



A simple preparation of an efficient heterogeneous gold catalyst for aerobic amine oxidation

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ABSTRACT

Numerous sophisticated techniques have been applied in the past years for the preparation of supported gold catalysts designed for oxidation reactions. Here we show that it is possible to arrive at an efficient catalyst without using any conventional step for the synthesis of supported gold nanoparticles. The reaction studied was the oxidative dehydrogenation of amines to imines with molecular oxygen. The catalyst precursors $\text{Au}(\text{OAc})_3$ and an oxide support were simply added to the reaction mixture and the active gold nanoparticles on the support were formed *in situ*. The corresponding imines were produced in 89–100% yield and the catalyst was proved to be truly heterogeneous and recyclable. Despite of the simplicity of the method, the activity of the catalysts was comparable, or even superior, to other known catalysts of the oxidative dehydrogenation of amines and to some commercially available supported gold catalysts.

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1. Introduction

The interest in gold catalysis has increased rapidly after the fundamental work by Bond, Hutchings, and Haruta in gold-catalyzed hydrogenation, hydrochlorination, and oxidation reactions, respectively [1–3]. It is now well established that the outstanding catalytic properties of gold is related to the appropriate preparation of nanoparticles. An important field of catalytic uses is oxidation [4–6], including the oxidation of aldehydes [7–9] and alcohols [10–14], and the epoxidation of olefins [15,16].

A recent application is the oxidative dehydrogenation of amines to imines with molecular oxygen, in which reaction even non-nanogold – i.e. gold powder – has detectable activity [17], although remarkably lower than that of small gold particles deposited onto an oxide support [18,19]. Imines are crucial intermediates in the synthesis of biologically active nitrogen compounds [20,21]. Selective oxidation of amines to the corresponding imines [22,23] offers an alternative route to the mostly applied synthesis, the condensation of an amine with a carbonyl compound. Table 1 presents an overview on the catalysts that are active with molecular oxygen as the only oxidant in the transformation of dibenzylamine to dibenzylimine, a commonly used test reaction. Note that depending on the catalyst, the oxidation of amines may lead to various other products, such as nitriles [24], oximes [25], amides [26], enamines

and heteroaromatic compounds [27], and carbonyl compounds and carboxylic acids [28].

Most of the gold catalysts used for aerobic oxidations have been prepared in a similar way: a gold salt, frequently HAuCl_4 , is applied in the presence of a support and the precursor salt is transferred to metal nanoparticles by reduction or calcination. For example, preparation of the $\text{Au}/\text{Al}_2\text{O}_3$ catalyst used for the oxidative transformation of amines to imines involves the impregnation of Al_2O_3 with a HAuCl_4 solution, a reduction step in H_2 at 300°C , and additional calcination at 700°C [18]. Equipments necessary for the last two steps are not commonly available in a synthetic laboratory.

Our aim was to develop a simple and efficient method for the synthesis of active gold catalysts. We have shown recently [19] that gold acetate adsorbed onto ceria from an aqueous solution is more active in the oxidative dehydrogenation of dibenzylamine to dibenzylimine (Scheme 1) than any other known catalyst (Table 1). Importantly, neither a reduction nor a calcination step was necessary to obtain the active catalyst, since the gold nanoparticles were formed in the reaction mixture, as demonstrated by *in situ* XANES and electron microscopy. Here we report a further development, in which case there is no need for any *ex situ* preparation step of the gold catalyst for the efficient transformation of amines to imines.

2. Experimental

2.1. Materials

The Au/CeO_2 (A) catalyst [29] was purchased from the laboratory of Professor Corma. The Au/TiO_2 (B) and Au/ZnO (C) catalysts and

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Table 1
Oxidative dehydrogenation of dibenzylamine to dibenzylimine with molecular oxygen.

