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Electronic Supplementary Information

Catalytic oxidation of aromatic amines to azoxy compounds over Cu-CeO$_2$ Catalyst using H$_2$O$_2$ as an oxidant

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Experimental Section

Characterisation techniques

The surface morphology, particle size, and elementary composition of as-prepared catalyst was investigated by various characterization techniques such as by XRD, ICP-AES, XPS, SEM, TEM, EXAFS,TPR and BET-surface area measurements.

Powder X-ray Diffraction(XRD) : The phase of as- prepared crystals was determined by Powder X-ray diffraction patterns which were recorded on a Rigaku- Geigerflex X-ray diffractometer fitted with a Cu Kα radiation as a source. Diffraction patterns in the 10º–80º region were recorded with a 0.04 step size (step time = 4 s). The line width of most intense XRD peak was used to determine the crystallite size by using Scherrer equation.

BET-surface area: The surface area of the catalyst was analyzed by N$_2$ adsorption-desorption isotherms at −196 ºC (Micrometrics ASAP-2020 surface analyser).

Scanning Electron Microscopy (SEM): SEM images were taken on a FEI Quanta 200 F, using a tungsten filament doped with lanthanum hexaboride (LaB$_6$) as an X-ray source, fitted with an ETD detector with a high vacuum mode, using secondary electrons and an acceleration tension of 10 or 30 kV. Samples were characterised 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 help of same spectrophotometer.

Transmission Electron Microscopy(TEM): The size and distribution of particles were estimated by transmission electron microscopy.TEM images were collected using a JEOL JEM 2100 microscope, and samples were prepared by mounting an ethanol-dispersed sample on a lacey carbon Formvar coated Cu grid.

X-ray Photoelectron Spectroscopy (XPS): The surface composition and oxidation state of sample was analysed by X-Ray photoelectron spectra (XPS), which were recorded on a Thermo Scientific K-Alpha X-Ray photoelectron spectrometer and binding energies (±0.1 eV) were determined with respect to the position of the C 1s peak at 284.6eV. The obtained spectra showed the presence of different oxidation states of copper oxide and cerium oxide.

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES): The presence of percentage of elemental constituents in the prepared catalyst were analysed by Inductively coupled plasma atomic Emission spectrometer (ICP-AES) model: PS 3000 uv, (DRE), Leeman Labs, Inc, (USA).

Temperature programmed reduction: The reducible behaviour of as-prepared catalysts was measured by H_2 temperature programmed reduction technique and TPR profile was recorded in Micromeritics, Auto Chem II 2920 instrument connected with a thermal conductivity detector (TCD). Samples were subjected in a U-tube quartz reactor for TPR analysis and the reactor was heated in the temperature range of 40–1000 °C with an increment of 10 °C min^{-1}, using helium as carrier.

EXAFS measurements of the Cu K-edge were carried out at the High Energy Accelerator Research Organization (KEK-IMMS-PF). The measurement was made in transition mode and spectra were taken at BL-7C and BL-9C. The electron storage ring was operated at 2.5 GeV and 450 mA, synchrotron radiation from the storage ring was monochromatized by a Si (111) channel cut crystal. The ionized chambers, which were used as detectors for the incident X-ray (Io) and transmitted X-ray (I), were filled with N_2 gas mixture, respectively. The angle of the monochromators was calibrated with Cu foil. The EXAFS raw data were analyzed with UWXAFS analysis package, [1]including background subtraction program AUTOBK[2] and curve fitting program FEFFIT.[3] The amplitude reducing factor, S_0^2 was fixed at 1.0. The backscattering amplitude and phase shift were calculated theoretically by FEFF 8.4 code.[4] ATOMS[5] was used to obtain the FEFF input code for the crystalline materials.

