

Review

## Mesoporous Silica Based Gold Catalysts: Novel Synthesis and Application in Catalytic Oxidation of CO and Volatile Organic Compounds (VOCs)

Hongjing Wu <sup>1,2</sup>, Giuseppe Pantaleo <sup>1</sup>, Anna M. Venezia <sup>1</sup> and Leonarda F. Liotta <sup>1,\*</sup>

<sup>1</sup> Institute for The Study of Nanostructured Materials (ISMN)-CNR, Via Ugo La Malfa 153, 90146 Palermo, Italy; E-Mails: wuhongjing@mail.nwpu.edu.cn (H.W.); pantaleo@pa.ismn.cnr.it (G.P.); venezia@pa.ismn.cnr.it (A.M.V.)

<sup>2</sup> Department of Applied Physics, Northwestern Polytechnical University (NPU), 127 Youyi Xilu, 710072, Xi'an, China

\* Author to whom correspondence should be addressed; E-Mail: liotta@pa.ismn.cnr.it; Tel.: +39-91-6809-371; Fax: +39-91-6809-399.

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**Abstract:** Gold nanoparticles, particularly with the particle size of 2–5 nm, have attracted increasing research attention during the past decades due to their surprisingly high activity in CO and volatile organic compounds (VOCs) oxidation at low temperatures. In particular, CO oxidation below room temperature has been extensively studied on gold nanoparticles supported on several oxides (TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, etc.). Recently, mesoporous silica materials (such as SBA-15, MCM-41, MCM-48 and HMS) possessing ordered channel structures and suitable pore diameters, large internal surface areas, thermal stabilities and excellent mechanical properties, have been investigated as suitable hosts for gold nanoparticles. In this review we highlight the development of novel mesoporous silica based gold catalysts based on examples, mostly from recently reported results. Several synthesis methods are described herein. In detail we report: the modification of silica with organic functional groups; the one-pot synthesis with the incorporation of both gold and coupling agent containing functionality for the synthesis of mesoporous silica; the use of cationic gold complexes; the synthesis of silica in the presence of gold colloids or the dispersion of gold colloids protected by ligands or polymers onto silica; the modification of silica by other metal oxides; other conventional preparation methods to form mesoporous silica based gold catalysts. The gold based catalysts prepared as such demonstrate good

potential for use in oxidation of CO and VOCs at low temperatures. From the wide family of VOCs, the oxidation of methanol and dimethyldisulfide has been addressed in the present review.

**Keywords:** gold; mesoporous silica; catalyst preparation; functionalization; CO oxidation; methanol; dimethyldisulfide oxidation

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## 1. Introduction

Gold has been used for coinage, jewelry, and other types of art for thousands of years due to its high stability in wet air. Chemical researchers rarely considered the catalytic activity of gold until the exciting discovery that gold possessed unique catalytic activity in the low temperature oxidation of carbon monoxide [1,2] and ethyne hydrochlorination to vinyl chloride [3], simultaneously and independently made by Haruta and Hutchings, respectively. For the first time these studies proved gold to be superior to other catalysts for these reactions, in contrast to the previous reports on the poor activity of gold.

The discovery that gold is active for heterogeneous oxidative reactions at low temperatures, especially for CO oxidation, motivated a considerable amount of research on the activity of gold based catalysts. Development of new processes based on the gold catalysts, would improve the selectivity of important chemical reactions, thus reducing the by-products and energy consumption and potentially limiting production of undesired chemicals that may be unfriendly to the environment or human health. Up to now, gold catalysts have been shown to have potential applications in environmental catalysis (CO oxidation, de-NO<sub>x</sub>, catalytic combustion of volatile organic compounds (VOCs), and photocatalysis), energy processing (the water-gas shift reaction, selective CO oxidation in excess H<sub>2</sub>, and steam reforming of methane), and chemical synthesis (selective hydrogenation and oxidation, C-C coupling, and partial oxidation of H<sub>2</sub> to form H<sub>2</sub>O<sub>2</sub>), with indubitable commercial potential [4–11].

Despite the numerous studies on the effects of different factors such as particle size, preparation methods, pretreatment conditions and choice of supports, the origin of the outstanding catalytic properties of gold nanoparticles is still under debate. It is generally accepted that gold nanoparticles are highly reactive in the ultra-fine particle size range, although the particles sized between 10–50 nm have also been reported to exhibit certain reactivity [12–16]. The role of supports appears to be a key point in determining the optimum size for activity since it affects the reaction pathways. In particular, for “inert” or inactive supports, the activity seems to depend critically on the particle size (high activity for size of 2 nm) because oxygen molecule dissociative adsorption can be enhanced due to a higher density of reactive defective sites or due to a gradual change in the electronic structure of gold when decreasing the size. Therefore, it is better to gradually reduce the particle size of gold until reaching the optimum size over the “inert” support for the possible improved activity.

Recently, the discovery of “inert” mesoporous silicas, such as SBA-15, MCM-41, MCM-48 and HMS, has stimulated intensive studies of “host-guest” chemistry inside the channels of mesoporous silicas, which have potential applications in catalysis, selective adsorbents, medicine, sensors, and nanomaterial fabrications [17–19]. The conventional methods used to prepare supported gold

materials, such as impregnation (Imp), co-precipitation (Cp), or deposition-precipitation (Dp), are not appropriate to obtain the required highly dispersed gold nanoparticles (Au-NPs) since they usually yield inactive large spherical particles which weakly bind to the support [20]. For example, the Dp method is not appropriate for the incorporation of Au-NPs into silica, because under the high pH conditions required to hydrolyze  $\text{HAuCl}_4$ , the weak interaction between the negatively charged silica surface and the  $[\text{Au}(\text{OH})_n\text{Cl}_{4-n}]^-$  species facilitates the mobility of gold particles, which can be easily sintered during the synthesis process, especially during the calcination step, yielding inactive catalysts. To overcome this drawback, various alternative methods have been proposed given that mesoporous silicas are very amazing supports due to their high surface area, thermal stability, ordered structure and excellent mechanical properties. Furthermore, to overcome the aggregation of large metal particles on the external surface of the host materials, Shi *et al.* [21] reported Pt nanoclusters within the pore channels of selectively modified mesoporous silica SBA-15 by a new *in situ* reduction process. Recently, Sun *et al.* [22] developed a novel *in situ* auto reduction route to synthesize monodispersed Ag nanoparticles inside the channels of SBA-15.

