



Bifunctional Cs-Au/Co₃O₄ (Basic and Redox)-Catalyzed Oxidative Synthesis of Aromatic Azo Compounds from Anilines

Charles O. Oseghale, Dele Peter Fapojuwo, Oyekunle Azeez Alimi, Christianah Aarinola Akinnawo, Batsile M. Mogudi, Oluwatayo Racheal Onisuru, and Reinout Meijboom*

Research Center for Synthesis and Catalysis, Department of Chemical Sciences, University of Johannesburg, PO Box 524, Auckland Park 2006, Johannesburg, South Africa Tel.: +27 (0)72 894 0293, Fax: +27 (0)11 559 2819 Corresponding Author* E-mail: rmeijboom@uj.ac.za (R.M.)

Graphical abstract



Abstract

An eco-friendly alkali-promoted (Cs-Au/Co₃O₄) catalyst, with redox and basic properties for the oxidative dehydrogenative coupling of anilines to symmetrical and unsymmetrical aromatic azo compounds, was developed. We realized a base additive and toxic molecular O₂ oxidant free process (using air), with reasonable reusability of the catalyst achieved under milder reaction conditions. Notably, the enhanced catalytic activity was also linked to increased basic site concentration, low reduction temperatures, and the effect of lattice oxygen on the nanomaterials. The increased basic strength of the cation-promoted catalyst improved the electron density of the active Au species, resulting in the higher yield of the desired aromatic azo compounds.

Keywords: Alkali-cations; Aniline; Basicity Gold; Oxidation.

Introduction

Concerns about the high energy consumption associated with large-scale chemical synthesis and environmental toxicity have fueled current attempts to create benign methods with a low negative environmental impact. Catalysis has been critical from the green chemistry perspective, owing to its ability to improve product selectivity and reduce reactor temperatures. Heterogeneous catalysis is of particular interest due to the ease with which it can be separated and the fact that it does not produce harmful byproducts throughout the reactions. Recently, gold catalysts for sustainable and green organic synthesis have attracted considerable scientific attention due to their broad range of applications and efficiency ^[1–5]. Initially thought inert, gold became apparent as a selective and active catalyst to others, such as platinum, for a range of reactions after a significant breakthrough in its usage at the nanoscale level ^[6]. Recent advancements in the gold catalyst's practical utility and applications, especially in gold metal and support interactions, have paved the way for new methods for their practical utility and applications. The higher catalytic activity of these gold catalysts has been attributed to their choice of support and, at times, the size of the gold nanoparticles. Catalyst design based on mutual cooperation between the gold and support has been shown to be advantageous for catalyzing a wide variety of reactions. Metal-support interactions have resulted in significant advancements in the development of commercially viable organic compounds. On the other hand, modifying (doping) support materials and catalysts with alkali metals has previously been shown to induce a phenomenon, increase their binding properties, and significantly improve the overall catalytic performance of the catalyst^[4,7].

Corma and coworkers demonstrated that this supported gold catalyst has the unique capacity to activate both a two-step, one-pot process to synthesize azo compounds from nitrobenzene through hydrogenation and the oxidative coupling of anilines to azobenzenes ^[8]. In the following years, Pd or Pt nanowires in the presence of KOH ^[9], Au/ZrO₂ through a photocatalytic route ^[10], and CuBr/pyridine ^[11] systems have all been investigated for this reaction.



Scheme 1: Synthetic routes for aromatic azo compounds. (a) ^[8], (b) ^[12,13], (c) ^[14,15].

Azo compounds with -N=N- functionalities are an essential class of chemicals used in food additives, pharmaceuticals, and other modern science applications such as liquid crystal displays ^[16], dyes ^[17], therapeutic agents ^[18,19], pigments ^[20], optical media storage ^[21], and reaction indicators ^[22]. They are mostly suitably accessed by oxidative dehydrogenative coupling of anilines. However, it has been reported that these azo compounds are synthesized via the diazonium route ^[12,13,23], which employs flammable organic bases, toxic oxidants, and nitrite salts in stoichiometric amounts, thereby generating inorganic waste in the process. These current methods have been linked with poorer yields, limited reusability, and severe reaction conditions (higher temperature and pressure) ^[12,13]. A more versatile chemical procedure, such as a multifunctional and effective heterogeneous catalyst for the selective synthesis of azo compounds under mild reaction conditions, is highly desired to supplement the traditional techniques.

