DOI: 10.1002/ange.201404543

Supported Catalysts

Gold-Catalyzed Direct Hydrogenative Coupling of Nitroarenes To Synthesize Aromatic Azo Compounds**

*Xiang Liu, Hai-Qian Li, Sen Ye, Yong-Mei Liu, He-Yong He, and Yong Cao**

Abstract: *The azo linkage is a prominent chemical motif which has found numerous applications in materials science, pharmaceuticals, and agrochemicals. Described herein is a sustainable heterogeneous-gold-catalyzed synthesis of azo arenes. Available nitroarenes are deoxygenated and linked selectively by the formation of N=N bonds using molecular H_2 without any external additives. As a result of a unique and remarkable synergy between the metal and support, a facile surface-mediated condensation of nitroso and hydroxylamine intermediates is enabled, and the desired transformation proceeds in a highly selective manner under mild reaction conditions. The protocol tolerates a large variety of functional groups and offers a general and versatile method for the environmentally friendly synthesis of symmetric or asymmetric aromatic azo compounds.*

Catalysis by supported gold has been intensively investigated in recent years, thus providing distinct reactivity, activity, and selectivity, all of which complement traditional platinum-group-metal (PGM) catalysis.[1] Gold has long been regarded to be catalytically inert. However, ever since the breakthrough discovery by Hutchings[2a] and Haruta et al.[2b] in the 1980s, it has become clear that gold, in its nanoscale form, is an active and often more selective catalyst than PGMs for a variety of reactions.[3] The activity of gold is typically attributed to a size effect, although in many cases the nature of the support also accounts for the superior effectiveness of the gold-based catalysts.[4] Recent advances in the understanding of catalysis by various gold-based nanostructures, and in particular the interplay between gold and the underlying support, have enabled new strategies to maximize the synthetic utility of particular gold catalysts and expand their catalytic applications in green synthetic chemistry.[5] In this regard, an integrated catalyst design, which relies on the synergy of the gold and support originating from the mutually beneficial cooperation between different active domains, has proven particularly effective toward these goals. Although this approach has delivered many useful transformations,[5] the development of an inherently clean and efficient process for step-economic construction of complex molecules, which are often elusive through classical catalytic systems, has remained a formidable challenge.

The azo moiety (-N=N- bond) is a common functionality in dyes and pigments (represents the most widely used and structurally diverse class of synthetic organic colorants by far),[6a] pharmaceuticals, food additives, and in many modern material science applications, including liquid crystal displays,[6b] optical storage media,[6c] and radical reaction initiators. The high value of the azo motif is reflected in the myriad strategies for its construction, the majority of which are the coupling reaction of diazonium salts with electron-rich aromatic compounds.[7] Nonetheless, it is widely appreciated that there remains a need for azo syntheses which are more concise, more selective, more versatile, and complementary to conventional routes.[7] In response to this need, much effort has been devoted to direct reductive coupling of nitroarenes, an approach which is of great importance because of the availability of substrates, the tolerance of a wide range of functionalities, and a simple one-pot procedure.[8–10] Although extensively studied, delivery of an efficient protocol using molecular H_2 as the ideal green reductant remains nontrivial. In particular, the inherent complexity of the multistep nitro reduction networks (see Scheme S1 in the Supporting Information)[11] must be tackled. Moreover, the desired level of selectivity is mostly achieved by the introduction of copious amounts of a base to suppress the unwanted side reactions catalyzed by PGMs.[12]

Thanks to the discovery that supported gold nanoparticles (NPs) are capable of uniquely facilitating the direct nitro-nitroso-hydroxylamine pathway, it is now possible for target-specific synthesis of substituted anilines and related derivatives by using catalytic nitro-group hydrogenation in a highly regio- and chemoselective manner.[13] Based on the fact that the azo compounds can be selectively synthesized through aerobic oxidative coupling of anilines,[7] an innovative integrated two-step process based on an initial nitro hydrogenation and subsequent oxidation have been proposed to access azo compounds directly from nitroarenes.[14] One major limitation of this procedure, however, is that it is potentially dangerous when applied to large-scale commercial applications. An industrial-friendly process for one-step nitro to azo conversion is thus of tremendous fundamental, as well as practical interest.[15] In view of the likely intermediacy of the azo compound in the selective hydrogenation of nitroarenes, and considering that the selectivity of the nitro reduction might be tuned in favor of azo products by rational regulation of the synergy between the metal and support in