Catalyst	Temp. (°C)	Time (h)	Conv. (%)	Yield (%)	TOF (h ⁻¹)	Ref.
Au(OAc) ₃ /CeO ₂	108	8	99.7	91	7.2	[19]
Au/Al ₂ O ₃	100	24	–	97	3.2 ^a	[18]
Au powder	100	24	–	64	0.001 ^a	[17]
Ru ₂ (OAc) ₄ Cl	50	18	97	72	1.3	[33]
Ru/Al ₂ O ₃	130	16	85	71	1.9	[34]
CuCl	80	12	–	90	3.8 ^a	[31]
RuHAp	130	24	98	91	0.24	[24]
trans-[Ru ^V (tmp)(O) ₂]	50	24	100	76	0	[35]

^a The approximate value of TOF is calculated based on the yield, instead of the conversion.

the Al₂O₃ support were generously provided by AuTek. The SiO₂ support (Aerosil® 380) was kindly supplied by Evonik (Degussa). The TiO₂ support (Aerioxide® P25) was purchased from Acros and the CeO₂ from Micro Coating Technologies. According to TG analysis, CeO₂ contained a small amount of nitrate that was removed by calcination at 500 °C for 4 h before use. The BET surface area after calcination was 117 m²/g. The Au(OAc)₃ (99.9%) was purchased from AlfaAesar.

2.2. Oxidative dehydrogenation of amines

According to the standard procedure, the reaction was carried out in a 25 mL two-neck pear-shaped flask equipped with a cooler to which a balloon, connected through a three-way tap and filled with oxygen, was attached. Ground gold acetate (2.6 mg) and 118.6 mg support were added and air was replaced with oxygen after evacuation. Through a septum, 3 mL solvent (dried with MS 4 Å) was injected and the stirring was turned on (1000 rpm). Then the amine (0.4 mmol) and an additional 2 mL of solvent were added and the flask was immersed into a pre-heated oil bath. In the case of the oxidative dehydrogenation of dibenzylamine at the end of the reaction diphenylamine was added as the internal standard for GC analysis. After oxidation of benzylamine and indoline the yields were determined by NMR after the catalyst was filtered off and the solvent was evaporated.

If not mentioned otherwise, the transformation of dibenzylamine with *ex situ* prepared catalysts was performed similarly. The reaction flask containing the catalyst was filled with oxygen, 1.5 mL of dried toluene was added, and the stirring was started (750 rpm). Dibenzylamine and then an additional 1.5 mL of toluene were added. The reaction was initiated by immersing the reactor into a pre-heated oil bath.

Turn over frequency (TOF) was calculated based on the conversion of the amine (Eq. (1)):

$$\text{TOF} = \frac{n(\text{amine converted})}{n(\text{Au})_{\text{total}} \times t} \quad (1)$$

In Eq. (1) the total amount of gold applied in the reaction was considered, since the fraction of surface gold atoms is frequently not available. When the conversion was not mentioned in the literature, the yields were used to estimate the TOF. These approximate TOF values are marked by an asterisk. The approximation did not cause a significant error since the yields were typically higher than 90%, except for the Au powder (64% yield, TOF = 0.001 h⁻¹ [17]). In this case the TOF would be only 0.0016 h⁻¹ even if 100% conversion is assumed (see Table 1). Note also that any comparison based

on TOFs is only semi-quantitative, since the reaction conditions are partly different and usually not optimized.

The gold content of the filtrate after the oxidation of indoline was determined (at ALAB AG, Switzerland) by inductively coupled plasma optical emission spectrometry (ICP-OES). The detection limit of the method was 3 ppm. After evaporation of the chlorobenzene the residue of the filtrate analyzed was 28.6 mg.

