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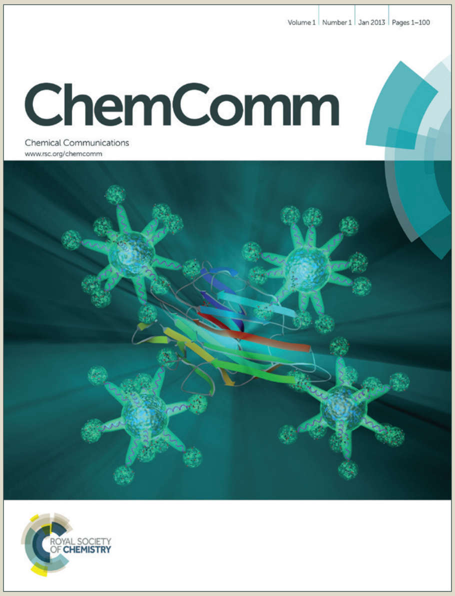

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

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Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Direct Oxyamination of Benzene to Aniline over Cu(II) nanoclusters supported on $CuCr_2O_4$ Spinel Nanoparticles Catalyst via simultaneous activation of C-H and N-H bonds

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We report a facile synthesis of highly efficient, reusable Cu (II) nanoclusters supported on $CuCr_2O_4$ spinel nanoparticles catalyst for the oxyamination of benzene to aniline with aqueous (H_2O_2 + NH_3) at mild reaction condition. 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 fields of application such as rubber processing chemicals, dyes and pigments, agricultural chemicals and 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 associated with high energy and time consuming, but also requires harsh operation conditions and generates huge amount of by-products, and causes severe environmental pollution, that 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 reacted with 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 direct amination of benzene with ammonia at 350 °C and 300–400 atm.[4] Generally, these methods suffer from the needs 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 $KCalmol^{-1}$) makes the "N–H activation" challenging.[10] Yuzawa et. al reported the amination of benzene by aqueous ammonia on Pt/TiO_2 photocatalyst under comparatively mild condition, but the yield of aniline was extremely low.[7] Use of H_2O_2 as oxidant has been proved to be promising for the oxyamination of benzene, but the yield of aniline was still not satisfactory.[11] However, since this reaction is endothermic (ΔG=53.7 KJ mol^{-1}), the yield of aniline is still low (<10%) even when the reaction is carried out at high temperature and pressure. Therefore, production of aniline by activation of aromatic C-H bond and introducing the new functional group $-NH_2$ in the aromatic nuclei via substitution of this hydrogen atom in a direct process at mild condition, with satisfactory yield is really an interesting as well as a challenging topic in the field of catalysis. Therefore, search for an effective catalyst to enhance the yield and selectivity to aniline is one of the most important issues for the researchers.

Copper chromium mixed oxides with a spinel structure had been recognized as an important class of bi-metallic oxides that act as a versatile catalyst.[12] Apart from its usage in chemical industries, copper chromite finds its major application as a burn rate modifier in solid propellant processing for space launch vehicles globally.[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.

