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

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Detailed Characterization Techniques:

1. X-ray power diffraction (XRD)

Powder X-ray diffraction patterns were collected on a Bruker D8 advance X-ray diffractometer fitted with a Lynx eye high-speed strip detector and a Cu K_{α} radiation sourceusing Cu Ka radiation with a wavelength of 1.5418 Å. Diffraction patterns in the 2°-80°region were recorded at a rate of 0.5 degrees (2q) per minute. The resulting XRD profiles were analyzed to identify the crystal phase of the compound using reference standards. The line width of the most intense XRD peak was taken for estimation of crystallite size by the Scherrer equation.

2. Scanning electron microscopy (SEM)

Scanning electron microscopy images were taken on a FEI Quanta 200 F, using tungsten filament doped with lanthanumhexaboride (LaB_6) as an x-ray source, fitted with an ETD detector with high vacuum mode using secondary electrons and an acceleration tension of 10 or 30 kV. Samples were analyzed by spreading them on a carbon tape. Energy dispersive X-ray spectroscopy (EDX) was used in connection with SEM for the elemental analysis. The elemental mapping was also collected with the same spectrophotometer. Samples were subjected to scanning electron microscope analysis to understand the shape, size, and morphology properties.

3. Transmission electron microscopy (TEM)

The particle size and distribution of the samples were analyzed by TEM, JEOL JEM 2100 microscope, and samples were prepared by mounting an ethanol-dispersed sample on a lacey carbon Formvar coated Cu grid.

4. X-ray photoelectron spectroscopy (XPS)

X-Ray photoelectron spectra were recorded on a Thermo Scientific K-Alpha X-Ray photoelectron spectrometer and binding energies (±0.1 eV) were determined. The resulting spectra were analyzed to identify the different oxidation states of the copper and chromium ions present in the sample. Prior to the analysis, the spectra were calibrated with reference to C1s observed at a binding energy of 284.5 eV.

5. Inductively coupled Atomic Absorption Spectroscopy (ICP-AES)

Chemical analyses of the metallic constituents were carried out by Inductively Coupled Plasma Atomic Emission Spectrometer; model: PS 3000 uv, (DRE), Leeman Labs, Inc, (USA).

6. Thermogravimetric Analyses (TGA) of the uncalcined catalyst were carried out in a PYRIS DIAMOND, PERKIN ELMER INSTRUMENTS, and TECHNOLOGY BY SII (SEIKO INSTRUMENTS INC), USA] instrument-balance by heating 2.15 mg samples at 5 °C min^{-1} in flowing air atmosphere.

7. Temperature Programmed reduction (TPR): TPR experiments were carried out in a Micromeritics, Auto Chem II 2920 instrument connected with a thermal conductivity detector (TCD). All samples were subjected for TPR in the temperature range of 40–1000 °C with an increment of 10 °C min^{-1}, using helium as carrier.

Detailed Experimental Procedure

Catalyst Preparation: In a typical preparation method, 5.6 g of $CuCl_2.2H_2O$ and 16.5 g $CrCl_3.6H_2O$ were dissolved in 180 g water to give a clear dark blue solution. The pH of solutions was measured by pH Meter, which was standardized for pH measurement prior to use. By gradual addition of few drop ammonia solution, the pH of the solution was made 9; the colour of the solution became greenish gradually. Then alcoholic solution of CTAB was added in the mixture, followed by intensive stirring for 2h to form gel. A solution of hydrazine monohydrate (80% aqueous solution) was added drop wise to the well stirred mixture at RT by simultaneous, vigorous agitation. All the reagents were used maintaining the ratio: Cu: CTAB: hydrazine: H_2O = 1: 0.75: 1: 300. The mixture was stirred vigorously for 30 min and subsequently sealed in a Teflon lined stainless-steel autoclave (250 mL capacity). The autoclave was heated to and maintained at 200° C for 18h and then allowed to cool to RT. The green fluffy solid products (precipitates) were collected by centrifugation at 5000 rpm and washed with water and ethanol several times prior to drying in air at 100 °C for 6h. The resulting dry powder was transferred to a quartz reactor inside a tubular resistance furnace for calcination. The calcination was operated at 750 °C in air at ramp of 1 °C min^{-1}.

Liquid Phase Catalytic Oxyamination: The catalytic oxyamination reaction was carried out in a thermostatic two-necked round bottomed flask at atmospheric pressure. In a typical experiment, 1g benzene and NH_4OH (30 wt%, 14.5 g) were mixed thoroughly in a thermostated two-necked round bottom flask containing 70 volume % acetic acid in acetonitrile (10 ml) at atmospheric pressure in open air,. Under reflux, the mixture was heated at 80 °C with continuous stirring. Then, 2.4 g H_2O_2 (50 wt %) was added in 3 parts in 10 min intervals to reduce the possible decomposition of H_2O_2 and possible deep oxidation of products. After the reaction was carried out for the required period, the reaction was stopped, and the resulting mixture was cooled to room temperature and neutralized by a 1M solution of Na_2CO_3. The liquid mixture was separated from the catalyst by filtration. The organic compounds were extracted with dicloromethane and analyzed by gas chromatography (GC, Agilent 7890, equipped with hydrogen flame detector and a capillary column, 30m length, 0.28 mm id, 0.25 μm film thikness). Methylamine was used as an internal standard to quantify the aniline produced. The main product (aniline) was identified by GC-MS.

