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Comparison of the Catalytic Activity of Gold Nanoparticles Supported in Ceria and Incarcerated in Styrene Copolymer

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Abstract The catalytic activity of gold nanoparticles supported on nanoparticulated ceria or incarcerated in a styrene copolymer has been compared for three general gold catalyzed reactions, namely the aerobic benzylamine and aniline oxidations and for phenylacetylene-amine-benzaldehyde coupling. Remarkable differences between the activity of both catalysts were observed.

Keywords Gold catalysts · Aerobic oxidation · Alkyne coupling

1 Introduction

Gold catalysis is currently a topic of much interest due to the relatively unexplored catalytic activity of this element compared to other noble metals [1–4]. There is a considerable number of examples showing that the catalytic activity of supported gold can be unique for some processes, exceeding that of other noble metals [2]. One of the most intriguing facts in gold catalysis is the strong dependence of the activity on the nature of the support [3, 4]. This is the case of the low-temperature CO oxidation for which nanoparticulated ceria renders gold nanoparticles more active than titania P-25 while deposition on silica makes gold nanoparticles inert for this reaction [4, 5]. Also, we have found that aniline coupling to form azobenzenes is strongly dependent on the nature of the support, titania being a convenient support while gold on active carbon was inactive [6].

Two of the most widely used types of supports for gold nanoparticles are metal oxides and organic polymers. Considering the influence of the support, an important issue in gold catalysis is to compare the activity among different supports. Typically comparison of the catalytic activity of gold nanoparticles depending on the supports is routinely performed in each work min the field of gold catalysis. However, up to now, no information about the relative catalytic activity of gold supported on nanoparticulate ceria or polymeric support has been provided from data of the same laboratory carrying out the experiments under the same conditions. This manuscript is aimed at providing this information.

In this context, it has recently reported that gold nanoparticles of small size and narrow size distribution entangled in the polymeric network of a styrene copolymer exhibit an exceedingly high catalytic activity for the room temperature aerobic oxidation of alcohols [7]. This polymer-entangled gold catalyst has also been found highly active for the aerobic oxidation of hydroquinones and their derivatives [8, 9]. Considering the remarkable performance of this catalyst based on gold nanoparticles entangled in styrene copolymer and that other metal oxide supports such as ceria nanoparticles are also highly active, it would be desirable to determine the relative performance of both types of gold supported catalysts under the same conditions for other gold-catalyzed reactions different from alcohol

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oxidation. It is the purpose of this report to compare the catalytic activity of gold nanoparticles supported on nanoparticulated ceria and in styrene copolymer for three general types of gold catalyzed reactions including two aerobic oxidations and one-three-component coupling.

2 Experimental

2.1 Preparation of Au/npCeO$_2$

First nanoparticulate ceria was produced. The preparation of nanoparticulated ceria was carried out following a reported procedure [10]. In short, an ammonia aqueous solution (1.12 L, 0.8 M) was added under stirring at ambient temperature over 375 mL of a Ce(NO$_3$)$_4$ (0.8 M). The colloidal dispersion of CeO$_2$ nanoparticles was heated in a poly(ethylene terephthalate) vessel at 100 °C during 24 h. The resulting yellow precipitate was filtered and dried under vacuum overnight. The cerium oxide synthesized has, owing to the small size of the nanoparticles, a very high surface area (180 m^2 g^{-1}).

Au was deposited on the nanoparticulated ceria using the deposition/precipitation procedure [11]. In brief, a solution of HAuCl$_4$·3H$_2$O (90 mg) in 160 mL of deionised water was brought to pH 10 by addition of a solution of NaOH 0.2 M. Once the pH value was stable the solution was added to a gel containing colloidal CeO$_2$ (4.01 g) in H$_2$O (50 mL). After adjusting the pH of the slurry at a value of 10 by addition of a 0.2 M solution of NaOH, the slurry was stirred vigorously for 18 h at room temperature. The Au/npCeO$_2$ solid was then filtered and exhaustively washed with several litres of distilled water until no traces of chlorides were detected by the AgNO$_3$ test. The catalyst was dried under vacuum at room temperature for 1 h. Then 3.5 g of the supported catalyst were added over 30 g of 1-phenylethanol at 160 °C and the mixture was allowed to react for 20 min. The catalyst was filtered, washed, with acetone and water, and dried under vacuum at room temperature. The total Au content of the final catalyst Au/npCeO$_2$ was 0.5 wt% as determined by inductively coupled plasma (ICP) chemical analysis after digesting at 60 °C the Au/CeO$_2$ in *aqua regia* (1:10 in weight). For the preparation of 2.0 wt% Au/npCeO$_2$ the method used was the same as above starting with 350 mg of HAuCl$_4$·3H$_2$O.

