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

David Gajan,^{†,‡} Kevin Guillois,[§] Pierre Delichère,[§] Jean-Marie Basset,[†] Jean-Pierre Candy,[†] Valérie Caps,^{*,§} Christophe Copéret,^{*,†} Anne Lesage,[‡] and Lyndon Emsley[‡]

Université de Lyon, Institut de Chimie de Lyon, C2P2-LCOMS UMR 5265 (CNRS - CPE - Université Lyon 1), ESCPE Lyon, 43, Bd. du 11 Novembre, F-69616 Villeurbanne, France, Université de Lyon, CNRS/ENS-Lyon/UCB-Lyon 1, Centre de RMN à Très Hauts Champs, 5 rue de la Doua, 69100 Villeurbanne, France, and Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON, CNRS/Université de Lyon), 2 Avenue Albert Einstein, F-69626, Villeurbanne Cedex, France

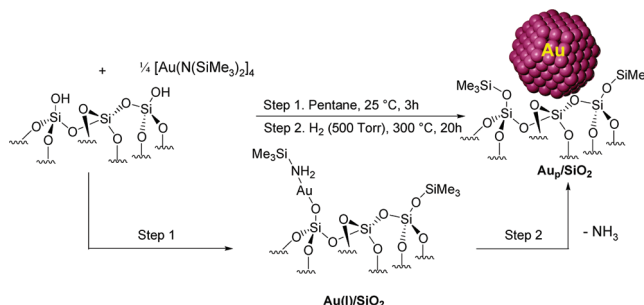
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We describe a method for the direct preparation of 1.8 nm gold nanoparticles (**AuNP**) on passivated silica via controlled functionalization of the silica surface with a Au^{I} complex, namely, $\{\text{Au}[\text{N}(\text{SiMe}_3)_2]\}_4$, followed 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).

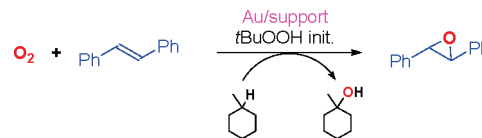
Although gold had been considered to be an inert metal, Haruta et al.¹ discovered that **AuNP** in the 2–5 nm range exhibited unique catalytic activity for the low-temperature oxidation of CO when associated with a reducible oxide. Other oxidation reactions involving supported gold catalysts and O_2 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 hydrocarbons⁶). 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 vacancies⁸ 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 mixture¹⁰ 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 carbon²¹). 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 $\{\text{Au}[\text{N}(\text{SiMe}_3)_2]\}_4$ ²² reacted at 25 °C with the silanols of a silica partially dehydroxylated at 700 °C [$\text{SiO}_{2-(700)}$], as evidenced by the disappearance of $\nu(\text{OH})$ silanol vibrations (3747 cm^{-1}) and the appearance of $\nu(\text{NH})$ 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

Scheme 1



Scheme 2



at 2958 and 2902 cm^{-1} are characteristic of the $\nu(\text{CH})$ 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 $\equiv\text{SiOH}$ groups resulting from reduction of the gold species were further converted into $\equiv\text{SiOSiMe}_3$ by reaction with $\text{H}_x\text{N}(\text{SiMe}_3)_{3-x}$.

By impregnation of a silica powder with a pentane solution of $\{\text{Au}[\text{N}(\text{SiMe}_3)_2]\}_4$ (1.1 equiv), the solid **Au(I)/SiO₂** remained white,

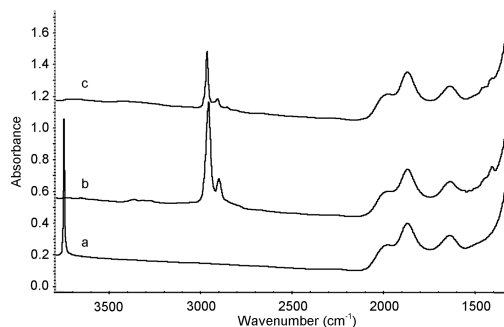


Figure 1. Preparation of **Au_P/SiO₂** monitored by FT-IR spectroscopy. (a) Silica partially dehydroxylated at 700 °C [$\text{SiO}_{2-(700)}$]. (b) After grafting of $[\text{Au}(\text{NSiMe}_3)_2]_4$ to give **Au(I)/SiO₂**. (c) After treatment under H_2 at 300 °C to give **Au_P/SiO₂**.

