gold−Fe_3O_4, respectively, thus creating more interfacial sites for CO oxidation.

The results reviewed above provide implications for future research: (1) Conceptually, the types of metal and the metal oxide component can be changed, and the metal−metal oxide interaction can be tuned. For instance, the metal-versus-metal oxide ratio, the size and shape of the metal particle, and the boundary area between the metal and metal oxide (e.g., Fe_3O_4) can be tuned. Systematic experiments are needed to study the influence of these parameters on catalytic performance in a number of reactions. The progress along this direction relies heavily on materials synthesis. (2) The interaction between the dumbbell and the support is still unclear. It is not clear whether the metal is in contact with the support, the modifier is in contact with the support, or both components are in contact with the support, and what the proportion of each scenario is. High-resolution TEM images are needed to unravel this mystery. (3) In addition, given the ambiguity in understanding the dumbbell−support interaction, the origin of the active sites is still unclear. Careful kinetic experiments plus detailed characterization are needed to correlate the activity with the structure.

6. ALLOY CATALYSTS AND IN SITU TRANSFORMATION

So far, we have limited our discussion to supported gold catalysts rather than gold-based bimetallic catalysts. To tune the catalytic performance of gold catalysts, it is worthwhile to explore the alloying of gold nanoparticles with another metal.[156−159] The alloyed metals can tune catalytic performance by an electronic effect or a geometric effect. Alternatively, the alloyed metals may also activate molecular oxygen for CO oxidation or become precursors to metal oxide components upon high-temperature oxidative treatment.

Mou and co-workers synthesized AuAg/Al-MCM-41 catalysts via a one-step approach.[160−162] The Au/Ag ratios were varied, and the catalyst with an Au/Ag ratio of 3/1 showed the highest activity in CO oxidation below room temperature. The unexpected high activity achieved by a combination of large alloy particles (∼33 nm) and a traditionally inert support (Al-MCM-41) was explained by the activation of oxygen by silver. The influence of the Si/Al ratio of Al-MCM-41 support on the activity in CO oxidation was further examined, and the highest activity was obtained when the Si/Al ratio was 24.[163] The structure defects generated in Al-MCM-41 were proposed to stabilize AuAg nanoparticles against sintering and generate reactive superoxide species (O_2^-) when oxygen was adsorbed. Sun and co-workers developed a one-pot synthesis of oleyamine-coated AuAg alloy nanoparticles and deposited these particles (8−9 nm in size) with different Au/Ag ratios onto a commercial SiO_2 support.[164] The one with a Au/Ag ratio of 1/1 showed the highest CO conversion, but all of these catalysts were inactive below 50 °C.

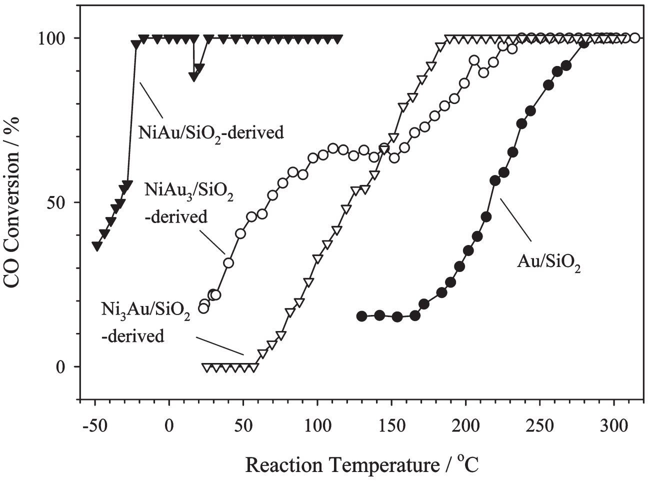

Figure 8. CO oxidation on Au/SiO_2 and Au−NiO/SiO_2 catalysts derived from $NiAu_3/SiO_2$, NiAu/SiO_2, and Ni_3Au/SiO_2 through pretreatment at 720 °C in H_2 and 300 °C in O_2.[172] Reproduced with permission of the American Chemical Society from Zhou, S. H.; Ma, Z.; Yin, H. F.; Wu, Z. L.; Eichhorn, B.; Overbury, S. H.; Dai, S. *J. Phys. Chem. C* 2009, *113*, 5758.

