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Aerobic oxidation of amines to imines catalyzed by bulk gold powder and by alumina-supported gold

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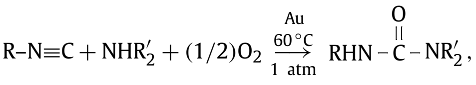
ABSTRACT

Both bulk gold powder (∼50 µm particle size) and alumina-supported gold (50–150 nm) are highly active catalysts for the aerobic oxidative dehydrogenation of amines (CH–NH) to imines (C=N) under the mild conditions of 1 atm O_2 and 100 °C. Reactions using the 5% Au/Al_2O_3 catalyst make efficient use of the gold metal and offer a practical synthesis of imines from amines. These studies add to the growing list of reactions that are catalyzed by bulk gold metal.

1. Introduction

Although catalysis by supported nano-sized gold metal particles (<5 nm) is a field of great interest [1–6], we recently reported that bulk gold powder, consisting of particles much larger than nanoparticles (50–150 µm), can catalyze reactions of isocyanides (Eqs. (1) and (2)) [7,8] and carbon monoxide (Eq. (3)) [9a] with amines and oxygen to produce carbodiimides and ureas in high yields under mild conditions:

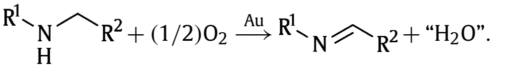
$$R\text{–}N{\equiv}C + H_2N\text{–}R' + (1/2)O_2 \xrightarrow[1\ \text{atm}]{\overset{\text{Au}}{60\,^\circ\text{C}}} R\text{–}N{=}C{=}N\text{–}R' + \text{“}H_2O\text{”}, \qquad (1)$$



$$R\text{–}N{\equiv}C + NHR'_2 + (1/2)O_2 \xrightarrow[1\ \text{atm}]{\overset{\text{Au}}{60\,^\circ\text{C}}} RHN\text{–}\overset{\overset{\large O}{\|}}{C}\text{–}NR'_2, \qquad (2)$$

$$O{\equiv}C + H_2N\text{–}R + (1/2)O_2 \xrightarrow[1\ \text{atm}]{\overset{\text{Au}}{60\,^\circ\text{C}}} O{=}C{=}N\text{–}R + \text{“}H_2O\text{”}. \qquad (3)$$
$$O{=}C(NHR)_2 \longleftarrow H_2N\text{–}R$$

Bulk gold particles also catalyze the oxidation of CO and glycerol under alkaline conditions [9b]. We also have described the bulk gold powder-catalyzed aerobic oxidation of secondary amines to imines (Eq. (4)) [10]:



(4)

All of these reactions [11] are especially notable because they are catalyzed by a bulk form of gold metal that was previously known to be a poor catalyst [1] of other reactions. As an extension of the reaction in Eq. (4), herein we report a gold powder-catalyzed oxidative dehydrogenation and coupling of primary amines to give imines. In addition, we describe the use of alumina-supported gold (Au/Al_2O_3) as a catalyst for the oxidative dehydrogenation of secondary and primary amines to imines. This catalyst was prepared by the incipient wetness impregnation method and contained relatively large gold particles (50–150 nm). Like gold powder, Au/Al_2O_3 is an excellent catalyst for the oxidative dehydrogenation of amines. In fact, the catalytic activity of 5 mg of gold in the Au/Al_2O_3 catalyst is greater than that of 1000 mg of bulk gold powder. The results described in this paper show that Au/Al_2O_3 is a useful catalyst for the practical synthesis of imines by the oxidative dehydrogenation of secondary and primary amines. They also demonstrate that the gold particles in these catalysts need not be nano-sized in order to be active in these reactions.

2. Experimental

The amines (pyrrolidine, piperidine, hexamethyleneimine) were dried and purified as described previously [12]. Toluene, diben-

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zylamine, 1,2,3,4-tetrahydroisoquinoline, *N*-benzylaniline, *n*-hexylamine, benzylamine, 4-chlorobenzylamine, 4-methylbenzylamine, *N*-benzylideneaniline, and *N*-benzylidenebenzylamine were purchased from Sigma Aldrich or Fisher and used as received. Authentic samples of *N*-hexylidenehexylamine [13], *N*-(4-methylbenzyl)-4-methylbenzaldimine, *N*-(4-chlorobenzyl)-4-chlorobenzaldimine, and 3,4-dihydroisoquinoline [14] were prepared as described previously, and authentic samples of other imines mentioned in this work were synthesized as described previously [10]. The O_2 (99.5%) was used as received. The shiny gold powder was prepared from $HAuCl_4$ by reduction with hydroquinone as described previously [15]; it had a surface area of 0.35 m^2/g [16]. As described previously [9], attempts to identify nano-sized gold particles in this powder using SEM (see below) and by studying the reaction of CO and O_2 showed no evidence of gold nanoparticles in the gold powder. The gold powder (10 g) was cleaned before being reused in subsequent catalytic reactions by treatment with piranha solution (40 mL, a 3:1 mixture of concentrated H_2SO_4 and 30% aqueous H_2O_2. Caution: H_2SO_4 must be added to H_2O_2 in a large beaker under slow stirring). After vigorous foaming and gas evolution for the first 5 min, the mixture was stirred for another 2 h, and then diluted with 200 mL of distilled water. After the mixture was filtered on a coarse frit, the gold was washed 10 times with 40 mL of water, followed by five washings in 40 mL of methanol. After drying under a nitrogen stream, the Au powder was heated overnight in air in a 110 °C oven. The gold powder that was used in the catalytic reactions was re-used and treated with H_2O_2/H_2SO_4 many times.