[†] C2P2.[‡] Centre de RMN à Très Hauts Champs.[§] Institut de Recherches sur la Catalyse et l'Environnement de Lyon.

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 $\sim 50\%$ of the available surface silanols [0.26 mmol SiOH/g for SiO₂₋₍₇₀₀₎]. The IR spectrum of this solid is similar to that obtained previously on the silica disk (e.g., the absence of remaining $\equiv\text{SiOH}$ group). The N–Au bond was cleaved upon grafting, and the liberated HN(SiMe₃)₂ probably reacted with adjacent unreacted $\equiv\text{SiOH}$ to give $\equiv\text{SiOSiMe}_3$ groups and H₂NSiMe₃. This is consistent with the formation of a 1:1 mixture of $\equiv\text{SiOSiMe}_3$ and a surface complex (here $\equiv\text{SiOAu}^{\text{I}}$), a phenomenon typically observed upon grafting of similar bis(trimethylsilyl)amide metal complexes.²³ Moreover, the two $\nu(\text{NH})$ bands at 3368 and 3286 cm^{−1} are characteristic of NH₂,²⁴ and this is consistent with the presence of H₂NSiMe₃, which is probably coordinated to Au^I (Scheme 1). These hypotheses were confirmed by solid-state NMR spectroscopy through (1) the presence of SiMe₃ signals (0 ppm) and consumption of OH [a very low intensity signal ($\sim 2\%$) 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 ¹³C signals at 0 and 6.4 ppm associated with $\equiv\text{SiOSiMe}_3$ and H₂NSiMe₃, respectively (Figure S2).

Further evidence of the presence of grafted Au^I species was obtained by adsorption of PMe₃. First, the ³¹P 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–PMe₃ complexes, they have been assigned to a 1:2 mixture of [$\equiv\text{SiOAuPMe}_3$] and [$\equiv\text{SiO}^-\text{Au}^+(\text{PMe}_3)_2$] (Scheme S1).²⁵ Second, the signal previously observed at 6.4 ppm and attributed to coordinated H₂NSiMe₃ in the ¹³C CP-MAS NMR spectrum of Au(I)/SiO₂ (Figure S2), is replaced by a signal at 14.2 ppm (Figure S4), assigned to the PMe₃ ligand of the two aforementioned Au^I surface species. The presence of these two species upon reaction of Au(I)/SiO₂ with PMe₃ shows that the well-defined $\equiv\text{SiOAu}(\text{H}_2\text{NSiMe}_3)$ species can be in slightly different environments, as already proposed for [$\equiv\text{SiO}$]Zr(CH₂tBu)₃.²⁶

Next, heating Au(I)/SiO₂ at 300 °C under H₂ (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/SiO₂) 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/SiO₂ 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 Au⁰ 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/SiO₂ shows only traces of surface silanols [<0.003 mmol/g, <0.01 OH/nm², i.e., $<1\%$ of the initial OH density of SiO₂₋₍₇₀₀₎], indicating passivation of the silica surface. The concomitant disappearance of the NH vibration is probably due to the reaction of the freed $\equiv\text{SiOH}$ groups with Me₃SiNH₂ previously coordinated to Au(I), which generates $\equiv\text{SiOSiMe}_3$ and NH₃ (Figure 1c).

This material, Au_p/SiO₂, 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 $\sim 80\%$ (Figure 3). Notably, an epoxide yield of $\sim 80\%$ 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

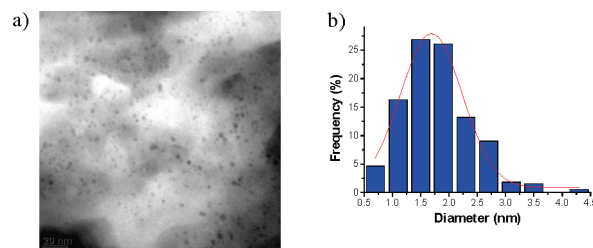


Figure 2. a) TEM image of Au_p/SiO₂ (2.79 wt % Au). (b) Au particle size distribution of Au_p/SiO₂.