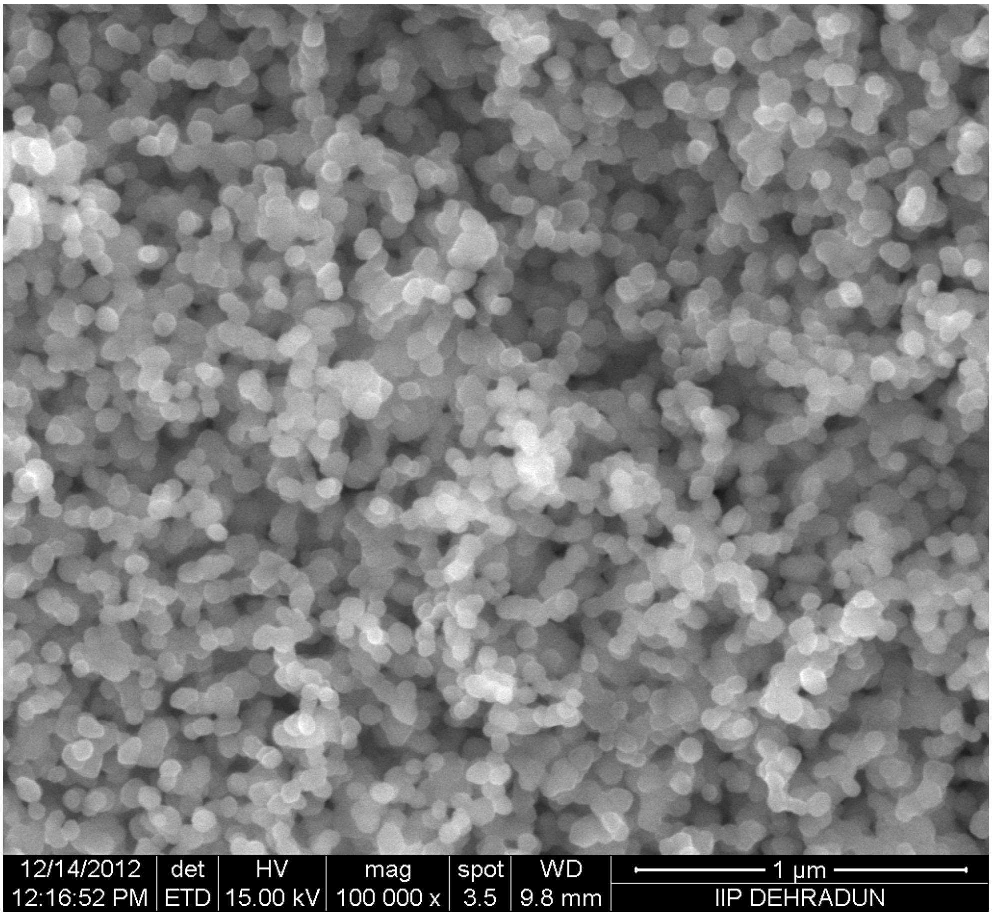


Fig. S1 SEM diagram of the catalyst

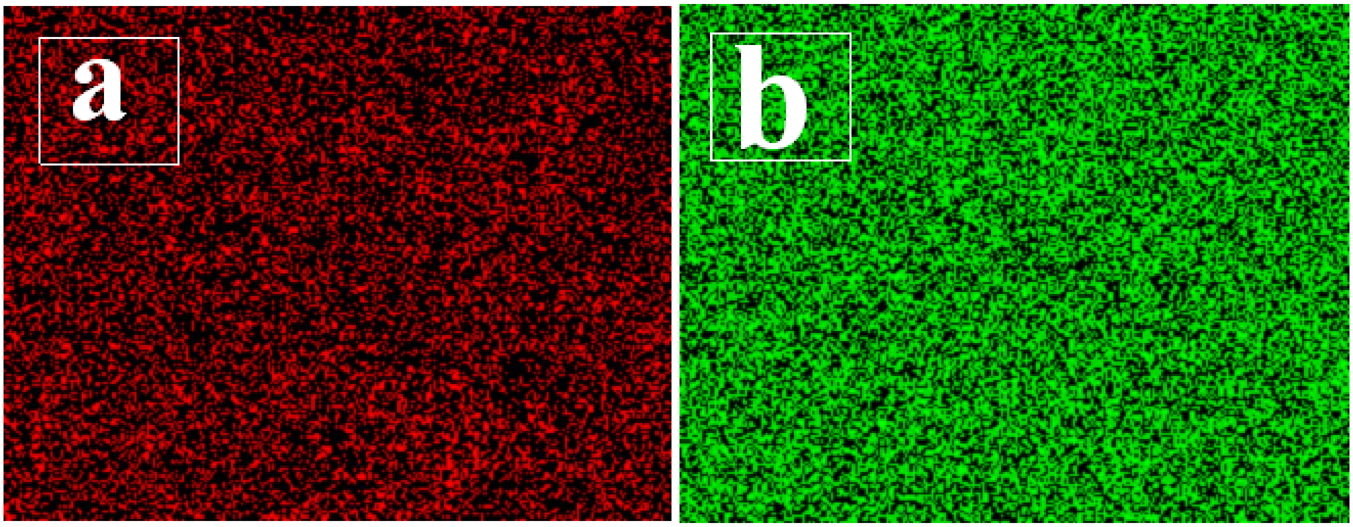


Fig. S2 Elemental Mapping of (a) Cu and (b) Cr in the Catalyst.