Catalytic activity

The liquid phase oxidation of aromatic amines were carried out in a double neck round bottom flask fitted with spiral water condenser in an oil bath taking 15 ml acetonitrile, 0.1 g catalyst, 1 g (substrate) aromatic amines, in which the drop wise addition of H_2O_2 (50% aq. solution) was performed to restrain its immediate decomposition under vigorous stirring. The mole ratio of substrate to aniline ratio was taken 1:3. The temperature of reaction was varied from RT to 70 ºC. Small aliquots of samples were withdrawn at regular intervals from the reaction mixture for the analysis into Gas Chromatograph (GC, Agilent 7890) connected with a HP 5 capillary column (30m length. 0.28mm i.d., 0.25μm film thickness) and flame ionisation detector (FID). The aniline conversion and azoxybenzene selectivity was calculated with the help of calibration curve which was obtained by manually injecting the authentic samples. Conversion of aromatic amines were calculated by [moles of reactant reacted] / [initial moles of reactant used] x 100 and selectivity of products were calculated by [total moles of product formed]/[total moles of reactant converted] x100 by drawing a calibration curve using authentic samples. The leaching test of active species in the reaction mixture was estimated by ICP-AES and found leaching of active metal at ppb level. The obtained products were also confirmed by GC-MS. At the end of process, solid catalyst was filtered, washed with acetone and dried at ambient temperature for the further use.

References

1. E. A. Stern, M. Newvill, B. Ravel, Y. Yacoby and D. Haskel, *Phys. B,* 1995, **117-120**, 208.
2. M. Newville, P. Livins, Y. Yacoby, E. A. Stern and J. Rehr, J. *Phys. Rev. B: Condens. Matter,* 1993, **47**, 14126-14131.
3. A. L. Aukudinov, B. Ravel, J. J. Rehr and S. D. Conradson, *Phys. Rev. B: Condens. Matter,* 1998, **58**, 7565-7576.
4. A. L. Ankudinov, A. I. Nesvizhskii and J. Rehr, J. *Phys. Rev. B: Condens. Matter,* 2003, **67**, 115120-1151201.
5. B. Ravel, *J. Synchrotron Radiat.,* 2001, **8**, 314-316.

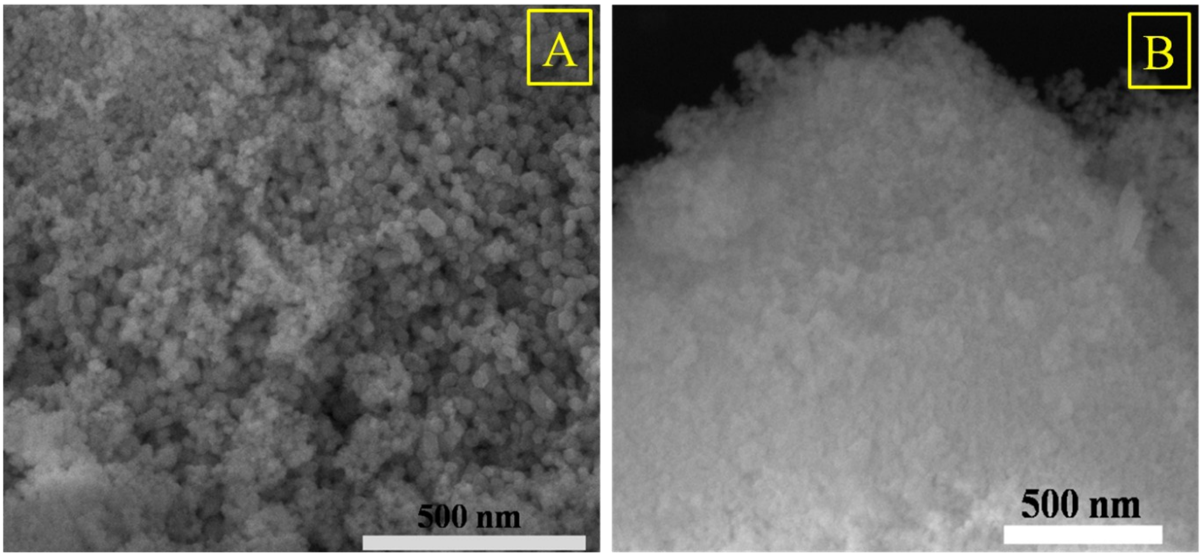


Fig.S1 SEM micrographs of 4% Cu-$CeO_2^{Imp.}$ and 4% Cu-$CeO_2^{Co.ppt.}$.