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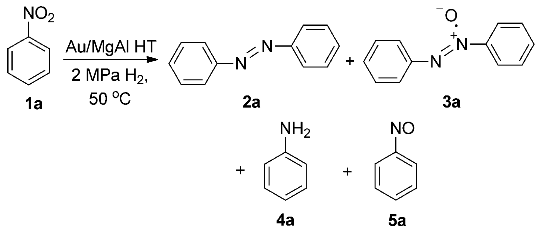
[**] This work was supported by the National Natural Science Foundation of China (21073042, 21273044), the State Key Basic Research Program of PRC (2009CB623506), the Research Fund for the Doctoral Program of Higher Education (20120071110011), and Science & Technology Commission of Shanghai Municipality (08DZ2270500).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201404543.

the gold catalyst system, we were motivated to explore gold deposited on functional support with tailored surface redox and acid–base properties as a catalyst for the direct hydrogenative coupling of nitro compounds.

We commenced our study by subjecting nitrobenzene (**1a**) to gold NPs (average diameter of approximately 2.5 nm) deposited on various inorganic oxide materials in the absence of any external additives under mild hydrogenation conditions, that is, 2 MPa of H_2 pressure in toluene at 50 °C. This initial screening identified gold on Mg-Al hydrotalcite (Mg/Al = 2) as a possible catalyst which could deliver appreciable levels of hydrogenative coupling activity, thus furnishing the desired azobenzene **2a** in a yield of approximately 34 % (see Table S1, entry 1). Consistent with most of the previous work on gold-catalyzed nitro reductions,[13] the observation of aniline (**4a**) as the sole or predominant product provides strong support for the operation of a highly selective and direct nitro-nitroso-hydroxylamine pathway (Scheme S1) over gold deposited on all other carriers (see Table S1). Further evaluation of a series of gold catalysts, with identical an gold loading (1.0 wt %), deposited on Mg-Al hydrotalcites (HTs) with different Mg/Al molar ratios (Mg/Al = 2–5, see the Supporting Information for preparation details) revealed that an impressive **2a** yield of about 65 % can be attained with the Au/Mg_4Al HT material (Table 1, entry 3).

Table 1: Hydrogenative coupling of nitrobenzene to azobenzene over Au/MgAl HT catalysts at 50 °C.[a]



Entry	Metal [wt %][b]	Mg/Al [mol/mol]	Au size [nm][c]	*t* [h]	Conv. [%][d]	Sel. [%][d] **2a**	**3a**	**4a**	**5a**
1	0.89	2	2.1	3.5	99	34	< 1	64	1
2	1.02	3	2.1	3.5	100	61	< 1	37	< 1
3	1.08	4	2.2	3.5	100	65	3	31	1
4	0.85	5	2.2	3.5	35	10	8	82	0
5	2.10	4	2.0	3.0	100	27	< 1	72	0
6	0.53	4	1.9	4.5	97	73	2	24	< 1
7	0.26	4	1.9	4.5	99	88	< 1	11	0
8	0.11	4	1.9	4.5	100	98	1	1	0

[a] Reaction conditions: nitrobenzene (1 mmol), catalyst (0.5 mol % Au), H_2 (2 MPa), toluene (5 mL), 50 °C. [b] Metal weight loadings determined by ICP analysis. [c] Evaluated by TEM. [d] Conversion and selectivity measured by HPLC analysis.

