Catalysis Letters Vol. 95, Nos. 3–4, June 2004 (© 2004)

Comparison of Au catalysts supported on mesoporous titania and silica: investigation of Au particle size effects and metal-support interactions

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Received 29 September 2003; accepted 19 March 2004

Au catalysts supported on mesoporous silica and titania supports were synthesized and tested for the oxidation of CO. Two approaches were used to prepare the silica-supported catalysts utilizing complexing triamine ligands which resulted in mesoporous silica with wormhole and hexagonal structures. The use of triamine ligands is the key for the formation of uniformly sized 2–3 nm Au nanoparticles in the silica pores. On mesoporous titania, high gold dispersions were obtained without the need of a functional ligand. Au supported on titania exhibited a much higher activity for CO oxidation, even though the Au particle sizes were essentially identical on the titania and the wormhole silica supports. The results suggest that the presence of 2–3 nm particle size alone is not sufficient to achieve high activity in CO oxidation. Instead, the support may influence the activity through other possible ways including stabilization of active sub-nanometer particles, formation of active oxygen-containing reactant intermediates (such as hydroxyls or O_2^-), or stabilization of optimal Au structures.

KEY WORDS: Au; silica; titania; CO oxidation; mesoporous oxides; TEM; FTIR.

1. Introduction

Both the exceedingly high activity of Au catalysts for CO oxidation reactions and the sensitivity of this activity to preparation techniques have been a subject of great interest in the catalysis community[1–3]. The rate of oxidation of CO for gold catalysts is more than one order of magnitude higher than those for similarly prepared Pt catalysts[4]. However, for comparable Au loadings, the reaction rate over different Au catalysts at room temperature may vary by more than four orders of magnitude depending upon the method of preparation. Two important but distinctly different factors have been suggested to be important for the control of the activity of Au catalysts, (1) Au particle structure effects, especially Au particle size and (2) support effects. The correlation between activity and Au particle size has been clearly demonstrated for Au on reducible metal oxides [5] as well as for Au islands deposited upon a TiO_2 thin film[6]. The results show that Au particles of approximately 2–3 nm in diameter exhibit optimal activity. Nevertheless, the fundamental reason for this size effect remains unresolved, since variation of the Au particle size also results in variation in Au-support contact area and possible electronic modulation by the support. Similarly, Au-support contact interactions are expected to be a major determinant of the resulting particle size. Results of experimental attempts to compare supported and unsupported Au are difficult to interpret, since aggregation of unsupported Au particles makes it very difficult to stabilize particles with comparable size distributions in both cases [7].

The development of mesoporous supports with mean pore diameters in the range of interest for Au catalysis offers the opportunity to use these supports as a means to control the sizes of catalytic particles deposited within their pore structure. The ability to prepare both silica and titania mesoporous supports provides an opportunity to compare the activity of Au particles of comparable sizes on a reducible and non-reducible support. In this paper, we present such a comparison. We have previously reported that stabilization of small Au particles in silica requires special care [8]. By functionalizing the silica mesopore walls, we have succeeded in stabilizing high loadings of Au particles with Au particle sizes comparable to those prepared onto mesoporous titania supports by the deposition–precipitation (DP) method. Our results indicate that equally sized Au particles supported on silica are far less catalytically active than those supported on titania. The results suggest that activity of Au particles is not determined by particle size alone, but support interactions must be considered.

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2. Experimental

Steady-state activity measurements for the oxidation of CO were carried out in a single pass fixed bed reactor. The outlet and inlet streams of the reactor were analyzed using an Infrared Gas Analyzer (Siemens Ultramat 23). A thermocouple placed in the catalysts bed was used to monitor the temperature of the reaction. The volumetric flow rate of the reactant mixture (1% CO in air with less than 3 ppm water) was held at 150 mL/min over 500 mg of catalyst for a corresponding space velocity of 18,000 mL/(g h). For the Au supported on mesoporous TiO_2 calcined to 200 °C, where a limited amount of catalyst was available, a higher space velocity of 45,000 mL/(g h) was used. Steady state CO conversion measurements were obtained at different temperatures in random order, typically allowing for at least 1 h between successive measurements in order for the reaction system to reach steady state.

