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PAPER

Mild, Selective and Switchable Transfer Reduction of Nitroarenes Catalyzed by Supported Gold Nanoparticles†

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A highly versatile and flexible gold-based catalytic system has been developed for controlled and selective transfer nitroarene reduction using 2-propanol as a convenient hydrogen source under mild conditions. Depending on the specific reaction conditions, multiple products including azoxyarenes, symmetric or asymmetric azoarenes, and anilines, can be respectively obtained via a controlled reduction of nitro aromatics with good to excellent yields in presence of a reusable mesostructured ceria-supported gold (Au/meso-CeO_2) catalyst. The overall operational simplicity, high chemoselectivity, functional-group tolerance, and reusability of the catalyst make this approach an attractive and reliable tool for organic and process chemists.

Introduction

The reduction of nitroarenes is an important process as the resultant N-containing products, such as aniline, azoxy, and azo compounds, are versatile intermediates and precursors in the preparation of dyes, pharmaceuticals, pigments, agrochemicals and polymers.[1] Despite a large number of procedures have been developed for the reductive transformation of nitroarenes,[2-4] still the development of catalytic methodologies that afford high chemo- and regio-selectivity under mild conditions represents an important challenge. Even more challenging is the selective conversion of one nitroarene compound into more than one target product by controlled reduction with the use of a single catalyst system. Such a process would be of particular value to synthetic chemistry due to its step-economical potential and cost-efficiency.[5] Compared with the great progress made in the selective reduction of nitro compounds to anilines, there are scarcely available reports of nitroarenes undergoing a controlled reduction to a range of different target products with an appreciable level of functional group selectivity.[6] Sakai et al. have recently shown that highly selective conversion of nitroarenes into azoxy-, azo-, hydrazo-, or aniline compounds could be realized by using a complex reducing system comprising trivalent indium salts coupled with hydrosilane as hydrogen source.[6b] Very lately, Kim et al. have described that the reduction of nitroarenes can be finely tuned to obtain three different products by using a simple Ru nanoparticle-ethanol combination. This protocol, however, showed only moderate activity and selectivity for the generation of azoxy- and azo- compounds.[6a] Therefore, finding a more benign and economical heterogeneous protocol which is chemoselective for the reduction of nitroarenes into both amines and the corresponding compounds of the reductive coupling under mild and general reaction conditions is highly desirable.

Over the past few years, supported gold nanoparticles (NPs) have emerged as powerful catalysts that can promote a wide range of chemical transformations under green and mild conditions.[7] For example, Corma et al. have discovered an excellent activity of TiO_2-supported gold NPs for highly selective reduction of substituted nitroarenes to corresponding anilines with H_2.[4n,8] We have recently developed an alternative Au-catalyzed transfer hydrogenation (TH) strategy which can facilitate more efficient chemoselective nitro group reduction in the presence of other sensitive functional groups under very mild conditions.[9] From our continuing studies on Au catalysis, we report herein that a single Au-based catalyst system enables highly selective staged reduction of a range of nitroarenes using 2-propanol as the hydrogen source. Our results have shown that the Au catalyst comprising gold NPs deposited on mesostructured ceria (Au/meso-CeO_2) is a highly versatile system for targeted synthesis of azoxy-, azo-, or aniline compounds in good to excellent yields starting from nitroarenes. This flexible nitro reduction approach using a robust and recyclable Au catalyst has several advantages over those reported previously. For instance, this catalyst does not require any kind of poisonous salts, and provides excellent yields achievable under mild conditions.

Results and discussion

Synthesis and characterization

Mesostructured ceria was synthesized through a surfactant assisted precipitation method, with the use of cetyltrimethyl ammonium bromide (CTAB) as templating agent.[10, 11] The nitrogen adsorption–desorption isotherms of meso-CeO_2 are of a typical type IV with a clear H1-type hysteresis loop, which is characteristic of highly ordered mesoporous materials (see Figure S1 in ESI†). When gold nanoparticles were deposited onto the meso-CeO_2, X-ray photoelectron spectroscopy (XPS) of the Au $4f_{7/2}$ core level showed a sole contribution from metallic Au^0 at a

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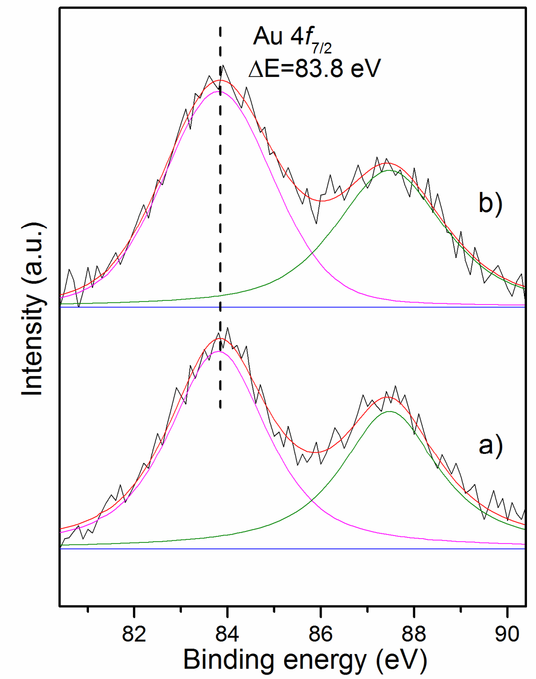

