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Heterogeneous Gold Catalysts for Efficient Access to Functionalized Lactones

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Abstract: A novel class of heterogeneous gold catalysts supported on zeolite beta-NH_4^+ was prepared by the deposition–precipitation method. This new class of catalyst showed interesting catalytic activities for the intramolecular cycloisomerization of γ-acetylenic carboxylic acids leading to functionalized γ-alkylidene γ-butyrolactones. Analysis of the supported gold species with in situ X-ray photoelectron spectroscopy (in situ XPS) suggests that cationic Au (possibly Au^{III}) can play an important role in such reactions. The high discrepancy in catalyst stability in favor of the Au supported on the zeolite system over bulk Au_2O_3 is explained by 1) the size of the particles and 2) the reversibility of the redox deactivating process ($Au^{III} \rightarrow Au^{I}$) in the presence of oxygen for the supported system. The efficiency of this system allowed reaction under mild heterogeneous conditions. The potential for catalyst recycling was also highlighted.

Keywords: butyrolactones • cycloisomerization reactions • gold • green chemistry • heterogeneous catalysis

Introduction

The work of Haruta[1] and Hutchings[2] pioneered the interest for gold in heterogeneous catalysis and demonstrated that it can catalyze the low-temperature oxidation of CO, ethyne hydrochlorination, and propylene epoxidation. The interest for this element thus expanded and numerous contributions demonstrating the effectiveness of supported gold in many other important reactions emerged.[3] Very recently, Corma and Serna reviewed the behavior of gold nanoparticles in catalysis[4] and showed that they may act as active redox catalysts for oxygen-containing hydrocarbons and as reduction catalysts for alkenes, alkynes, imines, carbonyls, and nitro compounds. Au/TiO_2 and Au/Fe_2O_3 proved to be effective in the hydrogenation of nitro compounds, also providing an alternative catalytic route for the production of cyclohexanone oxime.[4] It was also shown[5] that it is possible to modify the reactivity of the small particles of gold by supporting these on a nanocrystalline CeO_2 leading to very active catalysts for CO oxidation, homocoupling of aryl boronic acids, and Sonogashira's coupling reactions. The performance of these catalysts was attributed to stabilized Au^{III}, which was considered the active site for performing not only the oxidation of CO, but also C−C bond formation. Alternatively, nanocrystalline Au particles dispersed on a more neutral support like carbon can provide tunable active catalysts for the oxidation of alkenes using air, with high selectivity to partial oxidation products and significant conversions without a sacrificial reductant.[6] Anticipating that heterogeneous gold catalysts may be active for C−O bond formations, the cycloisomerization of carboxylic acetylenic acids was chosen as a standard reaction.

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Homogeneous transition-metal-catalyzed cyclization of 4-alkynoic acids constitutes a major route for the construction of 5-membered exocyclic enol lactones. Earlier studies have demonstrated interesting catalytic activities for a large variety of ruthenium,[7] rhodium,[8] palladium,[9] silver,[10] and mercury[11] complexes and clusters.[12] However, the effective systems require the presence of additives or ligands or/and strong bases, or the use of toxic Lewis acids and often lead to moderate regio- and stereoselectivies.[7–12] We recently described the high catalytic activities of simple, commercially available AuCl and $AuCl_3$ for the synthesis of functionalized lactones[13] in the absence of any base. However, the optimized system requires 2–5 mol % gold and is limited to *gem*-substituted substrates. Subsequently, the cyclization of unfunctionalized acetylenic acids has been reported by using a combination of AuCl and K_2CO_3.[14] The low substrate-to-metal ratio (i.e., T.O.N. = 10) and the presence of a homogeneous base still do not fit the twelve principles of green chemistry.[15] In contrast with the flurry of synthetic methodologies developed in homogeneous catalysis, reports of heterogeneous systems have been limited to bulk HgO.[8b,11a,b,g] Based on this background, we introduced the use of Au_2O_3 as an active, extremely selective catalyst for the cyclization of 4-pentynoic acids.[16] Substrate-to-catalyst ratios up to 1000 and the selective 5-*exo* mode of cyclization for both terminal and internal alkynes have been obtained. In this paper, we report the preparation and unprecedented study of the activity of selected supported gold catalysts for the cyclization of acetylenic carboxylic acids to enol lactones. Spectroscopic studies and structure-activity relationships show that the catalytic reaction possibly involves Au^{III} species and that a redox deactivation process leading to Au^{I} species is operating under the catalytic conditions. The effect of O_2 in air as a possible reoxidizing agent is postulated and investigations regarding the recyclability of the supported catalysts are reported.