Mou and co-workers subsequently prepared AuAg/Al-MCM-41 catalysts using a two step method in which the Al-MCM-41 support was functionalized by 3-aminopropyltrimethoxysilane (APTS), followed by the adsorption of $HAuCl_4$, reduction with $NaBH_4$, exposure to $AgNO_3$, and reduction with $NaBH_4$.[165] The catalyst with a Au/Ag ratio of 8/1 (alloy particle size 4.1 nm) showed the highest CO conversion below room temperature. Zhang and co-workers used a similar two-step approach to prepare AuAg/SiO_2 and AuAg/Al_2O_3. Silver was found to stabilize the AuAg alloy particles against thermal sintering, and the catalysts were highly active for CO oxidation.[166] In another study, Zhang and co-workers prepared AuCu/SBA-15 and AuCu/SiO_2 catalysts and demonstrated their good performance in CO oxidation in the absence or presence of H_2.[167,168] The advantage of using a two-step method is that the size of the alloy particles can be controlled to be small.

Han and co-workers prepared Pd/SiO_2, Au/SiO_2, and a series of Pd−Au/SiO_2 catalysts by an incipient wetness method.[169] The activity of the catalysts followed the sequence Au/SiO_2 > Pd_4Au_1/SiO_2 > Pd_8Au_1/SiO_2 > $Pd_{16}Au_1/SiO_2$ > Pd/SiO_2 > Pd_2Au_1/SiO_2 > $Pd_1Au_{1.6}/SiO_2$ > $Pd_1Au_{3.4}/SiO_2$; that is, the activity of Pd−Au/SiO_2 catalysts increased for bulk compositions from Pd/SiO_2 to Pd_4Au_1/SiO_2, but showed lower activity at higher gold contents.[169] Nevertheless, all of these Pd−Au/SiO_2 catalysts were less active than Au/SiO_2, and these catalysts, including Au/SiO_2, showed negligible CO conversions below room temperature.

Our group employed a butyllithium reduction method[170] for the solution-phase synthesis of NiAu alloy nanoparticles.[171,172]

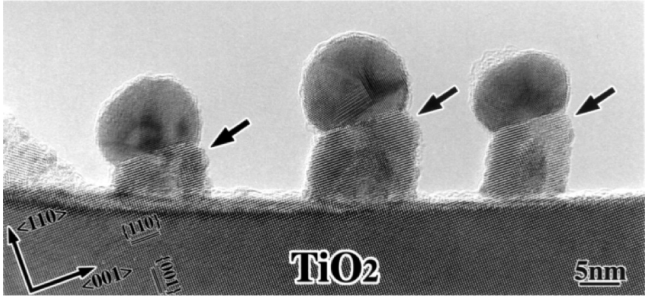

Figure 9. TEM image of gold nanoparticle−IrO_2 pillar structure on TiO_2 support.[175] This structure was formed by calcining Au−Ir/TiO_2 at 400 °C. The arrows point to the formed IrO_2 pillars. Reproduced with permission of the Japanese Society of Microscopy from Akita, T.; Okumura, M.; Tanaka, K.; Tsubota, S.; Haruta, M. *J. Electron Microsc.* **2003**, *52*, 119.

