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Gold Nanoparticles Supported on Passivated Silica: Access to an Efficient Aerobic Epoxidation Catalyst and the Intrinsic Oxidation Activity of Gold

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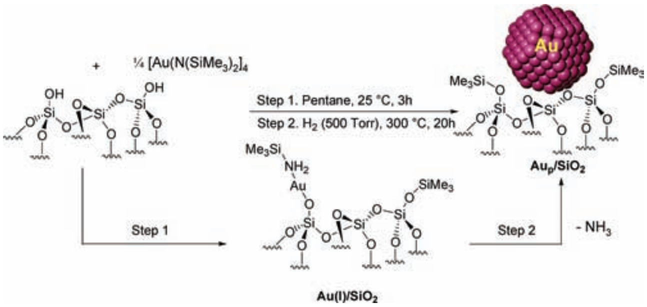
We describe a method for the direct preparation of 1.8 nm gold nanoparticles (**AuNP**) on passivated silica via controlled functionalization of the silica surface with a Au^I complex, namely, $\{Au[N(SiMe_3)_2]\}_4$, followed by mild reduction under H_2 (Scheme 1). This approach leads to a highly efficient gold catalyst for liquid-phase aerobic epoxidation of *trans*-stilbene. This tailor-made catalyst shows that **AuNP** are intrinsically active in aerobic epoxidation and in preferential oxidation of CO (PROX).

Although gold had been considered to be an inert metal, Haruta et al.[1] discovered that **AuNP** in the 2−5 nm range exhibited unique catalytic activity for the low-temperature oxidation of CO when associated with a reducible oxide. Other oxidation reactions involving supported gold catalysts and O_2 were then developed, such as the direct synthesis of H_2O_2 from H_2,[2] the epoxidation of propene,[3] and several liquid-phase aerobic oxidations (the oxidation of alcohols,[4] aldehydes,[5] and hydrocarbons[6]). For these reactions, the mechanism of O_2 activation is an important issue because dissociative chemisorption of O_2 on gold is unlikely.[7] In gas-phase oxidation, it relies on the presence of oxygen vacancies[8] and/or surface hydroxyls on the support,[9] and the gold−support interface probably plays a key role. However, in the presence of H_2, such as in the epoxidation of propene with a H_2/O_2 mixture[10] and in PROX,[11] alternative pathways involving the formation of highly reactive hydroperoxo species from O_2 and H_2 are possible.[12] Additionally, in liquid-phase aerobic epoxidation of alkenes, O_2 is probably activated by an alkyl radical produced from the hydrocarbon solvent and initiated by ROOH over gold (Scheme 2).[13,14] In all of these reactions, the size of the **AuNP** is also a key factor determining the activity.[15] Therefore, much effort has been devoted to controlling the size of **AuNP** on a variety of supports (TiO_2, CeO_2,[16] Fe_2O_3,[17] Al_2O_3,[18] MgO,[19] SiO_2,[20] and activated carbon[21]). However, there is a still need to develop methods for controlling the size of **AuNP** on supports with less reactive oxygenated surface functionalities.

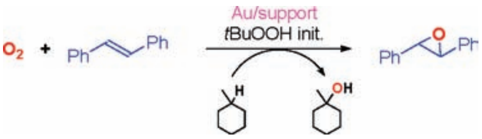
First, we describe the direct synthesis and characterization of **AuNP** supported on hydrophobic silica. Preliminary IR studies using a silica pellet showed that a pentane solution of $\{Au[N(SiMe_3)_2]\}_4$[22] reacted at 25 °C with the silanols of a silica partially dehydroxylated at 700 °C [$SiO_{2-(700)}$], as evidenced by the disappearance of ν(OH) silanol vibrations (3747 cm^{-1}) and the appearance of ν(NH) bands (Figure 1a,b). This is consistent with the protonation of the N atom bonded to Au by the surface silanol and grafting of this complex via an Au−O bond. Moreover, the peaks at 2958 and 2902 cm^{-1} are characteristic of the ν(CH) of the grafted $SiMe_3$ ligands. Upon a subsequent treatment under H_2 at 300 °C, the disk turned deep-red, indicating the formation of **AuNP** and implying the cleavage of the Au−O bond. Since the IR spectrum displayed only vibrations characteristic of the $SiMe_3$ groups but no O−H or N−H vibrations, this suggested that the ≡SiOH groups resulting from reduction of the gold species were further converted into ≡SiOSiMe$_3$ by reaction with $H_xN(SiMe_3)_{3-x}$.