2.3. Catalyst characterization

The particle size of gold nanoparticles was studied with scanning transmission electron microscopy (STEM). After the oxidation reaction the catalyst was filtered off, washed with ethyl acetate, and dried in vacuum at room temperature. The dry powder was dispersed in ethanol and deposited onto a perforated carbon foil supported on a copper grid. The investigations were performed on a Tecnai F30 microscope (FEI (Eindhoven), field emission cathode, operated at 300 kV). STEM images obtained with a high-angle annular dark field (HAADF) detector revealed Au particles with bright contrast (Z contrast). EDXS spot analysis confirmed that the bright patches corresponded to Au.

The specific surface area of CeO₂ was measured using nitrogen physisorption at 196 °C on a Micromeritics ASAP 2000 apparatus. The 5-point BET method was applied in the range 0.05 < p/p₀ < 0.25. The sample was degassed at 100 °C for several hours before the measurements.

The UV–vis spectrum was measured in a quartz cuvette by using the deuterium light source of a DH2000 spectrometer (Micropack).

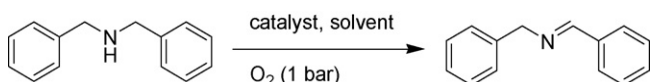
3. Results and discussion

3.1. Development of the catalyst preparation method

As mentioned in the introduction, dibenzylamine could be efficiently oxidized to dibenzylimine with molecular oxygen (Scheme 1), using Au(OAc)₃ adsorbed onto CeO₂ (Table 2, entry 1) [19]. According to XANES measurements and electron microscopy, the catalytically active species were gold nanoparticles, which formed *in situ* at the support surface. Interestingly, gold ions could not be detected in the liquid phase by XANES, suggesting that Au(OAc)₃ was anchored strongly onto CeO₂ and did not dissolve as an amine complex before its reduction to metal.

We tried to simplify the catalyst preparation and avoid the adsorption step, thus making the amine oxidation procedure more attractive as a laboratory method. At first, we ground gold acetate and CeO₂ together. Although grinding is not an efficient way to disperse the active component of the catalyst onto the support, the activity and selectivity were reasonably good (Table 2, entry 2).

We could go even further and omit any *ex situ* preparation step by directly adding the gold salt and the support into the reaction flask (Table 2, entry 3). Astonishingly, this *in situ* “evolved” catalyst was more active than the ground catalyst, and on the basis of the



Scheme 1. Gold-catalyzed oxidative dehydrogenation of dibenzylamine.

Table 2Comparison of gold acetate-based catalysts and commercial supported gold catalysts A–C^a.

Entry	Catalyst	Au content (wt%)	Conversion (%)	Selectivity (%)	Yield (%)	TOF (h ⁻¹)
1	Au(OAc) ₃ /CeO ₂ , adsorbed ^b	1.1	82	90	74	9.4
2	Au(OAc) ₃ /CeO ₂ , ground	1.1	49	94	46	5.7
3	Au(OAc) ₃ + CeO ₂ , not treated	1.1	61	95	58	7.1
4	Au/CeO ₂ (A)	2.5	52	95	49	6.0
5	Au/TiO ₂ (B)	1.0	63	63 ^c	40	7.3
6	Au/ZnO (C)	1.0	62	89	55	7.2

^a 0.2 mmol dibenzylamine, 3.47 μmol Au, 3 mL toluene, 108 °C, 5 h, and 1 bar O₂.^b 0.2 mmol dibenzylamine, 3.47 μmol Au, 4 mL toluene, 108 °C, 5 h, and 1 bar O₂, catalyst prepared according to Ref. [19].^c Benzaldehyde (15%) and benzaldehyde oxime (7%) as major by-products.

reaction rate (TOF) and imine yield its performance is similar to the best commercial supported gold catalysts (Table 2, entries 4–6). It is probable that at first a gold–amine complex is formed, which is reduced subsequently to Au nanoparticles.

