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## Deoxygenative coupling of nitroarenes for the synthesis of aromatic azo compounds with CO using supported gold catalysts†

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**A facile and efficient catalytic system based on a mesostructured ceria-supported gold (Au/meso-CeO<sub>2</sub>) catalyst was developed for the synthesis of various aromatic azo compounds by the reductive coupling of the corresponding nitroaromatics, using CO as the sole deoxygenative reagent, under additive-free and mild reaction conditions.**

Azo compounds constitute one of the largest classes of industrially synthesized organic compounds and are important intermediates for dyes, food additives, radical reaction initiators, and therapeutic agents because of their widespread and diverse biological activities.<sup>1</sup> Especially, those with aromatic substituents are known to serve as useful precursors to various products that have found numerous applications in materials science.<sup>2</sup> Despite many known methods,<sup>3</sup> there is an ongoing interest in the development of convenient and general protocols for the synthesis of these compounds. Hence, novel approaches such as copper-catalyzed oxidation of aromatic amines and a two-step, one-pot conversion of nitro compounds *via* the intermediacy of the corresponding anilines have been recently developed.<sup>4</sup> Despite all these achievements, the direct reductive coupling of readily available nitroarenes represents the most straightforward route to this class of compounds. In this regard, H<sub>2</sub> gas is undoubtedly one of the most attractive and popular means to effect reduction, thereby leading to a number of catalytic hydrogenative coupling procedures of nitroarenes.<sup>5</sup> However, it should be noted that the use of H<sub>2</sub> is not perfectly atom-economical as it might seem, given that current industrial production of H<sub>2</sub> relies overwhelmingly on fossil fuels and the fact the associated emissions have led to a net increase in the atmospheric CO<sub>2</sub> levels.<sup>6</sup> Moreover, the necessity for special handling of highly flammable H<sub>2</sub> gas and/or the requirement of external base additives to achieve an acceptable

level of selectivity has diminished the ultimate appeal and utility of these procedures.

So far, much less attention has been paid to the direct reductive coupling of nitroarenes to give azo compounds by exploiting carbon monoxide (CO) as an effective reagent. As one of the cheapest C<sub>1</sub> sources in the chemical industry, CO is now heavily used in a number of highly selective syntheses of a wide range of chemicals and fuels.<sup>7</sup> Aside from being a very useful C<sub>1</sub> building block, CO is also known to act as a reductant.<sup>8</sup> The use of CO instead of hydrogen gas or other hydrogen donor agents is particularly interesting in light of the fact that CO is produced in multiton quantities as a byproduct of the steel industry and thus represents an abundant source for chemical reduction.<sup>9,10</sup> However, most of such reductions proceed *via* the water-gas shift reaction (CO + H<sub>2</sub>O = H<sub>2</sub> + CO<sub>2</sub>) and therefore utilize hydrogen as the terminal reductant.<sup>11</sup> While conceptually more attractive in the context of without using an external hydrogen source, the potential of using CO as the sole reductant to obtain aromatic azo compounds from corresponding nitroarenes remains largely unexplored. In an early report on the interaction of CO with nitrocompounds in the absence of a catalyst, the conversion of nitroarenes into azo derivatives with yields up to 97.5% was achievable, but an exceptionally high CO pressure (3000 atm) was required.<sup>12</sup> A subsequent followup study in the 1960s showed that the reductive coupling of nitroarenes can take place in anhydrous benzene at 200 °C and a CO pressure of 200 atm by employing Fe(CO)<sub>5</sub> as the catalyst.<sup>13</sup> However, this system is not adequately effective and not very selective since only moderate yields of the corresponding azo derivatives in the range of 40–80% can be attained.

There is considerable current interest in the development of more benign organic synthesis methods facilitated by supported gold nanoparticles (NPs), which have emerged over the last decade as a promising new class of green catalytic materials to meet the ever-increasing demand for a clean and resource-efficient chemical synthesis.<sup>14</sup> As part of our continuing investigation into reduction chemistry by supported Au NPs, we recently reported the outstanding catalytic ability of Au NPs for the deoxygenation of nitroaromatics to anilines as well as epoxides to their corresponding

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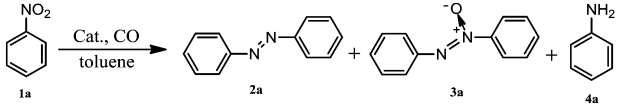
olefin compounds using CO/H<sub>2</sub>O as a reducing reagent.<sup>11b,e</sup> In such deoxygenation, a Au-hydride species was generated *in situ* from the reaction of H<sub>2</sub>O with CO, which led to highly chemoselective reduction. Being aware of the advantages of adopting the Au-based deoxygenation protocols and also utilizing the excellent catalytic activity of supported gold toward CO activation and related transformations,<sup>14</sup> we envisaged that the selective deoxygenation of nitroaromatics accompanied by the formation of the azo linkage in the reduced products would be plausible *via* gold-catalyzed deoxygenative couplings under a CO atmosphere and anhydrous conditions.