In continuation of our ongoing research on the use of alkali-promoted catalysts for sustainable catalysis ^[4,5,24], herein, we present a more environmentally friendly method for the oxidative coupling of anilines to symmetrical and unsymmetrical aromatic azo compounds using a Au-based catalyst with redox and basic properties. In general, the synthesis of unsymmetric aromatic azo compounds is very complex. Usually, it proceeds via the nitrosobenzene intermediates and diazonium salts pathway ^[13], using organic bases and a stoichiometric quantity of harmful oxidants such as nitrates, ferrates, mercury salts, and palladium salts, which produce inorganic wastes as a byproduct. This study describes a base additive and toxic oxidant-free reaction that utilizes air as the terminal oxidant aided by a convenient 3D-printed air-flow splitter. To our knowledge, this is the first Au-based catalyst with both redox and basic properties for the selective oxidative coupling of anilines to aromatic azo compounds (Scheme 1). Besides, ascribing the catalytic performance of this type of reaction to the concentration of basic sites in the catalyst has not been reported. Additionally, our catalyst's exceptional reusability makes our system more intriguing and competitive. Similarly, the effect of alkali-cations on the catalyst was investigated in terms of basicity, low reduction temperatures, and lattice oxygen defects.

Experimental

Materials

The palladium(II) acetate (98%), platinium(II) acetate (98%), gold(III) chloride trihydrate (99.9%), cobalt(II) nitrate hexahydrate (99%), manganese(II) nitrate tetrahydrate (97%), DMF (98%), acetonitrile (98%), ethanol (99%), 1, 4-dioxane (99%), toluene (99.9%), nitric acid (HNO₃) (70%), Pluronic (P-123), urea (\geq 99.9%), sodium borohydride (\geq 96%), 1-butanol (\geq 99.8%), aniline (\geq 99.5%), 4-methoxyaniline (99%), p-toluidine (99.6%), 4-fluoroaniline (98%), 4-chloroaniline (98%), nitrate salts of lithium (98%), sodium (98%), potassium (99%), calcium (98%) and cesium (98%) were supplied from Sigma-Aldrich and used without the need for further purification.

Catalyst synthesis

The deposition-precipitation technique was used to synthesize the undoped Au/Co₃O₄ and alkali metal salt $x(NO_3)$ (x = Cs, Na, Li, Ca, and K) doped x-Au/Co₃O₄ catalysts ^[25]. Typically, 1 g of mesoporous Co₃O₄-350 °C ^[5] was introduced to an aqueous solution of the metal salt (HAuCl₄.3H₂O) and agitated at room temperature (RT) for 2 h. Urea in a molar ratio of 2:1 to the

gold salt was added to the reaction mixture while maintaining the temperature and stirring speed at 80 °C and 450 rpm, respectively. After cooling to room temperature, freshly prepared NaBH₄ in a 10:1 molar excess was added to the reaction mixture and stirred for 4 h at RT. The alkali metal salt was then added to the mixture and agitated for 1 h at RT. The precipitate obtained was rinsed with excess distilled water (80 mL), dried, and calcined for 3 h at 350 °C. Mesoporous MnO₂ and the Pt and Pd-based catalysts using Pt(OAc)₂ and Pd(OAc)₂ precursors were synthesized according to the procedure earlier reported in ^[5]. The % composition of the catalysts ranges from 0.4-5%, with the main samples denoted as Co₃O₄, MnO₂, M/Co₃O₄, M/MnO₂, *x*-M/Co₃O₄ or M/Co₃O₄-*x*, and *x*-M/MnO₂ or M/MnO₂-*x*. Where M = Au, Pd, and Pt. The initial nanoparticle loading was set at 5 wt.%.

Catalyst characterization

The temperature-programmed oxidation (O₂-TPO) by O₂ was performed using a Micromeritics AutoChem II instrument at a temperature range of 50-700 °C (10 °C min⁻¹). Additionally, X-ray diffraction (XRD), N₂-sorption, Fourier transform infrared spectroscopy (FT-IR), temperatureprogrammed reduction by H₂ (H₂-TPR), transmission electron microscopy (TEM), inductively coupled plasma optical emission spectrometry (ICP-OES), Brunauer-Emmett-Teller (BET), scanning electron microscopy (SEM), temperature-programmed desorption by CO₂ (CO₂-TPD), gas chromatography spectroscopy (GC–MS/FID) and nuclear magnetic resonance spectroscopy (NMR), were performed; the instruments and methods employed for the characterization of the nanomaterials were the same as in our previously published works ^[4,5].