Figure 1. XPS of Au/meso-CeO_2: a) before reaction; b) after three runs. Note that the metallic state of Au practically undergoes no change after the three successive runs.

binding energy of 83.8 eV (Figure 1a). Almost identical X-ray diffraction (XRD) patterns were obtained for Au/meso-CeO_2 and meso-CeO_2 (Figure 2), indicating that the crystalline structure and the average size of the crystalline domain of the support were well maintained in the Au-containing samples. No diffraction lines of metal gold were observed in Au/meso-CeO_2, which indicated that the gold particles were highly dispersed and the sizes were very small (<5 nm). High resolution transmission electron microscopy (HRTEM) experiments have been carried out to observe a possible structure of the metallic Au particles (Figure 3a). According to the image, the average size of the meso-CeO_2 NPs was 4.8 nm, which confirmed the observations from the XRD data. The low Au loading and poor contrast between ceria and gold particles prevented to obtain the gold particle size distributions, but the existence of small Au particles can be confirmed by a careful lattice fringe analysis of the observed images (a detailed description for the relevant structural characterization has been provided in Table S3).

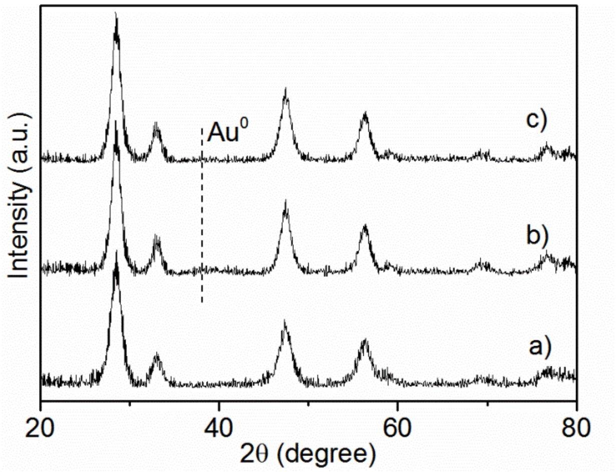

Figure 2. XRD diffractograms: a) meso-CeO_2, b) Au/ meso-CeO_2, and c) Au/meso-CeO_2 after three runs.

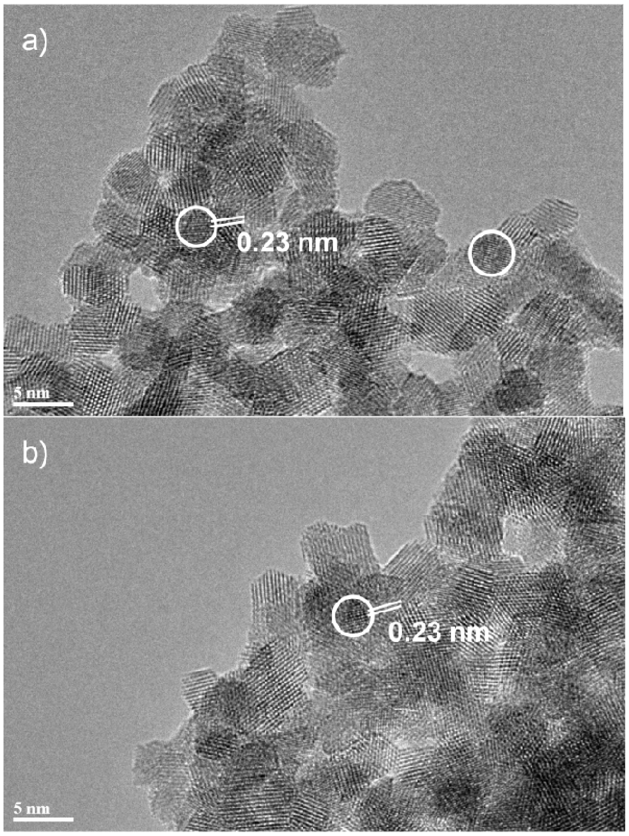

Figure 3. HRTEM images of Au/meso-CeO_2: a) before reaction; b) after three runs. The white circles indicate crystals showing the Au (111) planes. No aggregated gold particles were observed on the same sample after three times reuse.

Catalytic performance

At the start of our work, the transfer reduction of nitrobenzene (**1a**) was chosen as the model reaction for the optimization of catalytic activity and selectivity. Initially, the TH reactions were carried out with various heterogeneous catalysts in the presence of aqueous 2-propanol with 0.5 equiv. KOH at 30 °C. Azoxybenzene (**2a**), having high value as key intermediates for prodrugs and liquid crystals,[1e,1f] was obtained as the main reductive product. As can be seen in Table S1 (see ESI†), the ceria supported gold catalysts, in particular Au/meso-CeO_2 showed high activities for the transformation (Table S1, entries 1, 2). Most remarkably, the reaction with Au/meso-CeO_2 gave **2a** in full conversion with 99% selectivity (Table 1, entry 3). In this case, a noteworthy productivity with the average TOF and the TON of up to 20 h^{-1} and 100 was realized. It should be underlined that these values are nearly one order of magnitude greater than those in previously reported heterogeneous protocols such as a Ru/C-ethanol system for **2a** synthesis directly from nitroarenes (TOF: 1.2 h^{-1}, TON: 22, reaction at 60 °C).[6a] In the absence of the catalyst, however, the desired self-coupling product **2a** was not produced. No formation of **2a** was observed in the presence of just meso-CeO_2 (Table S1, entry 9). In the case of other supported gold catalysts, such as Au/TiO_2, Au/Al_2O_3,