By impregnation of a silica powder with a pentane solution of $\{Au[N(SiMe_3)_2]\}_4$ (1.1 equiv), the solid **Au(I)/SiO₂** remained white,

Scheme 1



Scheme 2



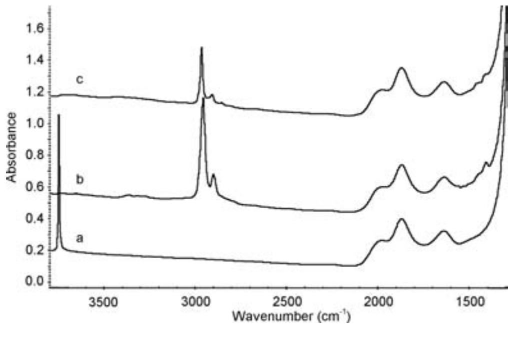


Figure 1. Preparation of **Au_p/SiO_2** monitored by FT-IR spectroscopy. (a) Silica partially dehydroxylated at 700 °C [$SiO_{2-(700)}$]. (b) After grafting of $[Au(NSiMe_3)_2]_4$ to give **$Au(I)/SiO_2$**. (c) After treatment under H_2 at 300 °C to give **Au_p/SiO_2**.

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but elemental analysis showed that it contained 3.0 ± 0.1 wt % Au. This corresponds to 0.15 mmol of Au/g of silica and therefore to the grafting of ~50% of the available surface silanols [0.26 mmol SiOH/g for $SiO_{2-(700)}$]. The IR spectrum of this solid is similar to that obtained previously on the silica disk (e.g., the absence of remaining $\equiv$SiOH group). The N−Au bond was cleaved upon grafting, and the liberated $HN(SiMe_3)_2$ probably reacted with adjacent unreacted $\equiv$SiOH to give $\equiv SiOSiMe_3$ groups and H_2NSiMe_3. This is consistent with the formation of a 1:1 mixture of $\equiv SiOSiMe_3$ and a surface complex (here $\equiv SiOAu^I$), a phenomenon typically observed upon grafting of similar bis(trimethylsilyl)amide metal complexes.[23] Moreover, the two ν(NH) bands at 3368 and 3286 cm^{-1} are characteristic of NH_2,[24] and this is consistent with the presence of H_2NSiMe_3, which is probably coordinated to Au^I (Scheme 1). These hypotheses were confirmed by solid-state NMR spectroscopy through (1) the presence of $SiMe_3$ signals (0 ppm) and consumption of OH [a very low intensity signal (~2%) at 1.8 ppm] in the ^1H magic-angle-spinning (MAS) solid-state NMR spectrum (Figure S1 in the Supporting Information) and (2) the presence of two ^{13}C signals at 0 and 6.4 ppm associated with $\equiv SiOSiMe_3$ and H_2NSiMe_3, respectively (Figure S2).

Further evidence of the presence of grafted Au^I species was obtained by adsorption of PMe_3. First, the ^{31}P cross polarization MAS (CP-MAS) NMR spectrum (Figure S3) displays two different resonances at 8.4 and −16.6 ppm, consistent with the presence of two types of Au^I−phosphine complexes. On the basis of chemical shift values of analogous Au^I-PMe_3 complexes, they have been assigned to a 1:2 mixture of [$\equiv SiOAuPMe_3$] and [$\equiv SiO^-Au^+(PMe_3)_2$] (Scheme S1).[25] Second, the signal previously observed at 6.4 ppm and attributed to coordinated H_2NSiMe_3 in the ^{13}C CP-MAS NMR spectrum of **Au(I)/SiO$_2$** (Figure S2), is replaced by a signal at 14.2 ppm (Figure S4), assigned to the PMe_3 ligand of the two aforementioned Au^I surface species. The presence of these two species upon reaction of **Au(I)/SiO$_2$**with PMe_3 shows that the well-defined $\equiv SiOAu(H_2NSiMe_3)$ species can be in slightly different environments, as already proposed for [$(\equiv SiO)Zr(CH_2tBu)_3$].[26]