2.1. Preparation of Au/Al_2O_3

The Au/Al_2O_3, with 5% Au (ww), was prepared overnight by incipient wetness impregnation of 4.0 g of γ-Al_2O_3 (specific surface area of 158 m^2/g) with an aqueous solution of 0.42 g of $HAuCl_4 \cdot 3H_2O$ in 1.5 mL of distilled water. The sample was allowed to dry overnight in air at room temperature. After drying in an oven at 100 °C for 1 h, the solid was reduced under a flow of H_2 with heating at a rate of 3 °C/min from room temperature to 300 °C and then holding at 300 °C for 1 h. In order to remove Cl^-, the catalyst was washed several times with hot water until a $AgNO_3$ test gave no AgCl precipitate. Finally, the solid was dried and calcined in air at 700 °C for 68 h.

2.2. Recycling of Au/Al_2O_3

After being used in a catalytic reaction, Au/Al_2O_3 (1.0 g) was cleaned by stirring (for 10 min) three times with 50 mL of CH_2Cl_2, three times with 50 mL of ethanol, and three times with 50 mL of hexane. It was then dried in an oven at 150 °C overnight.

2.3. Characterization of gold powder and Au/Al_2O_3

The gold powder and alumina-supported gold samples were analyzed by scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM), respectively. The SEM measurements were performed on a JEOL 840A microscope operated at 10 kV accelerating voltage and 0.005 nA of beam current. The STEM measurements with energy dispersive X-ray analysis (EDX) were performed on a Tecnai G2 F20 microscope operated at 200 kV. The samples were sonicated in isopropyl alcohol for five minutes; then, a drop of the suspension was placed on a lacy carbon copper grid (from Ted Pella, Inc.) and dried at ambient conditions. The average gold particle size and size distribution on the alumina support were determined by counting 55 particles. Energy dispersive X-ray analysis was used to establish that the contrasting particles on the surface of the larger alumina support were gold. The total surface areas of the Al_2O_3 and 5% Au/Al_2O_3 were determined by the BET method using N_2 adsorption at 77 K on a Sorptomatic 1990 instrument (Thermo Electron Corporation).

2.4. General procedure for the catalytic reactions

A mixture of amine (0.20 mmol) and gold powder (1.0 g) (or 5% Au/Al_2O_3, 100 mg) in toluene (5 mL) was prepared in a glass tube (2.5 × 18 cm, ∼85 mL volume). The O_2 gas (about 1.0 L) was introduced into a rubber balloon that was attached to a syringe needle, which was inserted into the septum covering the tube opening. The mixture was stirred vigorously (magnetic stir bar) at 100 °C for 24 h, and then worked up by filtration to remove the catalyst. Products of the reactions were identified by comparison of their mass spectra and GC retention times with those of authentic samples. Yields were determined by GC using authentic samples of the products as calibrants.

2.5. Preparative-scale oxidative dehydrogenation of 1,2,3,4-tetrahydroisoquinoline

The amine (1.0 g, 8.0 mmol) and 5% Au/Al_2O_3 (250 mg) in toluene (10 mL) were placed in a glass tube (2.5 × 18 cm, ∼85 mL volume) that was capped by a septum. A syringe needle attached to a rubber balloon containing O_2 (∼2.0 L) was inserted into the septum. The mixture was stirred vigorously (magnetic stir bar) at 100 °C for 80 h. After cooling to room temperature, the Au/Al_2O_3 catalyst was removed by filtration. The yield of the 3,4-dihydroisoquinoline was determined by GC using an authentic sample as the calibrant.