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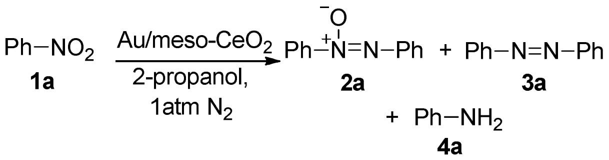
Table 1 Catalytic results of the transfer hydrogenation of nitrobenzene over Au/meso-CeO_2.[a]



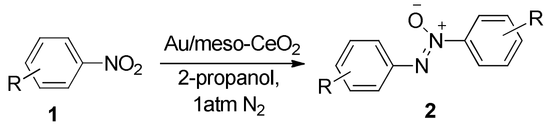
Entry	Base (equiv.)	H_2O (mL)	T (°C)	t (h)	Conv. (%)[b]	Sel. (%)[b] 2a	3a	4a
1	KOH(0.5)	-	30	7	100	78	18	4
2	KOH(0.5)	0.5	30	5	100	95	4	1
3	KOH(0.5)	1.0	30	5	100	>99	<1	-
4[c]	KOH(0.5)	1.0	30	5	100	98	2	-
5[d]	KOH(0.5)	1.0	30	5	-	-	-	-
6[e]	KOH(0.5)	1.0	30	5	-	-	-	-
7	KOH(0.5)	2.5	30	5	100	85	12	3
8	KOH(0.5)	5.0	30	5	100	32	67	1
9	KOH(0.5)	7.5	30	5	100	30	65	5
10	KOH(0.5)	5.0	40	5	100	3	95	2
11	-	5.0	60	5	38	-	3	97
12	-	5.0	80	3	>99	-	2	98

[a] Reaction conditions: Reaction conditions: 1 mmol nitrobenzene, 1 mol% Au, 5.0 mL 2-propanol, 1atm N_2. [b] Conversion and selectivity based on **1a** consumption. Determined by GC using *n*-dodecane as the internal standard. [c] Results for the third run. [d] 1 mol% Pd/meso-CeO_2. [e] 1 mol% Ru/meso-CeO_2.

Au/ZrO_2, Au/Fe_2O_3, and Au/ZnO, as well as Pd, Pt, and Ru supported on meso-CeO_2, inferior activity toward **2a** forma-tion was observed (entries 3-8 in Table S1 and entries 5 and 6 in Table 1).

With these findings in hand, the synthesis of azoxyarene derivatives from a variety of nitroarenes was examined. As illustrated in Table 2, the Au/meso-CeO_2 was highly efficient for the reductive coupling of various nitroarenes bearing structurally different functional substituents, giving the corresponding azoxy compounds in good to excellent yields. It is noted that both steric and electronic properties of the substituent affect the reductive coupling reaction significantly. In general, nitroarenes containing a substituent on the aromatic ring require a longer reaction time, and the yields of azoxyarenes are also lower. Notably, *m*-substituted nitrobenzenes had lower reaction rates and yields than *p*-substituted nitrobenzenes (Table 2, entries 2-5). Furthermore, the reaction of nitroarenes with electron-donating group can proceed faster with higher yields for **2** compared with nitroarenes with electron-withdrawing group (Table 2, entries 2-10). The reaction tolerates the presence of halogens (Table 2, entries 4-7), but a prolonged reaction time was needed for obtaining a high yield of the desired azoxyarenes. Of particular note is that the reducible function groups such as nitrile, ketone as well as ester moieties remained intact during the reduction process (Table 2, entries 8-10), demonstrating the high versatility of the present methodology for azoxy compounds synthesis.

Table 2 Synthesis of azoxyarenes from different nitroarenes.[a]

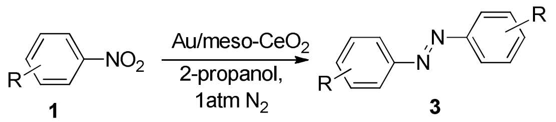


Entry	R	t (h)	Conv. (%)[b]	Yield (%)[b]
1	H	5	100	>99 (94)
2	*p*-CH_3	5	100	90 (84)
3	*m*-CH_3	7	100	84 (80)
4	*p*-Cl	8	97	80 (73)
5	*m*-Cl	8	93	75 (68)
6	*p*-Br	10	97	81 (75)
7	*p*-F	10	92	75 (69)
8	*p*-CN	10	90	70 (63)
9	*p*-COMe	6	96	89 (81)
10	*p*-COOMe	10	98	86 (79)

[a] Reaction conditions: 1 mmol nitroarene, 1 mol% Au, 0.5 equiv. KOH, 5.0 mL 2-propanol, 1.0 mL water, 30 °C, 1atm N_2. [b] Conversion and yields were determined by GC using *n*-dodecane as the internal standard; values in parenthesis are the yields of the isolated products.