Next, heating **Au(I)/SiO$_2$** at 300 °C under H_2 (500 Torr) for 20 h caused the white solid to turn red, indicating the formation of **AuNP**. Transmission electron microscopy (TEM) of this solid (**Au$_p$/SiO$_2$**) evidenced the formation of homogeneously dispersed particles (Figure 2a) with a size distribution centered at 1.8 ± 0.6 nm (Figure 2b). The X-ray photoelectron spectrum of **Au$_p$/SiO$_2$** at the Au 4f level (Figure S5) exhibits binding energies of 83.8 and 87.4 eV for Au $4f_{7/2}$ and Au $4f_{5/2}$, respectively, consistent with Au^0 having no to little interaction with the support.[27] The formation of small **AuNP** probably is a consequence of the low and controlled density of covalently bound gold complexes as well as the absence of OH groups and halide impurities, which can induce sintering.[28] Indeed, the IR spectrum of **Au$_p$/SiO$_2$** shows only traces of surface silanols [<0.003 mmol/g, <0.01 OH/nm^2, i.e., <1% of the initial OH density of $SiO_{2-(700)}$], indicating passivation of the silica surface. The concomitant disappearance of the NH vibration is probably due to the reaction of the freed $\equiv$SiOH groups with Me_3SiNH_2 previously coordinated to Au(I), which generates $\equiv SiOSiMe_3$ and NH_3 (Figure 1c).

This material, **Au$_p$/SiO$_2$**, exhibits the best catalytic performances observed to date in the liquid-phase epoxidation of *trans*-stilbene under aerobic conditions (Scheme 2).[14] After 50 h, nearly full conversion was achieved with an epoxide selectivity of ~80% (Figure 3). Notably, an epoxide yield of ~80% is greater than the yield of 5% expected from the stoichiometric reaction of stilbene with the peroxide initiator. By comparison, only 71% conversion and 50% epoxide yield were reached over the reference catalyst from World Gold Council (**Au/TiO$_{2\text{-WGC}}$**, 1.5 wt % Au, 3.5 ± 0.9 nm). This is attributed to the poor dispersion (wettability) of **Au/TiO$_{2\text{-WGC}}$** in the liquid phase, because the powder rapidly deposits onto the reaction vessel after only a few minutes of reaction, limiting the accessibility to the active sites. On the other hand, **Au$_p$/SiO$_2$**, which has a surface passivated with hydrophobic $SiMe_3$ functionalities, remains perfectly dispersed within the apolar medium throughout the duration of reaction. This leads to optimized mass transfer and hence increased initial reaction rates [from 0.023 mol (g of Au)$^{-1}$ h^{-1} for **Au/TiO$_{2\text{-WGC}}$** to 0.12 mol (g of Au)$^{-1}$ h^{-1} for **Au$_p$/SiO$_2$**] and, when the gold dispersion on the support (as measured by TEM) is taken into account, increased turnover frequencies per surface metal atom, from a maximum of 18 h^{-1} for **Au/TiO$_{2\text{-WGC}}$** to 40 h^{-1} for **Au$_p$/SiO$_2$**.

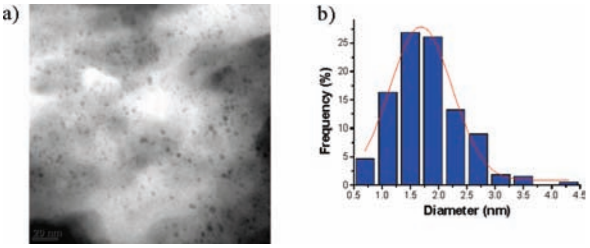

Figure 2. a) TEM image of **Au$_p$/SiO$_2$** (2.79 wt % Au). (b) Au particle size distribution of **Au$_p$/SiO$_2$**.

