Heterogeneous Catalysis

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Mesoporous Manganese Oxide Catalyzed Aerobic Oxidative Coupling of Anilines To Aromatic Azo Compounds

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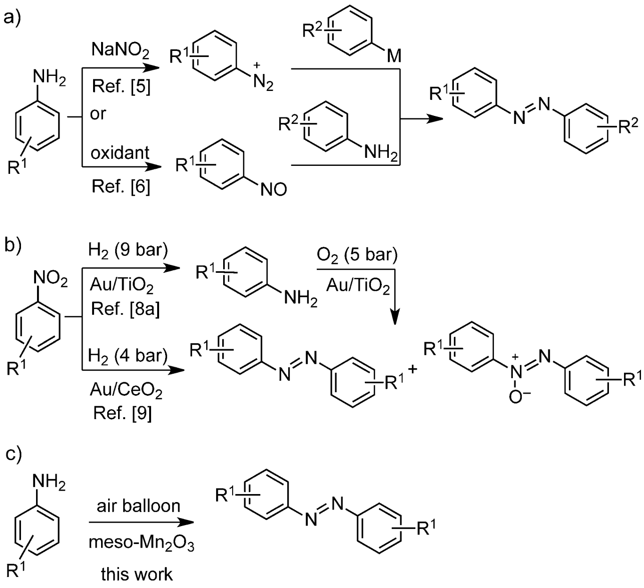
Abstract: *Herein we introduce an environmentally friendly approach to the synthesis of symmetrical and asymmetrical aromatic azo compounds by using air as the sole oxidant under mild reaction conditions in the presence of cost-effective and reusable mesoporous manganese oxide materials.*

Aromatic azo compounds are an important class of molecules used as dyes,[1] food additives,[2] pigments,[3a] indicators,[3c] and therapeutic agents,[3b,d] and as precursors in the synthesis of natural products.[4] Conventional methods for the formation of aromatic azo compounds involve the use of stoichiometric amounts of nitrite salts ($NaNO_2$) or toxic oxidants and proceed via diazonium[5] or nitrosobenzene intermediates[6] (Scheme 1 a). Catalytic pathways can make these conventional processes facile and more selective. A number of catalytic protocols have been developed for the synthesis of azo derivatives by the oxidation of anilines.[1] However, the existing systems[7] have several drawbacks, such as lower yields, undesirable overoxidation products, limited functional-group compatibility, the presence of additives, the use of harsh reaction conditions (high pressure, high temperature), and poor reusability of the catalyst. In 2008, Corma and co-workers made a breakthrough when they developed a Au/TiO_2-mediated synthesis of aromatic azo compounds from the corresponding aniline derivatives[8a,9] (Scheme 1 b).

In the following years, many important attempts were made to synthesis azo derivatives in good yields, for example, by the use of a $CuBr$/pyridine/O_2 reaction system,[10] a photocatalytic pathway in the presence of Au/ZrO_2,[11] and Pt or Pd nanowires in the presence of KOH.[12] Recently, Corma and co-workers reported another way of preparing azo compounds from aromatic nitro compounds: with Au/CeO_2 under high pressure of hydrogen.[8b,13] However, the use of precious metals (Au, Pt, or Pd), high pressure, and base additives make these processes industrially and environmentally unfriendly. Therefore, the development of cost-effective, efficient, heterogeneous catalysis for the synthesis of aromatic azo compounds under mild, atmospheric reaction conditions in the absence of additives is highly desirable.



Scheme 1. Catalytic routes for synthesizing aromatic azo compounds.