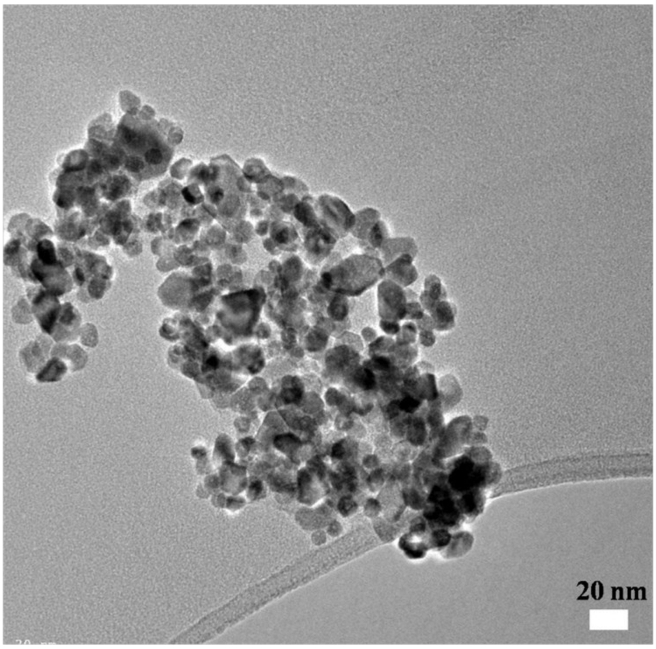


Fig. S 2 TEM image of 3.8% Cu-CeO_2 (spent catalyst).

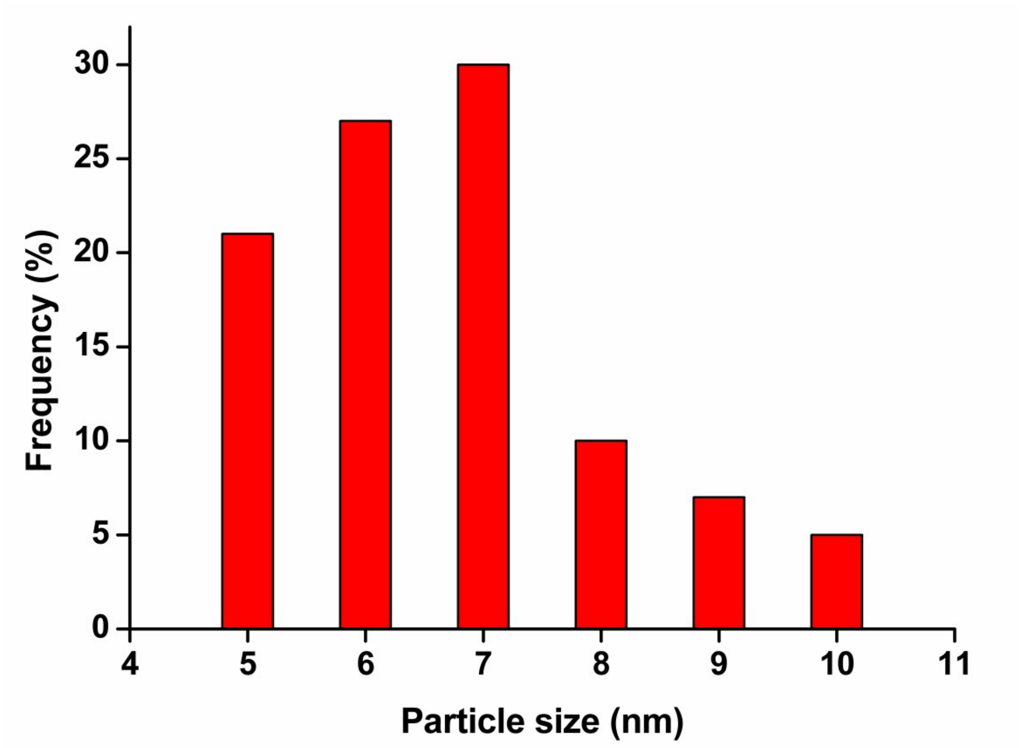


Fig. S 3 Cu particle size histogram (3.8% Cu-CeO_2).