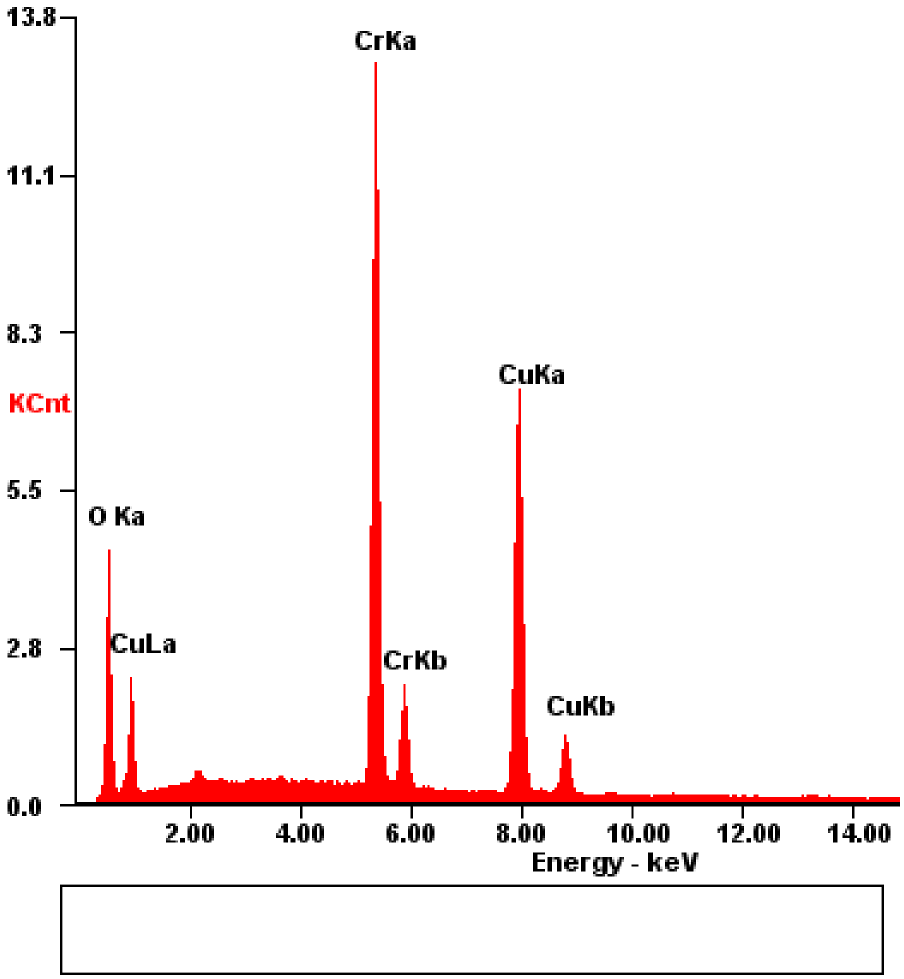


Fig. S3 SEM-EDAX of the Catalyst.

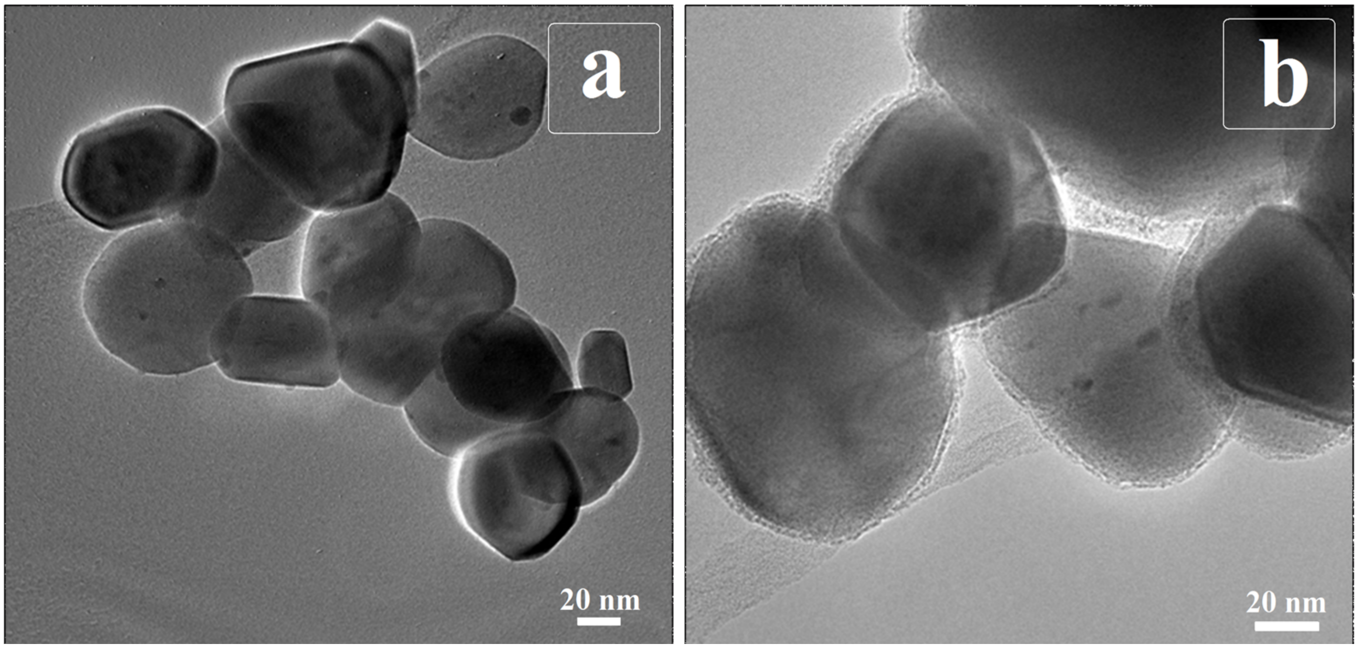


Fig. S4 TEM image of the a) Fresh and b) Spent Catalyst.