TEM measurements were obtained with a Hitachi HD-2000 electron microscope. Measurements were conducted in both bright field and dark field. The Sigmascan program was used as an aid to estimate particle sizes and to obtain particle size distributions. Surface area measurements were made using a Quantachrome Autosorb I system and the supplied software for all analyses of surface area and Barrett-Joyner-Halenda (BJH)[9] pore size distributions. Infrared measurements were made using a Nicolet 470 FTIR spectrometer with a homemade *in situ* cell. The catalyst was pressed into a thin pellet (about 20 mg/cm^2) and positioned in the IR beam. Background measurements were obtained in He at room temperature prior to introduction of CO. Spectra were collected until the gas phase CO spectrum stabilized and then He was flowed in the cell to remove the gas phase CO. The spectra shown were obtained after the gas phase CO was removed from the cell.

3. Results

3.1. Synthesis and structure of mesoporous catalysts

Two types of Au catalysts supported on mesoporous silica were considered, as well as Au catalysts supported on mesoporous titania. A significant difficulty with preparing Au catalysts supported on mesoporous silica is the weak interactions between Au and silica, which lead to significant agglomeration of the Au particles and loss of Au from the mesopores. We have combined complexation-mediated growth of Au nanoparticles with surfactant templating synthesis of the silica to prepare two types of Au catalysts supported on silica with substantially different porous supports. In one case, the pore structure was characterized by well-ordered, aligned and non-intersecting pores typified by MCM-41 [10], while in the second case, the pores were typified by a poorly ordered "wormhole" structure [11].

3.1.1. Hexagonal silica support

The preparation of Au supported on mesoporous hexagonally ordered silica was based upon the MCM-41 synthesis [10]. The complete synthesis, processing, and structural characterization are described elsewhere [8]. Briefly, this catalyst was prepared by a co-assembly synthetic procedure using $HAuCl_4$ and TEOS (tetraethoxyorthosilicate) as the precursors for Au and SiO_2, respectively, CTAB (cetyl trimethly ammonium bromide) as the template, and TMSPTA (trimethoxysilyl propyl diethylenetriamine) as the complexing ligand for the stabilization of the Au nanoparticles. The co-synthesis mole ratios used were 0.15 : 1 : 0.05 : 0.007 (CTAB : TEOS : TMSPTA : Au), implying a maximum Au loading of 2.2 wt%. For the catalysts discussed below, the as-synthesized material was treated for 1 h at 200 °C in a 4 % H_2/Ar mixture in order to reduce the Au ions. The surfactant was removed by ion exchange with ammonium chloride.

The resulting catalyst exhibited a high surface area and narrow pore size distribution with a mean mesopore size of 1.8–2 nm (table 1). The XRD patterns recorded after the final ion-exchange reaction indicate the presence of very broad peaks associated with small crystalline particles of Au. The Z-contrast STEM images of the reduced as-synthesized sample indicate the presence of Au nanoparticles (figure 1a) with an analyzed size distribution of approximately 2.6 ± 1.3 nm. The mesoporous structure of the silica is evident in the bright-field micrographs (not shown) with aligned pores separated by approximately 4 nm. These features are consistent with thin walls and the 2 nm pore diameter obtained by BJH analysis.

3.1.2. Wormhole silica support

The preparation of Au supported on mesoporous multi-dimensional ("wormhole" structured) silica was based upon a neutral templating method described by Tanev and Pinnavaia [12, 13]. The complete synthesis, processing and structural characterization have been described elsewhere [14]. Briefly this catalyst was prepared by a co-assembly synthetic procedure using $HAuCl_4$ and TEOS as the precursors for Au and Si respectively, dodecylamine as the template, and TMSPTA as the complexing ligand for the stabilization of the Au nanoparticles. The co-synthesis mole ratios used were 0.25 : 1 : 0.025 : 0.005 (surfactant : TEOS : TMSPTA : Au) implying a maximum Au loading of 1.6 wt%. After precipitation from the synthesis mixture, the surfactant was extracted by washing with ethanol and the catalyst was reduced in 4% H_2 /He mixture at 500 °C in order to form the Au nanoparticles. A subsequent 1-h calcination was performed by inserting the reduced catalyst into a hot oven, at 500 °C. This rapid upquenching appeared to result in decreased sintering and loss of Au from the mesopores [14].