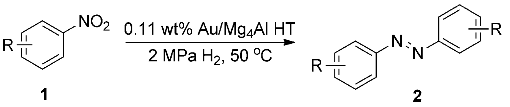
The dramatically improved hydrogenative coupling of **1a** over Au/Mg_4Al-HT, under the reaction conditions described above, clearly reflects the altered reaction pathway caused by the intimate interaction of the gold NPs with the underlying Mg-Al HT support. A preliminary analysis of the basic properties of the HT materials (see Table S2) indicates that a higher population of strong basic sites on the underlying supports is crucial for the desired reaction pathway. Further inspection of the support reveals that a prominent surface density of medium-strong acidic sites is also indispensable for the superior performance of the Au/Mg_4Al HT sample. In support of this view, the addition of either benzoic acid or pyridine greatly inhibited the hydrogenative coupling activity of the Au/Mg_4Al HT sample (see Scheme S2). These data, together with the set of catalytic data reported in Table 1, strongly suggest that the unique trifunctional character of the Au/Mg_4Al HT catalyst is essential for facilitating the conversion of **1a** into **2a** in a highly selective manner.

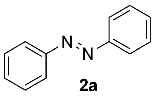
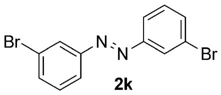
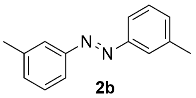
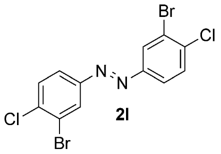
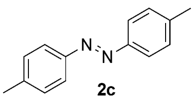
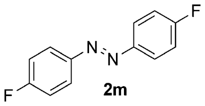
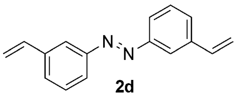
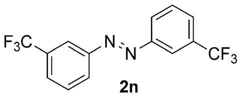
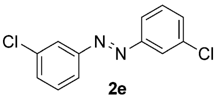
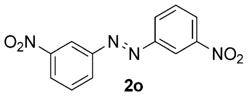
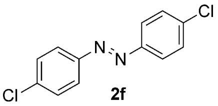
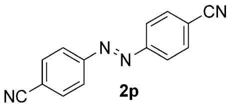
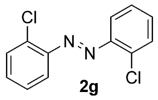
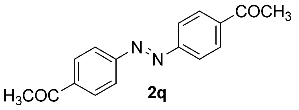
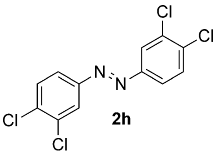
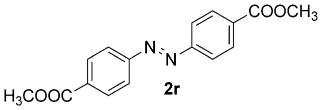
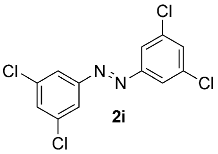
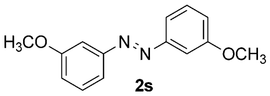
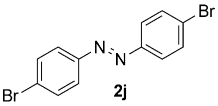
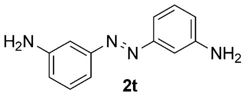
Encouraged by these promising results, we initiated a systematic study of a set of Mg_4Al-HT-supported gold samples with gold loadings ranging from 0.1 to 2.1 wt %. Much to our delight, when the gold loading was decreased to 0.11 wt %, the selectivity for **2a** increased significantly. Thus, an excellent yield of **2a** (98 %) was obtained at 50 °C after 4.5 hours when using a 0.11 wt % Au/Mg_4Al HT (Table 1, entry 8). Particularly noteworthy is that, at a temperature as low as 25 °C, the 0.11 wt % Au/Mg_4Al HT can also transform **1a** into **2a** with an extremely high selectivity, and a **1a** conversion of up to 99 % can be readily obtained (see Table S3, entry 8). Subsequent investigation of the various reaction parameters revealed that the solvent has a significant influence on the chemoselectivity of the reaction and toluene was the solvent of choice for the desired **2a** (see Table S3, entries 1–5). Increasing the H_2 pressure generally resulted in higher reaction rates but slightly lowered the selectivity for azobenzene. Therefore, a 2 MPa of H_2 pressure was enough to obtain the optimal reaction activity.