XPS: The Cu2p spectrum of the fresh sample is characterized by two spin orbit doublets with strong satellite peaks. The so obtained Cu2p$_{3/2}$ signals fitted satisfactorily to two principal peak components at ~ 935.2 and 933.8 eV. The BE for the Cu2p peak was in close agreement with that of $CuCr_2O_4$ indicating that, the main phase is $CuCr_2O_4$ spinel. The low energy component with Cu2p$_{3/2}$ at 933.8 eV is associated to Cu^{2+} in octahedral sites, whereas the high component at 935.2 eV is associated to Cu^{2+} in tetrahedral sites. The $Cr_{2p\ 3/2}$ core level spectra of the $CuCr_2O_4$ fresh catalyst appeared at 576.6 eV which shows the presence of Cr^{3+} ions in $CuCr_2O_4$ spinel and the O_{1s} binding energies appeared at 530.2 eV and 532.2 eV, revealed the presence of O^{2-} species in $CuCr_2O_4$ spinel.[1-3]

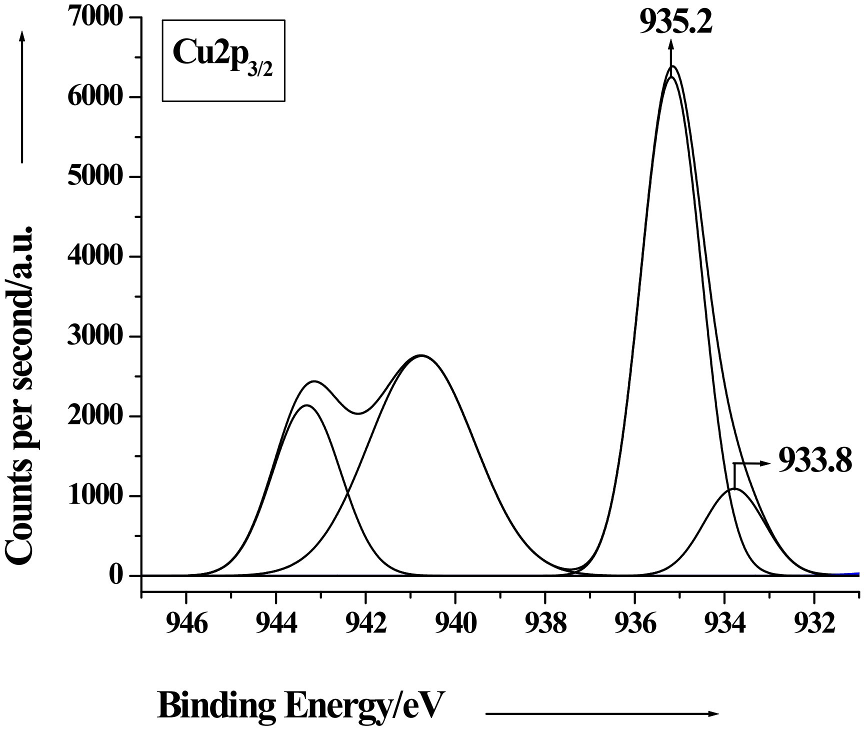


Fig. S5 Cu 2p$_{3/2}$ core level spectra of the catalyst.

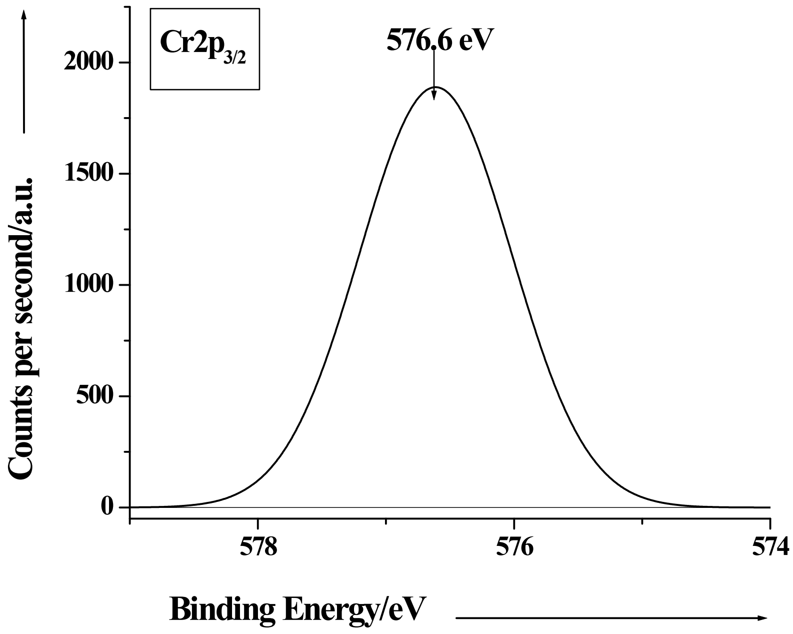


Fig. S6 Cr $2p_{3/2}$ core level spectra of the catalyst.

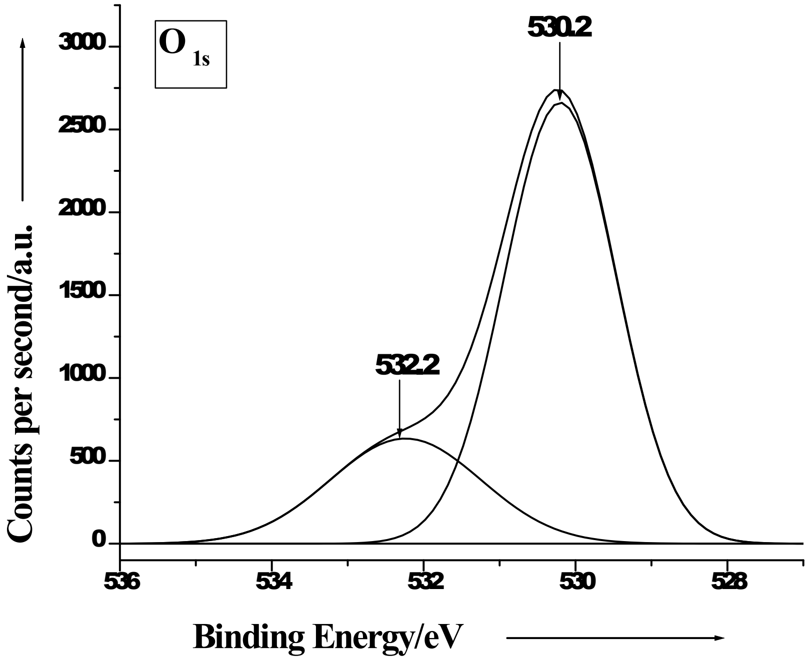


Fig. S7 O $_{1s}$ core level spectra of the catalyst.