The conditions applied in Table 2 are not optimized. Interpretation of the influence of various reaction parameters is not straightforward, since not only the oxidative dehydrogenation of the amine itself but also the properties of the *in situ* formed catalyst are affected. An example is the effect of solvent (Table 3, entries 1–3). The reaction was the fastest in chlorobenzene and the more polar butyl acetate seems to be less suitable. Beside the oxidation reaction itself, the solvent influences also the solubility and the stability of the amine complex, and thus the properties of the *in situ* formed gold nanoparticles. In addition, at close to the boiling point the partial pressure of oxygen (at a total pressure of 1 bar) varies strongly with the vapor pressure of the solvent.

In chlorobenzene the reaction rate could be improved by increasing the reaction temperature, without any negative effect on the imine selectivity (Table 3, entries 3 and 4). Working at higher temperature accelerates the removal of water co-product. In aerobic oxidations in the liquid phase, removal of water from the reaction mixture is frequently the rate limiting step [30]. In addition, water is detrimental to the imine selectivity, as it will be discussed later.

The last three entries in Table 3 demonstrate that not only CeO₂ but also other common supports, such as TiO₂, SiO₂, or Al₂O₃ are suitable for the *in situ* catalyst preparation method (entries 3 and 5–7). Among the supports, TiO₂ seems to be the least appropriate due to the moderate selectivity. It has been reported recently that TiO₂ in the form of anatase is a good catalyst for the oxidation of amines to oximes [26] (see also Table 2, entry 5), although in our case using the TiO₂ (“P25”) as support oximes did not form in detectable amounts (Table 3, entry 5).

To prove that the *in situ* prepared gold catalyst is truly heterogeneous, the reaction presented in Table 3, entry 3 was repeated and stopped after 3 h, at 60% conversion. The reaction mixture was filtered through two layers of a very fine filter (Whatman Glass Microfibre Filter GF/D; between the layers 2 g Celite was packed). After separation, the reaction was continued with the filtrate under the same reaction conditions for 2 h but the conversion did not change. Hence, the presence of dissolved active species can be excluded.

Table 3Effect of solvent, support and temperature on the oxidative dehydrogenation of dibenzylamine with some not treated Au(OAc)₃ + support systems^a.

Entry	Support	Temp. (°C)	Solvent	Conversion (%)	Selectivity (%)	TOF (h ⁻¹)
1	CeO ₂	108	Toluene	71	93	8.2
2	CeO ₂	108	<i>n</i> -Butyl acetate	25	88	2.8
3	CeO ₂	108	Chlorobenzene	80	90	9.3
4	CeO ₂	121	Chlorobenzene	91	90	10.5
5	TiO ₂	108	Chlorobenzene	66	86	7.6
6	SiO ₂	108	Chlorobenzene	68	91	7.8
7	Al ₂ O ₃	108	Chlorobenzene	82	92	9.4

^a 0.4 mmol dibenzylamine, 6.95 μmol Au, 5 mL solvent, 5 h, and 1 bar O₂.

The reusability of the *in situ* prepared catalyst was also investigated. After the experiment described in Table 3, entry 3 the catalyst was filtered off, washed with the solvent chlorobenzene and dried over night at room temperature in vacuum. The second run under the same conditions gave only 67% conversion, probably due to the presence of some surface impurity not removed by the simple washing with the solvent [18].

3.2. Characterization by electron microscopy

The gold catalysts prepared in various ways were characterized with electron microscopy. The small gold particles on CeO₂ are hardly recognizable because of the relatively small difference in Z of Ce and Au. Therefore, for this study titania-supported catalysts were used since on titania even sub-nm gold particles are clearly visible in the HAADF-STEM images. The bridging experiments in Table 3 demonstrate that both supports are suitable to prepare active catalysts.