Results and Discussion

We have chosen to immobilize gold on various supports by precipitation of $AuCl_3$ with NaOH on nanocrystalline CeO_2, MgO, and TiO_2. Taking into account the literature concerning the role of Au^{III}[4] in oxidation reactions we have also decided to prepare gold-exchanged zeolites (ZSM-5, beta, ferrierite) in which the zeolite was expected to play the same role as the chloride. Simple depositions/precipitations on zeolite beta in the H^+ or NH_4^+ forms were realized and led to the corresponding Au/beta-H^+ and Au/beta-NH_4^+ zeolites[17] The resulting catalysts were characterized by ICP-AES, adsorption–desorption isotherms of N_2 at 77 K, DR-UV/Vis spectroscopy, XPS (X-ray photoelectron spectroscopy), TEM (transmission electron microscopy), and EDX (energy-dispersive X-ray analysis). Table 1 compiles the analytical and textural data. Zeolites exhibit very high specific areas. High surface areas were also found for Au catalysts supported on CeO_2, MgO, or TiO_2.

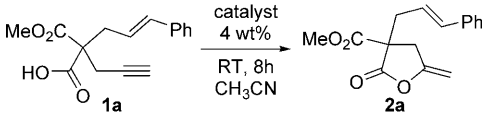
Table 1. Surface area and average particle size of supported catalysts.

Catalyst	Au loading [wt %]	Surface area [$m^2 g^{-1}$]	Average Au particle size [nm][a]
zeolite beta-H^+	–	420	–
zeolite beta-NH_4^+	–	464	–
Au/beta-H^+	4	294	5–7
Au/beta-NH_4^+	4	383	3–5
Au/CeO_2	4	82	5–11
Au/MgO	2	62	2–12
Au/TiO_2	4	42	5–8
exchanged Au/zeolite beta-NH_4^+	1.2	426	–

[a] Measured from TEM.

We decided to investigate the behavior of these 4 wt % Au catalysts in the cyclization of the standard acetylenic substrate **1a** (Table 2). Cyclization of acetylenic acids does not take place over gold supported on CeO_2 or MgO (Table 2, entries 1–2) at room temperature after 8 h. The main effect of increasing the temperature and time for the reaction in the presence of the Au/MgO catalyst was decomposition of the substrate and the formation of only 34 % of the desired product (Table 2, entry 3). Such behavior was rather surprising because CeO_2, and even more so, MgO exhibit Lewis base properties as supports, which should assist this reaction according to the precedent literature.[8b,11g,12,14,16] The Au/TiO_2 catalyst demonstrated moderate activity at room temperature after 8 h (Table 2, entry 4). Considering that a gold-exchanged beta zeolite may behave as a halide substitute due to its acidic properties, we then tested the efficiency of the exchanged zeolites in this reaction. Very low catalytic activity has been detected (Table 2, entries 5–6). The same behavior was found for the catalyst Au/beta-H^+ that has been prepared by using the deposition–precipitation method (Table 2, entry 7). However, we were pleased to find that Au/beta-NH_4^+ exhibited a high activity, as 99 % of the γ-lactone **2a** was isolated (Table 2, entry 8). It is important to note that the control experiments

Table 2. Au-catalyzed cyclization of carboxylic acid **1a**.[a]



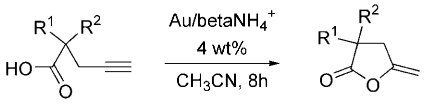
Entry	Catalyst	Conversion [%]	Yield [%][b]
1	Au/CeO_2	0	–
2	Au/MgO	0	–
3[c]	Au/MgO	80	34
4	Au/TiO_2	50	25
5	Au/ZSM-5	< 10	–
6	exchanged Au/zeolite beta-NH_4^+	< 10	–
7	Au/beta-H^+	0	–
8	Au/beta-NH_4^+	100	99
9	ZSM-5, Ferrierite, Beta-NH_4^+ or beta-H^+	0	–

[a] 1.5 mol % [Au], see Experimental Section for details. [b] Isolated yield. [c] 40 °C, 16 h.

performed by using pure zeolite (i.e., without any Au) either in the H^+ or NH_4^+ form, or on beta-H^+ treated in a solution with a pH corresponding to those at which the deposition/precipitation process was carried out led to zero conversion in this reaction (Table 2, entry 9). Moreover, the reaction was found to be very slow when conducted under argon and the best yields were obtained under an air atmosphere.

