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Direct catalytic oxyamination of benzene to aniline over Cu(II) nanoclusters supported on $CuCr_2O_4$ spinel nanoparticles *via* simultaneous activation of C–H and N–H bonds†

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We report the facile synthesis of a highly efficient, reusable catalyst comprising Cu(II) nanoclusters supported on $CuCr_2O_4$ spinel nanoparticles for the oxyamination of benzene to aniline (H_2O_2 + NH_3) under mild aqueous reaction conditions. The synergy between the Cu(II) nanoclusters and $CuCr_2O_4$ spinel nanoparticles plays the most vital role towards its high catalytic activity.

Aniline is one of the most important building blocks in chemistry as it is used as an intermediate in many different applications, such as rubber processing chemicals, dyes and pigments, agricultural chemicals, pharmaceuticals *etc.*[1] Commercially, aniline is produced in an indirect process where nitration of benzene is initially carried out using mixed acids, followed by further reduction of the nitro functionality to aniline by a reducing reagent. This multistep process is not only high energy and time consuming, but also requires harsh operation conditions and generates huge amounts of by-products, and causes severe environmental pollution, which hampers the green trends of global chemical manufacturing.[2] In 1917, Wibaut reported the direct synthesis of aniline by passing benzene and ammonia over a reduced Fe/Ni catalyst in the temperature range 550–600 °C.[3] However, since the direct amination of benzene is thermodynamically equilibrium limited, the yield of aniline is rather low, even under strict reaction conditions.[4] One probable trajectory to shift the thermodynamic equilibrium towards the forward direction is to remove the produced hydrogen. This has been achieved by using additives,[5] O_2,[3,4,6] or/and reducible metal oxides which react with the hydrogen to form water, or the use of a hydrogen-permeable membrane[4,7] that permitted hydrogen to diffuse away from the reaction system. DuPont reported the highest yield of 13.6% to aniline by the direct amination of benzene with ammonia at 350 °C and 300–400 atm.[4] Generally, these methods suffer from the requirement of expensive equipment that resists high temperature (from 100–1000 °C), high pressure (from 10 atm to 1000 atm) and strong corrosion. Aniline can also be synthesized by reacting aryl halides (Ar–X, X = Cl, Br) with acylamide,[8] or aminating benzene with hydroxylamine (NH_2OH).[9] Direct amination of benzene with ammonia, in contrast to the above processes, is practically attractive from the viewpoints of both atom economy, the direct use of raw materials and low price of NH_3. However, the strength of the N–H bond in ammonia (107 kcal mol^{-1}) makes the "N–H activation" challenging.[10] Yuzawa *et al.* reported the amination of benzene by aqueous ammonia on a Pt/TiO_2 photocatalyst under comparatively mild conditions, but the yield of aniline was extremely low.[7] The use of H_2O_2 as an oxidant has proved promising for the oxyamination of benzene, but the yield of aniline was still not satisfactory.[11] However, since this reaction is endergonic ($\Delta G = 53.7$ kJ mol^{-1}), the yield of aniline is still low (<10%) even when the reaction is carried out at a high temperature and pressure. Therefore, production of aniline by activation of the aromatic C–H bond and introducing the new functional group $-NH_2$ into the aromatic nuclei *via* substitution of a hydrogen atom in a direct process under mild conditions, with a satisfactory yield is really an interesting as well as a challenging topic in the field of catalysis. Therefore, the search for an effective catalyst to enhance the yield and selectivity to aniline is one of the most important issues for researchers.

Copper chromium mixed oxide with a spinel structure had been recognized as an important class of bi-metallic oxides that can act as a versatile catalyst.[12] Apart from its usage in chemical industries, copper chromite finds its major global application as a burn rate modifier in solid propellant processing for space launches.[13] Supported copper catalysts catalyze many industrially important reactions.[14] The catalytic properties of the active copper phase can be greatly influenced by the nature of the supported oxide and the dispersion of the active component.[15] However, the nature of the active species of these catalysts is still the subject of extensive investigation by many researchers.