3. Results and discussion

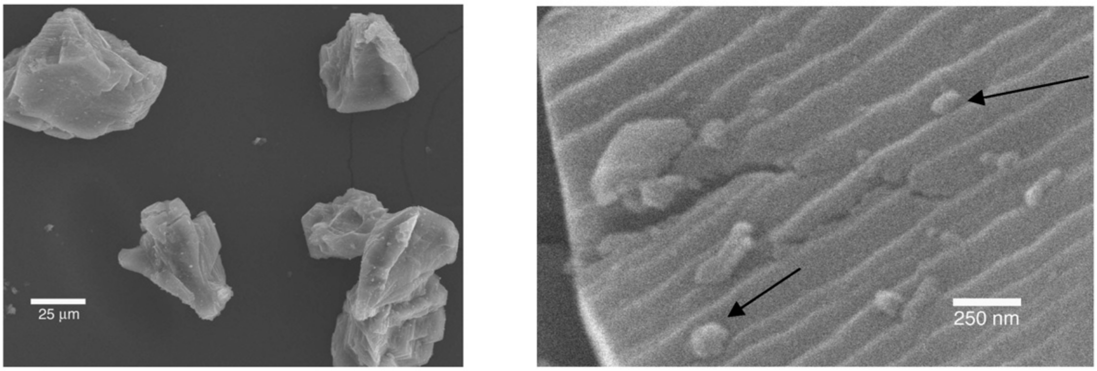
3.1. SEM characterization of gold powder

The bulk gold powder examined by SEM had been used in several catalytic reactions and had been treated with H_2O_2/H_2SO_4 solution several times. SEM was used because the gold powder particles were too large to be analyzed by TEM or STEM. Fig. 1 shows two SEM images of the bulk gold powder at 500× (a) and 50,000× (b). The particles have an average particle size of approximately 50 µm. The particles do not have a uniform shape but are relatively monodispersed in regard to size. High magnification (Fig. 1b) shows gold particles with ridges and much smaller particles (∼100 nm, black arrows) on the surface of the large particles. These small particles and ridges are possibly the most catalytically active sites.

3.2. Characterization of 5% Au/Al_2O_3

The specific surface area of the Au/Al_2O_3 catalyst, which was determined by the BET method, is 74.7 m^2/g. This is substantially smaller than that (158 m^2/g) of the Al_2O_3 itself. This decrease is likely due to sintering of the alumina under the 700 °C thermal treatment; these high temperatures have been observed previously to cause sintering of alumina [17].

Typical STEM images of the gold particles on the 5% Au/Al_2O_3 catalyst are shown in Fig. 2. Images were recorded in the scanning transmission mode to achieve higher contrast between the gold particles and the alumina support. The gold particles (white dots in Fig. 2) are fairly uniformly distributed over the alumina support (gray, darker regions). The white dots were identified as gold particles by EDX analysis, as illustrated in Fig. 3. The Cu peaks in this figure are due to the Cu grid that is used to support the sam-



(a) (b)

Fig. 1. Scanning electron micrographs of gold powder: (a) 500× magnification and (b) 50,000× magnification. Black arrows point to small Au particles on the surface of the much larger Au particles.

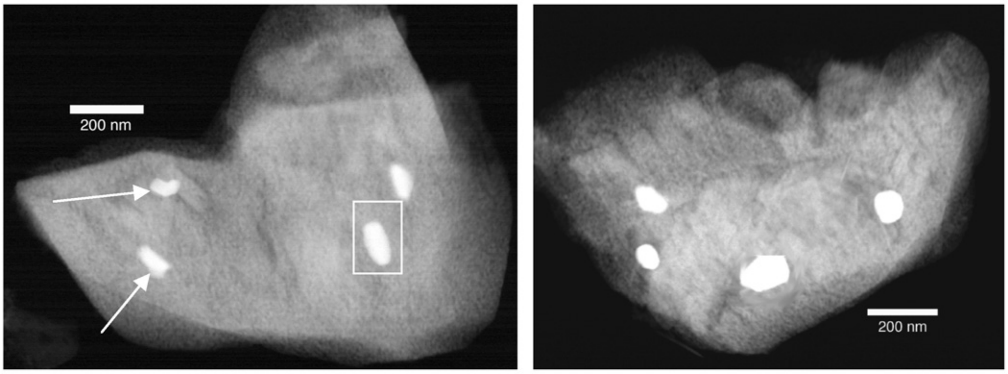


Fig. 2. Scanning transmission electron micrographs of the 5% Au/Al_2O_3 catalyst. White rectangle represents the area of the EDX analysis (Fig. 3). White arrows point to the Au particles on the surface of the alumina.