The scope of the reaction was then studied for various acetylenic acids either at room temperature or at 40 °C (Table 3). We first evaluated the efficiency of the system on malonic derivatives **1b–e** (Table 3, entries 1–6). Very good yields were observed for the cyclizations of acetylenic carboxylic acids **1b–d** bearing alkyl or alkenyl side chains (Table 3, entries 1–4). As expected, we observed that the reaction times were longer (8 h) than those attained under homogeneous conditions (2 h). However, when using heterogeneous catalysts it is noteworthy that comparable results were obtained for a low catalyst loading estimated to be 1.5 mol% of gold. No side reactions were observed on the alkenyl side chains during the course of the reaction at 40 °C (Table 3, entries 2–4). The presence of a benzylgroup also allowed a clean cyclization leading to the lactone in 71% isolated yield (Table 3, entry 6). Performing the reaction at room temperature corresponded to smaller reaction rates (Table 3, entries 5, 7). Encouraged by such results, we attempted to transform unsubstituted substrates, for which only degradation or formation of methylketone had been observed by using homogeneous gold chloride sources,[13] whereas perfect chemoselectivity was obtained when using either heterogeneous Au_2O_3 conditions[16] or homogeneous $AuCl/K_2CO_3$ conditions.[14] The cyclization of 2-(methoxycarbonyl)hex-5-ynoic acid (**1f**; Table 3, entries 7–8) needed a prolonged reaction time and a temperature of 40 °C to reach complete conversion, whereas the corresponding lactone **2f** was isolated in a modest yield of 50%, which may be due to the degradation of starting material. Indeed, in the case of the 2-phenyl-pent-4-ynoic acid **1g**, the corresponding *exo*-methylene lactone was obtained in 80% yield (Table 3, entry 9).

Table 3. Au-catalyzed cyclization of functionalized carboxylic acids.



2b-g

1b: $R^1 = CO_2Et$, $R^2 = n$Bu
1c: $R^1 = CO_2Me$, R^2 = but-2-enyl
1d: $R^1 = CO_2Me$, R^2 = allyl
1e: $R^1 = CO_2Et$, R^2 = Bn
1f: $R^1 = CO_2Me$, R^2 = H
1g: R^1 = Ph, R^2 = H

Entry	R^1	R^2	**2**	*T* [°C]	Yield [%][b] (Conv. [%])
1	CO_2Et	*n*Bu	**2b**	RT	60 (90)
2[a]	CO_2Et	*n*Bu	**2b**	40	85 (100)
3	CO_2Me	but-2-enyl	**2c**	40	80 (100)
4	CO_2Me	allyl	**2d**	40	88 (100)
5	CO_2Et	Bn	**2e**	RT	65 (70)
6	CO_2Et	Bn	**2e**	40	71 (100)
7[a]	CO_2Me	H	**2f**	RT	25 (40)
8[a]	CO_2Me	H	**2f**	40	50 (100)
9	Ph	H	**2g**	40	80 (85)

[a] 16 h. [b] Isolated yield

Reports on homogeneous catalysis did not underline the recyclability of the catalysts. Figure 1 presents the recycling results for the first five runs when using the substrate **1a** in the presence of Au/beta-NH_4^+. The reaction time was deliberately fixed at 8 h to allow a maximum conversion of the carboxylic acid to lactone. The supported catalytic system can easily be separated by centrifugation under ambient conditions. In addition, catalyst recovery is not hampered by decomposition as the presence of air has no detrimental effect, but on the contrary is a prerequisite to reach high activities. As can be seen, the supported catalysts were recycled without any significant loss of conversion and yield (Figure 1). No leaching of the gold seemed to occur, as the same ICP-AES analyses were obtained for the reused catalysts.