Most gold particles, formed from Au(OAc)₃ preadsorbed onto TiO₂ during the oxidative dehydrogenation of dibenzylamine [19], have diameters in the range 5–10 nm but some smaller and much larger (up to ca. 40 nm) particles are also seen (Fig. 1a). The particles are well dispersed over the support. When the catalyst is prepared by grinding Au(OAc)₃ and TiO₂ together, the typical diameters of the Au particles formed prior to amine oxidation are in the range 30–50 nm (Fig. 1b) but smaller particles of ca. 5 nm can be seen as well. When Au(OAc)₃ and TiO₂ are simply added to the reaction mixture, the *in situ* formed gold has also bimodal particles size distribution: besides the large particles in the range 20–40 nm, there are also small nanoparticles with an average diameter of around 5 nm (Fig. 1c). In the last two cases the gold particles are less evenly dispersed on TiO₂ than in the catalyst where Au(OAc)₃ was preadsorbed onto TiO₂ from a dilute aqueous solution [19]. An average particle size for these catalysts could not be calculated due to the very broad and uneven particle size distribution.

Fig. 1d shows the electron micrograph of the reference catalyst Au/TiO₂ (B). Here the gold particles are well dispersed and their size is in the range 1–12 nm. On the basis of the smaller gold particle size and the corresponding higher specific surface area, Au/TiO₂ (B) would be expected to be more active than our Au/TiO₂ formed *in situ* from Au(OAc)₃ and TiO₂ (Fig. 1c), which is not the case.