Catalytic activity for the oxidative coupling of anilines

The oxidation reactions were carried out in a carousel reactor equipped with twelve 50 mL tubes from the Radley Discovery Technologies. Typically, a 50 mL tube was charged with the catalyst (50 mg), toluene (3 mL), and 1 mmol (200 μ L) decane (internal standard) and aniline substrates (1 mmol). The mixture was heated to a reaction temperature in the range of 80-110 °C during a specified period while maintaining a stirring speed of 550 rpm under an air-flow. The air-flow was assisted by a 12-way 3D-printed air-flow splitter built on-site. After separating the catalyst, the mixture was cooled to room temperature, and the filtrate was analyzed using a GC-FID instrument. Prior to the NMR investigations, water (40 mL) was slowly added to separate the organic phase,

10.1002/ejoc.202100976

and the aqueous layer was extracted with ethyl acetate (2 x 20 mL). The mixed layer was washed with brine solution and dried over sodium sulphate. The remaining solvent was evaporated using a rotary evaporator, and the purification procedure was carried out using flash column chromatography on silica gel with ethyl acetate and hexane as eluents. The catalyst was separated using a simple filtering technique for the reusability experiments and then washed, dried, and activated in an oven before reuse.

Results and discussions

The soft template inverse-micelle and deposition-precipitation techniques were employed for the supports and catalysts syntheses. Alkali metal salts (*x*.NO₃) in trace amounts were used to dope the catalyst materials. However, these cations significantly enhanced the catalytic performance for the oxidative coupling of a diverse array of anilines to symmetric and unsymmetric aromatic azo compounds. As previously demonstrated by our group, alkali metal ions on the surface of reducible metal oxides and catalysts can improve the nanomaterials' basic strength concentration and catalytic activity ^[4,5,24]. According to Helwani and coworkers, the presence of these highly electropositive cations in catalysts, which create basic sites, can cause defects in the materials ^[26]. Increased basic site concentrations in materials also aided in the oxidation of alkylbenzenes ^[27]. With this, increasing the basicity of these catalysts can provide reasonable reactivity and activity for the oxidative coupling of anilines.

Structural characterization of the catalyst

The carbon monoxide temperature-programmed desorption (CO₂-TPD) measurement was used to determine the nanomaterial's relative basicity. As shown in Figure 1, the Cs promoted catalyst exhibited the highest basic concentration (1.058 mmol CO₂ g⁻¹) to the others. Comparing the basicity values of Cs-Au/Co₃O₄ to the unpromoted Au/Co₃O₄ showed the promotional effect of the alkali cations on the nanomaterials (Figure 1b). A fascinating finding is the increasing basicity of the catalysts, which corresponds with the size and charge of the cations; a similar pattern has been reported, with the Cs⁺ promoted catalyst being more basic than the others and providing a much higher activity for the reaction ^[4] (Figure 1a). In many oxidation reactions, the addition of organic bases (as additives) can enhance catalytic activity. However, an efficient and environmentally sustainable oxidation process should not involve the use of additives (bases or acids). In this study,

This article is protected by copyright. All rights reserved.

the bifunctional nature (basic and redox) of our catalytic system can promote the oxidative dehydrogenative synthesis of aromatic azo compounds without using base additives. Therefore, we believe that our catalyst's basic and redox nature plays an essential role in the selective oxidative coupling of the anilines.



Figure 1 CO₂-TPD of the catalysts. The gold catalyst loadings were set at 5 wt.%.

The physicochemical properties of the catalysts (pore diameters/volumes and BET surface areas) were also considered a factor in their high catalytic activity (Table S1 and Figure 2a). The 1% Au/Co₃O₄-Cs loading, along with the reduced particle size and intra-particle voids, provided more defects on the catalyst surface, which act as active catalytic sites. As a result, we hypothesized that the decreased surface area, pore-volume, and pore size of the promoted catalyst with a gold loading of up to 5% was the major reason for its slightly decreased catalytic activity. The TEM pictures displayed aggregated particle sizes as the gold loading on the support matrix increased (Figure 3). Additionally, the XRD study shows that the alkali-cations and AuNPs did not alter the structure of the mesoporous cobalt oxide since there were no peaks attributed to AuNPs in the spectra (Figure 2b).



Figure 2 (a) BET and (b) p-XRD of the nanomaterials.



This article is protected by copyright. All rights reserved.