Table 1
Comparison of silica and titania supported Au catalysts

Sample	BET surface area (m^2/g)	BJH pore size (nm)	TEM particle size (nm)		Lightoff T_{50} (°C)	Estimated loading (wt%)
			Before	After		
Au/hexagonal silica	725	1.9	2.6 ± 1.3	11 ± 5	280	2.2
Au/wormhole silica	1375	2.2	2.6	2.7 ± 0.9	190	1.6
Au/mesoporous titania (150 °C)	160	5.0	3.5	N/A	–10	9
Au/mesoporous titania (200 °C)			N/A	6.7 ± 2.8	30	14

Complete removal of the surfactant from the wormhole silica by washing in ethanol was verified by FTIR analysis. The XRD patterns of the as-synthesized catalyst as well as patterns obtained after each post-processing step, verified the presence of significant number of crystalline Au particles. The presence of the mesopores is indicated by a sharp BJH pore size distribution peaked at 2.2 nm (table 1). TEM images (figure 1b) indicate the presence of a large number of Au nanoparticles. The analysis of the particle size in this dark field micrograph is complicated by the high density of overlapping particle images, but measurements of distinct particles indicate an average particle size of 2.6 ± 0.8 nm in diameter. The pore structure can not be clearly observed in the TEM images (either as rows or as ordered pore openings) suggesting a "wormhole" type of structure [12].

3.1.3. Mesoporous titania support

The mesoporous titania was synthesized following published methods [15]. The as-synthesized mesoporous titania was calcined at 350 °C, a temperature chosen to prevent significant crystallization. Two Au samples supported on mesoporous titania were prepared by the DP method, using Au quantities sufficient to yield 9–14 wt%. Briefly, the dried mesoporous titania support was added to an aqueous solution of $HAuCl_4$, which was neutralized to pH 7 with KOH. Unlike the silica samples, no complexing ligand was needed in the case of the titania support. After the DP process, the samples were calcined at 150 or 200 °C, for the 9–14 wt% samples, respectively.

Gas adsorption measurements on the titania support prior to impregnation with Au indicates a well-defined but somewhat broadened pore size distribution with an average of approximately 5 nm and FWHM of approximately 1 nm. The surface area and pore volume were found to be 250 m^2/g and 0.29 cm^3/g, respectively. After Au impregnation and calcination, the pore size distribution broadens slightly and shifts to 6 nm, while the surface area and pore volume decrease to 160 m^2/g and 0.20 cm^3/g. The TEM image of the Au-impregnated catalyst following calcination at 150 °C (figure 1c) suggests Au particle sizes in the range of 3.5 ± 1 nm, consistent with the Au particles being contained within the mesopores. In several TEM images of this material, a hexagonal array of pore openings is apparent, suggesting that the mesopore structure in the titania is well ordered and exhibits the Im3m structure reported previously [15]. SEM images indicate that there are occasional large (> 15 nm) Au particles aggregated on external surfaces of the mesoporous titania crystallites, but comparison of the TEM and SEM images suggests that the majority of the Au is present within the pores.

3.2. Catalytic activity of mesoporous catalysts

CO oxidation "lightoff" (i.e., conversion versus temperature) curves for all the Au catalysts examined are shown in figure 2. In particular, the silica-supported catalysts are significantly less active than the titania-supported ones. Complete conversion of CO was observed at temperatures near 0 °C for Au supported on mesoporous titania. In contrast, over Au supported on silica, activity is only detected at 100 °C, and complete conversion of CO is not reached until 200 or 300 °C, for the wormhole and the hexagonal silica, respectively. The difference in activity is so wide, that it becomes experimentally difficult to compare measured rates at the same temperature. This is why specific rates or turnover frequencies are not used for the comparisons.

In comparing these results, it is important to consider the pre-treatment of the catalysts and the time on stream, since pre-treatments may be expected to affect Au particle size and structure. Au supported on the wormhole structured silica was initially treated in He at 200 °C for 30 min prior to obtaining the lightoff curve shown in figure 2. Extended time on stream (8 h) and a subsequent reduction at elevated temperature (1 h in 5% H_2 in He at 200 °C) had no effect on the activity. After completion of the activity measurements over several days, this catalyst was removed from the reactor and STEM images were obtained. A typical micrograph is shown in figure1b (right). Analysis of some 150 particles from two separate regions yielded a particle size of 2.6 ± 0.9 nm, comparable to that obtained from