2.2 Preparation of Au/PSt

2.2.1 *Synthesis of 2-(2-(2-(2-(4-vinylbenzyloxy)ethoxy) ethoxy)ethoxy)ethanol*

Tetraethyleneglycol (8.81 mL, 45.4 mmol) was carefully added to a suspension of NaH (1.82 g, 45.5 mmol, 60% in mineral oil) in anhydrous THF (70 mL) and the mixture was stirred at room temperature for 1 h. Then, 4-vinylbenzyl chloride (6.40 mL, 45.4 mmol) was added. The reaction was further stirred for 12 h, then cooled at 0 °C, diluted with diethyl ether and quenched by adding a saturated solution of ammonium chloride. The mixture was extracted with diethyl ether, the combined organic layers were dried over sodium sulfate and the solvent removed under reduced pressure. The crude was purified by flash chromatography to affort 2-(2-(2-(2-(4-vinylbenzyloxy)ethoxy)ethoxy)ethoxy)ethanol as pale yellow oil with a yield of 72%. ^{1}H NMR (CDCl$_3$) δ: 3.45–3.55 (m, 2H), 3.59–3.70 (m, 14H), 4.53 (s, 2H), 5.27 (d, 1H, $J = 10.4$ Hz), 5.80 (d, 1H, $J = 18.0$ Hz), 6.78 (dd, 1H, $J = 10.4$ and 17.9 Hz), 7.35 (d, 2H, $J = 8.4$ Hz), 7.48 (d, 2H, $J = 8.4$ Hz). ^{13}C NMR (CDCl$_3$) δ: 61.6, 69.4, 70.5, 70.6, 70.7, 72.1, 73.2, 113.8, 127.0, 128.2, 136.2, 137.0, 138.9.

2.2.2 *Synthesis of 4-Vinylbenzyl Glycidyl Ether*

To a stirred suspension of NaH (1.92 g, 48 mmol, 60% in mineral oil) in anhydrous THF (40 mL), glycidol (1.01 mL, 16 mmol) was added at 0 °C. The mixture was stirred for 1 h at room temperature and 4-vinylbenzyl chloride (4.50 mL, 32 mmol) was added. After 12 h, the reaction was cooled at 0 °C, diluted with diethyl ether and a saturated aqueous solution of ammonium chloride was added as quencher. The aqueous layer was extracted three times with diethyl ether, the combined layers were dried over sodium sulfate and the solvent removed under reduced pressure. The crude was purified by flash chromatography to affort product 4-vinylbenzyl glycidyl ether as pale yellow oil with a yield oh 60%. ^{1}H NMR (CDCl$_3$) δ: 2.60–2.67 (m, 1H), 2.80–2.88 (m, 1H), 3.18–3.25 (m, 1H), 3.39–3.45 (m, 1H), 3.77–3.83 (d, 1H, $J = 11.7$ Hz), 4.59 (s, 2H), 5.27 (d, 1H, $J = 10.7$ Hz), 5.78 (d, 1 H, $J = 17.4$ Hz), 6.75 (dd, 1H, $J = 10.7$ and 17.4 Hz), 7.34 (d, 2H, $J = 8.4$ Hz), 7.44 (d, 2H, $J = 8.4$ Hz). ^{13}C NMR (CDCl$_3$) δ: 35.8, 44.0, 50.8, 71.2, 113.0, 125.8, 129.3, 135.2, 136.4, 138.4.

2.2.3 *Synthesis of Styrene Copolymer*

The styrene copolymer was obtained by dissolving a mixture of styrene (1.05 g), 2-(2-(2-(2-(4-vinylbenzyloxy)ethoxy)ethoxy)ethoxy)ethanol (3.0 g), 4-vinylbenzyl glycidyl ether (2.0 g), and 2,2′-azobis(4-methoxy)-2,4-dimethylvaleronitrile (92.0 mg) in chloroform (11.0 mL). The solution was continuously purged with Ar and stirred for 72 h at room temperature. The resulting polymer solution was slowly poured into ether. The precipitated polymer was separated by centrifugation, washed several times with ether and dried for 24 h *in vacuo* to afford the desired copolymer as a white solid with a yield of 50%.