To further confirm the effectiveness of the present system, a 100 mmol scale hydrogenation of **1a** was carried out. The hydrogenative coupling reaction proceeds efficiently, and the corresponding azo compound could be obtained in 94 % yield (see Scheme S3). After the reaction, the 0.11 wt % Au/Mg_4Al HT sample was easily separated by filtration using ethanol as a solvent. Analysis by inductively coupled plasma (ICP) confirmed that no gold was present in the filtrate (limit of detection: < 7 ppb), thus indicating that the observed catalysis is truly heterogeneous. Furthermore, the recovered Au/Mg_4Al HT can also be reused at least four times without an appreciable loss of activity on this scale, for which the total turnover number (TON) approached 92 000 (Scheme S3).[16] Compared to the palladium-[12a,c] and platinum-based[12b] nanorods which require inorganic bases (such as KOH) to catalyze the hydrogenative coupling of nitroarenes, Au/Mg_4Al HT has a TON which is at least two orders of magnitude greater than that of the reported catalysts under additive-free reaction conditions. Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD) confirmed almost no change in the dispersion of the gold or metallic state of gold before and after reuse. These results are in good agreement with an excellent retention of the activity of this catalyst.

Preliminary mechanistic analysis of this hydrogenation reaction was performed by monitoring the conversion of **1a** into **2a** using high performance liquid chromatography. The kinetic time course revealed the formation and disappearance of the intermediate azoxybenzene **3a** (see Figure S1), and is consistent with the overall Harber mechanism as depicted in

Table 2: Au/Mg_4Al-HT-catalyzed hydrogenative coupling of nitroarenes to give symmetric azo compounds.[a]



Entry	Product	*t* [h]	Yield [%][b]	Entry	Product	*t* [h]	Yield [%][b]
1	 **2a**	4.5	98 (94)	11	 **2k**	18	97 (93)
2	 **2b**	5	87 (82)	12	 **2l**	36	95 (90)
3	 **2c**	11	80 (74)	13	 **2m**	25	62 (58)
4	 **2d**	12	90 (85)	14	 **2n**	10	97 (91)
5	 **2e**	7	> 99 (97)	15	 **2o**	24	98 (92)
6	 **2f**	9	95 (90)	16	 **2p**	30	87 (81)
7	 **2g**	15	79 (75)	17	 **2q**	33	85 (79)
8	 **2h**	24	98 (93)	18	 **2r**	30	80 (75)
9	 **2i**	35	97 (91)	19	 **2s**	10	12
10	 **2j**	24	88 (82)	20	 **2t**	9	n.d.

[a] Reaction conditions: nitroarene (1 mmol), catalyst (0.5 mol% Au), H_2 (2 MPa), toluene (5 mL), 50 °C. [b] Yield measured by HPLC analysis. Numbers within parentheses refer to yields of isolated products. n.d. = not detected.

Scheme S1. Note that the hydrogenative intermediates, nitrosobenzene (**5a**) and phenylhydroxylamine (**6a**), are not detected because of the strong interaction between these compounds and the catalyst surface,[11c,13d] and their fast condensation. To gain further insight into the pathway, the initial reaction rate for the hydrogenation of nitrobenzene along with **5a** and azoxybenzene were measured, and the corresponding rates were $r_1 = 0.52\,\text{mmol}\,\text{g}^{-1}\,\text{h}^{-1}$, $r_2 = 11.52\,\text{mmol}\,\text{g}^{-1}\,\text{h}^{-1}$, and $r_4 = 0.14\,\text{mmol}\,\text{g}^{-1}\,\text{h}^{-1}$, respectively (see Scheme S4). Additionally, we confirmed in a separate experiment that the condensation of nitrosobenzene and phenylhydroxylamine occurs spontaneously and rapidly, with a rate (r_3) that is much faster than those of all the above-mentioned processes. These kinetic experiments indicate that the initial reaction rates for each step of the overall sequential reaction decreases on the order: $r_3 \gg r_2 > r_1 > r_4$, thus revealing that the rate-determining step of the overall reaction in the present Au/HT-catalyzed system is hydrogenation of azoxybenzene.