Accepted Manuscril

Figure 3 TEM images and particle size distribution of the catalysts (a) (b) 1% Au/Co₃O₄-Cs, (c) (d) 3% Au/Co₃O₄-Cs and (e) (f) 5% Au/Co₃O₄-Cs.

Temperature-programmed reduction (H_2 -TPR) and oxidation (O_2 -TPO) measurements were used to determine the reduction-oxidation profiles of the nanomaterials (Figure 4). The catalyst activity was found to be related to the reducibility of materials; the low reduction temperatures observed for Cs-Au/Co₃O₄ in comparison to Au/Co₃O₄ indicate the catalyst's easy reducibility due to the presence of Cs^+ , which also reveals an increase in the accessibility and mobility of the lattice oxygen (Figure 4a). The two major reduction peaks of 143 and 312 °C (Cs-Au/Co₃O₄) and 224 and 284 °C (Au/Co₃O₄) indicate a two-step reduction of Co₃O₄-CoO (reducible capping oxygen at a lower temperature) and CoO to Co (bulk reduction at a higher temperature). On the other hand, it is thought that the Cs cation in the catalyst increases lattice oxygen supply, resulting in increased defects in the nanomaterials ^[28]. The defects contributing to the high adsorption capacity and efficient adsorption of nanomaterial substrates have been extensively studied ^[29]. In contrast to the temperature reduction profiles, the oxidation peaks shifted to higher temperatures for Cs-Au/Co₃O₄ (351 °C) than for unpromoted Au/Co₃O₄ (328 °C), indicating that the O₂ consumption at higher temperatures may be necessary for the oxidation reaction to proceed smoothly (Figure 4b). It is worth noting that the alkali cation (Cs) in the catalyst was critical for the nanomaterial's O₂ (at higher temperatures) and H₂ consumptions (at lower temperatures).



Figure 4 (a) H₂-TPR and (b) O₂-TPO profiles of Cs-Au/Co₃O₄ and Au/Co₃O₄. The measurements were conducted from RT to 600°C (10°C/min) under a stream of 10 % O₂/Ar for O₂-TPO and 10 % H₂/Ar for H₂-TPR.

Catalytic studies

Catalyst screening

Next, we screened the different catalysts at 100 °C for 8 h using aniline 1a as the model substrate (Table 1). With the 5% Au/Co₃O₄ catalyst, a moderate yield (60%) of the aromatic azo compound **2a** was obtained (Table 1, entry 1). Not satisfied with the effectiveness of this unpromoted catalyst, we further modified it by doping with different alkali-metal ions (x = Cs, Na, Li, Ca, and K). Notably, the Cs-promoted catalyst was found to be the most active, with excellent 2a yield obtained when compared to the others; this was attributed to the catalyst's highly electropositive nature, which increased the basic site concentration and improved its catalytic activity ^[26] (Table 1, entry 2). As previously stated, the charge and size of these alkali cations in the catalysts are well correlated with their catalytic activity. The 1% and 3% Au loadings provided a much better 2a yield than the 5%. Apart from the Au/MnO₂ catalyst and its Cs-promoted counterpart, which gave satisfactory reactions (Table 1, entries 9 and 10), the oxidative dehydrogenative coupling of **1a** with the Pd and Pt-based catalysts was unsuccessful, indicating the involvement of the active nanoscale gold species in the reactions. Likewise, increasing the time up to 24 h did not significantly improve the reaction, but instead, it gave a trace amount of the product (Table 1, entry 11-16). Besides, the choice of support was also crucial and has been linked to the high catalytic activity of many Au-based catalysts ^[30–34]. However, in this study, the unsaturated Au sites were the active species. At an 8 h reaction time, attempts to use the support for the oxidative coupling of **1a** to azobenzene resulted in a reduced **2a** yield and selectivity (Table 1, entry 17); however, when the reaction time was increased to 16 h, the conversion and yield improved somewhat (Table 1, entry 18). Additionally, the difference in catalytic activity between the gold and platinium or palladium catalysts may be attributed to the high affinity of these metals (Pt and Pd) for the adsorption and diffusion of the aniline substrates in the reaction, thereby altering its catalytic performance.