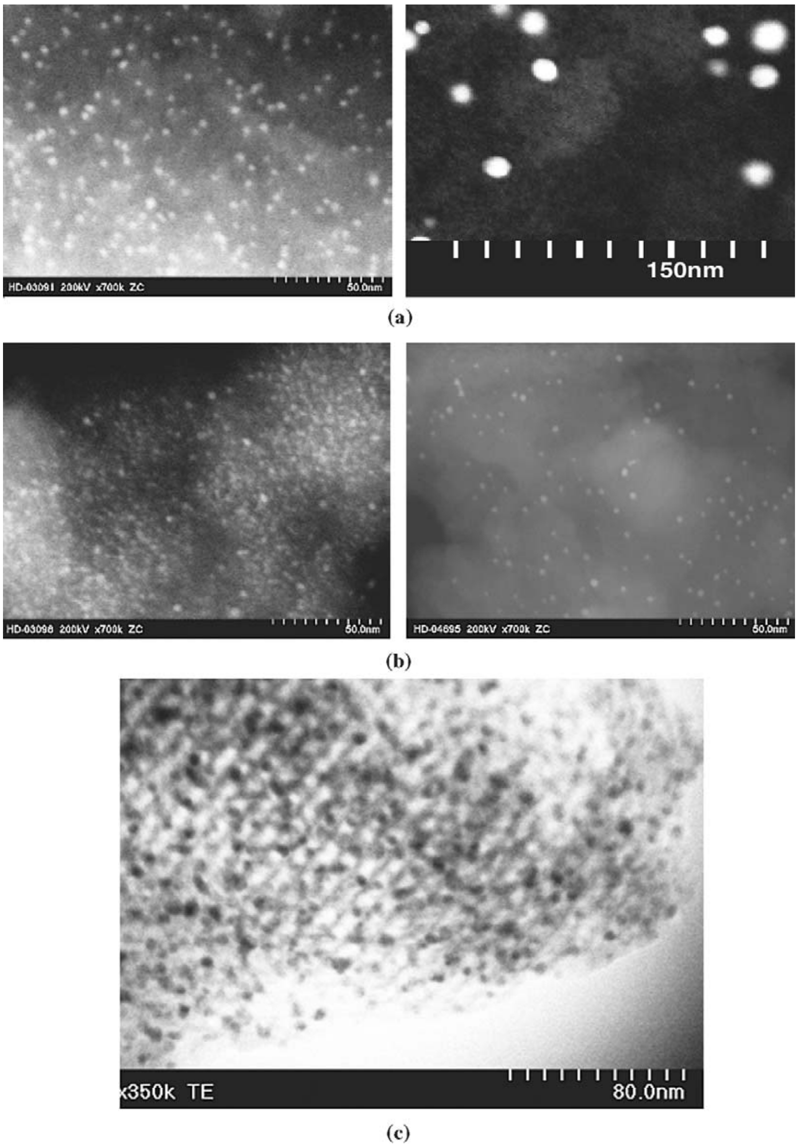

Figure 1. TEM images of the mesoporous catalysts are shown before (left) and after (right) measurement of lightoff curves for (a) Au/mesoporous silica (dark field); (b) Au/wormhole silica (dark field); and (c) Au/mesoporous titania before reaction only (bright field) calcined 150 °C. Images are rescaled to the exhibit the same magnification.

the fresh catalyst. Evidently, the Au particles on this support did not sinter appreciably as a result of treatments and exposure to reaction conditions.

Au supported on hexagonal silica was initially inactive up to 250 °C. After oxidation (5% O_2/He mixture at 400 °C for 1 h) to remove capping ligands from the Au particles, the lightoff curve in figure 2 was obtained. A second oxidation at 400 °C did not alter the activity. After completion of the activity measurements the catalyst was removed from the reactor and STEM images were obtained. A typical micrograph is shown in figure 1a (right side). Analysis of several hundred particles in images of four regions yielded a particle size of approximately 11 ± 5 nm. The particle size distribution further indicated a considerable number of particles with sizes near 2–3 nm, but the images were dominated by larger particles. Micrographs were also recorded of a sample which had not been in the reactor but was stored for approximately 6 months at room temperature. It exhibited a clear bimodal particle size distribution with large particles of approximately 12 nm in size, but also many particles with sizes around 2.5 nm. It is assumed that the larger particles are located on the external surfaces of the silica, while the more numerous 2.5-nm particles are contained within the mesopores. Evidently, even at room temperature, migration of Au out of the mesopores and sintering of the Au particles on the external surfaces occurs.