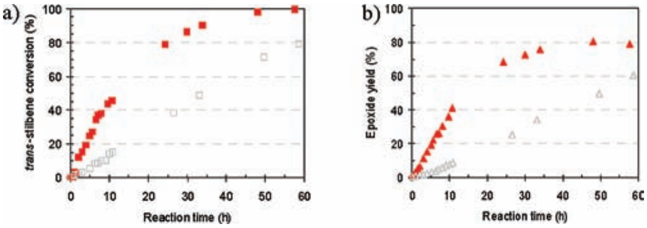

Figure 3. (a) *trans*-Stilbene conversion (squares) and (b) epoxide yield (triangles) as functions of time in the presence of **Au$_p$/SiO$_2$** (solid symbols) and **Au/TiO$_{2\text{-WGC}}$** (open symbols). Reaction conditions: *trans*-stilbene (substrate, 0.90 ± 0.05 mmol), methylcyclohexane (solvent, 20 mL/155 mmol), catalyst (2.0 ± 0.1 μmol of Au), *tert*-butylhydroperoxide (0.05 mmol), air (1 atm), 80 °C, 900 rpm.

Moreover, **Au$_p$/SiO$_2$** displays reasonable activity for low-temperature PROX, a key process for the purification of H_2 feed used in the polymer electrolyte fuel cell (PE-FC) technology. When this material is heated to 280 °C under a 2% CO + 2% O_2 + 48% H_2 mixture balanced in He, the conversion of CO first increases up to a maximum value and then decreases because of competition with H_2 oxidation for the limited amount of O_2 present in the feed (Figure 4). This activity profile remains similar over several cooling and heating steps (Figure S6) and TEM analysis of the sample after reaction (Figure S7) reveals similiar particle size as in the fresh catalyst. At the temperature of interest for fuel cell applications (80 °C), **Au$_p$/SiO$_2$** is a factor of ~2 more active in terms of rate per surface metal atom than **Au/SiO$_{2\text{-cd}}$** prepared by colloidal deposition (0.9 wt % Au, 4.0 ± 1.7 nm).[29] This is attributed to the gold particle size effect (1.8 vs 4.0 nm for **Au$_p$/SiO$_2$** and **Au/SiO$_{2\text{-cd}}$**, respectively).[15] It should be noted, however, that **Au$_p$/SiO$_2$** is (~4 times) less active than the reference catalyst from World Gold Council (**Au/TiO$_{2\text{-WGC}}$**, 1.5 wt % Au, 3.5 ± 0.9 nm), in agreement with the proposed role of the titania support in PROX, namely, promotion of O_2 activation by oxygen vacancies and OH groups. Thus, the significant activity of the fully passivated **Au$_p$/SiO$_2$**,

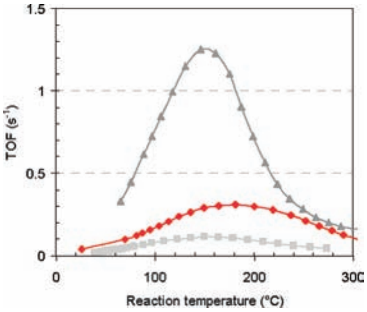

Figure 4. Turnover frequencies (TOF, s^{-1}) for CO oxidation over **Au$_p$/SiO$_2$** (diamonds), **Au/SiO$_{2\text{-cd}}$** (squares), and **Au/TiO$_{2\text{-WGC}}$** (triangles) as functions of temperature under PROX conditions.

despite the absence of any such promoter, indicates that gold is intrinsically active in the oxidation of CO under PROX conditions. Additionally, the negligible activity observed in the absence of H_2 suggests that H_2 plays a critical role in the activation of O_2 for silica-supported systems, probably through the formation of OOH species.

In conclusion, surface organometallic chemistry[30] allows the controlled formation of well-defined and dispersed [(≡SiO)Au^{I}] surface species (0.5/nm^2), which upon mild reduction (H_2, 300 °C) lead to the formation of small (1.8 ± 0.6 nm) Au particles supported on silica passivated with $SiMe_3$ functionalities (**Au$_p$/SiO$_2$**). This hydrophobic Au catalyst displays improved performances in liquid-phase aerobic epoxidation of *trans*-stilbene due to the smaller **AuNP** and better mass transfer. The catalytic reactivity of this OH-free material (**Au$_p$/SiO$_2$**) indicates that Au is intrinsically active in oxidation but requires the presence of H_2 or hydrocarbon, which is consistent with the formation of HOO or ROO intermediates. Given the accessibility of numerous bissilylamido organometallic complexes,[31] this synthetic strategy provides a general approach for the preparation of tailor-made supported metallic nanoparticles with controlled surface properties, and we are currently exploring its scope.

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Supporting Information Available: Full experimental details, Figures S1−S7, and Scheme S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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