Entry	Catalyst	Dopants	Conversion	Selectivity	Yield
			(%) ^[b]	(%) ^[b]	(%) ^[b]
1	5% Au/Co ₃ O ₄	-	63	94	60
2	5% Au/Co ₃ O ₄	Cs	88	98	87
3	5% Au/Co ₃ O ₄	Na	94	83	78
4	5% Au/Co ₃ O ₄	Li	91	90	81
5	5% Au/Co ₃ O ₄	Ca	86	82	70
6	5% Au/Co ₃ O ₄	Κ	94	79	74
7	*1% Au/Co ₃ O ₄	Cs	96	98	95
8	3% Au/Co ₃ O ₄	Cs	93	96	90
9	1.2% Au/MnO ₂	-	98	66	65
10	1% Au/MnO ₂	Cs	97	93	91
11 ^[c]	1% Pd/Co ₃ O ₄	-	n.r	n.r	n.r
12 ^[c]	1% Pd/Co ₃ O ₄	Li	n.r	n.r	n.r
13 ^[c]	1% Pd/Co ₃ O ₄	Cs	n.r	n.r	n.r
14 ^[c]	0.8% Pt/Co ₃ O ₄	-	n.r	n.r	n.r
15 ^[c]	1.3% Pt/Co ₃ O ₄	Cs	n.r	n.r	n.r
16 ^[c]	0.4% Pt/MnO ₂	Cs	n.r	n.r	n.r
17	Co_3O_4	-	31	35	11
18 ^[d]	Co_3O_4	-	60	28	17

Table 1	Catal	sts screening	[a]
---------	-------	---------------	-----

[a] Reaction conditions: Aniline **1a** (1 mmol), catalyst (50 mg), temperature (100 °C), toluene (3 mL) and 8 h reaction time. [b] Selectivity, conversion, and yield (%) determined by GC-FID. [c] 24 h. [d] 16 h. n.r = No reaction, although with a trace amount of the product detected for some of the catalysts.

Optimization of reaction parameters and substrate scope

For the solvent screening, the toluene showed the highest conversion and yield of **1a** and **2a** at 96 and 95%, respectively (Table 2, entry 1). The low reactivity of acetonitrile and ethanol may be due to the solvent's inability to bind to the catalyst's active Au sites, resulting in low conversions and yields (Table 2, entries 4 and 5). When the solvent volume was reduced to 1 mL, the conversion of **1a** improved significantly (Table 2, entry 6). Interestingly, when the reaction period was extended to 18 h, the Cs-Au/Co₃O₄ also showed solvent-free green oxidation of **1a** to **2a**; conversion and yield were 54% and 50%, respectively (Table 2, entry 7). Following that, we investigated the effect of time on the reactions. Extending the time from 8 to 24 h resulted in a substantial increase in **1a** conversion and **2a** yield (Table 2, entry 8). The temperature may be critical in this reaction. Increasing the temperature to 110 °C seems to have a detrimental effect on the **2a** yields, with the **1a** completely converted at > 99% (Table 2, entry 9). However, the reaction

was not favorable at temperatures below 50 °C. Notably, due to this catalytic system's basic and redox features, no side products were detected for several reactions, suggesting that the intermediate in this oxidation step was readily converted to the product. The effect of catalyst loading was also examined, and it was shown that reducing the catalyst loading to 20-30 mg had no discernible influence on the **2a** yield (Table 2, entry 10). When the amount is increased to 70 mg, a significant increase in the activity and reactivity of **2a** occurs (Table 2, entry 11). However, given the expense of the gold catalyst and its activity in this reaction, a loading of 50 mg of 1% Au/Co₃O₄-Cs or less is ideal. Based on the satisfactory reactions, we proceeded with 100 °C, 8 h, 50 mg, and **1a** (1 mmol) as the optimized reaction parameters for subsequent reactions.

Entry	Solvents	Time (h)	Temp	Catalyst	Conversion	Selectivity	Yield
			(°C)	(mg)	(%) ^[b]	(%) ^[b]	(%) ^[b]
1	Toluene	8	100	50	96	98	95
2	DMF	8	100	50	94	83	78
3	Dioxane	8	100	50	71	96	69
4	Acetonitrile	8	80	50	20	57	12
5	Ethanol	8	70	50	8	70	6.2
6 ^[c]	Toluene	8	100	50	98	98	97
7 ^[d]	-	18	100	50	54	91	50
8	Toluene	24	100	50	100	98	98
9	Toluene	8	110	50	100	85	85
10	Toluene	8	100	30	95	98	92
11	Toluene	8	100	70	100	>99	>99

 Table 2 Optimization of reaction parameters using 1% Au/Co₃O₄-Cs ^[a]

[a] Reaction conditions: Aniline 1a (1 mmol), catalyst (50 mg), temperature (100 °C), toluene (3 mL) and 8 h reaction time.
[b] Selectivity, conversion, and yield (%) determined by GC-FID.
[c] Toluene (1 mL).
[d] 1a (2 mmol), 18 h.