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† Electronic supplementary information (ESI) available: Detailed catalyst characterization techniques, experimental details, SEM images, TEM images, XPS diagrams, effects of different reaction parameters, the reaction mechanism *etc.* See DOI: 10.1039/c4cc02937b

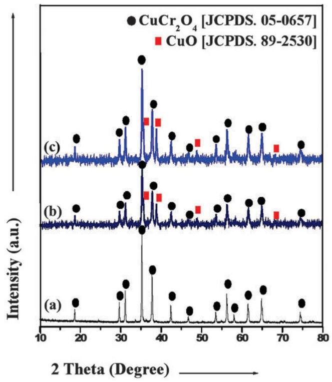

Fig. 1 XRD diffractogram of the (a) $CuCr_2O_4$ spinel (commercial), (b) used catalyst (after 5 cycles) and (c) prepared catalyst.

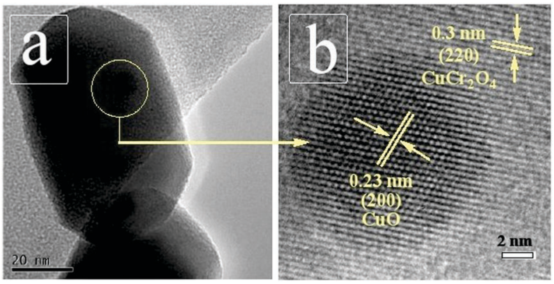

Fig. 2 TEM images of the catalyst at different magnifications.

Herein, we report a cationic surfactant, cetyltrimethylammonium bromide (CTAB), mediated catalyst preparation of Cu(II) nanoclusters, of ~10 nm in size, supported on $CuCr_2O_4$ spinel nanoparticles, of 30–60 nm in size. We also report the oxyamination of benzene to aniline with H_2O_2 and aqueous NH_3 under mild reaction conditions (80 °C) in liquid phase using our so prepared catalyst. A benzene conversion of 18% with an aniline selectivity of 96% was achieved over this catalyst. The catalyst was prepared by modifying our own preparation method (see the ESI†) varying the ratio of copper and chromium[16] and was characterized by XRD, XPS, SEM, TEM, TPR and TGA.

The X-ray diffraction patterns of the Cu–Cr catalysts (Fig. 1b) showed the typical diffraction lines of bulk $CuCr_2O_4$ with a maximum intensity peak at a 2θ value of 35.16° (JCPDS. 05-0657) accompanied by small peaks corresponding to crystalline monoclinic CuO (JCPDS 89-2530). Applying the Debye–Scherrer equation, the average crystallite sizes of the particles of $CuCr_2O_4$ and CuO were determined to be 35 nm (based on $2\theta = 35.16°$) and 13 nm (based on $2\theta = 35.6°$), respectively, and the data matched well with that obtained from the TEM results. This indicates the presence of supported Cu(II) oxide clusters on $CuCr_2O_4$ spinel nanoparticles. The topology of the catalyst was studied by scanning electron microscopy (SEM, Fig. S1, ESI†) which showed that a typical sample was composed of uniform nanoparticles in the range of 30–60 nm throughout. However, the transmission electron microscopy (TEM) image revealed that some particles are almost hexagonal (Fig. 2a) and 50 nm in size. Some spherical particles, 8–15 nm in size (Cu(II) nanoparticles), are seen to be anchored on these hexagonal particles. A representative high resolution TEM (HRTEM) image taken of a nanoparticle is shown in Fig. 2b. The lattice fringes with a d-spacing of 0.23 nm, corresponding to the spacing of the [111] planes of monoclinic CuO, is conveniently discriminated from that of the [220] planes of $CuCr_2O_4$, with a d-spacing of 0.30 nm.[13] The XPS binding energies (BE) of some characteristic core levels of Cu, Cr, and O in the Cu–Cr samples (Fig. S5–S7, ESI†) further support the fact that the main phase comprised the $CuCr_2O_4$ spinel, whereas a small amount of CuO is dispersed on the spinel phase of the catalyst surface. Furthermore, the coordination of Cu(II) oxide supported nanoclusters and the $CuCr_2O_4$ spinel nanoparticles was confirmed from TPR analysis (Fig. S8, ESI†).