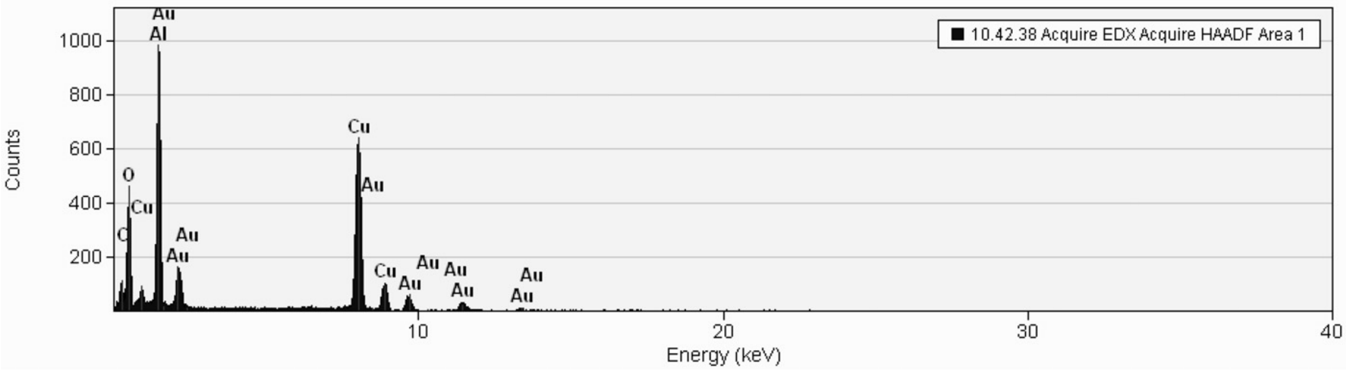


Fig. 3. Typical energy dispersive X-ray analysis of Au particles on the surface of the alumina (Fig. 2).

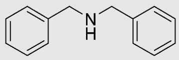
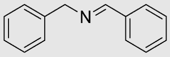
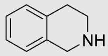
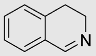
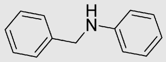
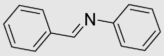
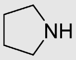
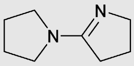
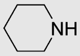
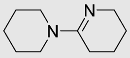
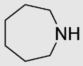
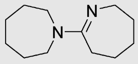
ple in the STEM and EDX studies. The gold particles are generally larger than 50 nm, as illustrated in the Au particle size distribution in Fig. 4. Although particles less than 20 nm could have been detected by the STEM instrument, none was observed. The shapes of the particles are quite irregular.

The relatively large sizes of the Au particles in the Au/Al_2O_3 catalyst are due, in part, to the use of the impregnation method of preparation [18]. Others have also observed that Au/Al_2O_3 prepared by this method contains relatively large particles [1,19,20]. Another factor leading to the large Au particles in the present case is the high temperature treatment (700 °C for 68 h) of the Au/Al_2O_3. Sintering of small gold particles would be expected as the melting point of Au is known to decrease as the size of the particle decreases [21]. It should be noted that smaller gold particles (∼1.9 nm) were observed in Au/Al_2O_3 that was treated at only 250 °C for 2 h [22].

3.3. Gold-catalyzed aerobic oxidation of secondary amines to imines

We reported previously the gold powder-catalyzed oxidative dehydrogenation of secondary amines, using O_2 as the oxidant, to give imines (Eq. (4)) [10] under a standard set of conditions (0.20 mmol amine, O_2 (∼1.0 L at ∼1 atm), gold powder (1.0 g) in 5 mL of toluene at 100 °C for 24 h). Yields from these reactions are given in column 4 of Table 1. The benzyl amines (entries 1–3) give the simple imine products (Eq. (4)), but the cyclic amines (entries 4–6) give products resulting from the coupling and oxidative dehydrogenation of two amine molecules (Eq. (5)):

Table 1
Gold-catalyzed aerobic oxidation of *secondary* amines to imines according to Eqs. (4) and (5)

Entry	Substrate	Product	Yield (%)	
			Au powder cat.[a]	Au/Al_2O_3 cat.[b]
1			64	97 (1[c])
2			87 (85[d])	89 (81[e])
3			9	18
4			93	98
5			75	95
6			22[f]	33

[a] Reaction conditions: amine (0.2 mmol), O_2 (~1.0 L at ~1 atm), gold powder (1.0 g) in 5 mL of toluene solvent at 100 °C for 24 h [10].
[b] Reaction conditions: amine (0.2 mmol), O_2 (~1.0 L at ~1 atm), 5% Au/Al_2O_3 (100 mg), in 5 mL of toluene solvent at 100 °C for 24 h.
[c] Only Al_2O_3 (100 mg) as catalyst.
[d] 0.4 mmol of pyridine added.
[e] Reaction conditions: amine (8.0 mmol, 1.0 g), O_2 (~2.0 L at ~1 atm), 5% Au/Al_2O_3 (250 mg), in 10 mL of toluene solvent at 100 °C for 80 h.
[f] At 60 °C in 5 mL of acetonitrile solvent for 40 h [10].