Herein we report the first demonstration of the efficient catalytic reductive coupling of nitroarenes under mild CO pressures, facilitated by a Au catalyst supported on mesostructured CeO<sub>2</sub> (*meso*-CeO<sub>2</sub>) featuring high redox capacities. The present catalytic system is highly effective in that turnover numbers (TONs) of up to ~2000 can be achieved, and is workable on a large scale. Even under atmospheric conditions, the catalytic activity of the *meso*-CeO<sub>2</sub> supported Au is much greater than those of previously reported systems requiring high CO pressures.<sup>13</sup> In addition, this new process works under mild conditions and enables the selective deoxygenative coupling of a wide range of functionalized nitroarenes while leaving other reducible or thermally labile functional groups intact.

To assess the viability of the proposed reaction, we first explored the conversion of nitrobenzene (**1a**) under mild processing conditions, *i.e.*, 5 atm of CO pressure in toluene at 150 °C. We initially examined the reduction of **1a** over a benchmark Au/TiO<sub>2</sub> catalyst (average Au particle size ~2.8 nm, Fig. S1a, ESI†), which has been widely studied and proven to be highly active for a large variety of functional group transformations.<sup>11b,e-g</sup> It is not surprising that aniline (**4a**) formation competes with the desired reductive coupling in a standard nondry toluene solvent (Table 1, entry 1). However, the use of freshly distilled toluene minimises the formation of **4a** (entry 2), and the appreciable formation of azobenzene (**2a**) and azoxybenzene (**3a**) with the overall yield of a modest 25% being attained. This result was encouraging and led us to further examine gold deposited on a series of other mineral supports such as Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, ZnO, ZrO<sub>2</sub> and hydrotalcite (HT, layered double Mg–Al hydroxide). These catalysts, however, were not found to be particularly active, and in most cases the unwanted **3a** was obtained predominantly (entries 3–7). Interestingly, when applying a commercial ultrafine ceria (Evonik Adnano 50) supported gold catalyst (Au/CeO<sub>2</sub>-50, average Au particle size ~3.3 nm, Fig. S1b, ESI†), appreciable levels of reductive coupling activity was observed, thus furnishing the desired **2a** in a favorable selectivity of approximately 58% at full **1a** conversion (Table 1, entry 8). A systematic study of the catalyst was then accomplished using a set of Au/CeO<sub>2</sub> samples with varied ceria specific surface areas ranging from 50 to 140 m<sup>2</sup> g<sup>-1</sup> (entries 8–10). To our delight, it was found that an excellent yield of **2a** of about 99% could be attained with a catalyst composed of gold deposited on *meso*-CeO<sub>2</sub> (*S*<sub>BET</sub> ~ 139 m<sup>2</sup> g<sup>-1</sup>, Fig. S2, ESI†) (entry 10).

In a scaled-up reaction at gram quantity (**1a**, 20 mmol), the Au/*meso*-CeO<sub>2</sub> catalyst provided a high isolated yield (96%) of

**Table 1** Deoxygenative coupling of nitrobenzene to azobenzene with CO in the presence of various catalysts<sup>a</sup>



Entry	Catalyst	Time (h)	Conv. <sup>b</sup> (%)	Sel. <sup>b</sup> (%)		
				2a	3a	4a
1 <sup>c</sup>	Au/TiO <sub>2</sub>	5	27	24	45	31
2	Au/TiO <sub>2</sub>	5	26	34	64	2
3	Au/Fe <sub>2</sub> O <sub>3</sub>	5	17	17	81	2
4	Au/Al <sub>2</sub> O <sub>3</sub>	5	28	86	10	4
5	Au/ZnO	5	37	77	18	5
6	Au/ZrO <sub>2</sub>	5	8	14	83	3
7	Au/HT	5	12	11	88	1
8	Au/CeO <sub>2</sub> -50	5	100	58	40	2
9	Au/CeO <sub>2</sub> -90	5	100	84	15	1
10	Au/ <i>meso</i> -CeO <sub>2</sub>	5	100	99	0	1
11 <sup>d</sup>	Au/ <i>meso</i> -CeO <sub>2</sub>	5	100	14	85	1
12 <sup>e</sup>	Au/ <i>meso</i> -CeO <sub>2</sub>	11	100	98	0	2
13 <sup>f</sup>	Au/ <i>meso</i> -CeO <sub>2</sub>	5	8	8	92	0
14 <sup>g</sup>	<i>meso</i> -CeO <sub>2</sub>	5	67	4	96	0