To further our understanding of using this base additive-free system, we investigated various substituted anilines with electron-donating and electron-withdrawing groups under the optimal reaction conditions (100 °C, 8 h). Notably, high selectivity and yields of up to 94% were achieved. As shown in Figure 5A, the yields of the desired aromatic azo compounds were well tolerated regardless of the substitution manner of the electron-rich and electron-deficient substituents. Except for the nitro substituted aniline 1i, which did not provide the intended product 2i, the other electron-withdrawing substrates (1f-1h) survived the reaction and were successfully converted to

azobenzene. The poor yields, on the other hand, showed the importance of electronic effects in the reactions. The no reaction (n.r.) observed for the nitro-substituted aniline **1i** may be attributed to the amine radical cation's instability and the presence of weak nucleophiles. The yield and conversion of the 1-naphthylamine substrate **1j** were much lower, presumably due to the bulky substituents' steric effect on the molecules. Interestingly, compound **1k** with an N-heteroatom was tolerated slightly; the poor conversion and yield may result from the poisoning effect of the pyridine N atom coordinated with the catalyst's metal center ^[35].

Given the remarkable activity of the catalyst (1% Au/Co₃O₄-Cs) in the synthesis of the symmetrical azobenzene, we hypothesized that the electron-rich substrates might undergo oxidative coupling to unsymmetric aromatic azo compounds under the optimized reaction conditions (Figure 5B). Unsymmetrically substituted azo compounds have been reported to be formed by coupling diazonium salts with both electron-deficient and electron-rich aromatic compounds in the presence of base additives and toxic oxidants, yielding a significant amount of aromatic azo compounds and water as a byproduct. To our delight, the oxidative dehydrogenative coupling of these electron-rich and electron-deficient substrates resulted in the formation of some active unsymmetrically substituted azobenzene and derivatives in the absence of base additives, diazonium salts, and hazardous oxidants. It is worth mentioning that the homocoupling of these aryl-substituted anilines with electron-withdrawing groups was slower than those with electron-donating groups.

This article is protected by copyright. All rights reserved.



ccepted Manuscri

This article is protected by copyright. All rights reserved.

10.1002/ejoc.202100976

Figure 5 Reaction conditions: Catalyst (50 mg), substrates (1 mmol), 100 °C, toluene (3 mL), and 8 h. Conversion and isolated yields determined by GC-FID analysis. [a] Reaction conditions: Catalyst (70 mg), substrate (1 mmol), 100 °C, and 18 h.

Control experiment and mechanism of the reactions

To gain mechanistic insight into the oxidative coupling of the anilines with our redox-base catalyst (Cs-Au/Co₃O₄), a series of control experiments were performed under the N₂ atmosphere and the results of which are presented in Scheme 2 [a]. Fortunately, just a trace amount of the aromatic azo compound was found, suggesting that air (O_2) was primarily responsible for initiating and catalyzing the transition of the anilines to symmetric and unsymmetric azo compounds. Additionally, since no crossover product was detected, Scheme 2 [b] shows that the reaction did not proceed through the nitrosobenzene pathway as a viable intermediate. Minor amounts of the nitrosobenzene intermediates were detected in the oxidative coupling reported by Corma and coworkers, resulting in a slightly reduced yield of the desired azobenzene ^[8]. However, our catalytic system utilized the synergistic combination of alkali metal cations, AuNPs, and Co₃O₄ support, with air as the terminal oxidant, compared to their system, which used molecular O_2 and pressure up to 5 bar. The low or no activity of these control experiments involving nitrogen when compared to the use of air could be ascribed to the labile lattice O₂ and adsorbed O₂ on the surface of the catalyst, indicating the role of O₂ supply from the air in these reactions since the loss of lattice O_2 is replenished by the O_2 coming from air ^[36]. Additionally, we found that the oxidation of 1, 2 diphenylhydrazine to azobenzene occurred more rapidly, which explains why the hydrazine intermediate (4¹) was not detected during the reaction (Scheme 2 [c]).



Scheme 2 [a] Control experiment with N_2 and [c] Reaction of 1, 2 diphenylhydrazine with 1% Au/Co₃O₄-Cs.