The use of catalytic systems based on transition-metal oxides has drawn significant attention for the synthesis of small organic molecules.[14] Recently, our research group introduced a new class of inverse-micelle-templated mesoporous manganese oxide materials [University of Connecticut (UCT) materials],[15,16] which were found to be effective in different organic transformations, such as the oxidation of alcohols[17] and amines,[18] the oxidation and esterification of long-chain alcohols, and methylbenzoic acid production by the oxidation of alkyl benzenes.[15] These mesoporous manganese oxide (meso-MnO_x) materials have versatile structural forms and high thermal stability, which influence their catalytic activity.[19] The redox cycle of manganese (Mn), along with its labile lattice oxygen molecules, have been found to be the dominant factors in the catalysis of different oxidation reactions.[18] Herein, we demonstrate a facile, cost-effective approach for the aerobic oxidative coupling of anilines in the presence of meso-MnO_x materials to synthesize diverse symmetrical and unsymmetrical aromatic azo compounds (Scheme 1 c). The absence of precious metals and additives, the use of air as the sole oxidant under atmospheric

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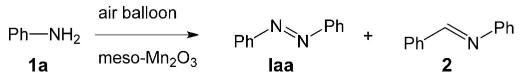
conditions, and the proper reusability of the catalyst make our catalytic protocol competitive with other existing systems.

According to a previous report, the metal-oxide-catalyzed oxidative coupling of aniline is initiated by the formation of radical intermediates through the transfer of electrons from aniline to a metal center.[8a] The target molecule (azobenzene) is formed after the successive loss of protons and electrons from the corresponding intermediates. Initially, we investigated the oxidative coupling of aniline as the model reaction for developing optimal reaction conditions. In a comparative study, aniline (**1a**) was converted into *trans*-1,2-diphenyldiazene (**Iaa**) by the use of different phases of manganese oxide materials synthesized by the UCT method (see Table S1 in the Supporting Information).[16] The Mn^{3+}-rich (as revealed from X-ray photoelectron spectra; see Figure S1 and Table S2 in the Supporting Information) meso-MnO_x material (meso-MnO_x-450) was found to be the best material in terms of conversion and selectivity (see Table S1). The meso-MnO_x-450 material had the crystalline Mn_2O_3 phase (see Figure S2) with a mesoporous size distribution (see Figure S3). The surface area was calculated to be 100 $m^2 g^{-1}$, and the pore size was 5.3 nm (see Table S3). A reaction with commercially available nonporous Mn_2O_3 produced the target compound in only 3% yield, which is similar to that observed under catalyst-free conditions (see Table S1). This result can be attributed to the presence of the mesoporous network of meso-Mn_2O_3, which not only provides a higher surface area (100 $m^2 g^{-1}$) than commercial Mn_2O_3 (11 $m^2 g^{-1}$), but also facilitates the adsorption and diffusion of aniline. A continual increase in conversion was observed as the catalyst loading was increased (see Figure S4), thus indicating that the system does not have limitations due to adsorption or mass transfer.

During the investigation of the effects of oxidants, higher conversion was observed for reactions conducted under air or oxygen than under nitrogen (see Table S4). This result indicates the importance of aerial oxygen in the reaction. The effects of different solvents with variable polarities were also surveyed (see Table S5), and toluene emerged as the best solvent, with 97% conversion. While optimizing the amount of solvent used, we found that 0.5 mL was optimal (> 99% conversion; Table 1, entry 5). The formation of a trace amount of imine **2** as a side product can be attributed to the condensation of benzaldehyde (from the oxidation of toluene) with aniline. This undesirable formation of benzaldehyde increased proportionally with the volume of toluene (Table 1, entry 1–5), thus reflecting higher selectivity towards the undesired formation of imine **2**. The use of oxidative additives, such as *tert*-butyl hydroperoxide (TBHP; Table 1, entry 6), enhanced the formation of benzaldehyde, thus leading to an increase in selectivity for the imine product to 79%. Hence, after extensive screening of all reaction parameters, we concluded that the optimal conditions were the use of 50 mg of *meso*-Mn_2O_3 in 0.5 mL of toluene at 110 °C under an air balloon (Table 1, entry 5). We used these reaction conditions for the rest of our study.