The success in this butyllithium reduction protocol lies in three key points: (1) the fast coreduction of the nickel and gold precursors by butyllithium; (2) the mass diffusion of nickel and gold in small bimetallic NiAu nanoclusters to form uniform NiAu nanoparticles; and (3) the stabilization of nickel atoms on particle surfaces by trioctylphosphine, so the migration of nickel atoms into the inner part of NiAu nanoparticles can be prevented.[172] The formed NiAu alloy nanoparticles were loaded onto SiO_2 support via colloidal deposition and tested in CO oxidation. The catalyst pretreated in H_2 at 720 °C and then in O_2 at 300 °C showed the highest activity; however, the actual working catalyst at this stage was not NiAu/SiO_2 but Au−NiO/SiO_2, an unexpected conclusion drawn from various characterization data. The nickel in NiAu alloy nanoparticles diffused toward the surface during H_2 treatment and then oxidized to NiO that situated around the gold nanoparticles after O_2 treatment. The influence of Ni/Au ratio in the pretreated catalyst was studied (Figure 8),[172] and the activity was the highest when the Ni/Au ratio was 1. The mean gold particle sizes of the four samples were determined by TEM to be 3.7, 3.6, 7.8, and 36.5 nm. The low activity of Au/SiO_2 was explained by the large size of the gold nanoparticles, whereas the lower activity of Ni_3Au/SiO_2-derived catalyst than NiAu/SiO_2-derived catalyst was explained as caused by the gold nanoparticles being covered by too much NiO.

The oxidative transformation of supported alloy catalysts under elevated temperatures is not limited to the case of NiAu/SiO_2 catalysts. In a next work, our group prepared an AuCu/SiO_2 catalyst and demonstrated its in situ transformation to the active Au−CuO/SiO_2 form upon oxidative treatment under elevated temperatures.[173] The Au−CuO/SiO_2 catalyst was active for CO oxidation below room temperature, whereas the as-synthesized AuCu/SiO_2, containing residual organic species, was not active. On the other hand, AuCu/SiO_2 prepared by reducing the active Au−CuO/SiO_2 catalyst at 300 °C was not active for CO oxidation at room temperature and became active only when AuCu/SiO_2 transformed back to Au−CuO/SiO_2 during CO oxidation under elevated temperatures. Similarly, Liu et al. found that a bimetallic Au−Cu phase on SBA-15 transformed into a gold core decorated with CuO_x patches during CO oxidation, and CO adsorbed on metallic gold reacted with active oxygen supplied by the CuO_x patches, thus leading to high activity in CO oxidation.[174] In another work, Akita and coworkers found that a gold nanoparticle−IrO_2 pillar structure on TiO_2 could be formed upon calcining Au−Ir/TiO_2 in air at 400 °C (Figure 9).[175] Results from first-principle calculations explained the enhanced thermal stability of gold nanoparticles owing to the formation of the IrO_2 pillar interacting with gold.[176]

The implication is that caution should be exercised when interpreting the catalysis data of gold-based alloy catalysts; sometimes the presumed "alloy catalysts" are not real alloy catalysts after oxidative pretreatments or under reaction conditions. Careful characterization before and after various stages of pretreatment or reaction testing is still needed. Additional experiments are still needed to expand the scope of this research because successful examples in this direction are still limited.

7. CONCLUDING REMARKS

Many advanced structured gold catalysts with high activity, selectivity, and stability have been designed via materials synthesis. They are different from those with simple metal−support interactions but often contain multiple interactions and components. The oxide components can be formed as shells, a matrix that encapsulates gold nanoparticles, coatings, amorphous oxide near gold nanoparticles, oxide nanoparticles attached to gold nanoparticles, or formed by transformation of alloys; that is, they have different formation routes and different morphologies. Oxide components can also be added to the support before loading gold.[32,177−179] The presence of additional interfaces between a metal and an oxide may bring new possibilities for tuning the structural properties and catalytic behaviors.