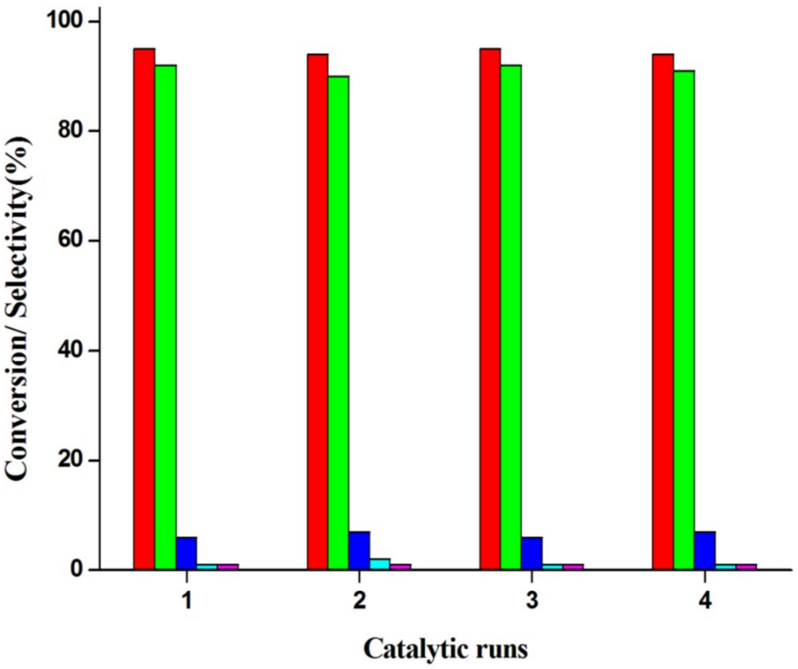


Fig. S4 Recyclability test of 3.8% Cu-CeO_2 for catalytic oxidation of aniline. (🟥) Conversion of aniline; (🟩) Selectivity of azoxybenzene;(🟦) Selectivity of nitrobenzene; (▢) Selectivity of azobenzene; (🟪) Selectivity of nitrosobenzene. Reaction conditions: Substrate (Aniline) = 1 g; Aniline: H_2O_2 = 1:3(mole ratio); solvent (Acetonitrile) = 15 ml; 50 ºC; Catalyst weight = 0.1 g; time = 6 h.

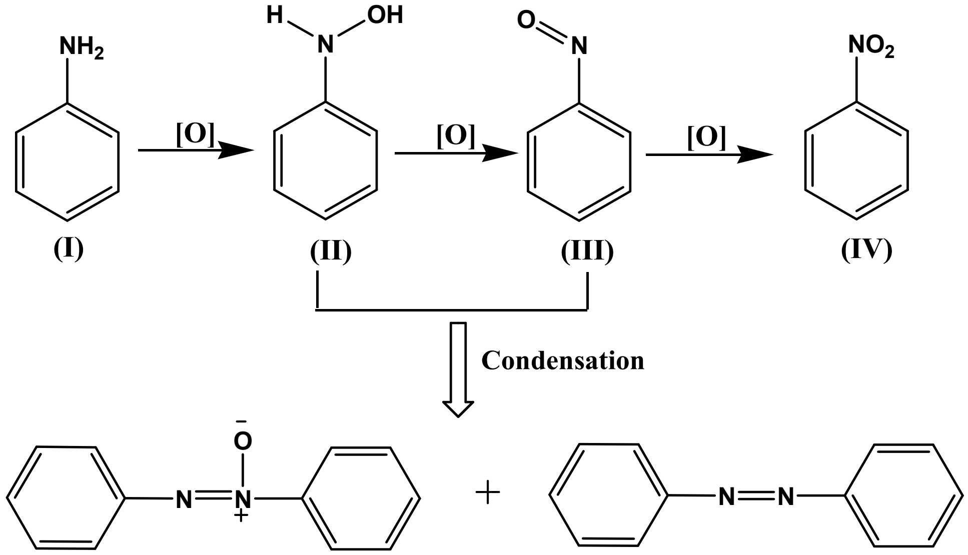
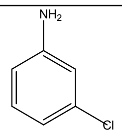
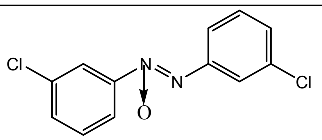
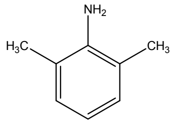
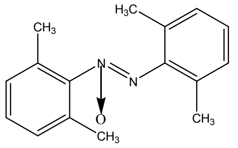
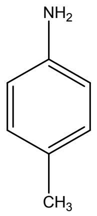
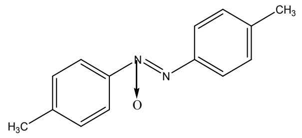
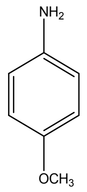
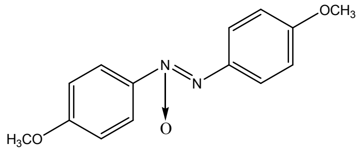
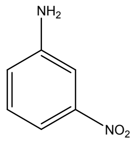
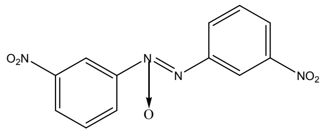


Fig. S5 Plausible mechanistic pathway of catalytic oxidation of Aniline over 3.8% Cu-CeO_2.