Table 1: Optimization of the oxidative coupling of aniline by meso-Mn_2O_3.[a]



1a **Iaa** **2**

Entry	Solvent volume [mL]	*t* [h]	Conv. [%][b]	Selectivity [%][b] **Iaa**	**2**	TON[c]
1	10	24	71	70	30	2.2
2	25	24	39	62	38	1.2
3	5	24	75	> 98	< 2	2.3
4	1	24	97	> 99	< 1	3.0
5	0.5	8	> 99	> 99	< 1	3.1
6[d]	10	36	58	21	79	1.8
7	no	36	51	100	0	1.6

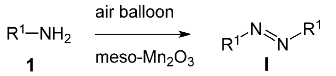
[a] Reaction conditions: **1a** (93 mg, 1.0 mmol), meso-Mn_2O_3 (50 mg, 0.32 mmol), toluene as the solvent, 110 °C, air balloon. [b] Conversion and selectivity were determined by GC–MS. [c] Turnover number: moles of aniline converted per mole of catalyst. [d] The reaction was carried out in the presence of TBHP.

To verify whether the observed catalysis was the result of solid meso-MnO_x or leached active metal species, we carried out the oxidative coupling of aniline and separated the catalyst from the system after a reaction time of 3 h (at about 64% conversion of aniline). The filtrate was then kept under the same reaction conditions for the next 7 h. Successive aliquots were taken after each hour and analyzed by GC–MS, but no further production of azobenzene was observed (see Figure S5). Moreover, inductively coupled plasma (ICP) analysis revealed a very low amount (79.6 ppb) of Mn in the filtrate. To check the reusability of the meso-Mn_2O_3 catalyst, we retrieved it from the reaction mixture by a simple filtration method with > 90% recovery. The reused catalyst was washed with excess toluene and acetonitrile, and finally reactivated at 250 °C (to remove the adsorbed species from the catalyst surface) for 50 min prior to reuse. The retrieved catalyst could be used at least five times, although a slight gradual decrease in performance was observed (see Figure S6).

We then focused our attention on evaluating the scope and general applicability of our catalytic protocol. Under the operationally simple and optimized reaction conditions, diverse aniline derivatives with electron-rich (Table 2, entries 2–5) and electron-deficient groups (entry 6) were converted into the corresponding aromatic azo compounds in excellent yield (as high as 98%) and with excellent selectivity (> 99%).

The reaction of a heterocyclic aniline analogue, **1g** proceeded to comparatively lower conversion (45%; Table 2, entry 7) with a greater amount of the catalyst. This result may be due to poisoning of the metal center of the catalyst by coordination with the pyridine N atom.[20] The excellent yield (82%) of the azo compound **Ihh** (Table 2, entry 8) derived from bulky 1-naphthylamine (**1h**) indicated that steric hindrance did not have a significant impact on this reaction. Moreover, **the** survival of halo-substituted compounds, such as 4-chloroaniline (**1f**), which was converted into the corresponding azo compound **Iff** (84%; Table 2, entry 6), is noteworthy, as the prevention of dehalogenation is a challenge in catalytic reactions involving halogen derivatives.[21] We found that this N,N coupling is only possible when the $-NH_2$ group is attached to an aromatic ring; with benzylamine (**1j**), the imine was formed by self-coupling (Table 2, entry 10).

Table 2: Aerobic oxidation of anilines to aromatic azo compounds by meso-Mn_2O_3.[a]