The oxyamination of benzene was carried out in liquid phase in a round bottom flask under atmospheric pressure using the prepared $Cu^{2+}/CuCr_2O_4$ spinel nanoparticle catalyst, where an aqueous mixture of $(H_2O_2 + NH_3)$ was added dropwise. The activity of the catalyst (designated as Cu(II)-SP) is shown in Table 1. A blank reaction was performed (in the absence of catalyst) and no product was detected in the reaction mixture (entry 1, Table 1), reflecting the necessity of the catalyst. We also noticed that temperature played a crucial role in the oxyamination reaction of benzene (Fig. S10, ESI†). No aniline was detected at 50 °C, and no decomposition of NH_3

Table 1 Oxyamination reaction of benzene over a catalyst comprising Cu(II) nanoclusters supported on $CuCr_2O_4$ spinel nanoparticles[a]

			S_P[c] (%)				
Entry	Catalyst	C_B[b] (%)	Φ_{NH_2}	Φ_{OH}	Others	Y_A[d] (%)	TON[e]
1	No catalyst	—	—	—	—	—	—
2	$Cu(NO_3)_2$	—	—	—	—	—	—
3	$CuCl_2$	—	—	—	—	—	—
4	$CuSO_4$	—	—	—	—	—	—
5	CuO	—	—	—	—	—	—
6	Cu_2O	—	—	—	—	—	—
7	Cr_2O_3	—	—	—	—	—	—
8	$CuCr_2O_4^{COM}$	—	—	—	—	—	—
9	$CuCr_2O_4^{NP}$	5	—	99.0	0	—	—
10	$CuO–CuCr_2O_4^{IMP}$	—	—	—	—	—	—
11[f]	Cu(II)-SP	18	96	3	1	17.3	54.1
12[g]	Cu(II)-SP	16.8	94.5	3.5	2	15.9	58.8
13[h]	Cu(II)-SP	9.5	70	28	2	6.7	20.8
14[i]	Cu(II)-SP	7.5	—	97	3	—	—
15[j]	Cu(II)-SP	6.5	99	—	—	6.5	20.2
16[k]	Cu(II)-SP	22	99	—	—	22	68.4
17[l]	Cu(II)-SP	0.8	99	—	—	0.8	2.5

[a] Reaction conditions: benzene = 1 g; solvent = 70% AcOH–MeCN (10 ml); catalyst = 0.1 g; benzene : H_2O_2 : NH_3 mole ratio = 1 : 3 : 2; time = 6 h and temperature = 80 °C. [b] C_B = conversion of benzene based upon the FID-GC (GC equipped with a flame ionization detector) = 100 × [initial amount (mol) of benzene − remaining unreacted amount (mol) of benzene]/initial amount (mol) of benzene. [c] S_P = selectivity of products = 100 × [total amount (mol) of product(s)/total amount (mol) of benzene consumed]. [d] Y_A = yield of aniline = [C_B × selectivity of aniline]/100. [e] TON = turnover number calculated by moles of aniline formed/one mol of Cu in the catalyst present as supported Cu(II) on spinel. [f] Fresh. [g] Spent (after 5 uses) catalyst comprising Cu(II) nanoclusters supported on $CuCr_2O_4$ spinel nanoparticles. [h] Solvent = 50% AcOH–MeCN. [i] MeCN. [j] AcOH. [k] Using NH_2OH. [l] Using TEMPO (radical scavenger) NP = nanoparticles and IMP= impregnation method.