In this paper, we review the current advanced ways of designing mesoporous silica based gold nanocatalysts. However, this paper does not deal with the Au@mesoporous  $\text{SiO}_2$  core/shell type catalysts, since such systems are not suitable for applications in low-temperature oxidation of CO and VOCs. We only focus on Au/ $\text{SiO}_2$  catalysts for environmental heterogeneous catalysis, therefore the newest publications on Au- $\text{SiO}_2$  composite systems appearing in 2012 and 2013, are not included in the present overview. In Section 2 and 3 we highlight the synthesis of gold catalysts with highly dispersed Au-NPs via conventional synthesis methods, modification of silicas by other metal oxides, pre-modification of mesoporous silicas, one-pot or simultaneous synthesis method, synthesis of silicas in the presence of gold colloids or the dispersion of gold colloids protected by ligands or polymers onto silicas, the use of cationic gold complexes, and finally other novel synthesis methods. In these sections we emphasize the synthesis of Au-NPs inside the channels of mesoporous silicas with single metal-support interface and their activity in CO and VOCs oxidation. We conclude (Section 4) with the understanding of structure-property correlation in CO oxidation and furnishing our assessment and perspectives. Although there are a number of reviews on various aspects of gold catalysis, few examples have specifically focused on the development of highly dispersed Au-NPs catalysts confined in the channels of mesoporous silicas.

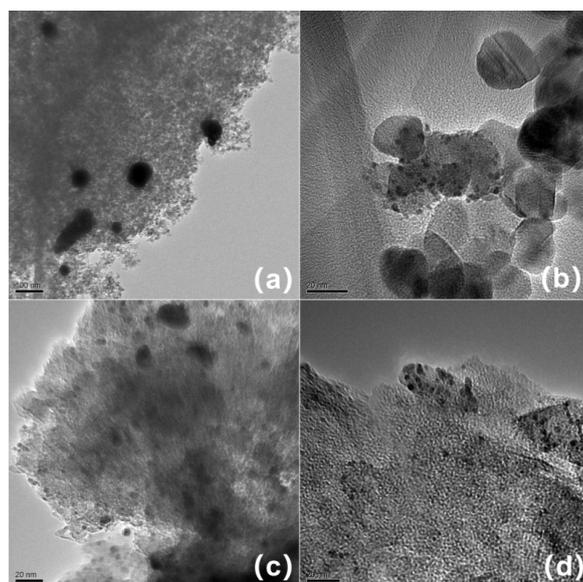
## 2. Synthesis of Mesoporous Silica Based Gold Catalysts and Applications in CO Oxidation

### 2.1. Synthesis of Au/ $\text{SiO}_2$ by Colloidal Deposition

When a non-reducible oxide, like silica, is used as a support it is very difficult to obtain an optimum particle size range of gold due to the weak interaction between gold and the irreducible support. In such cases, mesoporous silica with a well-defined pore size seems to be an appropriate support for the confinement of Au-NPs. In this respect, systems such as MCM-41 and SBA-15 are especially valuable, as their porous structure is periodic and their pore size can be controlled within a range of a few nanometers [23]. However, the Au/ $\text{SiO}_2$  catalysts prepared by the impregnation of  $\text{SiO}_2$  with  $\text{HAuCl}_4$  or  $\text{AuCl}_3$  have relatively large Au particles because the residual chloride ions facilitate the sintering of

Au-NPs in the calcination step [14]. Similarly, Au/SiO<sub>2</sub> catalysts prepared by the Dp method have a low catalytic activity in CO oxidation according to the above mentioned explanation [24]. To tackle the above-mentioned problems, we have synthesized a series of Au/MO<sub>x</sub> (M = Si, Al, Mg, Zn) by means of a colloidal deposition method [25]. As shown in Figure 1, we can compare the Au particle size ranges over different supports prepared by the colloidal deposition (Cd) method. The colloidal gold solution was prepared using poly (vinyl alcohol) as protecting agent to achieve such a particle size distribution. It can be clearly found that the more reducible the oxide supports are, the smaller is the particle size of gold. The large gold nanoparticles aggregate on the surface of amorphous silica with irregular shapes due to poor interaction between gold colloids and silica supports as previously reported in our paper [25]. These catalysts exhibit different catalytic activity toward oxidation of CO and VOCs depending on the various particle sizes of gold and the nature of the supports [25,26].

**Figure 1.** TEM images of the calcined catalysts prepared by a colloidal deposition method: (a) Au/SiO<sub>2</sub>; (b) Au/ZnO; (c) Au/Al<sub>2</sub>O<sub>3</sub> and (d) Au/MgO. Reproduced with permission from [25]. Copyright 2011 Elsevier B.V.

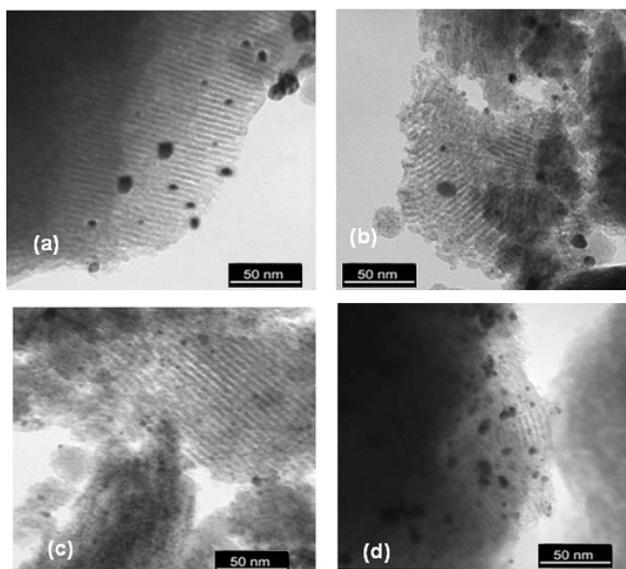


## 2.2. Synthesis of Au/Mesoporous Silica by Doping Oxides

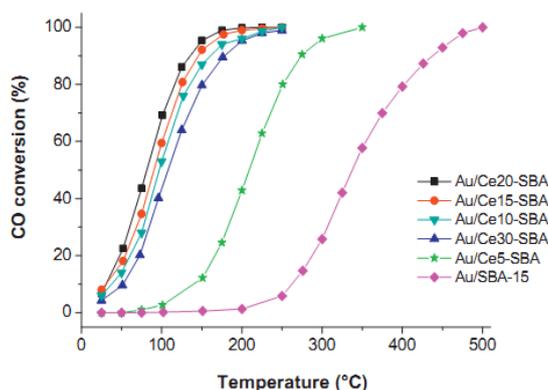
Our group prepared gold catalysts supported over SBA-15 with different CeO<sub>2</sub> loadings (5–30 wt.%) and their catalytic performances were evaluated in CO oxidation, chosen as a trial reaction [27]. The addition of proper metal oxides such as Co<sub>3</sub>O<sub>4</sub>, CeO<sub>2</sub>, TiO<sub>2</sub>, FeO<sub>x</sub> and CuO<sub>x</sub>, onto the silica support modified the acid-base and textural properties of the silica matrix and increased the binding effect and dispersion of the supported Au-NPs, finally improved their catalytic activity [27–33]. The changes of chemical environment of Au nanoparticles enhanced the interaction between Au-NPs and doping metal oxides, leading to an increase of catalytic activity and resistance to sintering or aggregation during the calcination or reaction step. In Figure 2, STEM images of four selected gold catalysts prepared by the Dp method show different particle size distributions. The optimum amount of doping CeO<sub>2</sub> is 20 wt.%, leading to major Au nanoparticles with size between 3–5 nm. Doping SBA-15 with CeO<sub>2</sub> significantly increases the CO conversion activity of gold supported catalysts (see Figure 3). By further increasing the