Herein, we report the cationic surfactant cetyltrimethylammonium bromide (CTAB) mediated preparation of nanoclusters of Cu (II) with size ~10 nm, supported on $CuCr_2O_4$ spinel nanoparticles catalyst with size 30-60 nm. We also report an oxyamination of benzene to aniline with H_2O_2 and aqueous NH_3 at mild reaction condition (80 °C) at 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 (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 the bulk $CuCr_2O_4$ with the maximum intensity peak at 2θ value of 35.16° (JCPDS. 05-0657) accompanied by small peaks of crystalline monoclinic CuO (JCPDS 89-2530). Applying Debye-Scherrer equation, the average crystallite size of the particles were determined to be 35 nm (based on 2θ= 35.16°) and 13 nm (based on 2θ= 35.6°) respectively and the data matched well with that obtained from 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 a typical sample composed of throughout uniform nanoparticles in the range of 30-60 nm. However, transmission electron microscopy (TEM) image revealed that some particles are almost hexagonal (Fig. 2a) with 50 nm in size. Some spherical particles with size 8-15 nm (Cu (II) nanoparticles) are seen to be anchored on these hexagonal particles. A representative high resolution TEM (HRTEM) image taken from a nanoparticle is shown in Figure 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 [211] planes of $CuCr_2O_4$ with a d-spacing of 0.30 nm can also be seen.[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 is comprised of $CuCr_2O_4$ 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 round bottom flask under atmospheric pressure using the prepared $Cu^{2+}/CuCr_2O_4$ spinel nanoparticles catalyst, where aqueous mixture of (H_2O_2 + NH_3) was added dropwise. The activity of the catalyst (designated as Cu (II)-SP) has been shown in Table 1. Blank reaction was performed (in absence of catalyst) and no product was detected in the reaction mixture (Entry 1, Table1), 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 was observed, suggesting the fact that, the amination process is solely dependent on decomposition of NH_3. Increment in temperature increased the yield of aniline, and the maximum yield, with highest selectivity to aniline (96%) was achieved at 80 °C. But above 80 °C, yield of aniline decreased rapidly due to the formation of unwanted by-products like biphenyl, phenol, nitrobenzene etc. At the same time conversion of benzene was not upto the mark; 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, 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 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 maxima of 17.3%, when 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 produced NH_3 molecules to react with H_2O_2 to facilitate oxidative coupling of NH_3 over the catalyst. Furthermore, in absence of aqueous NH_3, only phenol and some dihydroxybenzene was discovered in the reaction mixture (Fig. S13, ESI†). Unaltering benzene to H_2O_2 molar ratio, we monitored the effect of increment of 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 the decrement in the catalytic efficiency. So, initially, both the conversion of benzene and yield of aniline increased sharply, with the increment of NH_3 solution. When the concentration of aqueous ammonia was too high, basically it diluted the H_2O_2; and thereby decreased 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 evaporated ammonia, waning the catalytic system. These experimental findings were in consistent 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 pH of the medium (Entry 13-15, Table1). 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 $CuCr_2O_4$ spinel nanoparticles) were obtained in the reaction media with pH values in the rang 0.2-0.3, implying a strong correlation between acidic medium and the activation of N-H bond in NH_3. Maintaining all 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 went decreasing with time, due to the oxidative coupling of aniline in presence of excess H_2O_2 present 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 (Entry 2-6, Table 1). Experimental results showed that no aniline or nitrobenzene was produced, excluding the catalytic contribution of the free Cu^{2+} species to the N–H bond activation. Moreover, commercial Cr_2O_3, commercial $CuCr_2O_4$ and even $CuCr_2O_4$ spinel nanoparticles catalyst failed to produce aniline (Entry 7-9, Table 1), indicating the fact that, neither Cr_2O_3 nor $CuCr_2O_4$ spinel-framework individually was enough for activating N–H bond. Use of $CuCr_2O_4$ spinel nanoparticles produces phenol in the reaction medium (Entry 9, Table 1) ascertained the fact that, it can efficiently activate C-H bond in benzene. Therefore, it can be assumed rationally that the cooperative action of nanoclusters of Cu^{2+} and spinel framework assist the activation of the N–H bond in NH_3. A control experiment using aniline as the reactant (with other optimum reaction conditions unchanged) revealed that azoxybenzene, azobenzene, nitrosobenzene and nitrobenzene were produced by 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 solution 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 aqueous solution. We also conducted the control experiment by direct use of NH_2OH to detect the probable mechanistic path. We observed 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 radical scavanger (10% by weight wrt benzene) while conducting the experiment maintaining its all 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 obey the fact that, the direct synthesis of ammonia from benzene probably follows a free radical mechanism pathway via 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 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 per Kuznetsova et. al protonated amino radical ($^{\bullet}NH_3^+$) is generated in acidic medium that acts as the active aminating species, considering an inito quantum mechanical calculations for the amination of benzene.[9a] Cu (II) interacts with NH_2OH in acidic medium and generates protonated amino radical ($^{\bullet}NH_3^+$) by reduction of NH_2OH. The latter reacts with benzene to give unstable protonated aminocyclohexadienyl intermediate, which is oxidized by catalyst to give aniline. Cu (II) is regenerated by the unreacted H_2O_2 molecules present in the reaction mixture;[19] probably this is why excess amount of H_2O_2 is needed for this oxyamination reaction. Furthermore, benzene produces phenyl radicals in presence of H_2O_2 (stabilized by acetonitrile solvent). These radicals self-condense to form biphenyl as side product.