TPR: The TPR profiles of the catalyst show broad signals with four distinct peaks :120-210 °C, 400-510 °C, 510-545 °C and 540-665 °C region. The peaks in the range 400-665 °C attributes to the reduction of Cu^{2+} to Cu^{+} and Cu^{+} to Cu^{0} in $CuCr_2O_4$ spinel. The peak in 120-210°C range implies the reduction of small amount of Cu^{2+}species. TPR results indicate the presence of nanoclusters of Cu(II) oxide species dispersed on $CuCr_2O_4$ spinel.

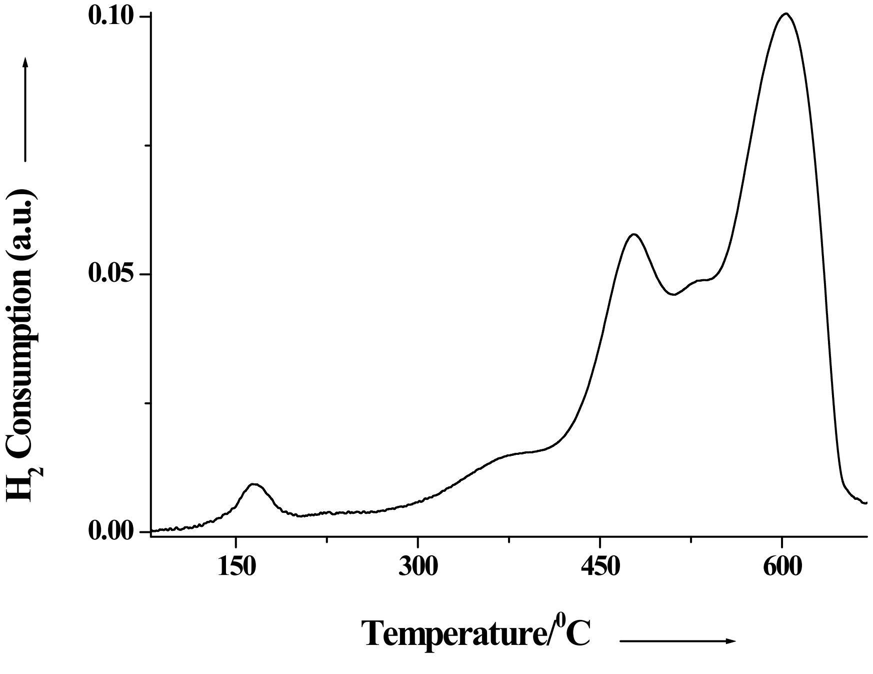


Fig. S8 TPR profiles of the catalyst.

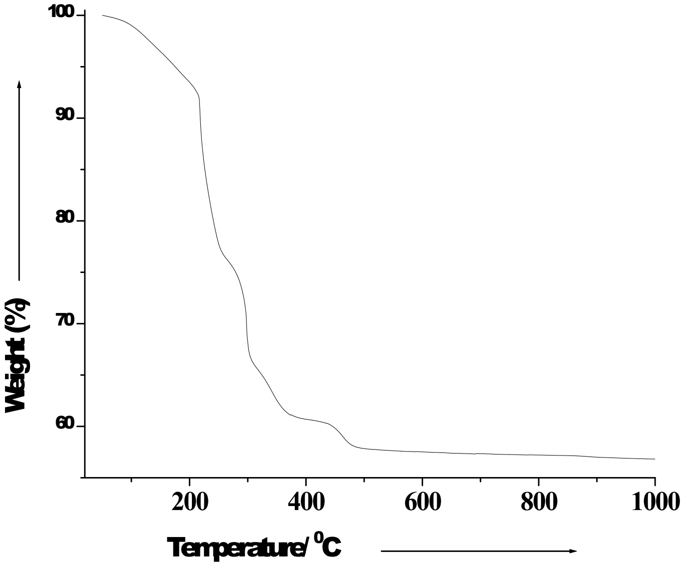


Fig. S9 TGA analysis of uncalcined catalyst.