To find out if our catalyst system might also be applicable for the direct synthesis of more valuable azoarenes, the effect of reaction parameters on the product distribution was investigated. With the Au/meso-CeO_2 catalyst, we first studied the effect of base additives on the reduction of **1a** at 30 °C. During exploration of different bases, we found that KOH was the most suitable additive, which showed the highest conversion and a high selectivity toward **2a** formation (Table S2, entries 2-4, 6). The reaction was also affected by the amount of KOH added and a 0.5 equiv. was enough to give the optimal yield (Table S2, entries 1, 5-8). The major product, however, was still **2a** under all the reaction conditions examined. Intriguingly, by increasing the amount of water in aqueous 2-propanol to 2.5 mL, we observed that appreciable amounts of azobenzene (**3a**) (ca. 12%) was produced as the main by-product (Table 1, entry 7).[12] We then hypothesized that, if the reaction was performed in a suitable aqueous 2-propanol solution, the reaction might be directed toward the selective formation of **3a**. We verified this by performing the reaction with different amount of water added (Table 1, entries 1-3, 7-9). To our delight, the crude mixture showed 67% **3a** selectivity in the presence of 5.0 mL water (Table 1, entry 8). For further optimization toward the selective synthesis of **3a**, subsequent studies were focused on the effect of the reaction temperature. Gratifyingly, **3a** was obtained in high selectivity of 95% when the temperature was slightly increased up to 40 °C (Table 1, entry 10).

Table 3 Synthesis of azoarenes from different nitroarenes.[a]



Entry	R	T (°C)	t (h)	Conv. (%)[b]	Yield (%)[b]
1	H	40	5	100	95 (88)
2	*p*-CH_3	35	6	100	93 (87)
3	*m*-CH_3	35	8	100	95 (90)
4	*p*-Cl	40	10	100	98 (91)
5	*m*-Cl	40	10	100	95 (89)
6	*p*-Br	40	10	95	92 (87)
7	*p*-F	40	10	95	90 (83)
8	*p*-CN	40	12	100	99 (95)
9	*p*-COMe	40	5	100	97 (91)
10	*p*-COOMe	40	9	97	94 (86)

[a] Reaction conditions: 1 mmol nitroarene, 1 mol% Au, 0.5 equiv. KOH, 5.0 mL 2-propanol, 5.0 mL water, 1atm N_2. [b] Conversion and yields were determined by GC using *n*-dodecane as the internal standard; values in parenthesis are the yields of the isolated products.

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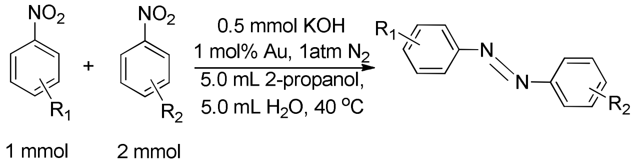
Having established the optimal catalytic system and reaction conditions for formation of azobenzene from nitrobenzene, other nitroarenes were investigated. As shown in Table 3, a range of nitroarenes were selectively transformed into the corresponding azoarenes. Again, the reaction activity is highly dependent on the electronic and steric properties of the substituent. Generally, the nitroarenes containing an electron-donating substituent on the benzene ring is more active than the nitroarenes containing an electron-withdrawing substituent (Table 3, entries 2-10). For example, a higher reaction temperature and longer reaction time is necessary for the *p*- or *m*-chlorine-containing nitrobenzene compared with the *p*- of *m*-CH_3-containing nitrobenzene (Table 3, entries 2-5). Furthermore, 4-nitrobenzonitrile, 4-nitroacetophenone and 4-nitrobenzoic acid methyl ester can also be converted to the desired azo compounds, without reduction of C=O or C≡N groups. In contrast to the previously reported catalytic systems, such as Au/ZrO_2 photocatalyst,[3c] worm-like nano-Pd,[3b] ultra-thin Pt nano- wires,[3a] or Ru/C[6a], the present Au-based protocol represents the most mild and efficient system for convenient and controlled synthesis of azoarenes directly from nitroarenes to date.

Encouraged by the excellent yields of the reductive self-coupling of nitroarenes, an effort was initiated to explore the feasibility of using the Au/meso-CeO_2-mediated protocol to produce asymmetrical azoarenes by the transfer hydrogenative cross-coupling of two different nitroarenes. To this end, we have set out to prepare three representative asymmetrical azoarenes with potential applications in dyes,[13] liquid crystals,[14] or optical storage media,[15] respectively. In a preliminary experiment, the reaction was carried with an equimolar mixture of **1a** and 4-chloronitrobenzene. A mixture of azoarenes, namely **3a** and 4-chloroazobenzene was obtained in 61% and 33% yields, respectively, based on **1a** conversion (Scheme S1 in ESI†). Formation of 4-chloroazobenzene corresponds to the cross coupling of N-phenylhydroxylamine, the possible and most reasonable pathway according to the literature,[8a] with 4-chloronitrosobenzene. Meanwhile, the more reactive **1a** favoured the preferential formation of self-coupling product of **3a**. To optimize the reaction further, the reaction was carried out in the presence of two equivalents of 4-chloronitrobenzene. In this case, the selectivity towards asymmetric 4-chloroazobenzene increased remarkably, and a high yield up to 87% was achieved. By using this newly established procedure, three asymmetrical azoarenes with industrial interest were successfully synthesized with moderate to good yields (see Scheme 1).

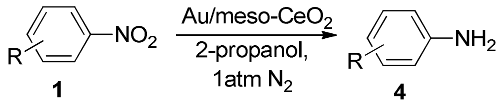
It is noteworthy that this simple Au-based transfer reduction method could also be applied to prepare anilines via the reduction of aromatic nitrobenzene. After carefully tuning the reaction conditions, we found that when the substrate **1a** was treated at a higher reaction temperature (80 °C) without introducing any base additives, the desired aniline (**4a**) could be obtained with excellent yield (Table 1, entries 11, 12). The scope of this new Au-based reduction protocol was established by using a wide range of nitroarenes with various reducible functional groups such as halogens, nitrile, ketone, or ester and in many cases the reaction was completed within 3-10 h with high yields (Table 4).