Based on the above, we proposed a probable reaction mechanism for the oxidative coupling of aniline catalyzed by 1% Au/Co₃O₄-Cs (Scheme 3). Although, similar to that described by Corma and coworkers ^[8], except for the azoxybenzene and nitrosobenzene intermediates, which were not detected in our reactions. In **step I**, the 1% Au/Co₃O₄-Cs absorbs oxygen (O₂) from the surrounding air through interaction with the active Au species. The aniline (**1a**) nitrogen atom is oxidized by adsorption on the oxygenated catalyst surface, forming an aniline radical cation (**3**), **step II**. Following that, the aniline radical species (**3**) combined with another aniline molecule (**1a***) to produce a 3e⁻ δ bond hydrazine radical intermediate (**4**), which was assumed to constitute the rate-determining step, **step III**. At **step IV**, the hydrazobenzene radical species (**4**) donates one electron and two protons by oxidation and removal of water molecules from the catalyst surface to form a hydrazine intermediate (**4**¹), which further undergoes oxidation rapidly, by going through **step IV** again to form the aromatic azo product **2a**, **step V**. A critical observation is that the aniline radical cation formed in **step II** was assumed to be involved in the reduction of the active Au⁺ to Au, which hypothetically resulted in the superficial release of the labile lattice O₂ from the air for the entire cycle.



Scheme 3 Plausible reaction mechanism for the oxidative dehydrogenative coupling reaction.

Reusability and heterogeneity studies

Notably, the 1% Au/Co₃O₄-Cs catalyst may be recycled and reused for up to six consecutive cycles with no substantial loss of catalytic activity using the simple filtration method (Figure 6). To prepare the catalyst for subsequent reuse, it was washed with 25 mL (x3) of toluene and reactivated at 120 °C to remove physically absorbed species. Following that, we performed a series of reactions using the filtrate after the catalyst separation (starting at 2 h reaction time). There was no observable change in the **1a** conversion or detectable amount of aromatic azo compounds (Figure S1). Additionally, an ICP-OES analysis of the filtrate after the sixth cycle showed a negligible amount of Au species. The results indicate that the reaction was catalyzed by the active Au species rather than leached Au ions.



Figure 6 Reusability studies of 1% Au/Co₃O₄-Cs with the optimized reaction conditions: 100 °C, 8 h, toluene (3 mL), air (1 atm), and catalyst (50 mg).

Conclusion

In conclusion, a novel bifunctional catalyst (Cs-Au/Co₃O₄) with redox and basic properties was designed for the oxidative coupling of anilines to symmetric and unsymmetric azo compounds. The reaction was carried out without toxic oxidants and base additives, with air as the terminal oxidant (aided by a 3D-printed air-flow splitter). The results indicate that the active Au species were responsible for the high catalytic activity and essential for activating the O_2 (air) and forming the radical intermediates. Additionally, the higher catalytic activity of the catalyst was easily correlated with the presence of the highly electropositive Cs⁺, which increased the basic site concentration of the catalyst and improved its catalytic efficiency. The basic and redox features of the catalyst, moderate reaction conditions, proper reusability, and the tested solvent-free green system all contribute to our system being more viable and competitive than others.