The reusability test of the catalyst (Table S1, ESI†) was conducted. ICP-AES was performed after each run to detect the Cu leached and the results are listed in Table S1, ESI† which showed that the catalyst retained most of its activity upon recycling in 5 consecutive catalytic runs and leaching of metals was hardly observed. Furthermore, the used catalyst was characterized by XRD (Fig. 1c) and TEM (Fig. S4, ESI†). The XRD patterns and the morphology for the used catalyst were not changed, which showed that the catalyst remained unchanged even after 5 reuses. Thus the catalyst demonstrated its good reusability and therefore true heterogeneous in nature.

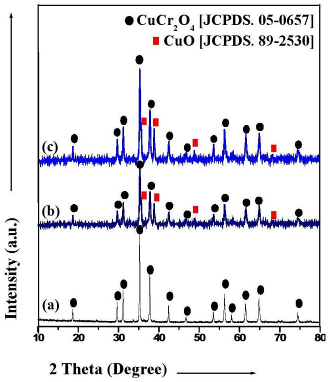

Fig. 1 XRD diffractogram of (a) $CuCr_2O_4$ spinel (commercial), (b) used catalyst (after 5 recycle) and (c) prepared catalyst.

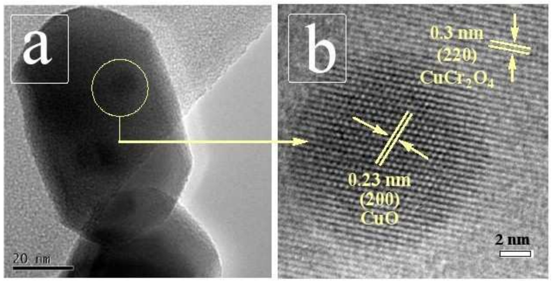

Fig. 2 TEM images of the catalyst at different magnifications.

Table 1 Oxyamination Reaction of Benzene over Cu(II) nanoclusters Supported on $CuCr_2O_4$ Spinel Nanoparticles Catalyst[a]

Entry	Catalyst	C_B[b] (%)	S_P[c(%)]			Y_A[d] (%)	TON[e]
			Φ_{NH2}	Φ_{OH}	Others		
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 Condition: benzene =1g; solvent = 70% AcOH-MeCN (10 ml); catalyst = 0.1g; benzene: H_2O_2: NH_3 mole ratio =1: 3: 2; time= 6 h; 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 and [g] spent (after 5 reuse) Cu(II) nanoclusters supported on $CuCr_2O_4$ spinel nanoparticles catalyst. [h] Solvent = 50% AcOH-MeCN, [i] MeCN and [j] AcOH. [k] Using NH_2OH and [l] Using TEMPO (radical scavanger) NP = nanoparticles, IMP= Impregnation Method.

Conclusions

To conclude, we report a facile route for the synthesis of nanoclusters of Cu (II) 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's recyclability. The component Cu (II) is found to exert a high influence on both the conversion rate and product selectivity. Furthermore, the catalyst can be resued several times without any significant activity loss. Probably, these effects stem directly from synergy between Cu (II) and $CuCr_2O_4$ spinel nanoparticles. The process may serve as a promising potential in the replacement of the traditional aniline production.

Acknowledgements

S.S.A. thanks CSIR and S.G. thanks UGC, New Delhi, India, for their respective fellowships. R.B. thanks CSIR, New Delhi, for financial support in the form of the 12 FYP Project (CSC- 0125, CSC- 0117). The Director of CSIR-IIP is acknowledged for his help and encouragement. The authors thank Analytical Section Division, IIP, for the analytical services.

Notes and references

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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, reaction mechanism etc. See DOI: 10.1039/c000000x/

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