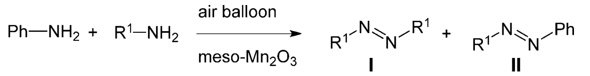


Entry	R^1	t [h]	Conv. [%][c]	Selectivity for I [%][c,d]	TON[e]
1	C_6H_5 (**1a**)	8	>99	>99 (93; **Iaa**)	3.13
2	4-MeC_6H_4 (**1b**)	7	>99	>99 (95; **Ibb**)	3.13
3	4-$OMeC_6H_4$ (**1c**)	4	>99	>99 (89; **Icc**)	3.13
4	3,5-$Me_2C_6H_3$ (**1d**)	4	88	>99 (**Idd**)	2.78
5	4-N(Me)$_2C_6H_4$ (**1e**)	8	>99	>99 (**Iee**)	3.13
6	4-Cl-C_6H_4 (**1f**)	6	84	>99 (**Iff**)	2.65
7[b]	2-$NH_2C_5H_5N$ (**1g**)	12	45	>99 (**Igg**)	0.71
8	1-naphthyl (**1h**)	12	82	>99 (**Ihh**)	2.59
9	2-Cl-4-MeC_6H_3 (**1i**)	16	97	>99 (**Iii**)	3.06
10	$C_6H_5CH_2$ (**1j**)	9	>99	0	0

[a] Reaction conditions: R^1NH_2 (1.0 mmol) and meso-Mn_2O_3 (50 mg, 0.32 mmol) were heated in toluene (0.5 mL) at 110 °C under air balloon. [b] The reaction was carried out with 100 mg of the catalyst. [c] Conversion and selectivity were determined by GC–MS on the basis of the concentration of the aniline starting materials. [d] The yield of the isolated product is shown in parenthesis in entries 1–3. [e] The TON value is the number of moles of the aniline derivative converted per mole of catalyst.

The excellent activity of the meso-Mn_2O_3-mediated homocoupling of anilines inspired us to study the feasibility of the protocol for the synthesis of unsymmetrical aromatic azo compounds. Unsymmetrical aromatic azo compounds are usually synthesized by treating diazonium salts with electron-rich aromatic compounds.[5,6] Initially, we examined reactions between *p*-anisidine (**1c**) and aniline (**1a**) in different molar ratios (Table 3, entries 1–3). A 1:3 molar ratio of *p*-anisidine to aniline was selected as the optimum ratio for the synthesis of the unsymmetrical aromatic azo compound **IIca** (35% selectivity; Table 3, entry 2). Various structurally different aromatic aniline derivatives, such as *p*-toluidine, 3,5-dimethylaniline, *p*-*N*,*N*′-dimethylaniline, *p*-chloroaniline, and napthylamine, were subjected to the reaction with aniline in this way. The unsymmetrical aromatic azo compound **IIba** was synthesized from *p*-toluidine (**1b**) and aniline (**1a**) with 56% selectivity (Table 3, entry 4).

Table 3: Aerobic oxidative cross-coupling of aniline with different aniline derivatives.[a]



Entry	R^1	Molar ratio[b]	Conv. [%][c]	Selectivity for II [%][c,d]	Yield [%][c]
1	4-$OMeC_6H_4$ (**1c**)	1:2	>99	28 (**IIca**)	28
2	4-$OMeC_6H_4$ (**1c**)	1:3	>99	35 (**IIca**)	35
3	4-$OMeC_6H_4$ (**1c**)	1:4	>99	37 (**IIca**)	37
4	4-MeC_6H_4 (**1b**)	1:3	>99	56 (**IIba**)	55
5	3,5-$Me_2C_6H_3$ (**1d**)	3:1	>99	92 (**IIda**)	91
6	4-N(Me)$_2C_6H_4$ (**1e**)	3:1	>99	43 (**IIea**)	43
7	4-ClC_6H_4 (**1f**)	3:1	>99	88 (**IIfa**)	87
8	1-naphthyl (**1h**)	3:1	80	72 (**IIh**)	58

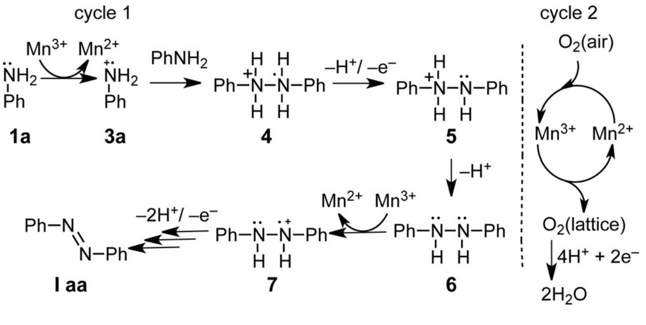
[a] Reaction conditions: R^1NH_2 and $PhNH_2$ (total amount, according to the molar ratio indicated: 1 mmol), meso-Mn_2O_3 (50 mg, 0.32 mmol), toluene (0.5 mL), 110 °C, air balloon, 12 h. [b] Aniline derivative/aniline. [c] Conversion and selectivity were determined by GC–MS on the basis of the concentration of the aniline starting materials. [d] Selectivity was calculated on the basis of the self-coupled (I) and cross-coupled products (II) derived from the limiting reagent.