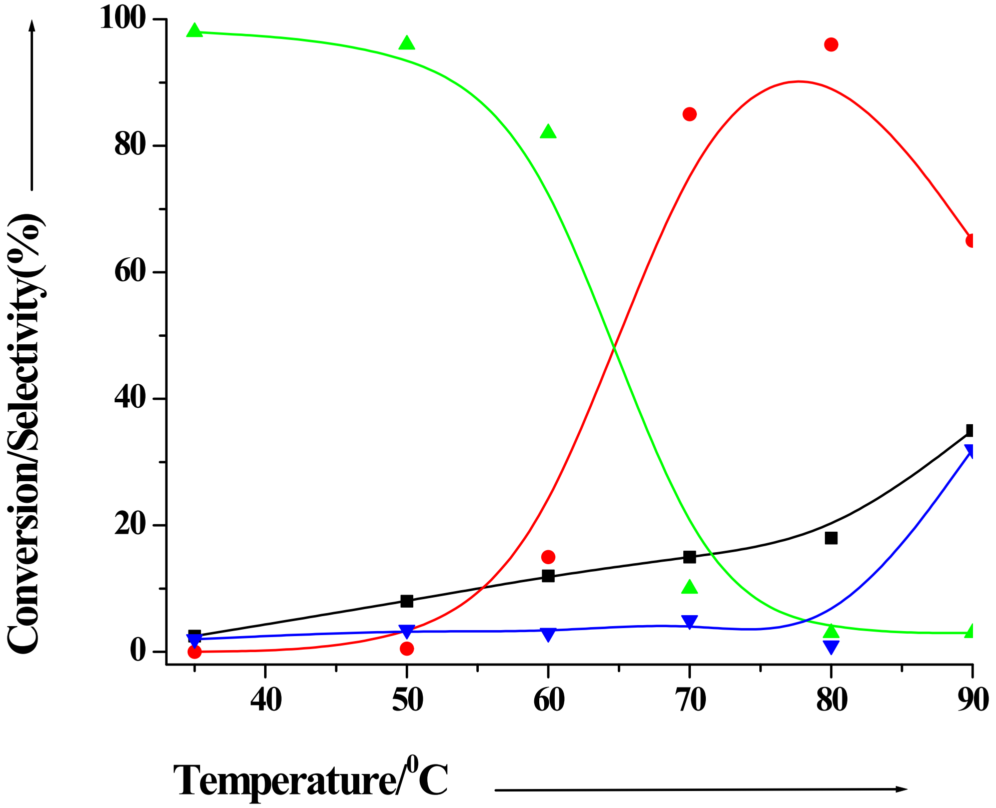


Fig. S10 Effect of temperature on oxyamination of benzene.
[■] Conversion of benzene; [●] Selectivity to aniline; [▲] Selectivity to phenol;
[▼]Selectivity to others.
Reaction Condition: benzene =1g; Catalyst = 0.1g; benzene: H_2O_2: NH_3 mole ratio =1: 3: 2; time= 6 h.

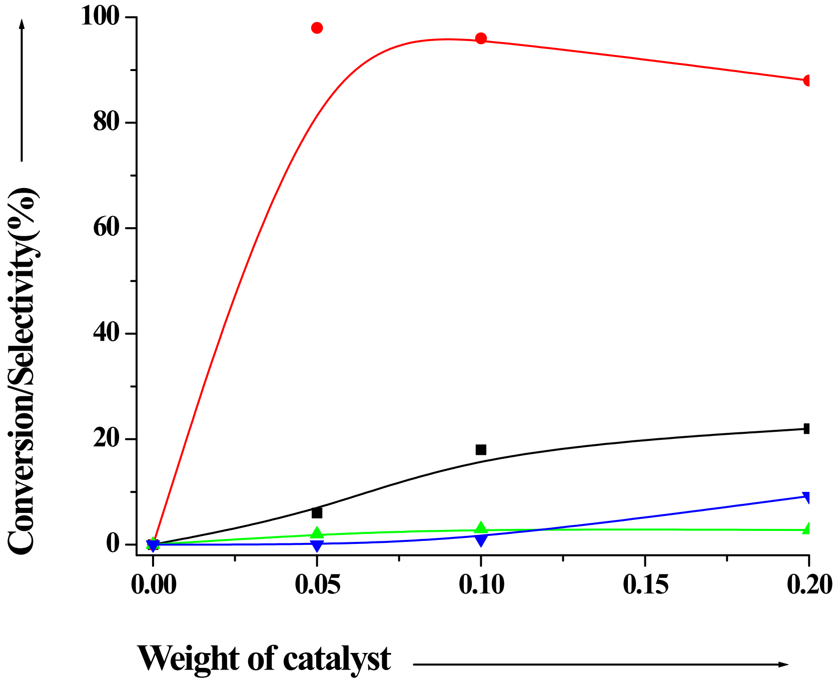


Fig. S11 Effect of catalyst weight on oxyamination of benzene.

[■] Conversion of benzene; [●] Selectivity to aniline; [▲] Selectivity to phenol; [▼]Selectivity to others.

Reaction Condition: benzene =1g; benzene: H_2O_2: NH_3 mole ratio =1: 3: 2; time= 6 h; temperature= 80°C