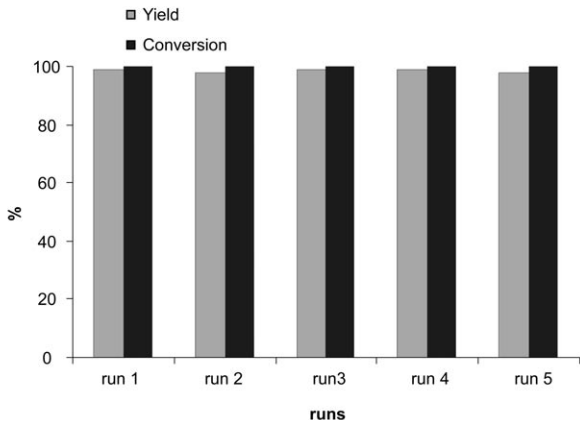


Figure 1. Recycling test for the cycloisomerization of carboxylic acid **1a** in the presence of the Au/beta-NH_4 catalyst.

A rationalization of the observed results was then pursued through more specific analysis of the effective catalyst. Figure 2 shows the TEM images (a,b) and EDX analysis (c) of the Au/beta-NH_4^+ catalyst. A quite narrow size distribution with the maximum centered at 4 nm can be observed from the bright-field TEM picture. As shown in Figure 2a, the morphology of the zeolite support was preserved. Based on the atomic-number (*Z*) sensitive nature of the high-angle annular dark-field (HAADF) contrast (*Z*-contrast), ADF-STEM analysis offered a better gold/zeolite contrast and revealed the existence of some gold oxide nanoparticles below 3 nm (Figure 2b). EDX analysis (Figure 2c) of the indicated area in Figure 2b confirmed the existence of gold in the sample.

During the catalyst preparation step, changing the precipitation pH, due to the precipitation rate, even in a small

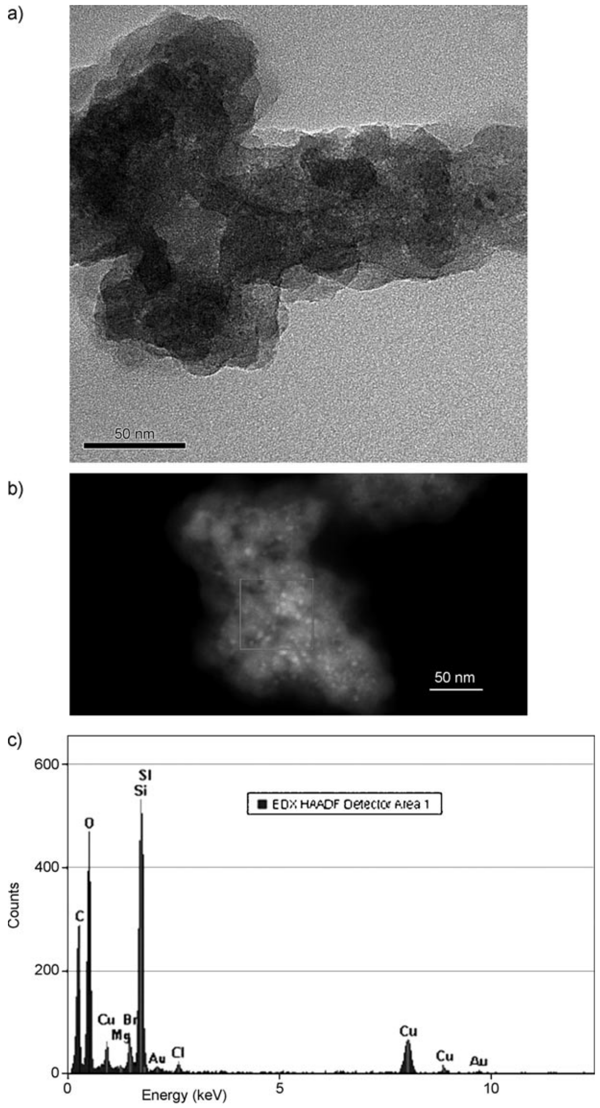


Figure 2. TEM images (a,b) and EDX analysis (c) of Au/zeolite beta-NH_4^+.

range (7.8–9.2) induced structural nonuniformities and changes of the size of the gold oxide particles (3–12 nm). Such a catalyst is no longer active in the cycloisomerization of acetylenic acids. The same structural nonuniformities and changes of the size of the gold oxide particles were observed for the catalysts supported on MgO and TiO_2. Because these catalysts are inactive too, we can conclude that for these reactions a narrow size distribution (e.g. 3–4 nm) of the gold particles is a prerequisite. Figure 3 depicts the TEM (a,b) and EDX (c) images for the catalyst Au/MgO. These images confirm a broader distribution of Au on the MgO support.