from World Gold Council (Au/TiO₂-wgc, 1.5 wt % Au, 3.5 ± 0.9 nm). This is attributed to the poor dispersion (wettability) of Au/TiO₂-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/SiO₂, which has a surface passivated with hydrophobic SiMe₃ 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/TiO₂-wgc to 0.12 mol (g of Au)^{−1} h^{−1} for Au_p/SiO₂] 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/TiO₂-wgc to 40 h^{−1} for Au_p/SiO₂.

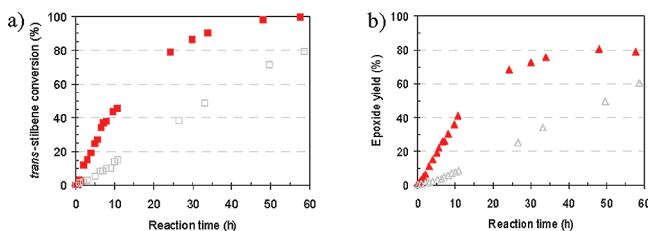


Figure 3. (a) *trans*-Stilbene conversion (squares) and (b) epoxide yield (triangles) as functions of time in the presence of Au_p/SiO₂ (solid symbols) and Au/TiO₂-wgc (open symbols). Reaction conditions: *trans*-stilbene (substrate, 0.90 ± 0.05 mmol), methylcyclohexane (solvent, 20 mL/155 mmol), catalyst (2.0 ± 0.1 μmol of Au), *tert*-butylhydroperoxide (0.05 mmol), air (1 atm), 80 °C, 900 rpm.

Moreover, Au_p/SiO₂ displays reasonable activity for low-temperature PROX, a key process for the purification of H₂ feed used in the polymer electrolyte fuel cell (PE-FC) technology. When this material is heated to 280 °C under a 2% CO + 2% O₂ + 48% H₂ mixture balanced in He, the conversion of CO first increases up to a maximum value and then decreases because of competition with H₂ oxidation for the limited amount of O₂ 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 similar particle size as in the fresh catalyst. At the temperature of interest for fuel cell applications (80 °C), Au_p/SiO₂ is a factor of ~ 2 more active in terms of rate per surface metal atom than Au/SiO₂-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/SiO₂ and Au/SiO₂-cd, respectively).¹⁵ It should be noted, however, that Au_p/SiO₂ is (~ 4 times) less active than the reference catalyst from World Gold Council (Au/TiO₂-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 O₂ activation by oxygen vacancies and OH groups. Thus, the significant activity of the fully passivated Au_p/SiO₂,

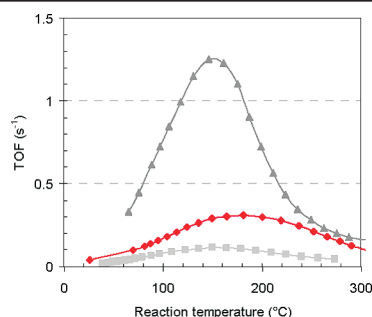


Figure 4. Turnover frequencies (TOF, s⁻¹) for CO oxidation over Au_p/SiO₂ (diamonds), Au/SiO_{2-ed} (squares), and Au/TiO_{2-wgc} (triangles) as functions of temperature under PROX conditions.

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 H₂ suggests that H₂ plays a critical role in the activation of O₂ for silica-supported systems, probably through the formation of OOH species.

In conclusion, surface organometallic chemistry³⁰ allows the controlled formation of well-defined and dispersed [(≡SiO)Au]⁺ surface species (0.5/nm²), which upon mild reduction (H₂, 300 °C) lead to the formation of small (1.8 ± 0.6 nm) Au particles supported on silica passivated with SiMe₃ functionalities (Au_p/SiO₂). 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/SiO₂) indicates that Au is intrinsically active in oxidation but requires the presence of H₂ or hydrocarbon, which is consistent with the formation of HOO or ROO intermediates. Given the accessibility of numerous bisilylamido 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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