CeO<sub>2</sub> content to 30 wt.%, the CO conversion worsens due to a limited effect and Au/Ce20-SBA-15 catalyst achieves 50% of CO conversion at 81 °C. Moreover, higher activity for Au/5(10) wt.% Fe<sub>2</sub>O<sub>3</sub>-SBA-15 catalysts, as compared to the responding Au/Fe<sub>2</sub>O<sub>3</sub> bulk system, can be obtained [31]. Regarding all these catalysts supported over promoted mesoporous silica, highly dispersed Au particles in intimate contact with the promoting active oxide are the key factors in CO oxidation activity. Moreover, the ordered pore system of the silica support may help in controlling the dispersion of the multicomponent active phase [32]. In the case of such three components systems the preferential formation of the active Au/MO<sub>x</sub> is decisive and enables the formation of more active sites compared with the bare active oxide supported Au-NPs [33]. SiO<sub>2</sub> as support for gold catalysts has presented excellent catalytic activity for CO oxidation through various advanced synthesis methods.

**Figure 2.** STEM images of as-synthesized catalysts: (a) Au/SBA-15; (b) Au/Ce5-SBA-15; (c) Au/Ce20-SBA-15 and (d) Au/Ce30-SBA-15. Reproduced with permission from [27]. Copyright 2012 Elsevier B.V.



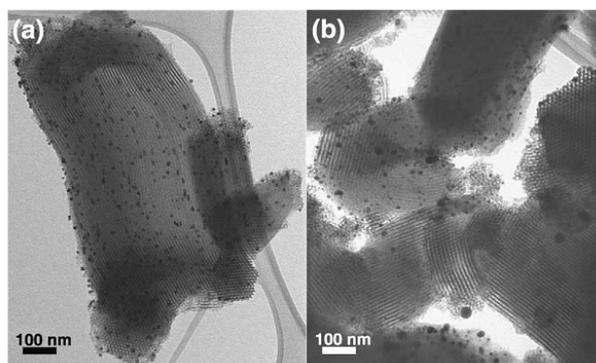
**Figure 3.** CO conversion (%) to CO<sub>2</sub> vs. temperature for Au/SBA-15 and Au/Ce<sub>x</sub>-SBA-15 catalysts (1 vol% CO + 1 vol% O<sub>2</sub> in He, flow rate: 50 mL min<sup>-1</sup>). Reproduced with permission from [27]. Copyright 2012 Elsevier B.V.



### 2.3. Synthesis of Au/Mesoporous Silicas by Pre-Modification

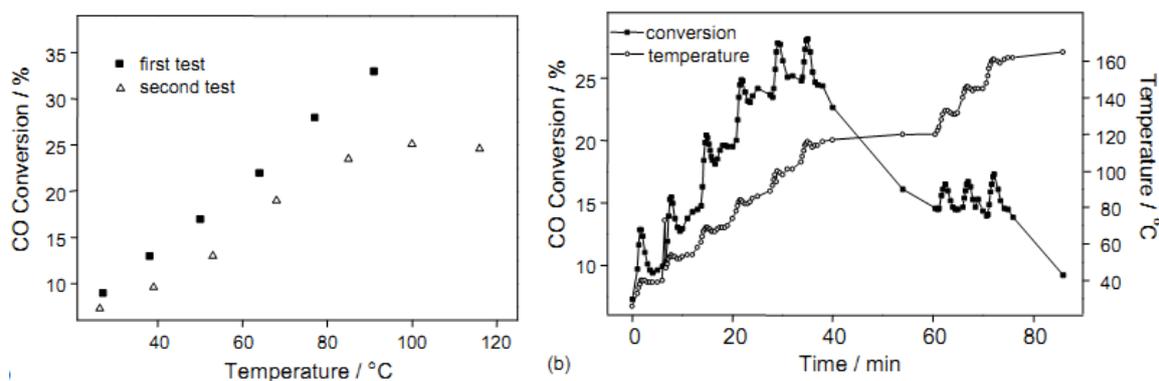
Generally, the preparation of active Au/SiO<sub>2</sub> catalysts with base solution methods is difficult and the resulting materials have very low activity in CO oxidation. This problem could be circumvented with the chemical vapor deposition (CVD) method although this method needs expensive equipment. Furthermore, Yang *et al.* [34,35] proposed a method to prepare highly dispersed metal nanoparticles in mesoporous silicas. To overcome the problem of depositing negatively charged solution species (AuCl<sub>x</sub><sup>-</sup>) on the negatively charged silica surface, the host silica was functionalized with a cationic organosilane (TPTAC) to generate a monolayer of positively charged groups on the pore surface. This facilitates a uniform distribution of negatively charged metal species after ion exchange and, upon reduction, results in highly dispersed metal nanoparticles supported in mesoporous silicas. This pathway provides an opportunity to synthesize gold nanoparticles on a silica support via a solution technique which could be highly active in CO oxidation. Figure 4 shows the TEM images of Au/SBA-15 catalysts before and after reaction at 160 °C. The Au nanoparticles with a particle size of 4.5 nm are highly dispersed in the channels of the host. After heating the catalyst to 160 °C during CO oxidation the Au-NPs is no longer well dispersed in the channels of the host and nanoparticles of 10–50 nm in size are formed on the outer surface of the host silica. It is suggested that the small Au nanoparticles gradually sinter and then the larger Au nanoparticles cannot be accommodated any longer in the channel system after CO oxidation.

**Figure 4.** TEM images of Au/SBA-15 (a) before and (b) after usage in CO oxidation reaction at 160 °C. Reproduced with permission from [35]. Copyright 2002 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.



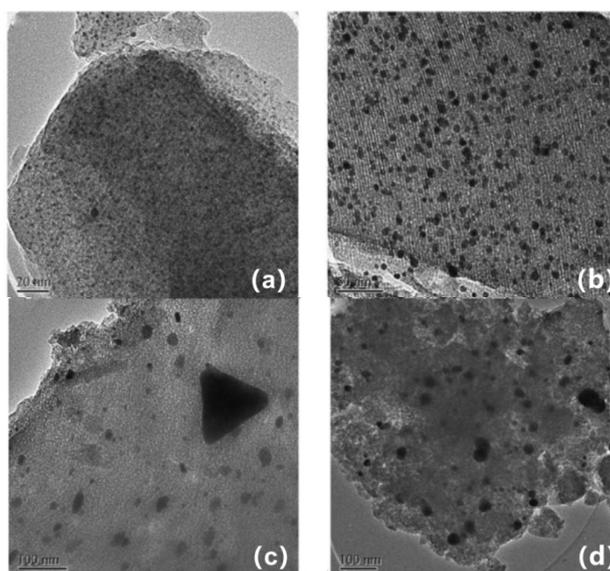
The results of the activity of this catalyst in CO oxidation are shown in Figure 5(a). The catalyst is found to be active even at room temperature. A CO<sub>2</sub> yield of 11% at 30 °C was observed under the reaction conditions given in the experimental part, which corresponds to a reaction rate of  $2.7 \times 10^{-4} \text{ mmol g}_{\text{cat}}^{-1} \text{ s}^{-1}$ . Figure 5(b) shows after each increase in temperature an initially higher reaction rate, leading to the hypothesis of a deactivation process occurring during the activity measurements. After reaction at 160 °C for about 20 min, the catalyst is almost inactive. The behavior described here is rather typical for the gold catalysts synthesized by the approach described above.