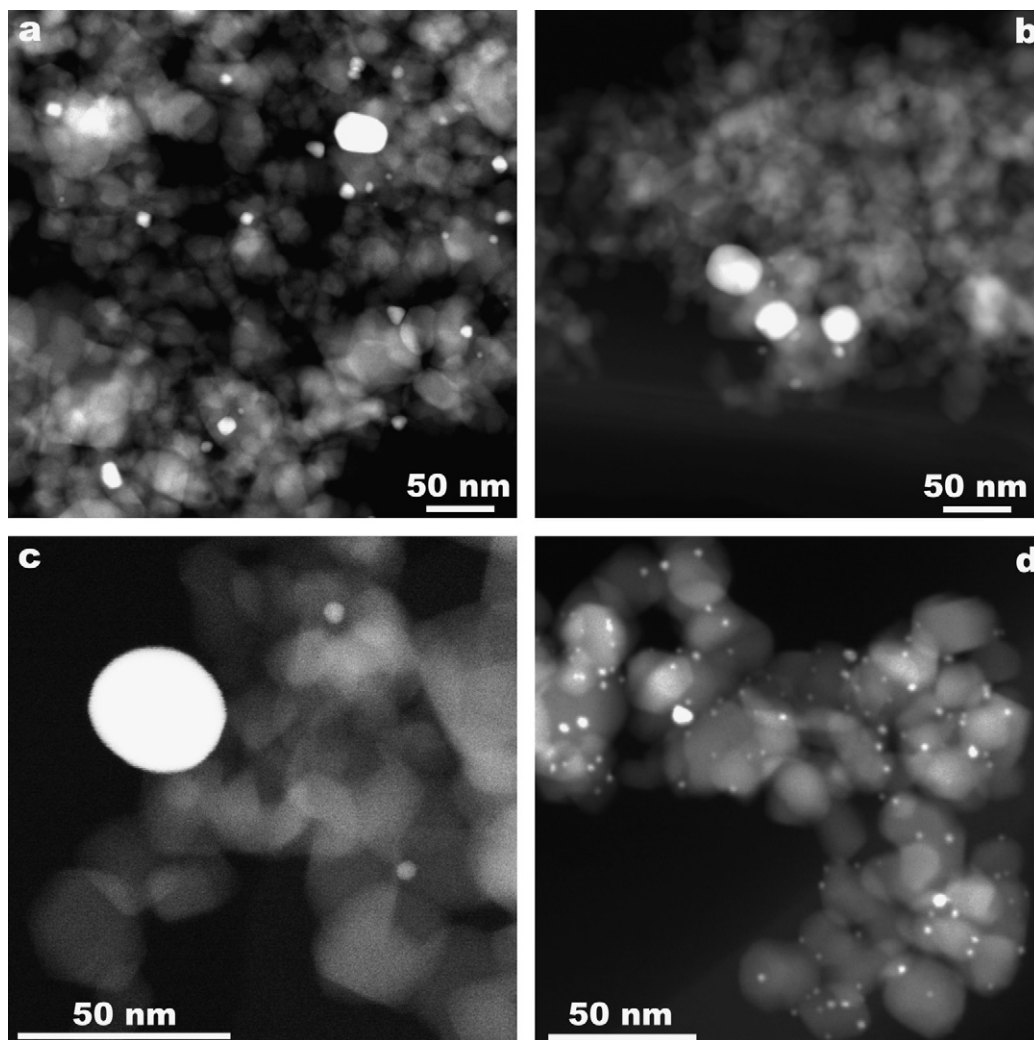


Fig. 1. Typical STEM images of the different catalysts after the oxidative dehydrogenation of dibenzylamine: (a) Au on TiO₂ formed *in situ* from Au(OAc)₃ adsorbed onto TiO₂ [19]; (b) Au on TiO₂ formed *in situ* from a ground mixture of Au(OAc)₃ and TiO₂; (c) Au on TiO₂ formed *in situ* from Au(OAc)₃ and TiO₂ directly added to the reaction mixture; (d) Au/TiO₂ (B) (unused reference catalyst).

Clearly, the particle size alone cannot explain the performance of various supported gold catalysts in the oxidative dehydrogenation of dibenzylamine.

3.3. Oxidative dehydrogenation of various amines

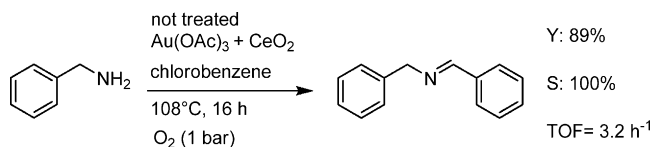
It is expected that in the *in situ* preparation of supported gold catalysts the amine substrate itself plays a key role in the formation and properties of the gold nanoparticles. To test the applicability of the catalyst preparation method, we extended the study to the oxidative dehydrogenation of a primary amine (benzylamine) and a heterocyclic amine (indoline).

The oxidative dehydrogenation of benzylamine yielded only dibenzylimine without any detectable side product (Scheme 2). Zhu et al. have shown recently the formation of imines through the

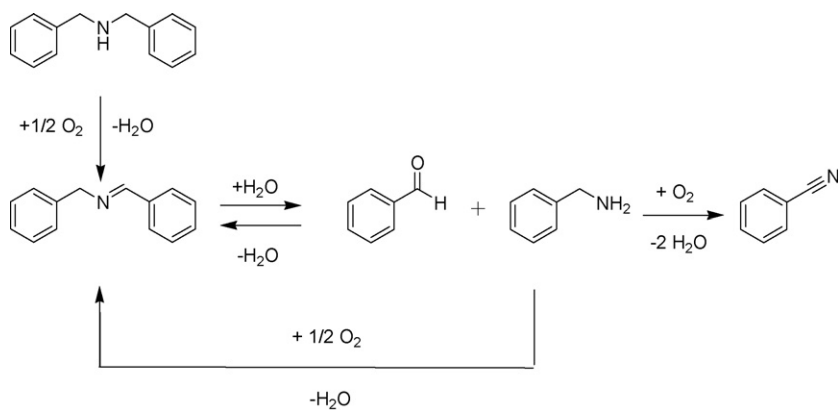
coupling and oxidative dehydrogenation of primary benzyl amines catalyzed by Au/Al₂O₃ [18]. In contrast, Cu-based catalysts facilitate the formation of imines together with the formation of some nitriles [31,32], and mainly nitriles are produced by the aerobic oxidation of primary amines with Ru-based catalysts [24,33–35].