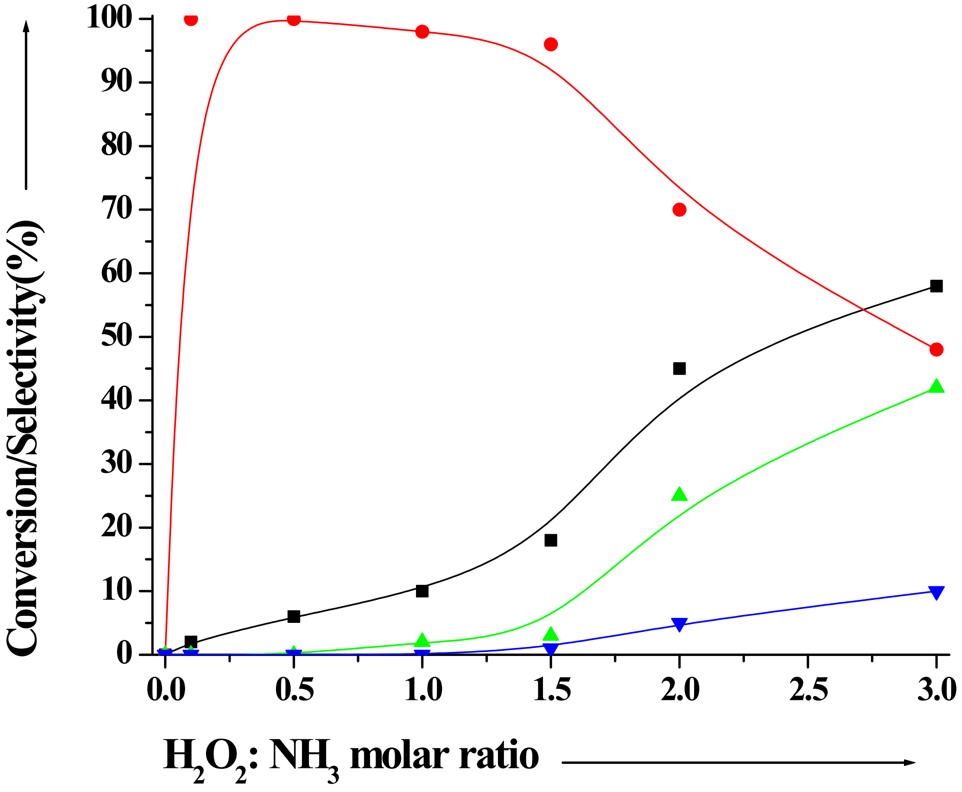


Fig. S12 Effect of H_2O_2: NH_3 molar ratio on oxyamination of benzene.
[■] Conversion of benzene; [●] Selectivity to aniline; [▲] Selectivity to phenol;
[▼]Selectivity to others.
Reaction Condition: benzene =1g; catalyst = 0.1g; benzene: NH_3 molar ratio= 1:2; time= 6 h; temperature= 80°C.

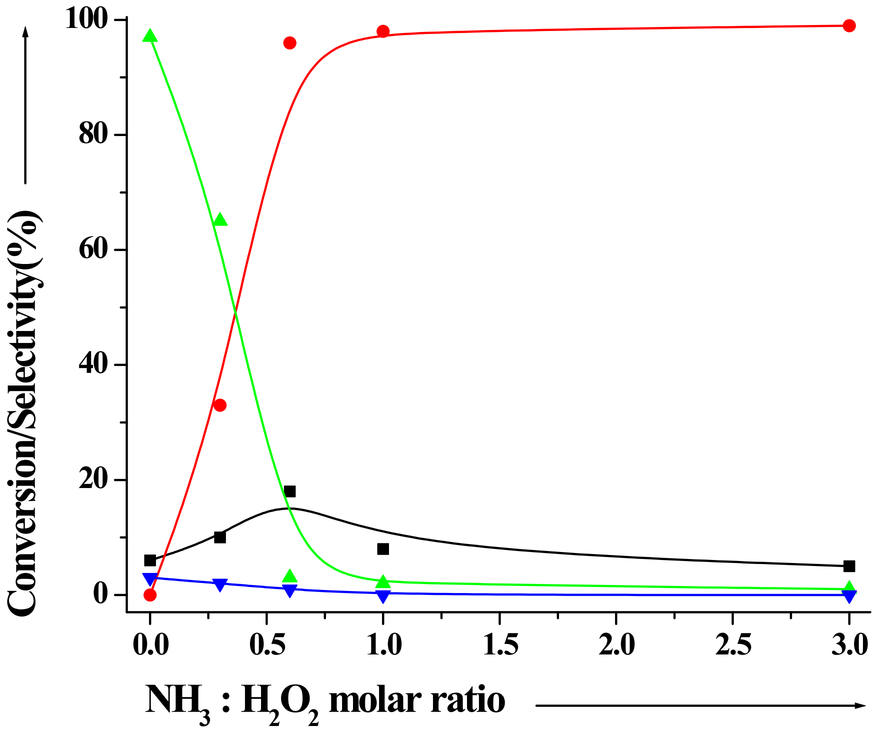


Fig. S13 Effect of NH_3: H_2O_2 molar ratio on oxyamination of benzene.
[■] Conversion of benzene; [●] Selectivity to aniline; [▲] Selectivity to phenol;
[▼]Selectivity to others.
Reaction Condition: benzene =1g; catalyst = 0.1g; benzene: H_2O_2 molar ratio= 1:3; time= 6 h; temperature= 80°C.

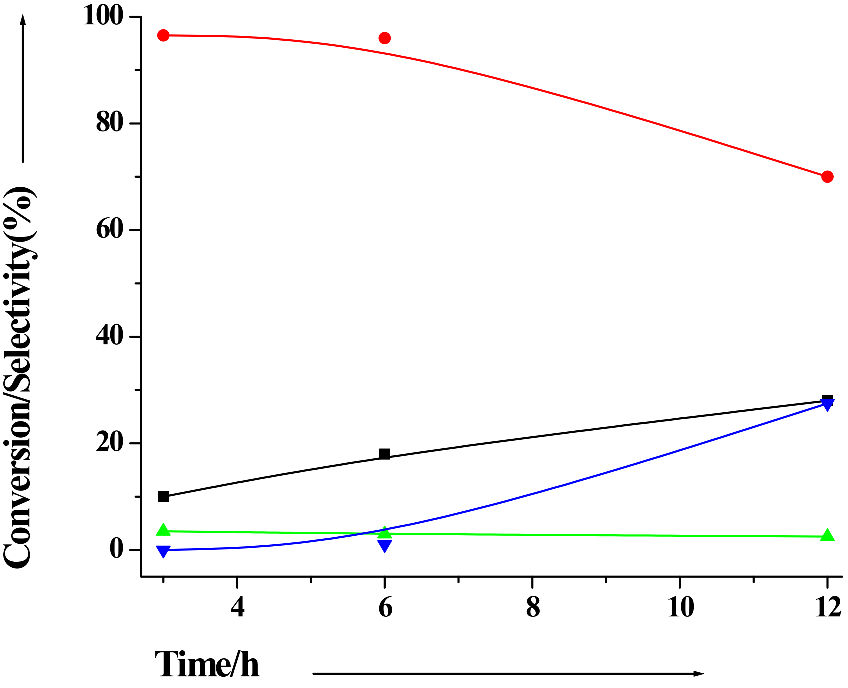


Fig. S14 Effect of time oxyamination of benzene.