**Figure 5.** Catalytic activity of Au/SBA-15 (a) CO conversion plotted against time for the first and second run and (b) CO conversion and temperature plotted against time for the second run. Reaction conditions: 1% CO in air, flow rate: 67 mL min<sup>-1</sup>. Reproduced with permission from [35]. Copyright 2002 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.



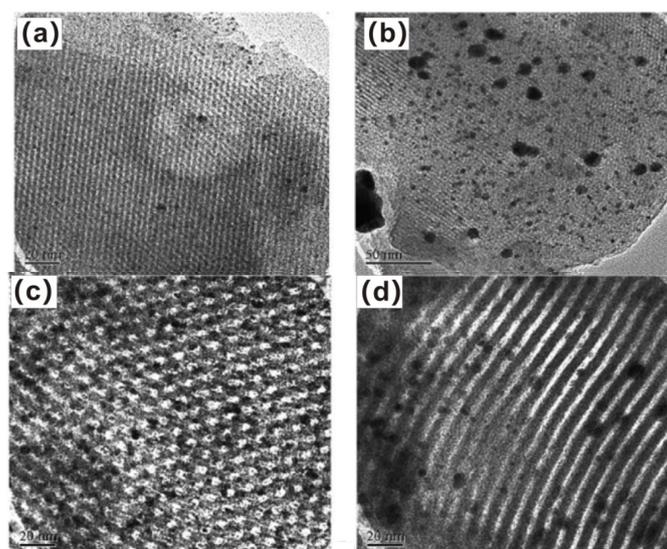
In 2005, Mou and coworkers [36] employed the well-studied mesoporous silica as supporting host to confine the Au-NPs and to study its catalytic effect on CO oxidation. So far the smallest size of uncalcined Au-NPs with particle size of about 2 nm can be obtained by 3-aminopropyltriethoxysilane (APTS) surface-functionalized MCM-41 (see Figure 6(a)). After calcinations, there is some degree of sintering of the Au-NPs in the MCM-41 material and they increase slightly in size (Figure 6(b)). From TEM of Au-NPs in Figure 6(b), one can see that the average particle size of Au-NPs increases to 5.1 nm. In order to compare the hosts, they also prepared Au/MCM-41 using unmodified MCM-41. From the TEM images in Figure 6(c,d), one can see that the Au-NPs are much larger than those prepared by the pre-modified synthesis method.

**Figure 6.** TEM images of MCM-41 modified with 3-aminopropyltriethoxysilane (APTS), then AuCl<sub>4</sub><sup>-</sup> adsorbed, and reduced by NaBH<sub>4</sub> (a) uncalcined, (b) calcined at 560 °C, (c) and (d) without modification with APTS. Reproduced with permission from [36]. Copyright 2005 Elsevier B.V.



Besides MCM-41, MCM-48 and SBA-15 are also used as the supports to prepare Au-NPs in the same process, e.g. modification of APTS, adsorption of  $\text{AuCl}_4^-$ , then reduction with  $\text{NaBH}_4$ . From Figure 7, we find that most of the Au-NPs are confined among the channels, although there are some large particles ( $>10$  nm) on the external surface. The average particle sizes of the Au-NPs follow the order: MCM-41 (5.1 nm)  $<$  SBA-15 (5.8 nm)  $<$  MCM-48 (6.9 nm). Figure 8 shows that all the Au/mesoporous silica catalysts, with the same Au loading of 4 wt.%, have the capability to catalyze the CO oxidation reaction at 80 °C. The smaller the size of Au-NPs, the higher is the CO oxidation activity. Indeed the relatively high activity of the calcined Au/MCM-41 catalyst may be due to the smaller size of Au-NPs. When the surface functional ligand (APTS) is not removed, its CO conversion is zero (Figure 8(D)). Meanwhile, the Au/MCM-41-Dp catalyst has no activity at 80 °C (Figure 8(E)). The results indicate that a size-activity effect plays a major role in CO oxidation.

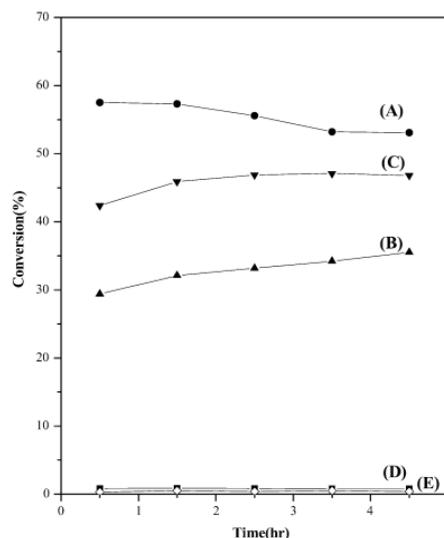
**Figure 7.** TEM of (a and b) MCM-48 and (c and d) SBA-15 modified with APTS, then  $\text{AuCl}_4^-$  adsorbed, reduction by  $\text{NaBH}_4$ , uncalcined and calcined at 560 °C, respectively. Reproduced with permission from [36]. Copyright 2005 Elsevier B.V.



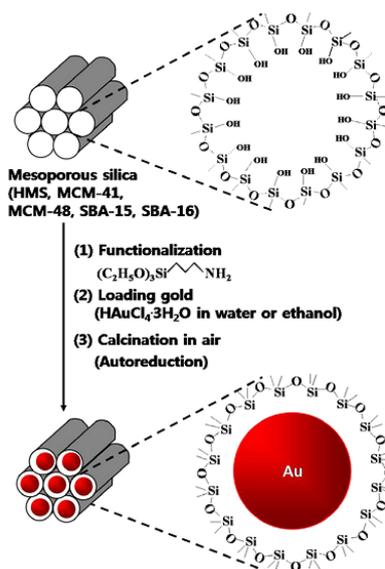
Recently, Dai's group has been interested in developing strategies that can effectively graft Au-NPs onto mesoporous silicas [37]. They systematically studied the influences of synthesis conditions and mesoporous structures on the size and thermal stability of supported Au-NPs upon calcination at 200 or 550 °C. The influences of the types of functional ligands (APTS and *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (DAPTS)) and solvents (water and ethanol) used in preparation, calcination temperatures (200 and 550 °C), and different pore structures (HMS, SBA-15, MCM-41, MCM-48 and SBA-16) on the size distributions of Au-NPs formed upon calcination were studied systematically [37]. HMS with bi-continuous wormhole structure, MCM-41 and SBA-15 with one-dimensional hexagonal structures, MCM-48 and SBA-16 with bi-continuous cubic structures are grafted by APTS or DAPTS, as shown in Figure 9. It can be found that APTS is the preferred grafting ligand, and water is the preferred solvent in order to get smaller Au-NPs. The thermal stability of Au-NPs on mesoporous silicas follows the order: SBA-15  $>$  HMS  $\approx$  MCM-41  $\approx$  SBA-16  $>$  MCM-48.