R_1=H, R_2=*p*-Cl; t=11 h; 87% yields based on $PhNO_2$;
R_1=H, R_2=*p*-$COCH_3$; t=13 h; 79% yields based on $PhNO_2$;
R_1=*m*-CH_3, R_2=*p*-Cl; t=9 h; 77% yields based on *m*-CH_3PhNO_2

Scheme 1. Direct synthesis of asymmetrical azobenzenes from different nitroarenes.

Table 4 Synthesis of anilines from different nitroarenes.[a]



Entry	R	T (°C)	t (h)	Conv. (%)[b]	Yield (%)[b]
1	H	80	3	>99	98
2	*p*-CH_3	80	5	>99	99
3	*m*-CH_3	80	5	92	91
4	*p*-Cl	90	8	>99	99
5	*m*-Cl	80	7	98	98
6	*p*-Br	80	10	96	96
7	*p*-F	80	10	94	94
8	*p*-CN	80	8	96	95
9	*p*-COMe	60	6	>99	99
10	*p*-COOMe	60	10	95	95

[a] Reaction conditions: 1 mmol nitroarene, 1 mol% Au, 5.0 mL 2-propanol, 5.0 mL water, 1 atm N_2. [b] Conversion and yields were determined by GC using *n*-dodecane as the internal standard.

The stability and reusability of the catalyst were tested in the reduction of **1a** to **2a**. It was found that the activity of the catalyst can be maintained even after 3 times of reuse, and the selectivity for **2a** was still up to 98% (Table 1, entry 4). Inductively coupled plasma atomic emission spectral (ICP-AES) analysis results showed that there was no leaching of gold during the reaction, verifying the inherent stability of the Au/meso-CeO_2 catalyst. XRD, HRTEM and XPS results confirmed no change in the dispersion of the Au NPs or metallic state of Au before and after reuse, which was in good agreement with an excellent activity retention of this catalyst (see Figures 1-3 and Table S3 in ESI†). Although the precise route and mechanism by which the reduction occurs are not yet fully understood, the transient Au-H species formed by the interaction with the hydrogen donor could be involved at the initial stage of the reaction.[9c] A plausible reaction pathway, consistent with the generally accepted Harber mechanism proposed for electrochemical hydrogenation of nitrobenzene and its derivatives,[16] is depicted in Scheme 2. In general, the nitro group of the substrate is firstly attacked by the

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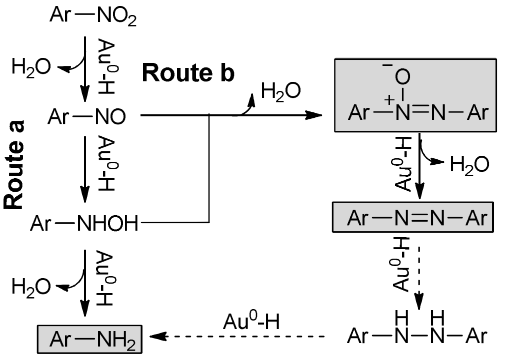

Scheme 2. A plausible reaction pathway for the reduction of nitrobenzene.

metal-hydride, leading to a direct hydride transfer from the 2-propanol to the reactant. At elevated temperatures and base-free conditions, the formation of anilines from nitrobenzenes proceeds smoothly via the intermediate formation of nitrosobenzene/N-phenylhydroxylamine molecules (Route a). A switch of the major reaction path way might occur, provided that suitable amount of KOH is introduced into the reaction system. Depending on the concentration of the aqueous 2-propanol and reaction temperature, either azoxybenzenes or azobenzenes can be selectively obtained in good to excellent yields (Route b). In the overall process, the fact that the reduction capability of the Au-H species can be finely tuned by optimising the reaction conditions is essential for controlling the reduction of the nitro group at different intermediate stages.

Conclusions

We have developed a highly efficient and flexible heterogeneous gold-catalyzed approach for controlled and chemoselective reduction of nitroarenes into three different target products of industrial importance. An essential feature of the present Au-based methodology is that the switchable products, including azoxy-, azo- and aniline compounds can be selectively obtained in high yields by simply varying the reaction conditions. We expect this method to be useful in the synthesis of more complex molecules by optimizing the step-economy in synthesis planning.

Experimental

General

Gold catalysts including 1 wt% Au/Al$_2$O$_3$ (Strem catalogue number: 79-0160), 1 wt% Au/TiO$_2$ (Strem catalogue number: 79-0165), and 1 wt% Au/ZnO (Strem catalogue number: 79-0170) were supplied by Mintek. 4.5 wt% Au/Fe$_2$O$_3$ (type C, lot no. Au/Fe$_2$O$_3$ no. 02-5) was supplied by the World Gold Council (WGC). Palladium chloride (PdCl$_2$), hexachloroplatonic acid hexahydrate (H$_2$PtCl$_6$·6H$_2$O), ruthenium chloride hydrate (RuCl$_3$·xH$_2$O), and chloroauric acid tetrahydrate (HAuCl$_4$·4H$_2$O), were supplied by Aldrich and used without further purification.