Anilines with electron-donating groups undergo homocoupling much faster (Table 2, entries 2–5) than those with electron-withdrawing groups (Table 2, entry 6). Therefore, for cross-coupling, an excess of the more electron deficient aniline was used to enhance the yield of the cross-coupled product (Table 3, entry 1–4). The molar ratio was flipped to 3:1 (Table 3, entry 5–8) for the reactions with aniline of aniline derivatives **1d**, **1e**, **1f**, and **1h**, which required equal or more time for homocoupling as compared to aniline In these reactions, the cross-coupled products were formed in moderate to high yields (Table 3, entries 5–8).

To investigate the kinetic aspects of the reaction, we conducted a time-dependent study (see Figure S7). The formation of a minute amount of the imine resulting from the coupling of aniline with benzaldehyde (formed by the oxidation of toluene) was tracked during the reaction. Kinetic experiments revealed a first-order rate equation with respect to aniline (**1a**; see Figure S8), with a rate constant of 0.32 h^{-1}. The apparent activation energy (E_a), as determined from an Arrhenius plot in the temperature range of 20–110 °C (see Figure S9), was 29.8 kJ mol^{-1}.

We conducted several experiments to gain an understanding of the mechanistic details of the catalytic process. In the presence of 2,6-di-*tert*-butyl-4-methylphenol (a radical inhibitor), no trace of azobenzene was observed. Rather, the reaction gave the product derived from the trapping of **3a** (Scheme 2) by 2,6-di-*tert*-butyl-4-methylphenol (see Figure S10). The formation of this intermediate suggests that our mechanism is similar to that proposed by Corma and coworkers.[8a] They assumed that the radical species **3a** formed from aniline (**1a**) was coupling with another molecule of aniline **1a** to form **4** (a compound with a 3 e^- σ bond), which through the successive loss of a proton, an electron, and another proton formed intermediate **6**. Intermediate **6** goes through all the aforementioned steps once again to provide the final product **Iaa**.

The generation of the radial intermediate **3a** caused the reduction of surface-active Mn^{3+} to Mn^{2+}, which led to the facile release of labile lattice oxygen (Scheme 2, cycle 2).[22] That lattice oxygen combines with the protons (4 H^+) and electrons (2 e^-) released in cycle 1 to form water. The supply



Scheme 2. Proposed mechanism of the reaction.

of oxygen from the air was crucial for this catalytic activity, as the lattice oxygen lost should be replenished by the oxygen from air.[18] This catalytic cycle is consistent with our observation of a diminished reaction rate when the reaction was performed under nitrogen only, instead of under air (see Table S2).

When 1,2-diphenylhydrazine (**6**) was heated with *meso*-Mn_2O_3 under the optimized conditions, azobenzene (**Iaa**) was formed in just 20 min. This reaction did not occur in the absence of the catalyst (Table 4). The very fast reaction rate could be the reason that intermediate **7** was not trapped.