These results enrich the literature data based on the thermal stability of metal nanoparticles supported on mesoporous materials.

**Figure 8.** CO conversion of the calcined mesoporous silica containing Au-NPs: (A) MCM-41; (B) MCM-48; (C) SBA-15; (D) uncalcined MCM-41 and (E) Au/MCM-41 prepared by Dp. Reaction conditions: feed gas: 1 wt.% CO balanced with air,  $T = 80\text{ }^{\circ}\text{C}$  and  $\text{WHSV} = 9 \times 10^4\text{ mL h}^{-1}\text{ g}^{-1}$ . Reproduced with permission from [36]. Copyright 2005 Elsevier B.V.



**Figure 9.** The general synthetic procedures of Au-NPs confined in channels of various mesoporous silicas. Reproduced with permission from [37]. Copyright 2009 Elsevier B.V.



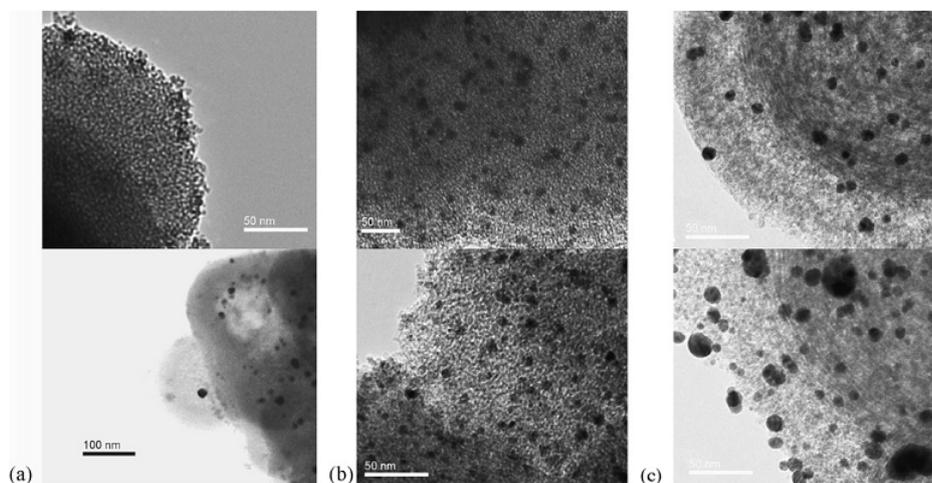
#### 2.4. One-Pot Synthesis of Au/Mesoporous Silica

Dai and coworkers [38] demonstrated and compared several synthetic protocols for the preparation of ordered mesoporous silica materials containing Au-NPs through a co-assembly synthesis method. The optimum methodology identified in that study involves: one-pot synthesis of the mesoporous

silica materials containing gold precursor complexes; reduction of the gold precursor complexes in the presence of surfactants; removal of the templating surfactants via an ion-exchange reaction. The size and distribution of the Au-NPs could be controlled by the complexing ligand and the unique micellar media. 2–5 nm Au-NPs have been successfully synthesized in mesoporous silica and may be an active catalyst for CO oxidation [38].

More recently, other authors [39,40] reported an *in situ* method to prepare the Au/Ti-HMS catalysts, and in particular, the intact HMS structure was maintained successfully. Nevertheless the Dp method is considered as an effective method to prepare supported gold catalysts due to the uniform size and excellent activity of the Au-NPs. However, the mesoporous materials such as HMS have very poor hydrothermal stability, so it is possible to destroy the intrinsic mesoporous structure under such harsh conditions of the Dp approach, which is confirmed in their papers. Figure 10 provides insights into the porosity framework structure of Ti-HMS after modification of Au-NPs. Typical wormhole-like pores of HMS materials exist in both *in situ* and NH<sub>3</sub>-Dp samples. In contrast, there are no wormhole structures existing in the urea-Dp sample. Uniform and small Au-NPs could be prepared by the NH<sub>3</sub>-Dp method, whereas, the Au-NPs prepared by the urea-Dp method are non-uniform. The results show that the preparation method influences the porous structure of the support, density and particle size of the Au-NPs, whereas no reaction data on the oxidation of CO or VOCs are reported.

**Figure 10.** TEM images of (a) Au/Ti-HMS (*in situ*); (b) Au/Ti-HMS (NH<sub>3</sub> Dp) and (c) Au/Ti-HMS (urea Dp). Reproduced with permission from [40]. Copyright 2010 Elsevier B.V.

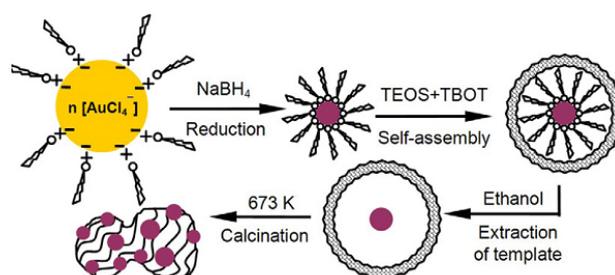


### 2.5. Colloidal Synthesis of Au-NPs Incorporated into Mesoporous Silica

Somorjai and coworkers [41] reported a two-step *in situ* procedure to encapsulate metal (Pt, Au, and Ag) nanoparticles in mesoporous structures. This two-step procedure can be summarized as follows: colloidal synthesis of the metal nanoparticles in the presence of a block copolymer; synthesis of mesoporous silica channels using the metal nanoparticles-copolymer unit as a template. Thus, the final material would have monodispersed metal nanoparticles that are accessible to gas phase molecules. In the 2–10 nm size range, the metal nanoparticles cause expansion of the mesoporous channels, while the 20 nm nanoparticles are found exclusively outside of the channels. It can be concluded that only less than 10 nm particle size of metal nanoparticles can be accommodated in these structures.

Song *et al.* [42] reported a novel synthesis method of Au/Ti-HMS through an *in situ*-reduction method as shown in Figure 11. Compared with the previously prepared Au/Ti-HMS (Dp) and Au/Ti-HMS (*in situ*), the optimum *in situ*-reduction sample possesses a much more uniform size of Au-NPs (<4 nm) that are more likely to be embedded into the HMS worm-like channels. However, the catalytic activity of this catalyst in CO or VOCs oxidation has still not been investigated by the authors.

**Figure 11.** Synthesis of Au/Ti-HMS by *in situ*-reduction. Reproduced with permission from [42]. Copyright 2011 Elsevier B.V.