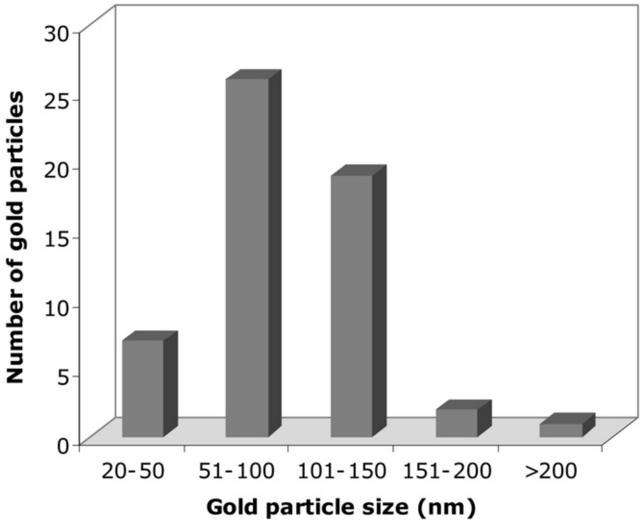
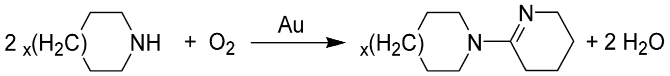


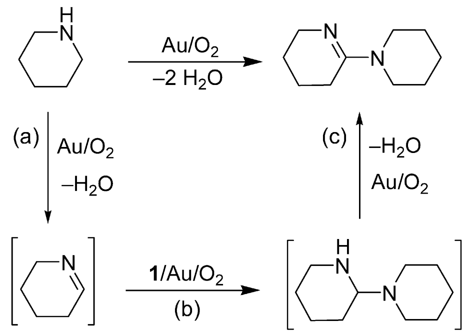
Fig. 4. Gold particle size distribution in 5% Au/Al_2O_3 as determined by TEM (55 randomly chosen particles measured).



(5)

A mechanism proposed [10] for this reaction (Scheme 1), based on additional studies, suggested the following steps: (a) oxidative dehydrogenation of the cyclic amine to give the imine, (b) addition of another molecule of amine across the imine double bond, and (c) oxidative dehydrogenation of the resulting diamine to give the product.

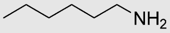
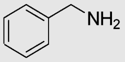
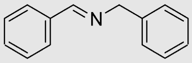
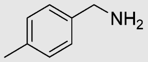
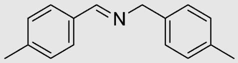
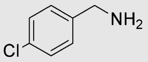
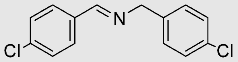
We have now investigated the possibility that Au/Al_2O_3 can catalyze the same reaction under the same conditions but using only 5 mg of gold metal in 100 mg of the 5% (w/w) gold-loaded Au/Al_2O_3 catalyst (rather than 1000 mg of gold powder). As is evident in column 5 of Table 1, yields of the imine products are as high or higher with the Au/Al_2O_3 catalyst than with gold powder. The benzyl amines dibenzylamine and 1,2,3,4-tetrahydroisoquinoline gave *N*-benzylidenebenzylamine and 3,4-dihydroisoquinoline in 97 and 89% yields, respectively (Table 1, entries 1 and 2). On the other hand, *N*-benzylaniline produced *N*-benzylideneaniline in only poor yield (18%), which is presumably due to the much less basic nitrogen in this amine, which reduces its tendency to adsorb to the gold surface. The 5-, 6-, and 7-membered cyclic amines (entries 4–6) gave the coupled imine products (Eq. (5)) in good yield especially for entries 4 and 5, which gave almost quantitative yields. To exclude the possibility that the Al_2O_3 support was catalyzing these reactions, the reaction of dibenzylamine with O_2 was performed with only Al_2O_3 (100 mg) as the catalyst (entry 1); the very low yield (1%) of imine shows that the Al_2O_3 support is not the catalyst. In an experiment designed to determine whether pyridine in the reaction mixture would reduce the product yield by competitively adsorbing to the gold powder [23], the reaction of 1,2,3,4-tetrahydroisoquinoline was performed in the presence of two equivalents of pyridine (entry 2); however, the added pyridine did not affect the yield of the 3,4-dihydroisoquinoline.



Scheme 1. Proposed mechanism for the oxidative dehydrogenation of cyclic secondary amines (illustrated for piperidine).