Catalyst preparation

Preparation of mesostructured ceria materials: Meso-CeO$_2$ was prepared by a template-assisted precipitation method.[10, 11] Typically, a NaOH solution (2 g in 300 mL of distilled water) was added to a stirred solution of Ce(NO$_3$)$_3$·6H$_2$O (4.34 g) and CTAB (2.19 g) in 200 mL distilled water at room temperature. The mixture was then maintained in a sealed glass vessel under stirring for 24 h. After thermal aging at 90 °C for 3 h, the pale yellow precipitate was filtered and washed with hot water (80 °C) to remove the residual CTAB. The resultant powder was dried at 100 °C for 6 h and then calcined at 450 °C for 4 h. The Brunauer-Emmett-Teller (BET) surface area of the as-synthesized meso-CeO$_2$ was 150 m^2·g^{-1}.

Preparation of Au/CeO$_2$ catalysts: Au/CeO$_2$ catalysts were prepared by a routine deposition-precipitation (DP) method.[10] An appropriate amount of aqueous solutions of chloroauric acid (HAuCl$_4$) was heated to 70 °C under vigorous stirring. The pH was adjusted to 9 by dropwise addition of NaOH (0.2 M), and then 1.0 g of CeO$_2$ powders (Evonic, Adnano 50, specific surface area: 50 m^2·g^{-1}) or meso-CeO$_2$ was dispersed in the solution. The mixture was aged for 1 h, followed by filtering and washing several times with deionized water to remove Cl$^-$. The resulting solid product was dried overnight before reduction at 300 °C for 2 h in 5 vol% H$_2$/Ar. The two catalysts were designated as Au/CeO$_2$-50 and Au/meso-CeO$_2$, respectively. The gold loading of the as-prepared catalysts was 0.49 wt% Au/CeO$_2$-50 and 0.5 wt% Au/meso-CeO$_2$ as determined by ICP-AES.

Preparation of Au/ZrO$_2$ catalyst: ZrO$_2$ powders were prepared by a conventional precipitation method following the reported procedure.[17] Au/ZrO$_2$ catalysts were prepared by a modified deposition-precipitation (DP) method by mixing ZrO$_2$ powders (2 g) with appropriate amounts of aqueous solutions of chloroauric acid (100 mL, 1 mM), the pH was adjusted to 9.0 by dropwise addition of 0.25 M NH$_4$OH. After 6 h stirring at 25 °C the catalyst was washed five times with deionized water and separated by filtration. The samples were dried at 110 °C in a forced air oven for 1 h, followed by reduction with a stream of 5 vol% H$_2$/Ar at 350 °C for 2 h. The BET surface area of the resultant Au/ZrO$_2$ catalyst was 113 m^2·g^{-1}. The concentration of gold in Au/ZrO$_2$ was 0.8 % Au by weight.

Preparation of Pt/meso-CeO$_2$, Pd/meso-CeO$_2$ and Ru/meso-CeO$_2$ catalysts: 1 wt% Pt/meso-CeO$_2$, 1 wt% Pd/meso-CeO$_2$ and 1 wt% Ru/meso-CeO$_2$ catalysts were prepared by incipient-wetness impregnation of the support, with aqueous solution of H$_2$PtCl$_6$·6H$_2$O, PdCl$_2$, and RuCl$_3$·xH$_2$O precursors of appropriate concentrations (typically 1.0 mL/g support). After a perfect mixing of the corresponding slurries, samples were dried under vacuum at room temperature for 12 h and then reduced in 5% H$_2$/Ar at 400 °C for 2 h.

Catalyst characterization

Elemental analysis: The Au loading of the catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer. The detection limit for Au is 7 ppb.

BET analysis: The BET specific surface areas of the prepared catalysts were determined by adsorption-desorption of nitrogen at liquid nitrogen temperature, using a Micromeritics TriStar 3000 equipment. Sample degassing was carried out at 300 °C prior to acquiring the adsorption isotherm.

X-ray diffraction (XRD) analysis: The crystal structures of mesostructured CeO$_2$ were characterized with powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer using the Ni-filtered Cu Kα radiation source at 40 kV and 40 mA.

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X-ray photoelectron spectroscopy (XPS): XPS data were recorded with a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The spectrometer was operated at 15 kV and 20 mA, and a magnesium anode (Mg Kα, hν = 1253.6 eV) was used. The C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (BE).

Transmission electron microscopy (TEM): A JEOL 2011 microscope operating at 200 kV equipped with an EDX unit (Si(Li) detector) was used for the TEM. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids.

High resolution transmission electron microscopy (HRTEM): HRTEM images for catalysts were taken with a JEM-2100F electron microscope operating at 200 kV. The size distribution of the metal nanoclusters was determined by measuring about 200 random particles on the images.

Catalytic activity test

General procedure for azoxy-, azox-, and aniline compounds synthesis via Gold-Catalyzed Reduction of Nitroarenes: Supported gold catalyst (1.97 mg Au, 0.01 mmol) was placed in a 25 mL two-neck flask, adding nitroarenes (1 mmol), a certain amount of KOH, 2-propanol and water. The reaction mixture was then vigorously stirred (800 rpm with a magnetic stir bar) at the designed temperature under 1 atm of N_2 atmosphere for the given reaction time. After completion of the reaction, the reaction mixture was filtered and the catalyst was washed thoroughly with ethanol. Then the filtrate was concentrated and dried under reduced pressure using a rotatory evaporator. The crude product was purified by column chromatography [silica 200–300; petroleum ether (60~90 ^{o}C)/ethyl acetate mixture] to afford the product. All the products were characterized identified by GC-MS and the spectra obtained were compared with the standard spectra. The conversion and yields were determined by GC-17A gas chromatograph equipped with a HP-FFAP column (30 m × 0.25 mm) and a flame ionization detector (FID).