## 2.6. Synthesis of Au/Mesoporous Silica by Gold Cationic Complex Precursor

Dai's group [43,44] has recently developed Au/SiO<sub>2</sub> catalysts by using Au(en)<sub>2</sub>Cl<sub>3</sub> as the gold precursor, and demonstrated their high activity in low-temperature CO oxidation. Furthermore, they furnished a systematic study on the fate of Au/SBA-15 upon high-temperature treatment in N<sub>2</sub> [45]. It has been found that significant decrease in surface area, deterioration of the mesoporous structure, and phase transformation from amorphous to cristobalite phase are registered when Au-NPs are supported onto SBA-15 support using Au(en)<sub>2</sub>Cl<sub>3</sub> as the precursor and the Au/SBA-15 is treated at 800–900 °C. More interestingly, part of the Au-NPs is encapsulated by the silica matrix upon high temperature treatment as shown in Figure 12. Moreover, the Au-NPs expelled to external surfaces of the silica matrix may contribute to the low activity observed, whereas Au-NPs trapped within may not be active, because the catalyst subjected to aqua regia leaching shows no activity at all in CO oxidation (see Figure 12 (d)).

**Figure 12.** (a) SEM; (b) bright-field TEM, and (c) dark-field TEM images of Au/SBA-15 treated under N<sub>2</sub> at 900 °C followed by leaching in aqua regia at room temperature for 3 days, and (d) its activity in CO oxidation (1% CO, balance air, flow rate: 37 mL min<sup>-1</sup>). Reproduced with permission from [45]. Copyright 2010 Elsevier B.V.

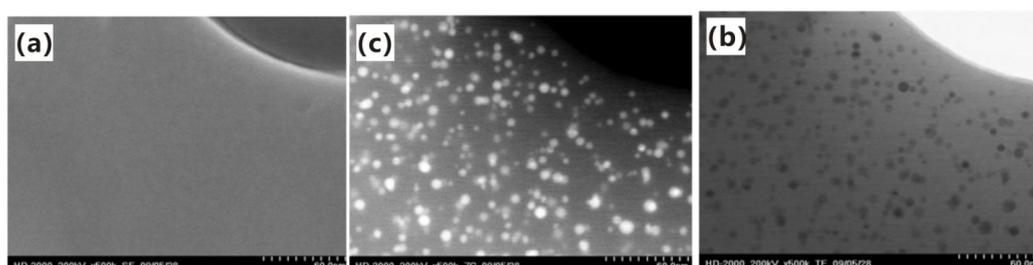
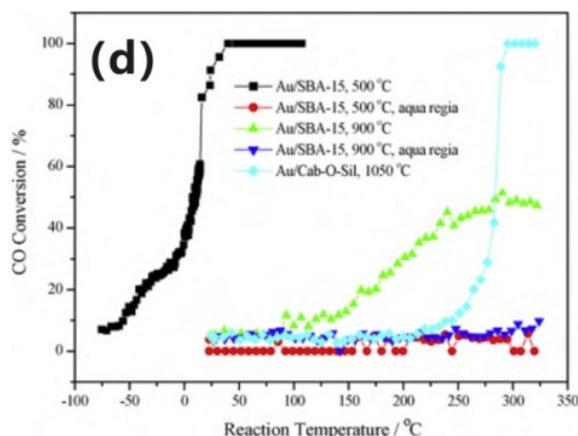


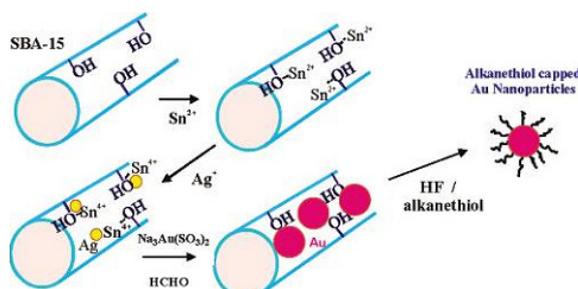
Figure 12. Cont.



### 2.7. Other Novel Synthesis of Au/Mesoporous Silica

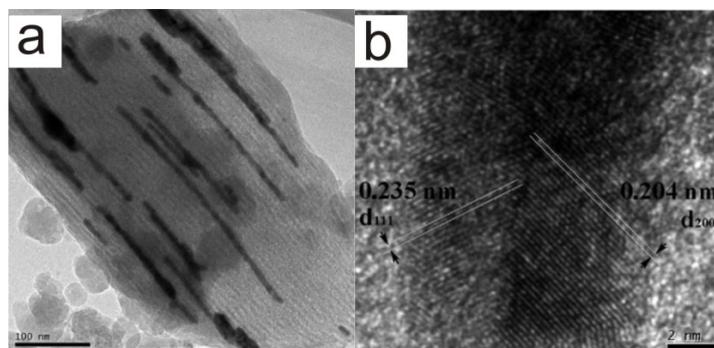
Except for the above-mentioned synthetic routes of mesoporous silica containing Au-NPs, Lennox *et al.* [46] reported the synthesis of monodispersed Au nanoparticles ranging from 5–9 nm in SBA-15 using another novel method: silver-catalyzed electroless deposition (see Figure 13). The synthesis results in an Au/SBA-15 material with a very large loading level of monodispersed Au-NPs aligned in the channels. Extraction of the SBA-15 entrapped Au-NPs from the materials by etching the SBA-15 framework with HF in the presence of alkanethiols results in milligram quantities of Au-NPs with low polydispersity.

**Figure 13.** Scheme of electroless synthesis Au/SBA-15 and alkanethiol-capped gold nanoparticles. Reproduced with permission from [46]. Copyright 2005 American Chemical Society.



Highly dispersed metal (Pd and Pt) nanoparticles and uniformly distributed metal (Au and Ag) nanowires have also been synthesized in ordered mesoporous silica SBA-15 *via* conventional incipient wetness impregnation followed by novel glow discharge plasma reduction reported by Liu *et al.* [47]. More interestingly, this novel glow discharge plasma reduction operates at room temperature and it eliminates the need for energy cost. Uniformly distributed Au nanowires have been successfully confined in the channels of mesoporous SBA-15 as shown in Figure 14. It can be observed that, due to the various natures of the noble metal, different morphologies of Au-NPs confined among the channels of mesoporous silicas can be formed.

**Figure 14.** (a) Typical TEM image of Au/SBA-15 nanocomposite and (b) high-resolution TEM image of Au nanowire confined in SBA-15. Reproduced with permission from [47]. Copyright 2008 American Chemical Society.



Meanwhile, another facile and unique methodology to synthesize the nanosized and uniform noble metal (Pt and Au) nanoparticles has been developed using mesoporous silica support including single-site titanium oxide moieties (Ti-HMS) under microwave irradiation [48]. Physical characterizations reveal that the smaller size of metal particles is formed on the microwave-assisted Ti-HMS support compared to the conventionally prepared impregnated samples. The obtained samples seem to be efficient catalysts for various reactions such as CO oxidation. For rough comparison of the efficiency of different preparation methods, the characteristic parameters of the resulting catalysts, in terms of size of produced Au-NPs, metal loading and  $T_{50}$  ( $^{\circ}\text{C}$ ) in the CO oxidation are listed in Table 1.