Table 1 Activities of different aromatic amines to corresponding azoxy compounds over 3.8%Cu-CeO_2.

S.No	Reactant	Product	Conversion C_r(%)	Selectivity S_p(%)
1			94	90
2			76	78
3			78	80
4			90	89
5			50	71

Reaction conditions: Substrate = 1gm; solvent (Acetonitrile) = 15ml; 50°C; time = 6h ; Substrate:H_2O_2= 1:3(mole ratio); 3.8%Cu-CeO_2 catalyst =0.1 g, C_r(%):conversion of An based on FID –GC result = moles of reactant reacted/initial moles of reactant used] × 100; S_p(%): selectivity of product calculated by total moles of product formed/total moles of reactant converted ×100.

Table 2 Comparative table for catalytic oxidation of aniline to azoxybenzene over different catalysts.

Entry	**Catalyst**	**Reaction condition**	**H_2O_2 used**	**C(%)**	**S(%)**	**Yield (%)**	**Reference**
1	Co-modified mesoporous silica	H_2O_2 (10mmol), CH_3CN (1ml), 80°C, 6 h, aniline (5mmol)	37%	100	100	100	C-F. Chang, S-T. Liu, *Journal of Molecular Catalysis A: Chemical* 299 (2009) 121–126.
2	TiO_2 in ionic liquids (ILs)	molecular oxygen -5 bars toluene, 100 °C, 24 h.	O_2	95	85	80.8	M. I. Qadir, J. D. Scholten and J. Dupont, *Catalysis science and technology*: DOI: 10.1039/C4CY01257G
3	Ti-SBA-50	0.5 g catalyst, 4.6 ml aniline (5 × 10^{-2}mol),20 mL acetonitrile oxidant/aniline = 0.2, 70 °C, 5 h.	30%	-	92	-	A. Tuel and L.G. Hubert-Pfalzgraf, *Journal of Catalysis* 217 (2003) 343–353.
4	ETS-10	catalyst = 60 mg; 70°C; substrate = 3.0 mmol; H_2O_2 = 3.0 mmol; methanol (10 ml); 6 h.	-	79.2	77.2	61.1	S. B. Waghmode, S. M. Sabne and S. Sivasanker, *Green Chemistry*, 2001, **3**, 285–288.
5	Titania pillared clays (Ti-PILC)	Methanol(10 ml); aniline=3 mmol; aniline/H_2O_2: 1 (mole ratio); Time: 8 h; catalyst conc. 20 wt.%; 300 K.	30%	50	99	49.5	N. Jagtap, V. Ramaswamy, Applied Clay Science 33 (2006) 89–98.
6	Mesoporoustitania microspheres	Catalyst = 25 mg; arylamines = 0.02 mol; arylamines/H_2O_2 molar ratio = 1 : 1.7;60 °C, 0.75h.	-	97.8	97.8	95.6	L. Yang, G. Shi, X. Ke, R. Shena and L. Zhang, CrystEngComm, 2014, 16,1620.
7	2.5%Ag/WO_3	catalyst = 0.10 g, room temperature; 24h; aniline : H_2O_2 molar ratio = 1 : 3, CH_3CN	50%	87	91	79.2	S. Ghosh, S. S. Acharyya, T. Sasaki and R. Bal, *Green Chem.*, 2015, 17, 1867–1876.
8	Cu-Cr_2O_4	70 °C, aniline : H_2O_2 molar ratio = 1:5, 1,4-dioxane (Solvent),10h	50%	78	92	71.8	S. S. Acharyya, S. Ghosh and R. Bal, *ACS Sustainable Chem. Eng.,* 2014, 2, 584.
9	3.8% Cu-CeO_2	catalyst = 10(wt%), 50 °C; time = 6 h; aniline : H_2O_2 molar ratio = 1 : 3, CH_3CN	50%	95	92	87.4	our work