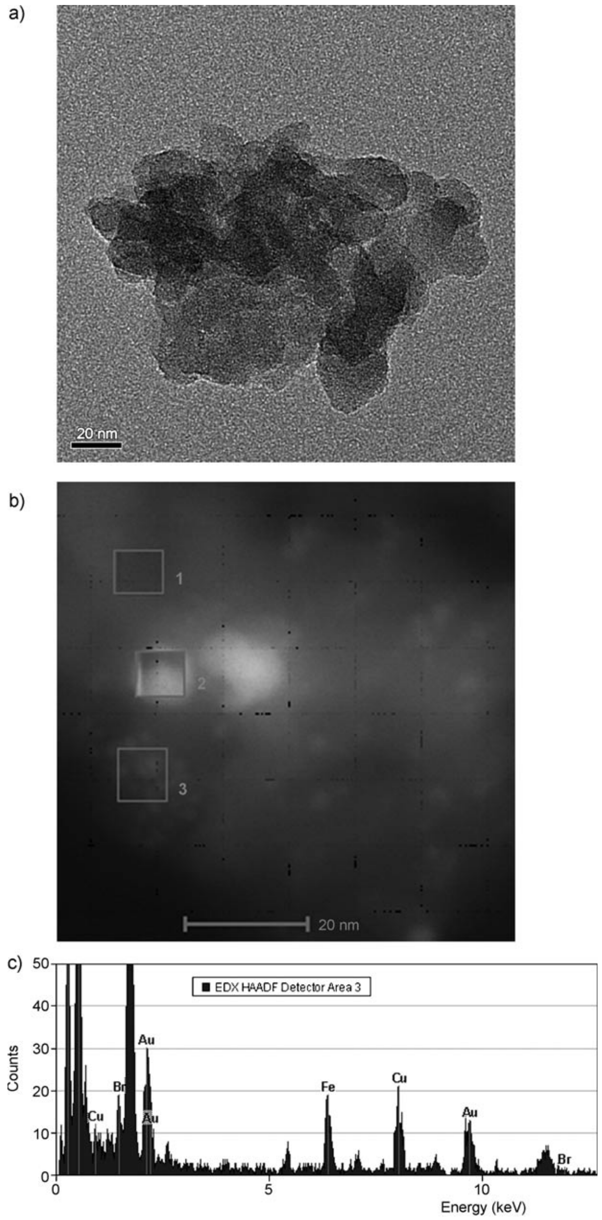


Figure 3. TEM images (a,b) and EDX analysis (c) of Au/MgO.

Another interesting observation in these experiments was related to the necessity to perform the catalytic experiments in the presence of air.

To clarify the observation that the catalyst is especially active under ambient conditions, we performed in situ XPS measurements by using the high-pressure X-ray photoelectron spectrometer described in the Experimental Section. In particular, the samples were exposed to argon, carbon monoxide (CO), and dioxygen (O_2) at pressures of 1 mbar during the XPS measurement. The resulting Au 4f spectra are displayed in Figure 4. In the presence of 1 mbar Ar, the Au $4f_{7/2}$ signal is centered at 84.5 eV. Exposing the sample to 1 mbar CO causes only small changes in the position and the shape of the signal. In contrast, the presence of O_2 shifts the peak center significantly to a higher binding energy, 85.1 eV, suggesting oxidation of the Au species. Considering the fact that this oxidation reaction occurs already at a very low oxygen partial pressure of 1 mbar, it appears not unlikely that a similar reaction occurs when the catalyst is in contact with the liquid phase under ambient conditions.