<sup>a</sup> Reaction conditions: 2.0 mmol **1a**, anhydrous toluene (5 mL) and Au 0.5 mol% at 150 °C under 5 atm of CO. <sup>b</sup> GC analysis using *tert*-butylbenzene as an internal standard. <sup>c</sup> As-received toluene from Aldrich. <sup>d</sup> 120 °C. <sup>e</sup> 1 atm of CO. <sup>f</sup> 5 atm of N<sub>2</sub> instead of CO. <sup>g</sup> 250 mg *meso*-CeO<sub>2</sub> was used.

the corresponding azo product (see Scheme S1, ESI†). In this case, a TON as high as 2000 was achieved, a value which is significantly higher than those obtained with previously reported systems requiring high CO pressure (Fe(CO)<sub>5</sub><sup>13</sup>; TON 20). These results indicated that Au/*meso*-CeO<sub>2</sub> constituted a practical catalyst for the deoxygenative coupling of nitroarenes producing azobenzenes amenable to gram-operations. After the reaction, the Au/*meso*-CeO<sub>2</sub> sample could be easily recovered by filtration using toluene as a solvent. Inductively Coupled Plasma (ICP) analysis confirmed that no Au was present in the filtrate (detection limit: <7 ppb), indicating that the observed catalysis is truly heterogeneous. Furthermore, the recovered Au/*meso*-CeO<sub>2</sub> can also be reused at least five times without an appreciable loss of activity (see ESI†), thus further demonstrating the utility of Au/*meso*-CeO<sub>2</sub> for achieving reductive coupling of nitro compounds, with catalyst loadings that are orders of magnitude lower than what have been previously employed for this transformation under additive-free conditions. In addition, the X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) confirmed almost no change in the dispersion of the Au or the metallic state of Au before and after reuse (see ESI†). These results are in good agreement with an excellent retention of the activity of this catalyst.

Consistent with the case identified for catalytic deoxygenation of nitroarenes to anilines using CO/H<sub>2</sub>O,<sup>11b,e-g</sup> we found that gold is exceedingly active for reductive coupling of nitroarenes with CO compared with other noble metals (Table S1, entries 1–5, ESI†). Subsequent experiments focused on the effect of the reaction temperature revealed that under otherwise identical reaction conditions the Au/*meso*-CeO<sub>2</sub> exhibited dramatically diminished the production of **2a** at 120 °C (Table 1, entry 11).

Upon solvent screening it was found that the reaction catalyzed by Au/*meso*-CeO<sub>2</sub> proceeded efficiently in a variety of solvents, with the highest rate reached in anhydrous toluene (Table S2, ESI†). Furthermore, it is revealed that the reaction can proceed smoothly even at atmospheric pressure, although a longer reaction time was required (entry 12). The reaction also proceeded under an inert atmosphere of N<sub>2</sub>, although the reaction rate decreased significantly with **3a** being formed as the major product (entry 13). In contrast, when replacing CO with H<sub>2</sub>, **4a** is formed preferentially even at low **1a** conversion levels (Table S3, ESI†).<sup>15</sup> We also tested other gold-based precursors or materials such as HAuCl<sub>4</sub>, Au<sub>2</sub>O<sub>3</sub> and bulk Au<sup>0</sup> powder (mean particle size, *ca.* 150 nm), but all of them gave no conversion (Table S1, ESI†). At this juncture, it is interesting to note that Au-free *meso*-CeO<sub>2</sub> can deliver appreciable reduction of **1a**, despite the fact that only the intermediate product of **3a** was formed predominantly (entry 14). Taken together, these results show that the combination of CO and Au NPs strongly associated with *meso*-CeO<sub>2</sub> is essential for achieving a high catalytic activity for selective reductive coupling of **1a** into **2a** under mild conditions.

With these promising results in hand, a variety of simple and readily available nitrobenzenes were further examined to demonstrate the general applicability of this novel CO-mediated catalytic system (Table 2). Both steric and electronic properties of the substituents in nitroarenes affect the coupling reaction significantly. Generally, nitrobenzenes containing a substituent on the aromatic ring mostly require a longer reaction time. The yields of *m*-substituted azo arenes were somewhat higher than those for the corresponding *o*- or *p*-substituted nitroarenes (Table 2, entries 3–7). The nitroaromatics bearing electron-withdrawing groups are converted smoothly and selectively into the desired products with good to excellent yields (74–91%) (entries 2–9). Electron-donating substituted nitroaromatics, such as 1-methyl-4-nitrobenzene and 1-methyl-3-nitrobenzene, also formed the corresponding azo compounds in good yields after 22 and 8 hours, respectively, of the reaction (entries 10 and 11). Furthermore, asymmetrical aromatic azo compounds, having a high value as key intermediates for prodrugs and liquid crystals, could also be synthesized with moderate yields upon using two different substituted nitroarenes as the reactants (Table S5, ESI†).<sup>16</sup>