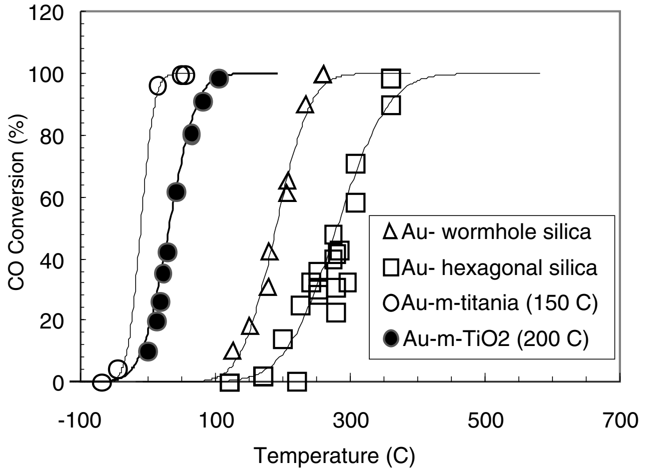

Figure 2. CO conversion (points) is shown as function of temperature for different supported Au catalysts: Au on wormhole mesoporous silica, Au on hexagonally ordered mesoporous silica, Au on mesoporous titania calcined at 150 °C, and Au on mesoporous titania calcined at 200 °C. Sigmoid curves guide the eye through the data. (Conditions provided in text.)

The Au catalysts supported on the mesoporous titania were pre-treated in the reactor in a 5% H_2–He mixture at either 150 or 200 °C for about 1 h before obtaining the lightoff curves shown in figure 2. For the sample calcined and reduced at 150 °C, the activity was very high with 100% conversion reached at 50 °C and measurable conversion (4%) observed even at −45 °C. This latter activity corresponds to a rate of 1 μmol CO/(s g_{Au}), and may be compared to literature values for Au supported on titania of 13–39 μmol CO/(s g_{Au}) at −38 °C [14,16]. The sample calcined and reduced at 200 °C, exhibited slightly higher lightoff temperatures, in part due to using a higher space velocity for this lightoff curve. Additional measurements indicated that the initial on-line pretreatment in 5% H_2 was not necessary to achieve this level of activity. Both titania-supported catalysts exhibited higher activity for CO oxidation than the silica, supported ones, regardless of whether they were pre-treated in H_2 or not.

3.3. FTIR spectra of adsorbed CO

Room temperature FTIR spectra obtained following CO adsorption on the Au catalysts supported on the mesoporous titania and the wormhole silica supports are shown in figure 3. The pre-treatment for the wormhole silica catalyst consisted of exposure to a 10% O_2–He mixture for 1 h at 200 °C. The sample was then cooled in He to room temperature. The mesoporous titania-supported catalyst was only pre-treated under He for 30 min at room temperature. For both samples, a mixture of 1% CO–He was then introduced at room temperature for several minutes, followed by purging with He to remove gas phase CO immediately prior to recording the spectra.

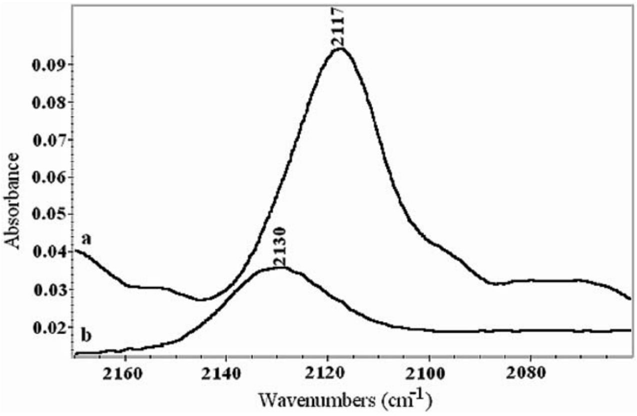

Figure 3. FTIR spectra of CO adsorbed at room temperature are shown for (a) Au supported on mesoporous titania and; (b) Au supported on wormhole silica.

The spectrum of the wormhole silica catalysts exhibits a CO band at 2130 cm^{-1} assigned to CO linearly bonded on Au [17]. A much stronger band is observed at 2117 cm^{-1} in the spectrum of CO adsorbed on Au supported on the mesoporous titania. This band can also be assigned to CO linearly bonded on Au [18]. These results indicate that Au in both samples is capable of adsorbing CO at room temperature. The observed differences in intensity and position of the two bands indicate that CO is more weakly held on the silica-supported Au particles. This may be the result of differences in Au-support interactions, CO coverage and/or Au oxidation state (in part due to differences in pretreatment conditions).