Apparently, the Au species in the zeolite is already in a reduced state when the gas is switched from Ar to CO, be-

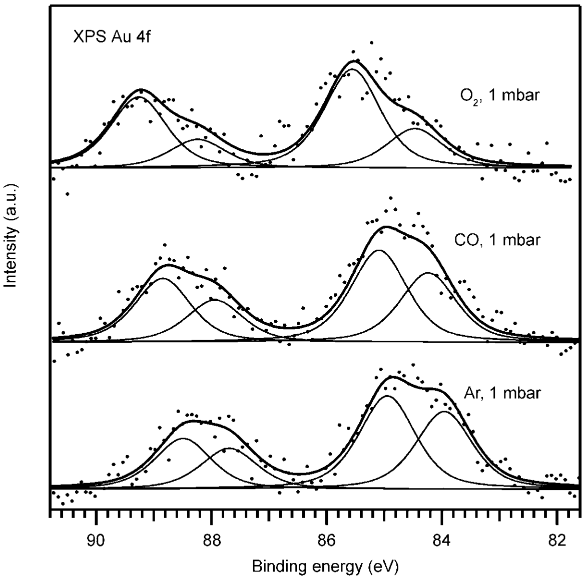


Figure 4. In situ high-pressure XP spectra of the Au/beta-NH_4^+ catalyst taken in the presence of 1 mbar Ar (bottom), 1 mbar CO (center), and 1 mbar O_2 (top).

cause otherwise reduction by CO would cause a major peak shift to lower binding energy. At the first glance, this is a surprising result, because the sample was exposed to ambient conditions prior to the XPS measurement and thus to a much higher oxygen pressure than in the high-pressure XPS experiment. The most likely explanation for this finding is the reduction of an initially oxidized Au species by reducing species (CO, H_2) in the residual gas of the vacuum chamber. The procedure of evacuating the load lock after introducing the sample and transferring the sample in the vacuum system to the high-pressure XPS chamber requires several hours. This time is probably sufficient for reducing oxidic Au species even at CO partial pressures in the low 10^{-10} mbar range, taking into account that AuO_x reacts rapidly with CO with a low activation barrier[17] (We note that X-ray-induced beam damage may also play a role in the decomposition of an AuO_x species, according to recent XPS investigation of Au_2O_3 on Au nanoparticles.[18]). Our considerations concerning the reduction of the oxidized Au species can be extended to the liquid phase and suggest why ambient conditions are crucial for the performance of the catalyst: most likely, the catalytically active oxidized gold is slowly reduced by a reactant or the solvent[19] and is reoxidized if air is admitted to the mixture.

Deriving the oxidation states of the Au species from the observed Au 4f binding energies is not straightforward. Firstly, influences of the final state of the photoemission process, for example screening effects, on the binding energy are difficult to quantify and depend on the local environment of the Au atoms or ions. This makes comparison with Au 4f binding energies of other Au compounds difficult. For example, the two components which can clearly be identified in the Au $4f_{7/2}$ signal may just result from two different local environments and may not represent different oxidation states. Secondly, residual charging of the sample may also occur in the presence of argon and thus make the absolute binding energies of all spectra uncertain (in contrast to the relative binding-energy shifts for the different gases). These cautioning remarks aside, we could compare our results to the Au $4f_{7/2}$ binding energy of bulk Au_2O_3, 85.9 eV.[20] The value we observed in the presence of 1 mbar O_2, 85.5 eV (position of the most intense contribution), is slightly lower and may thus represent a lower oxidation state of Au than +3, for example, a (metastable) Au^{II} species. Alternatively, the relatively broad peak may contain contributions from Au^{III} and Au in lower oxidation states. The spectra taken in Ar and CO show at least two contributions centered around 84 and 85 eV. This suggests that part of the Au is not in the zero oxidation state, even in the presence of CO, but forms an oxidized species, which cannot be reduced easily with CO. One may speculate that this Au species is incorporated into the zeolite framework such that reduction is prevented. Oxygen exposure would then lead to further oxidation, resulting in the formation of the catalytically active species.

Conclusion

We have found that gold supported on zeolite beta-NH_4^+ catalyzes the intramolecular addition of carboxylic acids to alkynes leading to functionalized lactones. XPS confirmed the role of oxidized Au species in such reactions, and provided evidence regarding the effect of air in preserving the catalyst activity. The efficiency of this system allowed reactions under mild heterogeneous conditions previously unobserved. The heterogeneous catalyst was efficiently recycled four times. The high activity observed for this system and the oxidoreduction mode of activation of the Au nanoparticles may have further reaching implications in the design of new catalytic systems for the formation of C–O or C–N bonds.