was observed, suggesting that the amination process is solely dependent on the decomposition of NH_3. An increment in temperature increased the yield of aniline, and the maximum yield with the highest selectivity to aniline (96%) was achieved at 80 °C. However above 80 °C the yield of aniline decreased rapidly due to the formation of unwanted by-products like biphenyl, phenol, nitrobenzene *etc.* At the same time the conversion of benzene was not at its maximum; this phenomenon may be attributed to the decomposition of H_2O_2 molecules that remained unreacted in the aqueous (H_2O_2 + NH_3) mixture. We also noticed that the optimum molar ratio of $H_2O_2:NH_3$ was 1:1.5; when the reaction was allowed to continue without adding H_2O_2, no conversion of benzene was detected (Fig. S12, ESI†). Unhindering the benzene to NH_3 molar ratio, when the amount of H_2O_2 was increased, we noticed that initially the yield of aniline and the conversion of benzene increased. The yield of aniline reached a maximum of 17.3% when the $H_2O_2:NH_3$ molar ratio was 1:1.5. The amount of phenol and dihydroxybenzene started increasing rapidly with the increment of this molar ratio; further increment in the concentration of H_2O_2 compelled NH_3 molecules to react with H_2O_2 to facilitate the oxidative coupling of NH_3 over the catalyst. Furthermore, in the absence of aqueous NH_3, only phenol and some dihydroxybenzene were discovered in the reaction mixture (Fig. S13, ESI†). Keeping the benzene to H_2O_2 molar ratio constant, we monitored the effect of the amount of NH_3 on the reaction. When the concentration of aqueous ammonia was too low, the contact between the catalyst, the reagents and benzene was hindered, which resulted in a decrease in the catalytic efficiency. Therefore, initially, both the conversion of benzene and yield of aniline increased sharply, with the increment of the NH_3 solution. When the concentration of aqueous ammonia was too high, it diluted the H_2O_2 concentration and thereby decreased the intimate contact between the reagents, benzene and the catalyst, resulting in the poor yield of aniline, although the selectivity of the latter increased sharply. Furthermore, with the addition of excess ammonia solution in the reaction mixture a large amount of benzene molecules escaped from the reaction mixture with the evaporated ammonia, waning the catalytic system. These experimental findings were in line with the fact that, the active species responsible for the oxyamination reaction of benzene was generated by the (H_2O_2 + NH_3) mixture solely, whereas, the initiation of the reaction starts with the C–H bond activation by H_2O_2. It is worth mentioning that, the oxyamination reaction is highly dependent on the pH of the medium (entries 13–15, Table 1). No aniline was detected in the absence of acetic acid. The higher aniline yields as well as TONs (based on excess Cu^{2+} supported on the $CuCr_2O_4$ spinel nanoparticles) were obtained in the reaction media with pH values in the range 0.2–0.3, implying a strong correlation between the acidic medium and the activation of the N–H bond in NH_3. Maintaining all of the optimum conditions, when the reaction was allowed to run for hours, we noticed that, the highest selectivity for aniline was observed at 6 h and it sharply decreased with time after that due to the oxidative coupling of aniline in the presence of excess H_2O_2 in the medium (Fig. S14, ESI†).