Recovery and reuse of Au/meso-CeO$_2$: The catalyst was collected after filtration washed with acetone for three times and then with distilled water for several times. The catalyst was then dried at 100 ^{o}C for 12 h before used for next reaction.

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Notes and references

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† Electronic Supplementary Information (ESI) available: experimental data, TEM, ^{1}H and ^{13}C NMR data. See DOI: 10.1039/b000000x/0

1 (*a*) H.-U. Blaser, H. Steiner and M. Studer, *ChemCatChem*, 2009, **1**, 210; (*b*) S. Nishimura, *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*, Wiley, Chichester, 2001, pp. 315-387; (*c*) J. P. Adams and J. R. Paterson, *J. Chem. Soc. Perkin Trans. 1*, 2000, 3695; (d) D. H. Rosenblatt and E. P. Burrows, *The Chemistry of Amino, Nitroso and Nitro Compounds and their Derivatives*, Wiley-VCH, Chichester, 1982, pp 1085; (e) J. van der Veen and A. H. Grobben, US patent 3907768, 1975.

2 (*a*) F. A. Khan and C. Sudheer, *Tetrahedron Lett.*, 2009, **50**, 3394; (*b*) Y. Lu, J. Liu, G. Diffee, D. Liu and B. Liu, *Tetrahedron Lett.*, 2006, **47**, 4597; (*c*) D. K. Dutta, *Synth. Commun.*, 2006, 36, 1903; (*d*) J. R. Hwu, A. R. Das, C. W. Yang, J.-J. Huang and M.-H. Hsu, *Org. Lett.*, 2005, **7**, 3211; (*e*) S. Wada, M. Urano and H. Suzuki, *J. Org. Chem.*, 2002, **67**, 8254; (*f*) P. Ren, S. Pan, T. Dong and S.Wu, *Synth. Commun.*, 1996, **26**, 3903.

3 (*a*) L. Hu, X. Cao, L. Chen, J. Zheng, J. Lu, X. Sun and H. Gu, *Chem. Commun.*, 2012, **48**, 3445; (*b*) L. Hu, X. Cao, L. Shi, F. Qi, Z. Guo, J. Lu and H. Gu, *Org. Lett.*, 2011, **13**, 5640; (*c*) H. Zhu, X. Ke, X. Yang, S. Sarina and H. Liu, *Angew. Chem., Int. Ed.*, 2010, **49**, 9657; (*d*) A. Grirrane, A. Corma and H. García, *Science*, 2008, 1661; (*e*) Y. Moglie, C. Vitale and G. Radivoy, *Tetrahedron Lett.*, 2008, **49**,1828; (*f*) G. R. Srinivasa, K. Abiraj and D. C. Gowda, *Synth. Commun.*, 2006, **33**, 4221; (*g*) G. R. Srinivasa, K. Abiraj and D. C. Gowda, *Tetrahedron Lett.*, 2003, **44**, 5835.

4 (*a*) D. Cantillo, M. Baghbanzadeh and C. O. Kappe, *Angew. Chem., Int. Ed.*, 2012, **51**, 10190; (*b*) L. Huang, P. Luo, W. Pei, X. Liu, Y. Wang, J. Wang, W. Xing and J. Huang, *Adv. Synth. Catal.*, 2012, **354**, 2689; (*c*) K. Layek, M. L. Kantam, M. Shirai, D. N.-Hamane, T. Sasaki and H. Maheswaran, *Green Chem.*, 2012, **14**, 3164; (*d*) R. Dey, N. Mukherjee, S. Ahammed and B. C. Ranu, *Chem. Commun.* 2012, **48**, 7982; (*e*) I. Sorribes, G. Wienhöfer, C. Vicent, K. Junge, R. Llusar and M. Beller, *Angew. Chem. Int. Ed.*, 2012, **51**, 7794; (*f*) P. Lou, K. Xu, R. Zhang, L. Huang, J. Wang, W. Xing and J. Huang, *Catal. Sci. Technol.*, 2012, **2**, 301; (*g*) K. Imaamura, K. Hashimoto and H. Kominami, *Chem. Commun.*, 2012, **48**, 4356; (*h*) M. Makosch, J. Sá, C. Kartusch, G. Richner, J. A. van Bokhoven and K. Hungerbühler, *ChemCatChem*, 2012, **4**, 59; (*i*) G. Wienhöfer, I. Sorribes, A. Boddien, F. Westerhaus, K. Junge, H. Junge, R. Llusar and M. Beller, *J. Am. Chem. Soc.*, 2011, **133**, 12875; (*j*) Y. Motoyama, Y. Lee, K. Tsuji, S.-H. Yoon, I. Mochida and H. Nagashima, *ChemCatChem*, 2011, **3**, 1578; (*k*) L. He, L. C. Wang, H. Sun, J. Ni, Y. Cao, H. Y. He and K. N. Fan, *Angew. Chem. Int. Ed.*, 2009, **48**, 9538; (*l*) L. Liu, B. Qiao, Z. Chen, J. Zhang and Y. Deng, *Chem. Commun.*, 2009, 653; (*m*) A. Corma, P. Serna and H. Garcia, *J. Am. Chem. Soc.*, 2008, **130**, 8748; (*n*) A. Corma and P. Serna, *Science*, 2006, **313**, 332.