As illustrated in Fig. 2, oxidative dehydrogenation of benzylamine with the Au/CeO₂ catalyst formed *in situ* from Au(OAc)₃ and CeO₂ is slower than the transformation of dibenzylamine. Still, in the oxidative dehydrogenation of benzylamine, the TOF at 89% conversion was 3.2 h⁻¹, and the catalyst seems to be considerably more active than the “conventionally” prepared Au/Al₂O₃ (TOF^a = 0.3 h⁻¹ [18]).

The higher selectivity of benzylamine oxidation are understandable when considering the reaction route involving the oxidation of both benzyl- and dibenzylamines (Scheme 3). Oxidative dehydrogenation of dibenzylamine gives dibenzylimine and water, but also benzonitrile, benzylamine, and benzaldehyde are formed. The latter two byproducts are the result of the hydrolysis of dibenzylimine with the coproduct water [36] and benzonitrile is formed by oxidative dehydrogenation of benzylamine. The amounts of the byproducts after 5 h reaction in chlorobenzene were 0.4%, 7.8%, and 0.5% for benzylamine, benzaldehyde, and benzonitrile, respectively. The low benzylamine/benzaldehyde ratio can be explained by the previously described route, the coupling and oxidative dehydro-



Scheme 2. Oxidative dehydrogenation of benzylamine with Au on TiO₂ formed *in situ* from Au(OAc)₃ and TiO₂ directly added to the reaction mixture.



Scheme 3. Gold-catalyzed oxidative dehydrogenation of dibenzylamine, and gold catalyzed coupling and oxidative dehydrogenation of benzylamine to form dibenzylimine.

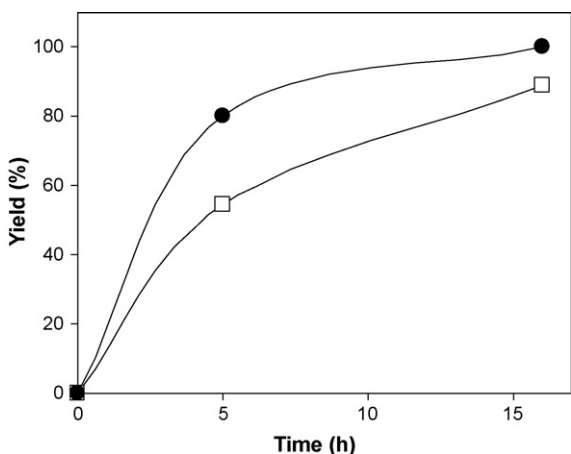
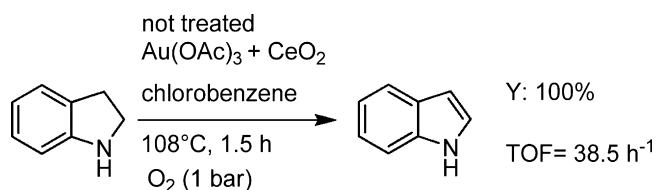


Fig. 2. Kinetics of the oxidative dehydrogenation of dibenzylamine (●) and coupling and oxidative dehydrogenation of benzylamine (□) to dibenzylimine by adding $\text{Au}(\text{OAc})_3$ and CeO_2 directly into the reaction mixture. Reaction conditions: 0.4 mmol amine, 6.95 μmol Au, 5 mL chlorobenzene, 108 °C, and O_2 at 1 bar total pressure.

generation of benzylamine to dibenzylimine. The small amount of benzonitrile indicates that the direct oxidation of benzylamine to benzonitrile is very slow. We can conclude that under the reaction conditions applied here the coupling and oxidative dehydrogenation of benzylamine to dibenzylimine is much faster than the hydrolysis of dibenzylimine and the oxidation of benzylamine to benzonitrile. The high selectivity of the coupling and oxidative dehydrogenation of benzylamine can be explained also by the Le Chatelier's principle: benzylamine is present in much higher concentration during its oxidative dehydrogenation than as a by-product during the oxidative dehydrogenation of dibenzylamine to dibenzylimine.