4. Discussion

Several factors which influence the CO oxidation activity of gold catalysts have been identified in the literature [3]. Notably, Au crystallite size has been considered to be one of the most important factors. In an early paper, Bamwenda *et al.* [4] reported CO oxidation activity data for Au deposited on TiO_2 by DP and other synthetic methods. The highest activity was obtained for a Au loading of 3.1 wt% (the highest attempted), which gave rise to particle sizes of 2.9 nm. Smaller particles obtained from lower loadings, and bigger particles (obtained using a different deposition technique) yielded lower activities. Subsequent studies of CO oxidation on Au islands deposited on TiO_2 single crystal surfaces demonstrate a particle size effect with optimal activity for islands of 3.5 nm [6,19]. Although this particle size effect is not well understood or proven to be the dominant factor, the correlation between "small" Au particle sizes and high CO oxidation activity, is by now considered as "well established."

The present results allow a comparison of the activity of three Au catalysts with nearly identical initial Au particle sizes, supported on three different supports (table 1). In each case, most of the particles are within the "optimal" particle size range of 2–4 nm. It is clear that despite the similar Au particle sizes, the catalytic activities, as indicated by lightoff temperature, vary considerably. In particular, the titania-supported Au particles (3.5-nm average size) are substantially more active than the optimally sized 2.6-nm Au particles on the wormhole silica support. The results provide clear evidence that the chemical nature of the support is also important, and seemingly not just for the purpose of stabilizing the optimally sized particles [20]. Previously, the importance of the support has also been discussed in the literature [21-23] and various mechanisms involving reactant or spectator species adsorbed on the support have been proposed [2,3,18].

In making this comparison, it is important to consider whether the surfaces of the less active Au particles supported on silica are somehow blocked by chemisorbates or oxidized to a less active state. Functional ligands are necessary in our synthetic approach to limit the growth of gold particles on silica, so it may be possible that residual from these ligands block the reaction. In the case of the wormhole silica, the calcination to 500 °C should have completely oxidized any remnants of the functional ligands, and the on-line treatments should render the surface of the Au particles into a state similar to that of the more active Au particles on the titania support. The FTIR results demonstrate that the Au particles can adsorb CO, and the position of the CO stretch is consistent with adsorption on metallic Au. Therefore, the lower activity of the wormhole silica catalyst can not be attributed simply to "capping" of the Au surface by the triamine functional ligands.

A second important consideration is whether the size of the Au particles increases under reaction conditions leading to de-activation of the silica supported catalysts as compared to titania. TEM images of the hexagonal silica catalyst did indeed indicate that substantial particle growth occurred under reaction conditions and may have contributed to the low activity of this catalyst. However, for the wormhole catalyst TEM micrographs obtained before and after the reactivity measurements confirmed that the Au particle size distribution, visible by TEM, did not change substantially as a result of either exposure to the reaction conditions or pre-treatment. Consequently, for this silica supported catalyst, particle growth is apparently not the factor responsible for the lower observed activity.

A third consideration is the difference in Au loading, since the titania-supported catalysts had substantially higher Au loadings. Ideally one would compare turnover frequencies, so that the loading and dispersion factors are eliminated. However, it is not possible to do so in the present case because the difference in activity is so wide, that it becomes experimentally difficult to compare rates at the same temperature. Nevertheless, the factor of 4–6 difference in loading is expected to give at most a shift of 20–30 °C, as compared to the 200 °C shift observed in figure 2. Therefore, differences in Au loading alone can also not explain the much higher activity of the titania-supported catalysts.

The low activity observed when non-reducible silica is used as the support suggests that a different mechanism is operating on this catalyst as compared to the titania-supported one. As stated above, it has been postulated that oxygen located at the interface between titania and the Au clusters contributes to the high activity of titania-supported Au catalysts [3]. In the absence of a support that can provide such oxygen, the activation of gas phase oxygen must take place on the Au particles. Such a reaction mechanism, in which CO and O_2 are co-adsorbed and directly react on the Au particle, has been considered theoretically on a Au_{10} cluster [24]. The calculated energy barriers were consistent with CO oxidation occurring below room temperature, but only if corner sites of very low coordination are present. Experimental evidence for such a direct mechanism also derives from studies of unsupported Au nano-particles (76 nm in diameter) which can catalyze CO oxidation, although at 0 °C they are two orders of magnitude less active than Au/TiO_2 [7]. Based on results of FTIR and isotope exchange studies, Boccuzzi *et al.* have also proposed that the direct oxidation of CO takes place on the surface of metallic particles and is faster than the oxidation by support oxygen species [18]. However, the present comparison between silica and titania-supported catalysts suggests that the direct CO oxidation pathway is the slower one, since this mechanism should function equally well on 2–3 nm Au particles on either support. Therefore, it appears that all available results can not be explained by a simple application of these two mechanisms.