As for the limitations of the research, many papers, adopting a "proof-of-concept" approach, simply reported the synthesis, characterization, and catalytic performance of new catalysts. The synthesis was often new, but delicate and tedious. The characterization relied on traditional tools such as XRD, TEM, ultraviolet−visible spectroscopy (UV−vis), and XPS. The catalytic reactions chosen were simple, and some data were sure to obtain because some catalytic organic reactions can inherently achieve 100% conversion in sufficient time and with high selectivity. There was virtually no demonstration of the applications of these catalysts in other more demanding reactions, and there was little variation in other experimental parameters relevant to catalysis. Sometimes the stability of the catalyst was not tested or tested inappropriately: the CO conversion observed was always 100% as a function of time on stream, making it impossible to observe possible deactivation. Similarly, sometimes the recyclability of catalysts was not studied properly; the conversions of the organic substrate in each run were always 100% because the reaction time was too long. The issues associated with inappropriate testing of stability and recyclability of catalysts have been commented critically.[180,181] After all, the objective of many studies was to demonstrate the synthetic protocols, and catalytic reactions were merely a screening tool rather than a destination.

In addition, the correlations between physicochemical properties and catalytic performance are preliminary. Many publications, including ours, simply concluded that one catalyst was better than another, because the gold nanoparticles in the former were smaller than those in the latter. Such a conclusion is not surprising and lacks insight. The resolution of TEM was not high enough for observation of tiny gold clusters and their distributions. Either the oxidation state of gold species was not studied or the observed oxidation state did not represent the actual oxidation state of the working catalyst, since the XPS experiments were conducted ex situ or only fresh catalysts (i.e., catalysts that had not undergone any catalytic reaction) were used for XPS measurements. Even though one detects the presence of both metallic and cationic gold species on a catalyst, it does not necessarily mean that the catalyst has to rely on both species to work properly. It also does not mean that other gold catalysts cannot work properly without the presence of both species. Therefore, meaningful correlations are still needed on the basis of solid and relevant data.

The limitations mentioned above may lead to directions in future research. Given that the catalysts are new, it is essential that more applied work and fundamental research be carried out. As for applied catalysis, it is worthwhile to explore the applications of these new catalysts in reactions other than CO oxidation and simple organic reactions. Some newly designed catalysts have transition metal oxide components (e.g.,MnO_x and FeO_x) that can catalyze the selective oxidation and dehydration of organic molecules. It is therefore desirable to take full advantage of the functions furnished by both gold nanoparticles and the metal oxide components. In addition, it would be worthwhile to adopt a so-called "molecular engineering" approach (i.e., to design new structured catalysts according to specific requirements in catalytic reactions[182]) instead of developing new catalysts from a materials perspective and then looking for suitable reactions that can demonstrate the usefulness of these catalysts. In addition to catalysis, the application of gold-based nanocomposites in other fields (e.g., biosensoring and biomedical applications,[183−186] electrochemical and photoelectrochemical applications[187]) can be explored.

As for fundamental research, it is essential to build up the correlations between physicochemical properties and catalytic performance. Delicate materials synthesis techniques may provide new opportunities for fine-tuning the sizes of gold nanoparticles and other catalyst components as well as the interfacial structures.[170,188,154,189,190] Meaningful correlations can be obtained by changing the physicochemical parameters via controlled synthesis and by carrying out careful kinetic studies. In situ XPS, X-ray absorption, and infrared spectroscopy, coupled with kinetic studies, may be useful to follow the changes in the oxidation states of gold under various treatment and reaction conditions.[191,192] High-resolution TEM—in particular, operated in an in situ mode—may be useful for monitoring the changes in size and morphology of gold nanoparticles or clusters under different treatment and reaction conditions.[193−197] Theoretical calculations are useful to understand the experimental observations.[176,198] In all, an integrated approach needs to be considered in future research.

In closing, we conclude that much has been done in designing new gold catalysts, and the recent progress is impressive. This is a field in which materials scientists and catalysis researchers share a common interest, and it will certainly continue for years to come. Nevertheless, most work has focused on the synthetic protocols and simple reaction testing, whereas still much is ahead about the practical applications and fundamental research using these new catalysts. We believe that future research along the latter directions is challenging and rewarding.

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