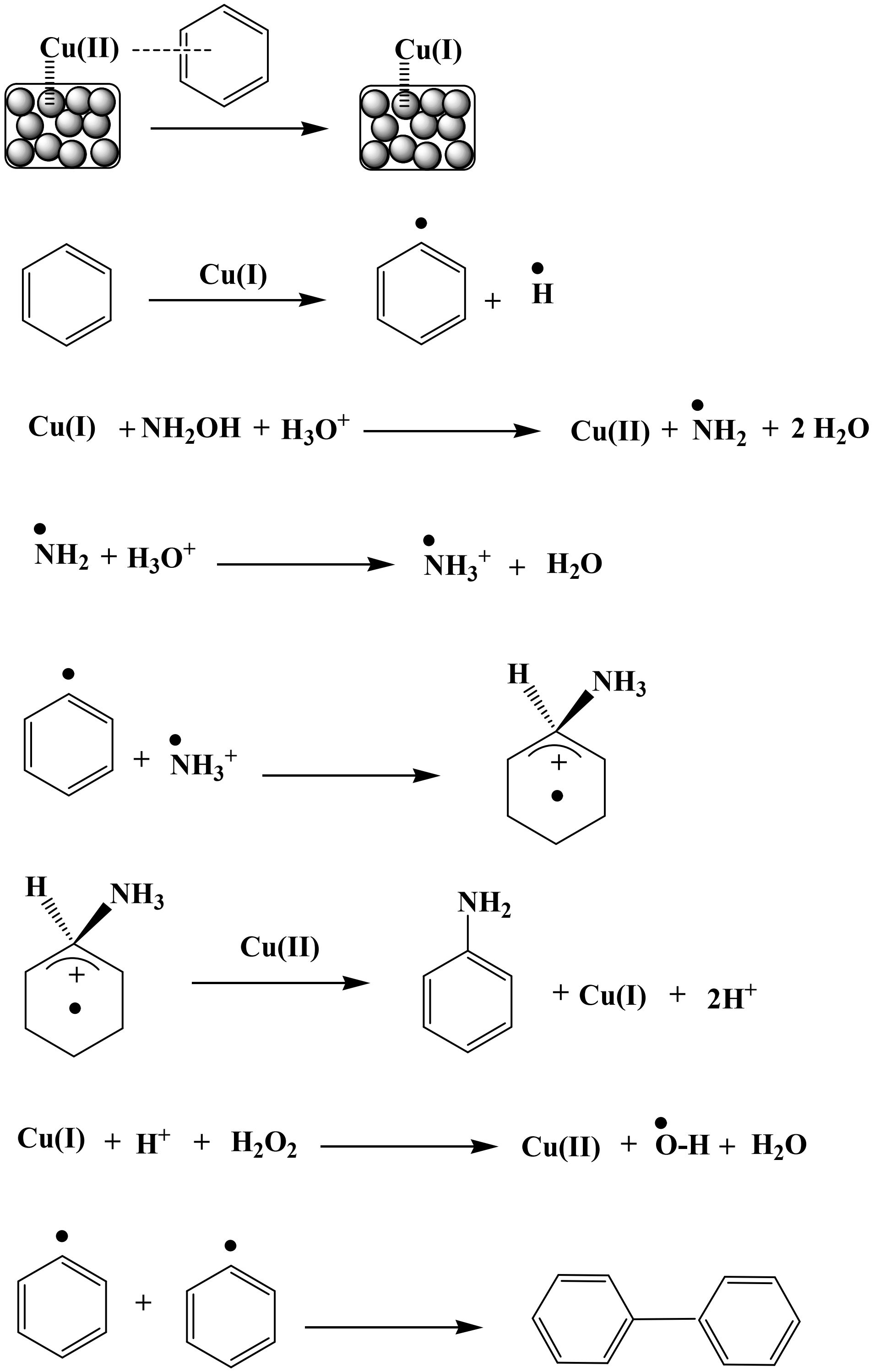
[■] Conversion of benzene; [●] Selectivity to aniline; [▲] Selectivity to phenol; [▼]Selectivity to others.

Reaction Condition: benzene =1g; catalyst = 0.1g; benzene: H_2O_2: NH_3 mole ratio =1: 3: 2; temperature= 80°C.

Table S1 The reusability of Cu(II) nanoclusters Supported on $CuCr_2O_4$ Spinel Nanoparticles Catalyst.[a]

Recycling No	C_B[b] (%)	S_P[c] (%)			Y_A[d] (%)	Cu loading[e] (wt %)
		Φ_{NH2}	Φ_{OH}	Others		
1	18	96	2	1	17.3	2.6
2	17.5	95.5	2.5	1	16.7	2.5
3	17	95	2	2	16.1	2.5
4	17	95	2	2	16.1	2.4
5	16.8	94.5	3	1.5	15.9	2.2

[a] Reaction Condition: benzene =1g; 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. [c] S_P = Selectivity of products. [d] Y_A = Yield of aniline. [e] Excess Cu loading (wt%) on $CuCr_2O_4$ spinel determined by ICP-AES.



Scheme S1. Mechanism of Oxyamination of Benzene over Cu(II) nanoclusters supported on $CuCr_2O_4$ spinel Nanoparticles Catalyst.

References.

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