Au catalysts supported on silica have not been studied much due to the difficulty of stabilizing small Au particles on this support. More specifically, Au can not be deposited on silica by methods most frequently used for other metals, because of the high acidity [22], the low melting point of Au [25] or the isoelectric point of silica [8]. Attempts have been made to deposit/precipitate Au onto a silica support of unspecified structure [5]. This catalyst showed a lightoff temperature of approximately 200 °C. Subsequent work with Au simply impregnated onto silica yielded a lightoff temperature of nearly 400 °C. The low activity of these catalysts has been attributed to the large particle sizes obtained by these methods[23]. Au supported on mesoporous MCM-41, prepared by vapor deposition, yields particles in the size range of 2.2–3.1 nm and is active for CO oxidation with lightoff temperatures (T_{50}) of -15 to -10 °C [25]. In this case, the mean Au particle size exceeded the pore size, suggesting growth on external surfaces. In a subsequent study, Okumura *et al.* reported that Au could be deposited by CVD onto a powder silica (surface area 310 m^2/g) to yield gold particles with a size distribution of 6.6 ± 3.8 nm. This catalyst exhibited higher activity (lower lightoff temperature) than titania-supported Au catalyst prepared by DP even though the average Au particle is more than three times larger on the silica support [23]. It is interesting that in our present study, the wormhole silica-supported catalyst with a smaller size distribution than the CVD-prepared sample, exhibits lower activity. The high activity of CVD-deposited Au on irreducible silica and alumina indicates that oxidation by support species is not a necessary condition for high activity. Furthermore, the present results suggest that small (i.e., 2–3 nm) Au particle size is not a sufficient condition for high activity.

Various contributing factors for the observed difference in activity of the supported Au catalysts may be considered. First, it is possible that the optimal size, demonstrated for titania supports [5,6] is not the same for all support types. This hypothesis suggests that polarization or electronic effects may play a role, for example, by weakening the CO bonding as indicated by the shift in the CO stretch in FTIR. A second factor is that the structure of the support may play a role in the morphology of the Au particles or their contact with the support. Morphology of the Au particles relates to the number of low coordination sites, postulated to be more active. Contact between Au and support may be important for transfer of lattice or molecular oxygen or for reactions involving hydroxyl or silanol groups. It has been recently demonstrated for example, that hydroxyls play an important role in CO oxidation by Au supported on alumina [26]. A third factor is that the charge state of the Au is important and may vary on different supports. For example, it has been shown that Au catalysts supported on iron oxide are most active when both cationic and reduced Au are present [27]. A fourth possibility is that Au particles formed by co-assembly may nucleate in the mesopore walls so that a portion of their surface is unavailable for catalytic processes. However, FTIR results suggest that the surface is not entirely blocked in this way, since CO adsorption is observed. Finally, another possible explanation is that the catalytic activity may be actually associated with sub-nanometer-sized Au clusters, undetected by "routine" TEM. The relative abundance of these undetected clusters could depend upon support type and preparation conditions and they could be generally less stable on silica supports. Preliminary high resolution dark field STEM images indicate the presence of such clusters on titania supports [28] and experiments are in progress to characterize these clusters and correlate their presence with CO oxidation activity.

5. Summary and conclusions

Au catalysts were prepared on wormhole and hexagonally structured mesoporous silica and on mesoporous titania supports. Stabilization by triamine complexing ligands and possibly rapid upquenching calcinations are responsible for achieving nanosized Au particles, (i.e., 2–3 nm) on the mesoporous silica. The Au particles in the wormhole-structured silica support maintain their small size distribution under reaction conditions. Nevertheless, they are substantially less active for the oxidation of CO than Au supported on mesoporous titania. Since previous results have demonstrated high CO oxidation activity for other silica-supported Au catalysts, it is suggested that confinement, surface hydroxyls, support structure or the presence of sub-nanometer Au clusters may play a role in the activity of supported Au catalysts.

Acknowledgments

Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

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