For the purpose of demonstrating that these catalytic reactions could be used to prepare larger amounts of imine products, 1.0 g of 1,2,3,4-tetrahydroisoquinoline was heated at 100 °C in 10 mL of toluene with 250 mg of 5% Au/Al_2O_3 under 2 L of O_2 at 1 atm pressure for 80 h. Although the reaction time was longer than that

Table 2
Gold-catalyzed aerobic oxidation of *primary* amines to imines according to Eq. (6)

Entry	Substrate	Product	Yield (%)	
			Au powder cat.[a]	Au/Al_2O_3 cat.[b]
1		C_6H_{13}–N=CHC_5H_{11}	5	29
2			56 (49[c], 4[d])	92 (3[e], 71[f])
3			61	96
4			7	59

[a] Reaction conditions: amine (0.2 mmol), O_2 (∼1.0 L at ∼1 atm), gold powder (1.0 g), in 5 mL of toluene solvent for 24 h at 100 °C.
[b] Reaction conditions: amine (0.2 mmol), O_2 (∼1.0 L at ∼1 atm), 5% Au/Al_2O_3 (100 mg), in 5 mL of toluene solvent at 100 °C for 24 h.
[c] 0.4 mmol of H_2O added.
[d] 0.4 mmol of bromobenzene added.
[e] Only Al_2O_3 (100 mg) as catalyst.
[f] With re-used catalyst.

(24 h) used for the smaller quantities, a high yield (81%) of the imine product was obtained.

3.4. Gold-catalyzed aerobic oxidation of primary amines to coupled imines

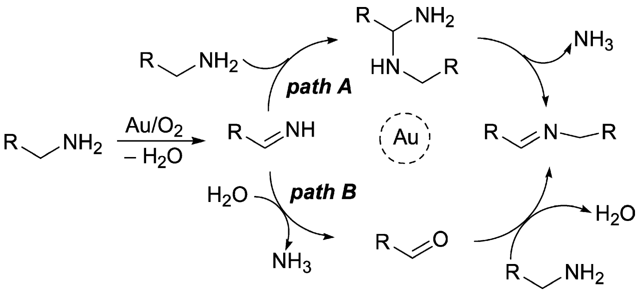
During the course of our studies of the oxidative dehydrogenation of secondary amines, we observed that primary benzyl amines undergo coupling and oxidative dehydrogenation to give imines according to Eq. (6):

$$2\text{R–CH}_2\text{NH}_2 + (1/2)\text{O}_2 \xrightarrow{\text{Au}} \text{R–CH=NCH}_2\text{R} + \text{“H}_2\text{O”} + \text{“NH}_3\text{”}. \qquad (6)$$

The reactions were performed under the same conditions (0.2 mmol amine, 1 L of O_2 at 1 atm in 5 mL of toluene at 100 °C for 24 h) using 1.0 g of gold powder or 100 mg of 5% Au/Al_2O_3. As shown in Table 2, low yields of the imine product (entry 1) were obtained from the aliphatic *n*-hexylamine. On the other hand, high yields of the imine were achieved with the benzyl amines (entries 2–4). In the benzylamine series, the highest yield was obtained from the benzylamine with the electron-donating *p*-methyl group, and the lowest yield was obtained with the electron-withdrawing *p*-chloro group. These effects can be understood by assuming that the most electron-donating group favors amine adsorption on the gold surface. Of course, it is possible that the *p*-substituent affects other steps in the mechanism. The slower rate of the *p*-chloro-derivative may be due to deactivation of the catalyst, as bromobenzene added to the gold powder-catalyzed reaction of benzylamine (entry 2) greatly inhibits the reaction.

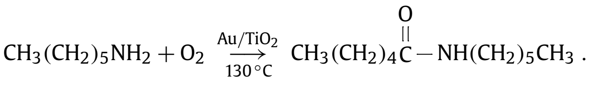
In all of the reactions, the product yields under the standard conditions are significantly higher with the Au/Al_2O_3 catalyst than with the gold powder (Table 2). It should be noted that when the reaction of benzylamine was conducted under an argon atmosphere, rather than O_2, or in the absence of a gold catalyst, only a trace of the imine product was detected. Also, when Al_2O_3 alone was used as the catalyst, only a low yield (3%, entry 2) of product was observed. When the Au/Al_2O_3 catalyst was re-used a second time after it was washed with CH_2Cl_2, EtOH, and hexanes, the yield was lower (71%). The lower activity of the recycled catalyst may be due to incomplete cleaning of the gold surface or pulverization of the Au/Al_2O_3 catalyst to smaller particles, which is observed visually during stirring with a magnetic stirbar.