**Table 1.** Main data of research papers on CO oxidation over Au/mesoporous silica reported in this review.

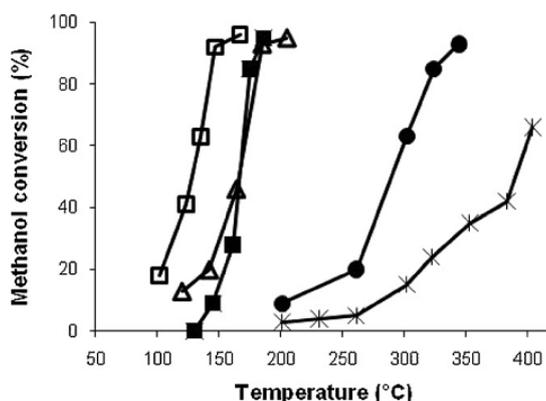
Catalysts	Preparation methods	Average Au particle size (nm)	Au loadings (wt.%)	$T_{50}$ ( $^{\circ}\text{C}$ )	Refs.
Au/SiO <sub>2</sub>	Colloidal deposition	~30–100	1.5	-	[25,26]
Au/Ce20-SBA-15	Doping oxide	~3–5	2.0	81	[27]
Au/mesoporous silica	Pre-modification	~4–7	4–5	~80	[34–37]
Au/mesoporous silica	One-pot synthesis	~2–5	0.7–7.0	-	[38–40]
Au/mesoporous silica	Colloidal synthesis	~2–10	2.0	-	[41,42]
Au/SBA-15	Cationic complex precursor	~3–4	~2.0–9.0	10	[43–45]
Au/SBA-15	Silver-catalyzed electroless deposition	~5–9	large	-	[46]

### 3. Catalytic Oxidation of Volatile Organic Compounds (VOCs)

The role of gold in the total oxidation of different types of saturated and unsaturated hydrocarbons, unsaturated carbonyl compounds, alkynes, and alkadienes, the so-called volatile organic compounds (VOCs), has also been extensively studied [49]. We have recently reviewed the synthesis and applications of gold supported catalysts in oxidation of VOCs [50]. Few mesoporous silica gold based catalysts have been investigated up to now in such a field. Recently, a series of Au/FeO<sub>x</sub>/SBA-15 catalysts were prepared by two preparation methods, conventional and one non-conventional: Au Dp on FeO<sub>x</sub>/SBA-15 (C-Fe Dp-Au) and bimetallic carbonyl cluster deposition on SBA-15 (C-FeAu),

respectively [29]. The catalyst prepared by using cluster impregnation shows the best performance in terms of methanol combustion as shown in Figure 15, a strong interaction between Au and iron oxide species was observed for the bimetallic cluster-derived material. Furthermore, the achieved catalytic performance in methanol total oxidation compares very favorably with literature reports.

**Figure 15.** Methanol conversion as a function of reaction temperature for SBA-15 supported catalysts: SBA-15 (✱), C-Fe (●), C-FeAu (□), C-Fe Dp-Au (Δ), and Dp-Au (■). Reaction conditions: reactant mixture 0.3 vol% methanol, 10 vol.% O<sub>2</sub>, N<sub>2</sub> balance. Space velocity (GHSV):  $7.6 \times 10^{-3} \text{ mol h}^{-1} \text{ g}^{-1}$ . Reproduced with permission from [29]. Copyright 2011 Elsevier B.V.

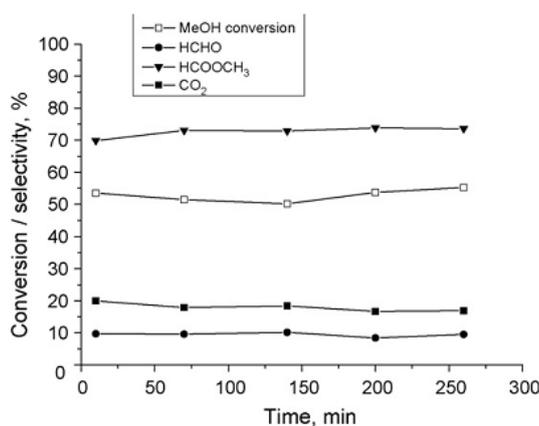


On the other hand, Sobczak and coworkers [51] studied the catalytic performances of Au/MCM-41 (prepared by a hydrothermal method) for the oxidation removal of methanol at low temperatures. Their work described the syntheses, characterization and catalytic application of silicate MCM-41 support modified with Au, V and Nb by their introduction during the synthesis, performed with the use of HCl or H<sub>2</sub>SO<sub>4</sub> as pH adjustment agent. They found that the basicity of Au/MCM-41 was diminished by the introduction of transition metal species (V and Nb). The catalysts prepared by the use of H<sub>2</sub>SO<sub>4</sub> revealed a higher acidity, better ordering of mesopores, and a lower activity in methanol oxidation than those prepared with the use of HCl. The latter exhibited higher activity in methanol oxidation to CO<sub>2</sub> (Figure 16). In addition, Solsona *et al.* recently reported that gold deposited on a cobalt containing siliceous mesoporous structure, UVM-7, presented good catalytic performance in the total oxidation of propane and toluene [52]. The improved activity of the bimetallic AuCo-samples if compared to gold free cobalt catalysts can be explained on the basis of the enhanced reducibility of some cobalt species in the presence of gold, which facilitated the redox cycle. The high reducibility of cobalt species in the bimetallic catalysts is probably due to the formation of Co<sub>3</sub>O<sub>4</sub> domains at the gold-CoO interface perimeter.

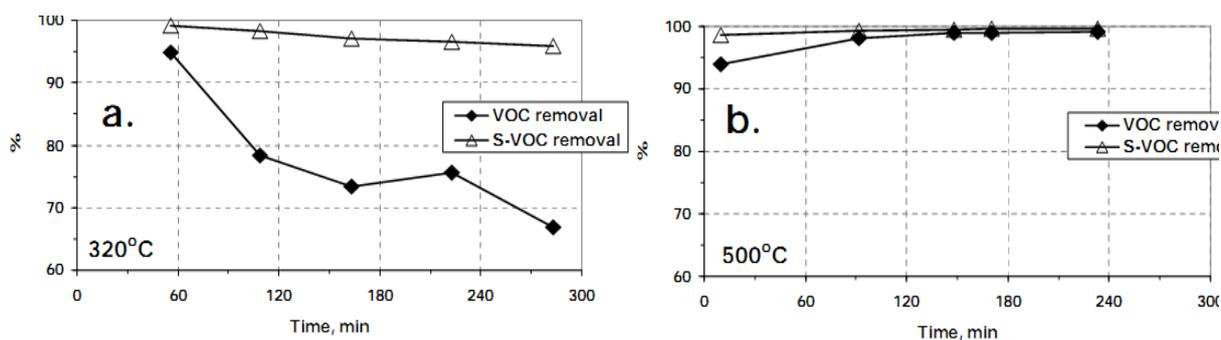
Recently, Kucherov and coworkers [53,54] reported that Au nanoparticles demonstrated quite unusual oxidative activity in low-temperature methanol (MeOH) and dimethyldisulfide (DMDS) removal from air. Au-NPs were introduced into the zeolite by ion exchange (IE) between a solution of HAuCl<sub>4</sub> in water ( $8.25 \times 10^{-4} \text{ M}$ ; pH = 5.0) and the NH<sub>4</sub>-form of zeolite. In detail, the 1.1 M ammonia solution was added dropwise to the HAuCl<sub>4</sub> solution keeping the pH below 5.5 (end point NH<sub>3</sub>: Au = 4.0). Complete transformation of the anion [AuCl<sub>4-x</sub>OH<sub>x</sub>]<sup>-</sup> to the cation complex