2.2.4 Synthesis of Au/PSt

This catalyst was prepared as reported [7]. Briefly, Au/PSt was obtained by dissolving ($AuClPPh_3$) in a small amount of THF and adding this solution to a mixture of styrene copolymer and $NaBH_4$ in THF at room temperature. The color of the solution immediately turned red. Hexane was then added to form microcapsules, which were filtered, washed, and dried under vacuum. The microcapsules were next heated at 150 °C for 5 h to cross-link the side chains and then washed with THF and water to afford Au/PSt as a deep-purple solid.

2.3 Procedure for Oxidation of Benzylamine to *N*-benzylidenebenzylamine

Benzylamine (107.16 mg, 1 mmol) dissolved in toluene (2 mL) in the presence the solid catalyst (Au/benzylamine mol ratio 1%), was stirred in a glass reactor (2.0 mL, SUPELCO), pressurized with O_2 (5 bars) and heated to 100 °C. The conversion was determined by GC analysis and the products identified by GC–MS.

2.4 Procedure for Aerobic Oxidation of Aniline to Azobenzene

Aniline (93.13 mg, 1 mmol) dissolved in toluene (2 mL) in the presence the solid catalyst (Au/aniline mol ratio 1%) was stirred in a glass reactor (2.0 mL, SUPELCO), pressurized with O_2 (5 bars) and heated to 100 °C. The conversion was determined by GC analysis and the products identified by GC–MS.

2.5 Procedure for Three-component Coupling of Benzaldehyde, Piperidine and Phenylacetylene

Phenylacetylene (132.8 mg, 1.3 mmol), piperidine (102.2 mg, 1.2 mmol), benzaldehyde (106.1 mg, 1 mmol) and H_2O (1 mL) in the presence the solid catalyst (Au/benzaldehyde mol ratio 0.12%) in a closed glass reactor (2.0 mL, SUPELCO) were heated to 100 °C. The oil was separated from water and analyzed by GC and identified by GC–MS.

3 Results and Discussion

Herein we have synthesised ceria supported gold nanoparticles (Au/CeO_2) [5] and polystyrene entangled gold nanoparticles (Au/PSt) [7] and compared them with each other. The weight percentage of gold on the catalysts was determined by ICP chemical analysis (Au/CeO_2) and quantitative X-ray fluorescence (Au/PSt). Au/PSt was prepared as previously reported in the literature by cross-linking a copolymer having three different styrene monomers. The two monomers required for the synthesis of PSt, namely 2-(2-(2-(2-(4-vinylbenzyloxy)ethoxy)ethoxy)ethoxy)ethanol and 4-vinylbenzyl glycidyl ether, in combination with styrene were previously synthesized and characterized by ^1H- and ^{13}C-NMR spectroscopy. ^1H-NMR spectra of both monomers are represented in Fig. 1. During preparation of Au/PSt we notice that the amount of Au loaded in the polymer is difficult to control. This problem could be associated to the way in which the gold nanoparticles interact with the polymer and remain entrapped by the polymer chains. Therefore, to adjust the gold loading to the target value, it is necessary to perform several trials until a sample with the desired gold content is obtained. In contrast, the deposition/precipitation method widely used in the literature to obtain gold nanoparticles supported on metal oxides appears reliable and reproducible with respect to gold loading [11].

A series of Au/CeO_2 and Au/PSt at two different gold loadings about 0.5 and 2 wt% was used throughout this comparative study. Figures 2 and 3 show representative TEM images of catalysts Au/CeO_2 and Au/PSt, respectively.