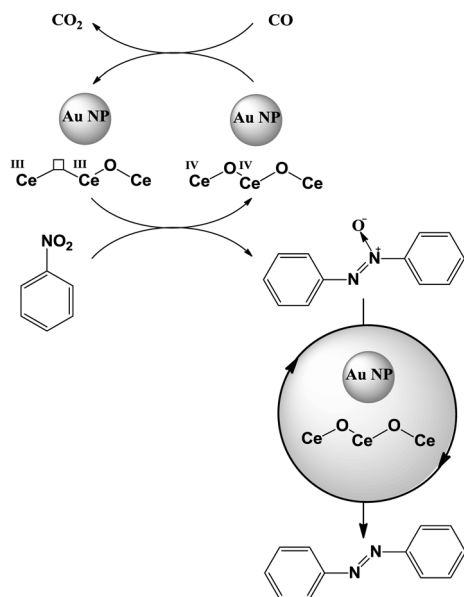
Taking into account the previous mechanistic investigation on related systems<sup>17</sup> and our experimental observations, a proposed surface-redox reaction pathway involving the Ce<sup>4+</sup>/Ce<sup>3+</sup> couple through cooperation between gold and the CeO<sub>2</sub> support is depicted in Scheme 1. The first step involves fast CO-induced catalyst reduction *via* abstraction of the lattice oxygen at the Au/CeO<sub>2</sub> perimeter interface to produce an oxygen vacancy. Subsequent deoxygenative coupling of the nitro group of **1a** occurring on the resultant vacancy sites provides the azoxybenzene, which then undergoes a further deoxygenation to give the azobenzene species,<sup>15,18</sup> thereby completing the catalytic cycle. This redox-coupling route is well supported by the following results: (1) an evaluation of the material redox behavior by CO-temperature-programmed reduction (CO-TPR) measurements revealed that the reactive removal of the surface

Table 2 Au/*meso*-CeO<sub>2</sub> catalyzed deoxygenative coupling of nitroarenes to give symmetric azo compounds<sup>a</sup>

Entry	Products	Time (h)	Yield <sup>b</sup> (%)
1			
1		5	99 (95)
2		33	74 (70)
3		15	91 (86)
4		28	85 (79)
5		5	91 (85)
6		28	74 (68)
7		16	86 (81)
8		20	86 (79)
9		15	79 (73)
10		22	86 (79)
11		8	92 (85)

<sup>a</sup> Reaction conditions: 2 mmol substrate, anhydrous toluene (5 mL), Au/*meso*-CeO<sub>2</sub> (Au 0.5 mol%) at 150 °C under 5 atm of CO. <sup>b</sup> GC yield using *tert*-butylbenzene as an internal standard. Numbers within parentheses refer to yields of isolated products.

oxygen from Au/CeO<sub>2</sub> occurred at much lower temperatures than other Au-based catalysts (Fig. S5, ESI†), thus verifying the distinguished deoxygenation activities of the Au/CeO<sub>2</sub> samples, (2) by monitoring the deoxygenation of **1a** with reaction time, we established that the reaction proceeds *via* the intermediacy of the azoxy compound,<sup>19</sup> indicative of a sequential deoxygenation



Scheme 1 Proposed mechanism for deoxygenative coupling of nitrobenzene with CO in the presence of Au/meso-CeO<sub>2</sub> as the catalyst.

pathway (Fig. S6, ESI<sup>†</sup>), and (3) a systematic study of the influence of the support surface areas in the Au/CeO<sub>2</sub>-based materials showed an excellent correlation between the oxygen storage capacity (OSC) and corresponding activity for selective **3a** deoxygenation (Fig. S7, ESI<sup>†</sup>), thus underscoring the importance of the greater surface oxygen mobility for facilitating the crucial CO-induced reductive coupling *via* a redox-mediated pathway.

In conclusion, we have successfully developed a facile and efficient gold-catalyzed approach for the synthesis of aromatic azo compounds directly from reductive coupling of the corresponding nitroarenes by using CO as the sole reductant. The reaction is very mild, general, scalable, and tolerant of various functionalities. This reductive coupling method, using a robust and reusable gold catalyst with the inexpensive and abundantly available CO as the appealing reductant under mild conditions, can make a significant contribution not only to reveal the synthetic potential of supported gold catalysts but also to establish a more benign and industrially viable process.

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