$[\text{Au}(\text{NH}_3)_4]^{3+}$  was controlled with an ion-meter (I-500) by using a  $\text{NH}_4^+$ -ion selective electrode [54]. No formation of elemental S was detected in the cases of gold catalysts supported on HZSM-5, H-beta, or MCM-41. Whereas, formation of  $\text{SO}_2$  and elemental S was revealed for pure  $\text{TiO}_2$  supported Au and Au-Pd catalysts [54]. Gold catalysts supported on HZSM-5, H-beta, or MCM-41 exhibited efficient DMDS-to- $\text{SO}_2$  oxidation at temperature above 290 °C. Not only formation of small nanoparticles of gold but also a specific interaction between gold and  $\text{TiO}_2$  support seems to be responsible for the relatively high catalytic behavior of the Au/ $\text{TiO}_2$  sample compared with those of Au/HZSM-5, Au/H-beta and Au/MCM-41 [54]. Au/HZSM-5 is also less active and less S-resistant compared with the bimetallic Au-Pd catalysts. Continuous coking of the Au/HZSM-5 catalyst is accompanied by gradual loss of the efficiency of VOC removal at 320 °C (Figure 17). However, the monometallic Au/HZSM-5 catalyst is able to provide an efficient removal of VOC+S-VOC at a relatively high operation temperature of 500 °C (see Figure 17).

**Figure 16.** Conversion and selectivity in the methanol oxidation reaction on Au/MCM-41(HCl). Reaction conditions: reactant mixture 4 mol% methanol, 8 mol%  $\text{O}_2$ , 88 mol% He balance. Flow rate: 40 mL  $\text{min}^{-1}$ . Reproduced with permission from [51]. Copyright 2008 Elsevier B.V.



**Figure 17.** Efficiency of VOC and S-VOC removal on 0.9 wt.% Au/HZSM-5: long-term test at 320 and 500 °C. Reaction conditions: reactant mixture 1100 ppm  $\text{CH}_3\text{OH}$  + 1060 ppm of  $(\text{CH}_3\text{S})_2$  + air; 75 200  $\text{h}^{-1}$ . Reproduced with permission from [53]. Copyright 2007 Elsevier B.V.



#### 4. Concluding Remarks

In this review we have provided a survey of the development of highly dispersed mesoporous silica based gold catalysts. It is well known that the conventional methods such as impregnation, deposition-precipitation, colloidal deposition, *et al.*, to prepare highly dispersed Au-NPs confined in the channels of mesoporous silicas are not efficient. Therefore, several typical examples have been highlighted of the novel syntheses of highly dispersed Au-NPs incorporated into mesoporous silica supports with relatively weak metal-support interaction and then reduced by various methods to increase the interaction between Au-NPs and the support. Compared to conventional synthesis methods, we presented several novel synthetic routes, such as the synthesis of Au/mesoporous silica by doping metal oxides to enhance the interaction between Au-NPs and metal oxides which result in the formation of multifunctional metal-support interfaces; the pre-modification of mesoporous silica by various bi-functional ligands before incorporating Au-NPs; the one-pot or *in-situ* synthesis of mesoporous silica containing Au-NPs; the colloidal synthesis of Au-NPs incorporated into mesoporous silica; the synthesis of Au/mesoporous silica by Au cationic complex precursor; and finally other novel or post-modification of Au/mesoporous silica. We need to emphasize here that most of the reviews in this field deal with new preparation methods, synthetic details and applications of mesoporous silica [55], while very limited examples of the mesoporous silica based gold catalysts and their catalytic properties in the oxidation of CO or VOCs are reported.

In this review, the majority of reported mesoporous silica based gold catalysts were prepared by loading Au-NPs on mesoporous silica supports. To enhance the dispersion of available Au nanoparticles, improve the thermal stability, and understand structure-property corrections, it is desirable to build up a large specific surface area, as well as stable and single interface catalytic architectures by various noble synthesis methods. It has been claimed that three strategies such as pre-modification, post-modification and co-modification could be adopted to modify Au/SiO<sub>2</sub> systems by adding the modifier or additive [56]. By controlling the sequence of introducing gold and the modifier, different interfaces enhancing the catalytic activity in CO oxidation could be constructed [56]. Moreover, this promotional effect may be due to the modification of the chemical state of gold, the particle size of gold, the thermal stability of Au nanoparticles, or even the creation of new active sites for CO oxidation [56]. In most of our cases, only the single Au-SiO<sub>2</sub> interface in the channels of Au/mesoporous silica systems can be found after removal of organic functional ligands or polymer. The interaction between Au-NPs and silicas could be enhanced by means of the close contact structures or Au-SiO<sub>2</sub> interfaces of these catalysts, but the reasons for the improved catalytic activity of these catalysts have not been clarified. The small particle size of Au nanoparticles inside the channels of mesoporous silicas or the addition of modifier on mesoporous silicas may also promote the catalytic activity considerably. Although variations in catalytic activity are clearly observed in the above-mentioned examples, the fundamental reasons for the above promoting effects require further study.

We propose several ideas for further research. First, although we observed the phenomenon in various mesoporous silicas, the essential reasons for the sintering resistance of Au nanoparticles during calcination process are not clear. For example, the particle size, the morphology and distribution of Au-NPs confined in the various mesoporous silica supports depend on the synthetic routes and on the

type of mesoporous silica supports. Thus, detailed and systematic experimental work and even theoretical calculations on these catalyst systems are needed. Second, in order to fully understand the novel synthesis of Au-NPs incorporated into mesoporous silica supports, all of the detailed physical characterization before and after thermal treatment is required. Third, most of the catalysts have only been tested in CO oxidation because it is a sensitive probe reaction and very useful in environmental protection. However, a deep physico-chemical investigation of CO oxidation over these novel catalysts should be done, especially with *in situ* spectra measurements and first-principle calculations, which could be helpful for understanding the reaction pathways, active sites, and mechanism of CO oxidation. Finally, it would be worthwhile to explore various applications of these catalysts in other reactions, such as combustion of VOCs, selective oxidation and hydrogenation, oxidative desulfurization and further examples.

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### Conflicts of Interest

The authors declare no conflict of interest.

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