To investigate the possible catalytic activity of Cu species in the amination, various commercial Cu-compounds were employed separately as catalysts (entries 2–6, Table 1). The experimental results showed that no aniline or nitrobenzene was produced, excluding the catalytic contribution of the free Cu^{2+} species to N–H bond activation. Moreover, commercial Cr_2O_3, commercial $CuCr_2O_4$ and even a $CuCr_2O_4$ spinel nanoparticle catalyst failed to produce aniline (entries 7–9, Table 1), indicating the fact that, neither Cr_2O_3 nor the $CuCr_2O_4$ spinel-framework individually was enough to activate the N–H bond. Use of $CuCr_2O_4$ spinel nanoparticles produces phenol in the reaction medium (entry 9, Table 1), which ascertained the fact that, it can efficiently activate the C–H bond in benzene. Therefore, it can be rationally assumed that the cooperative action of the Cu^{2+} nanoclusters and the spinel framework assist the activation of the N–H bond in NH_3. A control experiment using aniline as the reactant (with the other optimum reaction conditions unchanged) revealed that azoxybenzene, azobenzene, nitrosobenzene and nitrobenzene were produced by the oxidation of aniline. In a different control experiment, phenol was used as the reactant. No aniline was obtained, indicating that phenol was not the possible intermediate for aniline formation. We believe that, the amination and hydroxylation reactions are competitive, while the formation of aniline and other oxygenates of aniline are progressive. Furthermore, when aqueous solutions of $(NH_4)_2SO_4$, NH_4Cl or even $(NH_4)_2OAc$ with H_2O_2 were used instead of the aqueous NH_3 solution, the product was not aniline, but phenol (trace amount), indicating that the reactive species for the amination was not NH_4^+, but NH_3 in the aqueous solution. We also conducted a control experiment with the direct use of NH_2OH to detect the probable mechanistic path. We observed a 22% yield of aniline in this case (entry 16, Table 1). Moreover, we also used (2,2,6,6-tetramethyl-piperidin-1-yl)oxyl (TEMPO) as a radical scavenger (10% by weight wrt benzene) while conducting the experiment maintaining all of the optimum conditions. A drastic change in the conversion of benzene was noticed (entry 17, Table 1).

From the above experimental findings, it is rational to say that the direct synthesis of aniline from benzene probably follows a free radical mechanism pathway *via* the formation of NH_2OH as suggested by Mantegazza *et al.*[17] Nanoclusters of Cu(II), which are supposed to be the active site in the catalyst, probably act as a π-acid site and invite dense π-electron clouds of benzene molecules. Benzene addition reduces Cu(II) to Cu(I) species in acidic medium, and the latter take part in the oxyamination mechanism (Scheme S1, ESI†).[18] As described by Kuznetsova *et al.*, a protonated amino radical ($^{\bullet}NH_3^+$) is generated in acidic medium which then acts as the active aminating species, based on *ab initio* quantum mechanical calculations for the amination of benzene.[9a] Cu(II) interacts with NH_2OH in acidic medium and generates a protonated amino radical ($^{\bullet}NH_3^+$) by reducing NH_2OH. The latter reacts with benzene to give an unstable protonated aminocyclohexadienyl intermediate, which is oxidized by the catalyst to give aniline. Cu(II) is regenerated by the unreacted H_2O_2 molecules present in the reaction mixture;[19] this is probably why an excess amount of H_2O_2 is needed for this oxyamination reaction. Furthermore, benzene produces phenyl radicals in the presence of H_2O_2 (stabilized by the acetonitrile solvent). These radicals self-condense to form biphenyl as a side product.

A reusability test of the catalyst (Table S1, ESI†) was conducted. ICP-AES was performed after each run to detect Cu leaching and the results are listed in Table S1, in the ESI.† The test showed that the catalyst retained most of its activity upon recycling after 5 consecutive catalytic runs and hardly any leaching of metals was observed. Furthermore, the used catalyst was characterized by XRD (Fig. 1c) and TEM (Fig. S4b, ESI†). The XRD patterns and the morphology for the used catalyst were not changed, which showed that the catalyst remained unchanged even after 5 cycles. Thus the catalyst demonstrated good reusability and was therefore truly heterogeneous in nature.

To conclude, we report a facile route for the synthesis of Cu(II) nanoclusters supported on $CuCr_2O_4$ nanoparticles. The material displayed excellent catalytic performance in the sustainable oxyamination reaction of benzene to aniline in a direct process using NH_3 and H_2O_2, achieving high efficiency in terms of activity, selectivity, mild conditions and catalyst recyclability. The component, Cu(II), is found to exert high influence on both the conversion rate and product selectivity. Furthermore, the catalyst can be reused several times without any significant activity loss. These effects probably stem directly from the synergy between the Cu(II) and $CuCr_2O_4$ spinel nanoparticles. The process may serve as a promising replacement of traditional aniline production.

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