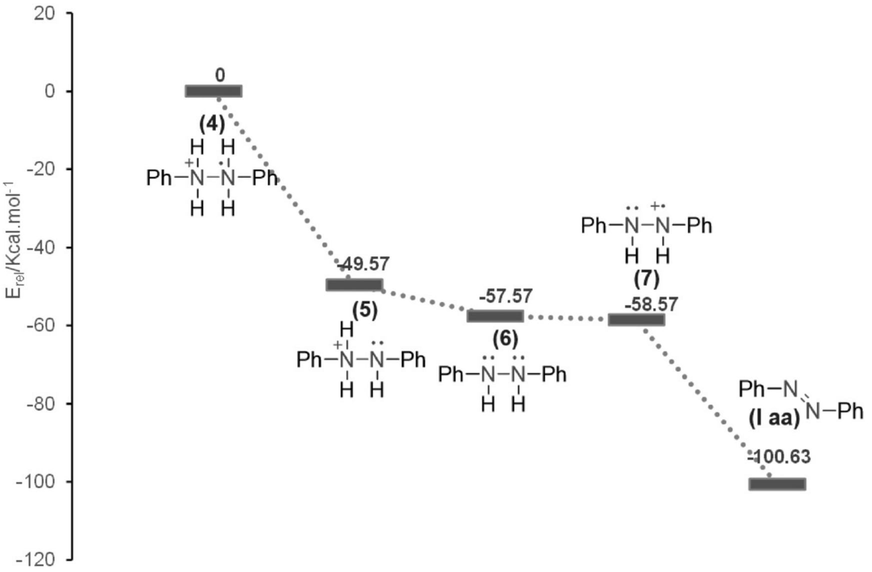
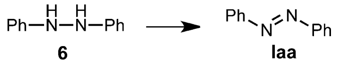


Figure 1. Energy profile of the reaction in the gas phase, as determined by DFT calculations.

Table 4: Reactivity of 1,2-diphenylhydrazine (**6**) in the presence and absence of meso-Mn_2O_3.[a]



6 → **Iaa**

Entry	Catalyst	Conversion [%][b]	Selectivity for **Iaa** [%][b]
1	meso-Mn_2O_3	>99	>99
2	none	0	0

[a] Reaction conditions: 1,2-diphenylhydrazine (**6**; 1 mmol) and meso-Mn_2O_3 (50 mg, 0.32 mmol) were heated in toluene (0.5 mL) at reflux (110 °C) under an air balloon for 20 min. [b] Conversion and selectivity were determined by GC–MS.

To further validate the reaction mechanism, we also performed quantum-mechanical computations on the system in the gas phase by using density functional theory (DFT) as implemented in the Vienna ab initio package. Furthermore, to estimate the Mn oxidation states, DFT calculations were carried out on mesoporous manganese oxide (meso-MnO_x). A DFT energy profile for the reaction in the gas phase is shown in Figure 1. The relative energies [kcal mol^{-1}] are based on the summation of the representative total energies E_{tot} of all species. Our Bader charge analysis based on DFT calculations supports the hypothesis that in step 1, the active Mn^{3+} species was reduced to Mn^{2+}. The calculated charge on Mn was 2.18 e^-. In step 2, the generated radical is further stabilized by coupling with another molecule of aniline, and the resulting intermediate readily loses two protons and an electron in steps 3 and 4 to give the more stable intermediate 1,2-diphenylhydrazine (**6**). In the subsequent steps (transformation of **6** into **Iaa**), our DFT computations support the suggested mechanism, according to which a similar pathway is followed to that for the conversion of **1a** into **4**.

In conclusion, we have developed a facile, cost-effective, and mild reaction procedure for synthesizing diverse symmetrical and unsymmetrical aromatic azo compounds by the use of inexpensive meso-MnO_x materials. A variety of aniline derivatives underwent oxidative homocoupling and cross-coupling in moderate to excellent yields (35–99 %). Air as the terminal oxidant, the absence of precious metals and additives, and the atmospheric conditions with proper reusability make our catalytic protocol superior to other reported systems. Through mechanistic investigations, we were able to reveal the involvement of surface-active Mn^{3+} species, labile lattice oxygen, and radical intermediates in the catalytic cycle. A manganese-mediated electron-transfer mechanism from aniline was proposed and was supported by DFT calculations. Studies aimed at modifying the reaction mechanism to make the reaction more facile are under way.

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