5 (*a*) N. A. Afagh and A. K. Yudin, *Angew. Chem. Int. Ed.*, 2010, **49**, 262-310; (*b*) N. Z. Burns, P. S. Baran and R. W. Hoffmann, *Angew. Chem., Int. Ed.*, 2009, **48**, 2854.

6 (*a*) J. H. Kim, J. H. Park, Y. K. Chung and K. H. Park, *Adv. Synth. Catal.*, 2012, **354**, 2412; (*b*) N. Sakai, K. Fujii, S. Nabeshima, R.Ikeda and T. Konakahara, *Chem. Commun.*, 2010, **46**, 3173; (*c*) D. D. Laskar, D. Prajpati and J. S. Sandhu, *J. Chem. Soc., Perkin Trans. 1*, 2000, 67.

7 (*a*) M. Stratakis and H. Garcia, *Chem. Rev.*, 2012, **112**, 4469; (*b*) T. Mallst and A. Baiker, *Annu. Rev. Chem. Biomol. Eng.*, 2012, **3**, 11; (*c*) Della Pina, E. Falletta, L. Prati and M. Rossi, *Chem. Soc. Rev.*, 2008, **37**, 2077; (*d*) A. Corma and H. Garcia, *Chem. Soc. Rev.*, 2008, **37**, 2096-2126; (*e*) A. S. K. Hashmi and G. J. Hutchings, *Angew. Chem. Int. Ed.*, 2006, **45**, 7896; (*f*) F. Z. Su, Y. M. Liu, L. C. Wang, Y. Cao, H. Y. He and K. N. Fan, *Angew. Chem., Int. Ed.*, 2008, **47**, 334.

8 (*a*) A. Corma, P. Concepción and P. Serna, *Angew. Chem. Int. Ed.*, 2007, **46**, 7266; (*b*) M. Boronat, P. Concepción, A. Corma, S. Gonzalez, F. Lllas and P. Serna, *J. Am. Chem. Soc.*, 2007, **129**, 16230.

9 (*a*) X. B. Lou, L. He, Y. Qian, Y. M. Liu, Y. Cao and K. N. Fan, *Adv. Synth. Catal.*, 2011, **353**, 281; (*b*) L. He, F. J. Yu, X. B. Lou, Y. Cao H. Y. He and K. N. Fan, *Chem. Commun.*, 2010, **46**, 1553; (*c*) F. Z. Su, L. He, J. Ni, Y. Cao, H. Y. He and K. N. Fan, *Chem. Commun.*, 2008, 3531.

10 M. M. Wang, L. He, Y. M. Liu, Y. Cao, H. Y. He and K. N. Fan, *Green Chem.*, 2011, **13**, 602.

View Article Online
DOI: 10.1039/C3CY00533J

11 B. Campo, G. Santori, C. Petit and M. A. Volpe, *Appl. Catal., A*, 2009, **359**,79.

12 Note that the solvent plays a vital role in reactants adsorption or products desorption. The concentration of aqueous 2-propanol may favor the adsorption of azoxybenzene on the surface of Au catalyst, facilitating the azobenzene formation. See: F. Figueras and B. Cop, *J. Mol. Catal. A: Chemical*, 2001, **173**, 223.

13 K. Hunger, *Industrial dyes: Chemistry, Properties, Applications*, Wiley, Chichester, 2007.

14 Y. Zhao and T. Ikeka, *Smart Light-Responsive Materials: Azobenzene-Containing Polymers and Liquid Crystals,* Wiley, Chichester, 2009.

15 T. Ikeda and O. Tsutumi, *Science*, 1995, **268**, 1873.

16 F. Haber, *Z. Elektrochem.* 1898, **4**, 506.

17 X. L. Du, Q. Y. Bi, Y. M. Liu, Y. Cao, H. Y. He and K. N. Fan, *Green Chem.*, 2012, **14**, 935.

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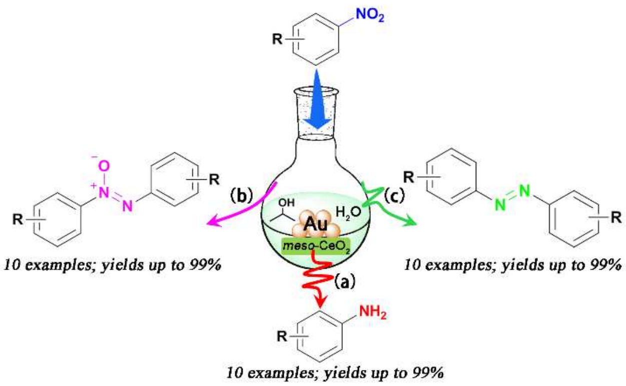
Graphical Abstract

Mild, Selective and Switchable Transfer Reduction of Nitroarenes Catalyzed by Supported Gold Nanoparticles

Xiang Liu, Sen Ye, Hai-Qian Li, Yong-Mei Liu, Yong Cao,* and Kang-Nian Fan



A highly efficient mesostructured ceria-supported gold catalyst system has been developed for controlled and selective transfer reduction of nitroarenes into azoxyarenes, azoarenes, or anilines with good to excellent yields using 2-propanol as a hydrogen resource under mild conditions.