Phenylhydroxyamine and azobenzene hydrogenation experiments also revealed why such high selectivity was observed. Under otherwise identical reaction conditions, the

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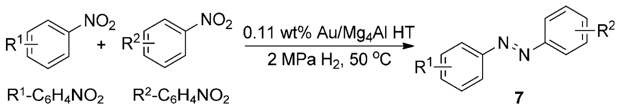
hydrogenative conversion of phenylhydroxylamine over 0.11 wt % Au/Mg_4Al HT closely resembles that for the corresponding H_2-free transformation under an N_2 atmosphere (see Table S4, entries 1 and 2). Conversely, aniline has been identified as a predominant product when subjecting phenylhydroxylamine to hydrogenation over other supported gold systems (Table S4). These findings, together with the lack of aniline formation during the **1a** to **2a** conversion reveal that both the disproportionation of phenylhydroxylamine and the reduction of the latter to aniline are practically inhibited over 0.11 wt % Au/Mg_4Al HT during the coupling process. Moreover, it was found that the hydrogenation of azobenzene proceeded sluggishly in the presence of 0.11 wt % Au/Mg_4Al HT (see Scheme S5). Taken together, all these results suggest that the 0.11 wt % Au/Mg_4Al HT catalyst biases the condensation to give the desired azobenzene via the intermediacy of azoxybenzene by suppressing the rate of both hydrogenation of phenylhydroxylamine and azobenzene to aniline. Furthermore, additional studies focused on the comparison with other noble metals showed that the presence of gold is indispensable for hydrogenative coupling of **1a** to **2a** (see Table S5). These results confirm that the relatively low hydrogen delivery capacity of a low loading of gold on Mg_4Al HT is one of the key aspects for maintaining a low and steady concentration of phenylhydroxylamine, and allows the reaction to proceed in a selective manner.

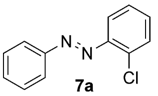
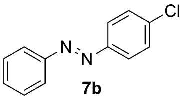
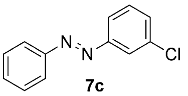
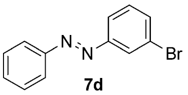
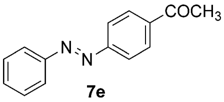
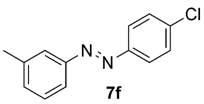
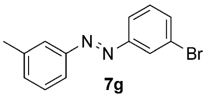
To demonstrate the general applicability of the novel catalyst and the scope of the process, a wide range of simple and readily available nitroarenes were tested without further optimization (Table 2). We were pleased to find that various functionalized nitroarenes, especially electron-deficient (entries 4–18) substrates, are converted smoothly and selectively into the desired products with good to excellent yields. The catalytic hydrogenation of electron-rich nitroarenes, such as 3-nitroaniline or 1-methoxy-3-nitrobenzene, was found to be problematic as no or a low yield of the azo product was formed (entries 19 and 20). However, the electron-donating methyl-substituted nitrobenzenes, 1-methyl-3-nitrobenzene and 1-methyl-4-nitrobenzene, were fully converted and gave the corresponding azos in good yields after 5 and 11 hours, respectively, of reaction (entries 2 and 3). Furthermore, steric properties of the substituent affect the reductive coupling significantly. Specifically, nitroarenes containing a substituent on the aromatic ring require a longer reaction time (entries 1–3). The yields of *m*-substituted azo arenes were somewhat higher than those for the corresponding *o*- or *p*-substituted nitroarenes (entries 2, 3, 5, 6, 10, and 11).

It is noteworthy that halogenated nitroarenes can be employed as selective hydrogenative coupling reagents. Both mono- and dihalogenated nitroarenes were tolerated, thus leading to the corresponding chloro-, bromo-, fluoro-, or dihalogenated azo compounds without any dehalogenation (Table 2, entries 5–13), a side reaction often encountered with other procedures,[17] including catalytic hydrogenation. In addition to halogen substituents, sensitive reducible function groups such as olefin, nitrile, ketone, as well as ester moieties were well tolerated without undergoing reduction to any substantial extent during the reduction process (entries 4 and 16–18). Moreover, this Au/Mg_4Al HT reduction system was also applicable to dinitroarenes to obtain the corresponding azo compound in excellent yield (entry 15), thus demonstrating the versatility of the present methodology for azo compound synthesis.