Particle size distribution for Au/CeO_2 and Au/PSt at 0.5 wt% was determined from TEM images by counting a statistically relevant number of particles in each case. Figure 4 presents the results. As it can be seen there, both catalysts show narrow size distribution with an average gold particle size of 4.8 and 3.4 nm for Au/CeO_2 and Au/PSt, respectively. No significant differences were observed when the loading was about 2 wt%, the average

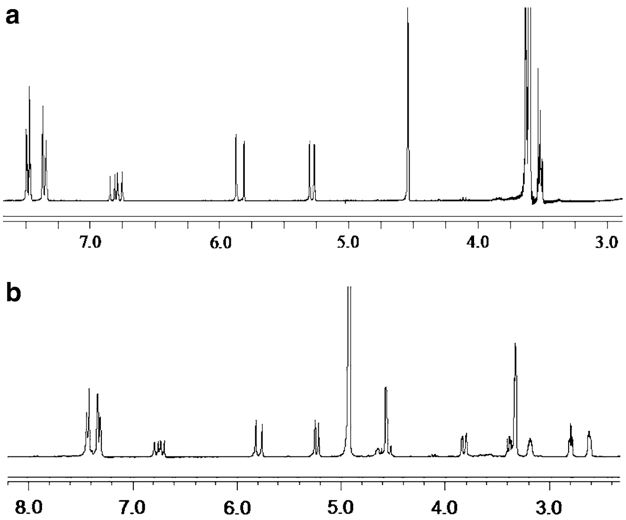


Fig. 1 ^1H-NMR spectrum of 2-(2-(2-(2-(4-vinylbenzyloxy)ethoxy)ethoxy)ethoxy)ethanol (**a**) and 4-vinylbenzyl glycidyl ether (**b**)

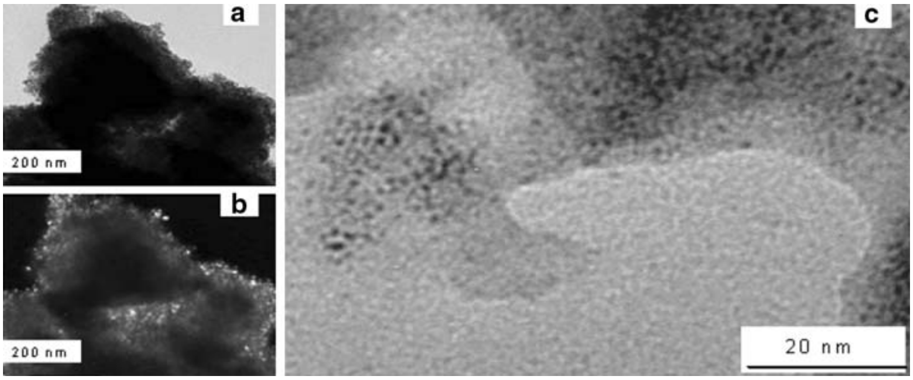


Fig. 2 Bright (**a**) and dark field (**b**) TEM images of 0.5 wt% Au/CeO$_2$ and (**c**)