Experimental Section

Synthesis of supported catalysts: Beta zeolite (1 g; PQ Corporation) was vigorously stirred for 3 h with a solution of NH_4NO_3 (100 mL, 1 M) at 353 K. After this time, the slurry was filtrated and carefully washed, dried for 6 h at 333 K, and calcined for 24 h at 773 K. Au-supported catalysts were prepared by the deposition–precipitation method, by adding the support (1 g) to an aqueous solution of $HAuCl_4$ (10^{-3} mol L^{-1}) previously adjusted at pH 8.5 with a NaOH solution (0.2 mol L^{-1}). The slurry was maintained at 343 K, under vigorous stirring for 3 h. After stirring, the sample was filtered, washed with deionized water until elimination of chloride, and then dried under vacuum at 333 K for 24 h. Au/TiO_2, Au/MgO, and Au/CeO_2 were prepared in a similar way. MgO was prepared from commercially available $Mg(OCH_3)_2$ solution (Aldrich, 8.7 wt % in methanol), methanol, and deionized water. The solution of $Mg(OCH_3)_2$ was mixed with water in methanol (molar ratio 1:2) at room temperature and left for gelation (2 days). After drying under vacuum at 333 K for 24 h, the oxide was heated at 773 K in air for 1 h, which resulted in an oxide with the surface area of 142 m^2 g^{-1}. CeO_2 was prepared by following the methodology proposed by Rambabu et al.[21] and exhibited a surface area of 182 $m^2 g^{-1}$. TiO_2 was obtained by sol-gel with $Ti(OBu)_4$ (Aldrich) as a precursor. $Ti(OBu)_4$ (10 mL) was mixed with isopropyl alcohol (4 mL), and then water and nitric acid (0.01 M) were added to this solution in a molar ratio $Ti(OBu)_4/H_2O/HNO_3$ of 1:4:0.01. This mixture was left for 7 days for gelification. The gel was then dried under vacuum at 333 K for 24 h and heated at 673 K in air for 2 h, which resulted in TiO_2 with a surface area of 116 $m^2 g^{-1}$.

XPS characterization methods: The in situ XPS measurements were performed with a high-pressure X-ray photoelectron spectrometer, which can be operated at pressures of up to 1 mbar at the sample and is, therefore, suitable for measurements within the "pressure gap" regime. The apparatus has been described in detail elsewhere.[22] Briefly, the experimental setup is based on a modified hemispherical electron-energy analyzer (Omicron EA 125), a modified twin anode X-ray source (Specs) ($Al_{K\alpha}$ radiation, $h\nu = 1486.6$ eV), and several differential-pumping stages between the sample region and the electron detector. The vacuum system has a base pressure in the 10^{-10} mbar range. The reaction gas is provided in situ by either background dosing or beam dosing; the latter uses a directed gas beam from a tube with a small cross section and permits higher local pressures. In this work, only background dosing was employed. All in situ XPS measurements were performed at maximum gas pressure (1 mbar). As a favorable side effect of the presence of the gas phase, photoinduced charging of the (nonconducting) samples is reduced because partial ionization makes the gas phase conductive. The conductivity (and, thus, the degree of residual charging) depends on the charge carrier density and, therefore, on the ionization probability of the gas. This leads to different charging of the samples for the different gases and, as a result, we find small deviations (<1 eV) in the positions of all photoemission signals for different gases. To account for this effect, we made the reasonable assumption that the silicon in the zeolite framework is chemically not affected by the different gases (Ar, CO, and O_2) in this pressure range and that any differences in the positions of the Si 2s signals are due to charging. Therefore, the shifts of the Si 2s signals can be used to correct the positions of the Au 4f signals. This procedure was applied in Figure 4 to correct the position of the spectra (a) and (b) relative to spectrum (c). For the general calibration of the energy scale of the spectrometer, we used the Fermi edge and the Au $4f_{7/2}$ signal ($E_B \equiv$ 84.0 eV) of a clean Au(111) sample.

Catalytic procedure: A mixture of acetylenic acid (0.26 mmol) and gold catalyst (20 mg) in acetonitrile (1.2 $mol L^{-1}$) was stirred under an air atmosphere at room temperature or 40 °C. After completion of the reaction, the mixture was centrifugated. By simple decantation, the catalyst was removed from the reaction mixture and the solvents were evaporated under reduced pressure to give the corresponding lactone. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 300 instrument and were in accordance with the literature.[7–14,16]

Acknowledgements

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