References

- [1] M. Zhang, C. Zhu, L.-W. Ye, Synthesis (Stuttg). 2017, 49, 1150–1157.
- [2] G. J. Hutchings, ACS Cent. Sci. 2018, 4, 1095–1101.
- [3] Y. Zhang, G. Wang, L. Yang, F. Wang, A. Liu, Coord. Chem. Rev. 2018, 370, 1–21.
- [4] C. O. Oseghale, B. M. Mogudi, O. R. Onisuru, C. A. Akinnawo, D. P. Fapojuwo, R. Meijboom, *ChemCatChem.* 2021, 13, 1311–1316.
- [5] C. O. Oseghale, B. M. Mogudi, C. A. Akinnawo, R. Meijboom, *Appl. Catal. A Gen.* 2020, 602, 117735.
- [6] X. Liu, H. Li, S. Ye, Y. Liu, H. He, Y. Cao, Angew. Chem. Int. Ed. 2014, 53, 7624–7628.
- [7] C. O. Oseghale, O. R. Onisuru, D. P. Fapojuwo, B. M. Mogudi, P. P. Molokoane, N. P. Maqunga, R. Meijboom, *RSC Adv.* 2021, *11*, 26937–26948.
- [8] A. Grirrane, A. Corma, H. García, *Science* (80-.). 2008, 322, 1661–1664.
- [9] L. Hu, X. Cao, L. Chen, J. Zheng, J. Lu, X. Sun, H. Gu, *Chem. Commun.* 2012, 48, 3445–3447.
- [10] H. Zhu, X. Ke, X. Yang, S. Sarina, H. Liu, Angew. Chem. Int. Ed. 2010, 49, 9657–9661.
- [11] C. Zhang, N. Jiao, Angew. Chem. 2010, 122, 6310–6313.
- [12] M. Barbero, I. Degani, S. Dughera, R. Fochi, P. Perracino, *Synthesis (Stuttg)*. 1998, 1998, 1235–1237.
- [13] H. A. Dabbagh, A. Teimouri, A. N. Chermahini, Dye. Pigment. 2007, 73, 239–244.
- [14] K. Krageloh, G. H. Anderson, P. J. Stang, J. Am. Chem. Soc. 1984, 106, 6015–6021.
- [15] Z. Liu, M. Jiang, J. Mater. Chem. 2007, 17, 4249–4254.
- [16] Y. Zhao, T. Ikeda, Smart Light-Responsive Materials: Azobenzene-Containing Polymers and Liquid Crystals, John Wiley & Sons, 2009.
- [17] E. Merino, *Chem. Soc. Rev.* **2011**, *40*, 3835–3853.
- [18] W. J. Sandborn, Am. J. Gastroenterol. 2002, 97, 2939.
- [19] R. G. Anderson, G. Nickless, Analyst 1967, 92, 207–238.
- [20] K. Hunger, **2003**.
- [21] S. Hvilsted, C. Sánchez, R. Alcalá, J. Mater. Chem. 2009, 19, 6641–6648.
- [22] Ashutosh, N. D. Pandey, J. K. Mehrotra, *Colourage* 1979, 26, 25.
- [23] M. C. Barbero, S. Dughera, Eur. J. Org. Chem 2006, 4884.
- [24] B. M. Mogudi, P. Ncube, N. Bingwa, N. Mawila, S. Mathebula, R. Meijboom, Appl. Catal.

B Environ. 2017, 218, 240–248.

- [25] T. A. Le, J. K. Kang, S. H. Lee, E. D. Park, J. Nanosci. Nanotechnol. 2019, 19, 3252–3262.
- [26] Z. Helwani, M. R. Othman, N. Aziz, J. Kim, W. J. N. Fernando, *Appl. Catal. A Gen.* 2009, 363, 1–10.
- [27] S. K. Jana, P. Wu, T. Tatsumi, J. Catal. 2006, 240, 268–274.
- [28] V. P. Santos, M. F. R. Pereira, J. J. M. Orfao, J. L. Figueiredo, *Appl. Catal. B Environ.* 2009, 88, 550–556.
- [29] M. J. Climent, A. Velty, A. Corma, *Green Chem.* **2002**, *4*, 565–569.
- [30] Y. Khan, T. Kilpiö, M. Marin, V. Russo, J. Lehtonen, R. Karinen, T. Salmi, *Chem. Eng. Sci.* 2020, 221, 115695.
- [31] S. Verma, Y. Hamasaki, C. Kim, W. Huang, S. Lu, H.-R. M. Jhong, A. A. Gewirth, T. Fujigaya, N. Nakashima, P. J. A. Kenis, ACS Energy Lett. 2017, 3, 193–198.
- [32] O. R. Schade, K. F. Kalz, D. Neukum, W. Kleist, J.-D. Grunwaldt, *Green Chem.* 2018, 20, 3530–3541.
- [33] Y. Liu, H. Dai, J. Deng, S. Xie, H. Yang, W. Tan, W. Han, Y. Jiang, G. Guo, J. Catal. 2014, 309, 408–418.
- [34] H. Yang, H. Dai, J. Deng, S. Xie, W. Han, W. Tan, Y. Jiang, C. T. Au, *ChemSusChem* 2014, 7, 1745–1754.
- [35] B. Karimi, A. Biglari, J. H. Clark, V. Budarin, Angew. Chem. Int. Ed. 2007, 46, 7210–7213.
- [36] S. Dharmarathna, C. K. King'ondu, L. Pahalagedara, C.-H. Kuo, Y. Zhang, S. L. Suib, Appl. Catal. B Environ. 2014, 147, 124–131.