Oxidation of indoline to indole was remarkably faster than the two reactions discussed previously. Quantitative transformation without any detectable byproduct was achieved within 1.5 h, with a TOF of 38.5 h^{-1} (Scheme 4). For comparison, in former reports on this reaction the TOF values varied between 18 and 25 h^{-1} [33,34].



Scheme 4. Gold-catalyzed oxidation of indoline.

Another special feature of this reaction was that the filtrate after reaction was not colorless but purple, indicating the presence of some very small, colloidal gold particles. Still, the amount of gold remained in solution was negligible, below the detection limit of the ICP-OES analysis. We could not find any gold in the filtrate also by STEM analysis combined with EDX. In contrast, with UV-vis spectroscopy we could detect the plasmon resonance for metallic gold between 500 and 600 nm. In a control experiment we repeated the oxidation of indoline and stopped the reaction after 30 min, at a conversion of 79% and 100% selectivity. After separation of the catalyst, no further reaction was detectable in the filtrate in the subsequent 50 min reaction under otherwise identical conditions. It concludes that the amount of gold in the filtrate was negligible.

The catalyst filtered off after the reaction was studied with STEM. Here again, TiO_2 was used in the oxidation reaction instead of CeO_2 to allow detection of the gold particles. The particle size distribution was relatively narrow ranging from less than 1 to 6 nm, and no larger particles could be found. Fig. 3 shows an example where the whole particle size range is seen but in most other regions of the sample the proportion of the 4–6 nm particles was low and particles below 2 nm were dominant. A comparison of Figs. 3 and 1c reveals that

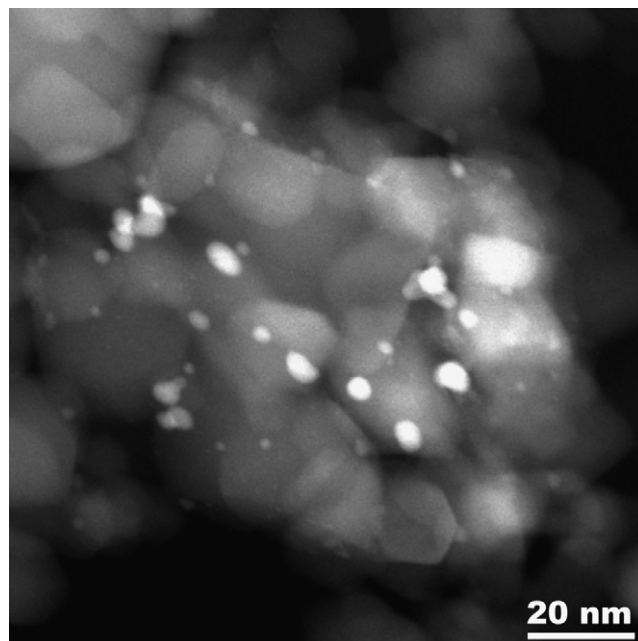


Fig. 3. STEM image of the Au on TiO_2 catalyst formed *in situ* from $\text{Au}(\text{OAc})_3$ and TiO_2 directly added to the reaction mixture of indoline oxidation.

the gold particles formed from the Au(OAc)₃ + TiO₂ mixture in the presence of indoline are remarkably smaller than those produced with the contribution of dibenzylamine.

4. Conclusions

In conclusion, we have developed a very simple route for the synthesis of gold catalysts for the oxidation of amines. There is no need for any *ex situ* preparation step before the reaction because the active gold nanoparticles are generated *in situ*. The method can be easily applied in a synthetic chemical laboratory, not equipped for the preparation of heterogeneous catalysts. Despite of the simplicity of the method, the activity and selectivity of the catalyst in amine oxidation are excellent. The method can be applied for the oxidative dehydrogenation of various amines to imines.

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