Prior to the studies reported herein, there were a few previous investigations of the conversion of primary amines (often benzylamines) to coupled imines. There are photolytic conversions in the absence of an oxidizing agent, with the formation of H_2, over Pt/TiO_2 [13], ZnS [24], and Hg [25,26] catalysts. The reaction of HgO and I_2, as oxidizing agent, with primary amines gives the coupled imines [14]. Copper (I and II) salts catalyze the oxidation (O_2) of benzylamines to the *N*-benzylidenebenzylamines, as in Eq. (6) [27,28]. Also, heteropolyoxometallate clusters containing Mo and V catalyze the oxidation in Eq. (6) [29,30]. The two mechanisms (Scheme 2) that have been proposed for the oxidation of primary amines (Eq. (6)) both proceed by way of oxidative dehydrogenation of the amine to the imine intermediate RCH=NH. In path A, this intermediate is attacked by a second molecule of the primary amine to give an aminal which loses NH_3 to give the coupled imine product $RCH{=}NCH_2R$; this path was proposed for the oxidative dehydrogenation using I_2 and HgO [14]. In path B, the initially formed imine reacts with trace amounts of H_2O to give the aldehyde RCH=O, which subsequently reacts with a second molecule of the amine to give the imine product; this mechanism was proposed for the reaction (Eq. (6)) using the $Na_6PMo_2V_2O_{40}$ catalyst [29]. In the gold metal-catalyzed reactions described herein, it is likely that the first step is the oxidative dehydrogenation because this gold-catalyzed reaction occurs with a variety of *secondary* amines [10]. The next step could be either reaction with amine (path A) or with H_2O (path B). In the toluene reaction solvent, little water would be present. To determine whether or not H_2O might promote the reaction in path B, 0.4 mmol of H_2O was added to the reaction of 0.2 mmol of benzylamine (entry 2, Table 2). The yield of product actually decreased from 56% to 49%, which indicates that a substantial increase in the H_2O concentration does not accelerate the reaction. Although this result is not definitive, path A is most consistent with our results for the gold-catalyzed reactions (Eq. (6)).



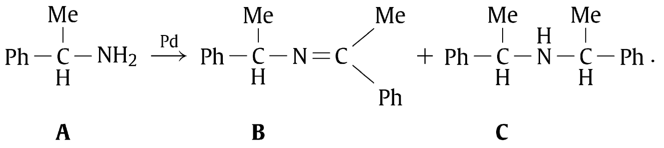
Scheme 2. Possible mechanisms for the gold-catalyzed aerobic oxidation of primary amines to imines according to Eq. (6).

To our knowledge, the only previously reported gold-catalyzed oxidative dehydrogenation of primary amines is that using nanogold particles in the form of Au/TiO_2 [31]. With this catalyst, neat *n*-hexylamine reacts with O_2 (1 atm) at 130 °C to give *N*-hexylbutanoic amide (Eq. (7)):



$$CH_3(CH_2)_5NH_2 + O_2 \xrightarrow[130\,^\circ\mathrm{C}]{Au/TiO_2} CH_3(CH_2)_4\overset{\overset{O}{\|}}{C}-NH(CH_2)_5CH_3\,. \tag{7}$$

Thus, nanogold catalyzes a quite different reaction of primary amines and O_2 than that catalyzed by bulk gold (Eq. (6)). However, specially prepared palladium black catalyzes the dehydrogenation of α-phenylethylamine **A** (Eq. (8)) at 100° under an argon atmosphere [32]:



(8)

Presumably, NH_3 is the other product of the reaction. The proposed mechanism involves initial dehydrogenation of **A** to give an intermediate imine hydride species $[Ph(Me)C{=}NH]PdH_2$ which undergoes attack at the imine carbon by a second molecule of amine **A**. The resulting aminal (analogous to the intermediate in path A of Scheme 2) then breaks down to products **B**, **C**, and NH_3. Product **C** arises from the transfer of the two hydrogen atoms from Pd. The formation of **B** from the aminal intermediate occurs by loss of NH_3 as proposed for the gold-catalyzed reaction in path A of Scheme 2. Thus, the Au- and Pd-catalyzed reactions appear to proceed by similar imine and aminal intermediates, but O_2 in the gold-catalyzed reaction participates in the formation of the imine intermediate. This involvement of O_2 also prevents the formation of Au-hydride species on the metal, as occurs in the Pd-catalyzed reaction which leads to the amine product **C**. The reactions of primary amines with the palladium black catalyst were not performed under an O_2 atmosphere. If they had been, and they followed path **A** (Scheme 2) proposed for the Au-catalyzed reaction, **B** would have been the only expected product.

4. Conclusion

These investigations show that bulk gold powder and supported gold (5% Au/Al_2O_3), prepared by traditional incipient wetness impregnation, are excellent catalysts for the oxidative dehydrogenation of secondary and primary amines. Both catalysts consist of particles that are much larger than those (<5 nm) found in nanogold catalysts. The gold powder particles were about 50 µm in diameter, while the Au particles on Au/Al_2O_3 were much smaller (50–150 nm). Both types of gold catalysts convert non-cyclic secondary amines in the presence of O_2 to simple imine products $R^2CH{=}NR^1$ (Eq. (4)). Cyclic secondary amines are proposed to initially form an imine which reacts with a second amine molecule to give an aminal that undergoes oxidative dehydrogenation to the final coupled imine product (Scheme 1). Primary amines also first form an imine, which reacts with a second molecule of amine to give the $RCH{=}NCH_2R$ imine product (Eq. (6)). These reactions illustrate a type of bulk gold-catalyzed conversion that is very different from the previously reported reactions of isocyanides ($C{\equiv}N–R$) and $C{\equiv}O$ with amines and O_2 (Eqs. (1)–(3)). The use of small amounts of gold in Au/Al_2O_3, while achieving high yields of products, makes these catalysts useful for the synthesis of imines on a preparative scale.