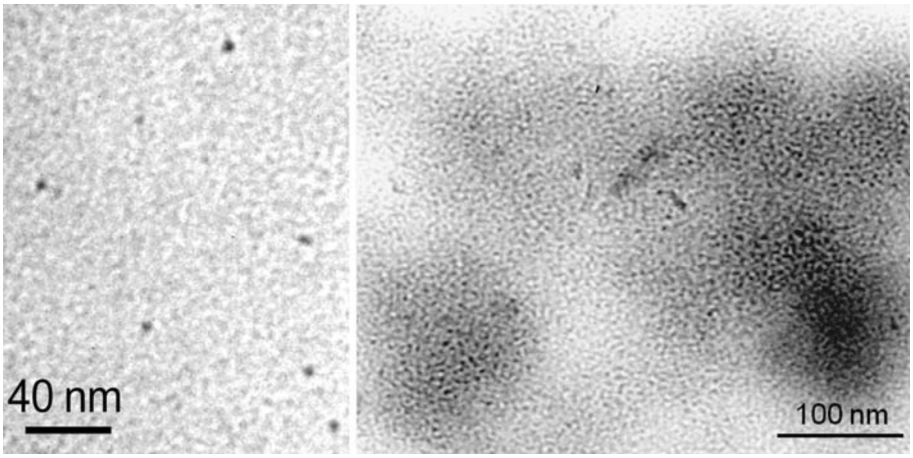


Fig. 3 Bright field TEM images of 0.5 wt% Au/PSt polymer

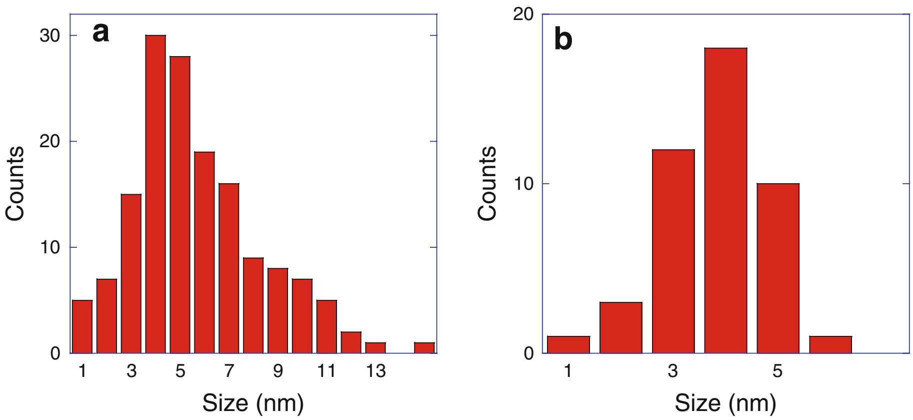
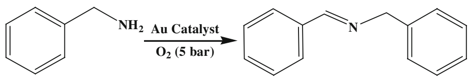


Fig. 4 Particle size distribution od Au/CeO2 (**a**) and Au/PSt (**b**)

particle size being for both catalysts below 5 nm. From the TEM study it can be concluded that regardless the support and at the loading used, no influence of the particle size on the catalytic performance should be expected.

The first reaction tested was the aerobic oxidation of benzyl amines to *N*-benzylidene benzyl amine. This reaction has been recently investigated by Angelici, who has shown that even micrometric bulk gold nanoparticles can be active for this reaction [12, 13]. This reaction has been found to be influenced by the nature of the support and the particle size. The preferred catalyst for this aerobic oxidation was gold supported on active carbon that exhibits an improved performance over gold supported on titania [14]. Also, it was found that for benzyl amine oxidation the smaller the particle size, the higher the activity of the catalyst. Thus, considering the structural similarity between active carbon and PSt since both are organic solids constituted by aromatic six members rings and the small particle size of gold nanoparticles in Au/PSt, it can be anticipated that this Au/PSt will exhibit high activity.

Table 1 Oxidation of benzylamine to *N*-benzylidenebenzylamine[a]



Catalyst	Conversion (%)[b]				Yield/%[c]
Time/h	1	4	6	24	
0.5% Au/CeO_2	48	80	95	>99	99
2% Au/CeO_2	19	41	61	97	95
0.5% Au/PSt	22	50	93	>99	97
1.6% Au/PSt	3	15	33	76	73

[a] Reaction conditions: benzylamine (107.16 mg, 1 mmol) dissolved in toluene (2 mL) in the presence the solid catalyst (Au/benzylamine mol ratio 1%), stirred in a glass reactor (2.0 mL), pressurized with O_2 (5 bars) and heated to 100 °C

[b] The conversion was determined by GC analysis and the products identified by GC–MS

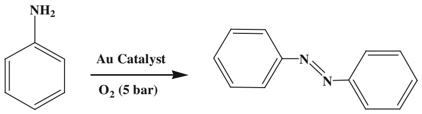
[c] The yield was determined by GC analysis at 24 h reaction time

The results obtained are indicated in Table 1. As it can be seen there, we noticed a negative influence of the gold loading on its catalytic activity, the best performing catalysts being those with lower loading. This effect has been previously also observed and attributed to the presence in the catalyst of larger particle size as the loading increases [7]. This somewhat larger particle size would reduce the overall efficiency of gold with loading due to the smaller surface area of the gold particles. In our case, we have not observed significant particle size changes comparing loading of 0.5 and 1.6 wt%, Thus, it could be that it is the increase in the dispersion of gold nanoparticles on the support, i.e. the percentage of surface area covered by gold, the factor that is reducing the catalytic activity and favoring low loadings due to higher dispersion. From the results shown in Table 1, it can be concluded that for this aerobic oxidation of benzyl amines, Au/CeO_2 and Au/PSt samples at the lowest gold loading (0.5%) exhibit similar catalytic efficiency even if the first catalyst has a shorter induction period. What appears clear is that an increase in the catalyst gold loading has a detrimental effect on the performances of both types of catalysts.