Given that the surface-mediated condensation of nitroso and hydroxylamine intermediates is a central step in the formation of the azo linkage, we have explored the possibility of the gold-catalyzed cross-coupling to prepare more industrially important asymmetric aromatic azo dyes by using a mixture of two different nitroarenes of very different reactivity. These azo dyes are traditionally synthesized through coupling of the diazonium salt of the electron-poor partner with the electron-rich arene.[7] The problems inherent in this procedure are the use of expensive and very unstable starting materials and the release of large amounts of toxic waste. Thus, the development of more environmentally acceptable processes, which make use of more readily available and easily handled feedstocks, is highly desired. It should be noted at this point that upon mixing the two

Table 3: Au/Mg_4Al-HT-catalyzed hydrogenative coupling of nitroarenes to unsymmetrical azo compounds.[a]



Entry	Substrates R^1	 R^2	Products	*t* [h]	Yield [%][b]
1	H	*o*-Cl	 **7a**	7	75 (70)
2	H	*p*-Cl	 **7b**	6.5	87 (80)
3	H	*m*-Cl	 **7c**	5	92 (87)
4	H	*m*-Br	 **7d**	6	90 (83)
5	H	*p*-$COCH_3$	 **7e**	9	79 (71)
6	*m*-CH_3	*p*-Cl	 **7f**	7	89 (83)
7	*m*-CH_3	*m*-Br	 **7g**	8	90 (82)

[a] Reaction conditions: R^1-$C_6H_4NO_2$ (0.5 mmol), R^2-$C_6H_4NO_2$ (1.5 mmol), catalyst (1 mol% Au bases on R^1-$C_6H_4NO_2$), H_2 (2 MPa), toluene (5 mL), 50°C. [b] Yield measured by HPLC analysis based on R^1-$C_6H_4NO_2$ consumption. Numbers within parentheses refer to yields of isolated products. Meanwhile, the R^2-$C_6H_4NO_2$ that was present in threefold excess also gives appreciable amounts of hydrogenative byproducts including anilines as well as self-coupling azo and azoxy derivatives.

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different nitroarenes preferential self-coupling may occur as an unwanted side reaction, particularly for the intrinsically more reactive partner. Despite such challenges, one may assume that it is possible to achieve a high selectivity for desired cross-coupling, provided that one partner proved much more reactive than the other. This selectivity is especially good when the less reactive partner is present in excess (see Table S6), wherein the lack of reactivity in the reduction with this partner favored the preferential trapping of the reactive-partner-generated phenylhydroxyamine with the surface-abundant nitroso species derived from the less reactive partner. Indeed, we were able to obtain seven asymmetrically substituted azobenzenes with potential applications in dyes,[6a] liquid crystals,[6b] or optical storage media,[6c] in high selectivity and conversion (Table 3) using the Au/Mg_4Al HT catalyst. To the best of our knowledge, a simple ligand-free heterogeneous catalytic system that does not require external additives and is highly efficient for direct hydrogenative coupling of a wide range of nitro substrates has not been reported to date.

In summary, aromatic azo compounds can be selectively and directly synthesized from hydrogenative coupling of nitroarenes without any external base or additives. This green synthetic reaction, mediated by a robust hydrotalcite-supported gold catalyst, proceeds chemoselectively in a highly efficient manner under mild reaction conditions using H_2 as a clean reductant. The new catalytic protocol exhibits a broad substrate scope, thus providing a variety of symmetrical and asymmetrical aromatic azo compounds in good to excellent yields. The catalytic system described here promotes a sophisticated multistep process by controlled manipulation of the reaction pathways, and may present a new strategy toward the development of versatile multitask, heterogeneous catalysts, and also contribute to the design of catalytic systems for accessing higher levels of complexity.

Received: April 22, 2014
Published online: June 6, 2014

Keywords: arenes · azo compounds · gold · reduction · supported catalysts

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