Although Au/Al_2O_3 with large gold particles is highly effective for the oxidative dehydrogenation of amines, it would be of considerable interest to compare its catalytic activity with that of Au/Al_2O_3 catalysts that contain nanogold particles (<5 nm) [22]. Another future study might examine the selectivity of the Au/Al_2O_3 catalyst in O_2 oxidations of amines that also contain other oxidizable functional groups.

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References

[1] G.C. Bond, C. Louis, D.T. Thompson, Catalysis by Gold, Imperial College Press, London, 2006.
[2] G.C. Bond, D.T. Thompson, Appl. Catal. A Gen. 302 (2006) 1.
[3] D.T. Thompson, Top. Catal. 38 (2006) 231.
[4] M.S. Chen, D.W. Goodman, Catal. Today 111 (2006) 22.
[5] (a) G.J. Hutchings, M. Haruta, Appl. Catal. A Gen. 291 (2005) 2;
(b) G.J. Hutchings, Catal. Today 100 (2005) 55.
[6] B.K. Min, C.M. Friend, Chem. Rev. 107 (2007) 2709.
[7] M. Lazar, R.J. Angelici, J. Am. Chem. Soc. 128 (2006) 10613.
[8] M. Lazar, B. Zhu, R.J. Angelici, J. Phys. Chem. C 111 (2007) 4074.
[9] (a) B. Zhu, R.J. Angelici, J. Am. Chem. Soc. 128 (2006) 14460;
(b) W.C. Ketchie, Y.-L. Fang, M.S. Wong, M. Murayama, R.J. Davis, J. Catal. 250 (2007) 94.
[10] B. Zhu, R.J. Angelici, Chem. Commun. (2007) 2157.
[11] R.J. Angelici, J. Organomet. Chem. 693 (2008) 847.
[12] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, second ed., Pergamon, New York, 1980.
[13] B. Ohtani, H. Osaki, S.-I. Nishimoto, T. Kagiya, Chem. Lett. (1985) 1075.
[14] K. Orito, T. Hatakeyama, M. Takeo, S. Uchiito, M. Tokuda, H. Suginome, Tetrahedron 54 (1998) 8403.
[15] B.P. Block, Inorg. Synth. 4 (1953) 14.
[16] M.J. Robertson, R.J. Angelici, Langmuir 10 (1994) 1488.
[17] P. Marginean, A. Olariu, Appl. Catal. A Gen. 140 (1996) 59.
[18] M. Haruta, Caltech. 6 (2002) 102.
[19] M.M. Schubert, S. Hackenberg, A.C. van Veen, M. Muhler, V. Plzak, R.J. Behm, J. Catal. 197 (2001) 113.
[20] Y.-F. Han, Z. Zhong, K. Ramesh, F. Chen, L. Chen, J. Phys. Chem. C 111 (2007) 3163.
[21] P. Buffet, J.-P. Borel, Phys. Rev. A 13 (1976) 2287.
[22] C. Baatz, U. Prüße, J. Catal. 249 (2007) 34.
[23] B.C. Barlow, I.J. Burgess, Langmuir 23 (2007) 1555, and references therein.
[24] S. Yanagida, H. Kizumoto, Y. Ishimaru, C. Pac, H. Sakurai, Chem. Lett. (1985) 141.
[25] P. Krajnik, R.R. Ferguson, R.H. Crabtree, New J. Chem. 17 (1993) 559.
[26] A.A. Baum, L.A. Karnischky, D. Mcleod Jr., P.H. Kasai, J. Am. Chem. Soc. 95 (1973) 618.
[27] Y. Maeda, T. Nishimura, S. Uemura, Bull. Chem. Soc. Jpn. 76 (2003) 2399.
[28] S. Minakata, Y. Ohshima, A. Takemiya, I. Ryu, M. Komatsu, Y. Ohshiro, Chem. Lett. (1997) 311.
[29] R. Neumann, M. Levin, J. Org. Chem. 56 (1991) 5707.
[30] K. Nakayama, M. Hamamoto, Y. Nishiyama, Y. Ishii, Chem. Lett. (1993) 1699.
[31] S.K. Klitgaard, K. Egeblad, U.V. Mentzel, A.G. Popov, T. Jensen, E. Taarning, I.S. Nielsen, C.H. Christensen, Green Chem. 10 (2008) 419.
[32] S.-I. Murahashi, N. Yoshimura, T. Tsumiyama, T. Kojima, J. Am. Chem. Soc. 105 (1983) 5002.