The second reaction that was studied was the aerobic oxidative coupling of aniline to azobenzene. In contrast to the previous reaction for which gold supported on active carbon was a highly active catalyst, for the aerobic oxidation of aniline it has been determined that the nature of the support plays an extremely important role [6]. Actually, it has been reported that nanoparticles of CeO_2 exhibit already significant activity that is boosted further when gold nanoparticles are deposited on it [6]. In contrast, gold supported on active carbon was found inactive to promote this oxidation [6]. Therefore, this aniline oxidation presents a different scenario than the previous oxidation of benzyl amine for which active carbon and metal oxides were found to be suitable supports. Therefore for the aerobic aniline oxidation, we anticipated based on the similarity in structure and composition between active carbon and PSt for which aromatic rings are present, that active carbon and PSt could behave similarly. If this were the case, then, Au/PSt should be notably inactive to promote aniline coupling. The results are shown in Table 2. As it can be seen there, our expectations were correct and Au/PSt was remarkably inactive as catalyst to promote the aerobic oxidation of aniline. Azobenzene could only barely be detected using 0.5 wt% Au/PSt. This catalytic behavior sharply contrasts with the excellent performance of Au/CeO_2. Complete conversions with over 93% selectivity were obtained for Au/CeO_2.

The last reaction that was tested was the three component coupling of benzaldehyde, piperidine and phenylacetylene to form *N*-(1,3-diphenyl-2-propynyl)piperidine. The reaction and the catalytic results obtained are indicated in Table 3. Again, as in the previous two processes studied, the catalytic performance of Au/PSt was notably inferior to that of Au/CeO_2. We have concluded in previous studies that the cationic gold Au(III) species are the active sites for this reaction [10] and that this positive gold species becomes stabilized by using CeO_2 as support [5]. Apparently, the data from Table 3 suggest that the population of positive Au(III) in Au/PSt is very minor.

Table 2 Aerobic oxidation of aniline to azobenzene[a]



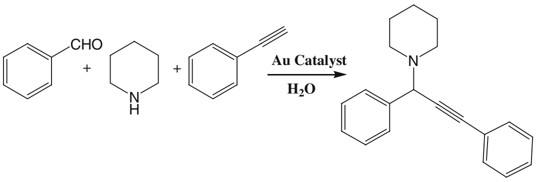
Catalyst	Conversion/%[b]		Yield (%)[c]	Selectivity (%)
Time/h	6	10	10	10
0.5% Au/CeO_2	98	100	93	93
2% Au/CeO_2	29	31	23	74
0.5% Au/PSt	1	2	–	–
1.6% Au/PSt	No reaction			

[a] Reaction conditions: Aniline (93.13 mg, 1 mmol), toluene (2 mL) in the presence the solid catalyst (Au/aniline mol ratio 1%), stirred in a glass reactor (2.0 mL), pressurized with O_2 (5 bars) and heated to 100 °C

[b] The conversion was determined by GC analysis and the products identified by GC–MS

[c] The yield was determined by GC analysis at 10 h reaction time

Table 3 Three-component coupling of benzaldehyde, piperidine and phenylacetylene[a]



	Conversion (%)[b]			Yield (%)[c]
	1 h	4 h	6 h	
0.5% Au/CeO_2	53	90	98	97
2% Au/CeO_2	60	95	>99	99
0.5% Au/PSt	15	56	87	83
1.6% Au/PSt	14	23	33	30

[a] Reaction conditions: phenylacetylene (132.8 mg, 1.3 mmol), piperidine (102.2 mg, 1.2 mmol), benzaldehyde (106.1 mg, 1 mmol), H_2O (1 mL) in the presence the solid catalyst (Au/benzaldehyde mol ratio 0.12%) in a closed glass reactor (2.0 mL) and heated to 100 °C

[b] Determined by GC analysis based on benzaldehyde (the water phase was also analyzed)

[c] Yields of isolated product based on benzaldehyde at 6 h reaction time

4 Conclusions

Our study provides comparative data of the influence of the support on the catalytic activity of gold nanoparticles for three reactions. Based on these three reactions it can be concluded that Au/CeO_2 is the catalyst of choice and outperforms Au/PSt. Thus, although the activity of Au/PSt for the aerobic oxidation of benzyl amines is remarkable, Au/PSt is notably inefficient for the aerobic oxidative coupling of aniline. The present data suggest a parallelism between the catalytic behavior of gold supported on active carbon and Au/PSt. One point of concern is the experimental difficulty in anticipating the final gold loading on Au/PSt based on the amount of $AuClPPh_3$ present in the synthesis. Considering the influence of gold loading on the catalytic activity, this poor reliability can complicate catalyst preparation.

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