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Supporting Information

Low Temperature Catalytic Oxidation of Aniline to Azoxybenzene Over Ag/Fe₂O₃ Nanoparticle Catalyst Using H₂O₂ as an Oxidant

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1. Catalyst characterization

Thermogravimetric analysis (TGA) was performed in air on a Netzsch STA449F3 thermal analyzer maintaining flow rate of 20 mL/min and heating rate of 10°C/min. FT-IR spectrum was recorded on KBr matrix with Bruker 3000 Hyperion Microscope with Vertex 80 FT-IR system. XRD measurements were carried out on a Bruker AXS D8-Advance powder X-ray diffractometer with Cu-K α radiation (λ =1.5418Å) with a scan speed of 2°/min. Transmission electron microscopy images were obtained on a JEOL, JEM2100 equipment. The sample powders were dispersed in ethanol under sonication and TEM grids were prepared using a few drops of the dispersion followed by drying in air. Nitrogen adsorption-desorption isotherms were obtained with a Micromeritics ASAP 2010 surface area and porosity analyzer. Scanning electron microscopy (SEM) images were obtained on a FEI Quanta 200 F, using a tungsten filament doped with lanthanum hexaboride (LaB6) 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 elemental analysis. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo Scientific K-Alpha X-ray photoelectron spectrometer and binding energies ($\pm 0.1 \text{ eV}$) were determined with respect to the position of C 1s peak at 284.8 eV. TPR experiments for the samples were carried out in a Micromeritics, Auto Chem II 2920 instrument connected with a thermal conductivity detector (TCD). TPR analysis for all the samples were done in the temperature range of 40–1000 °C with an increment of 10 C min⁻¹, using helium as carrier gas. Magnetism of the material was studied using a Lakeshore VSM 7410 at 300 K.

2. TEM Image



Figure S1. Tem image of spent catalyst

3. XPS Spectra



Figure S2. XPS spectra of spent catalyst.



Figure S3. FTIR diagram of (a) fresh and (b) spent (c) uncalcined Ag/ α -Fe₂O₃ nanoparticle catalyst and (d) that of CTAB



Figure S4. TG analyses of the uncalcined Ag/ α -Fe₂O₃ catalyst.



Figure S5. TG analyses of the catalysts after calcination.



Figure S6. UV/DRS spectrum of Ag/ α -Fe₂O₃ nanostructured catalyst.



Figure S7. VSM of Ag/α -Fe₂O₃ nanostructured catalyst.

4. Mechanism



Scheme S1. Mechanism of oxidative coupling of aniline to azoxybenzene

5. Comparison Table

Table S1 Comparative table for catalytic oxidation of aniline to azoxybenzene over different catalysts

Entry	Catalyst	Reaction condition	H ₂ O ₂ used	C (%)	S (%)	Yield (%)	Reference
1	Ti-SBA-50	0.5 g catalyst, 4.6 ml aniline $(5 \times 10-2mol),20$ mL acetonitrile oxidant/aniline = 0.2, 70 °C, 5 h.	30%		92		J. Catal. 217 (2003) 343–353.
2	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	Green Chem. 3 (2001) 285–288.
3	TiO ₂ in ionic liquids (ILs)	molecular oxygen -5 bars toluene, 100 °C, 24 h.	O ₂	95	85	80.8	Catal. Sci. Technol.5 (2015)1459-1462
4	Titania pillared clays (Ti-PILC)	methanol(10 ml); aniline=3 mmol; aniline/H ₂ O ₂ : 1 (mole ratio); Time: 8 h; catalyst conc. 20 wt.%; 300 K.	30%	50	99	49.5	Appl Clay Sci. 33 (2006) 89–98.
5	2.5%Ag/WO ₃	catalyst = 0.10 g, room temperature; 24h; aniline : H_2O_2 molar ratio = 1 : 3, CH ₃ CN	50%	87	91	79.2	Green Chem. 17 (2015) 1867–1876.
6	Cu-Cr ₂ O ₄	70 °C, aniline : H_2O_2 molar ratio = 1:5, 1,4- dioxane (Solvent),10h	50%	78	92	71.8	ACS Sustainable Chem. Eng. 2 (2014) 584-589.
7	Ag/Fe ₂ O ₃	catalyst = 0.1g, 50 °C; time = 12 h; aniline : H ₂ O ₂ molar ratio = 1 : 3, CH ₃ CN	30%	91	94	85.54	Present work
8	Ag/Fe ₂ O ₃	catalyst = 0.1g, 50 °C; time = 8 h; aniline : H ₂ O ₂ molar ratio = 1 : 3, CH ₃ CN	50%	92	94	86.48	Present work

6. NMR Spectra

(a) Azoxybenzene: ¹H NMR (500 MHz, CDCl₃): δ: 8.30 (2H, d), 8.17 (2H, d) 7.54-7.46 (6H, m, ArH); ¹³C NMR (CDCl₃) δ 148.3, 144.0, 131.6, 129.6, 128.8, 125.5, 122.3.

(b) 3, **3'-Dimethylazoxybenzene**: ¹HNMR (500 MHz, CDCl₃): δ 7.73–7.71 (4H, m), 7.41–7.24 (4H, m), 2.45 (6H, s). ¹³C NMR (CDCl₃) δ 121.5, 123.5, 126.0, 126.5, 128.5, 130.0, 130.7, 131.2, 134.1, 142.8, 142.4.

(c) 3, **3'-Dichloroazoxybenzene:** ¹H-NMR (500 MHz, CDCl₃): δ 8.32-8.0 (3H, m), 7.57-7.55 (1H, m), 7.48-7.26 (3H, m); ¹³C NMR (CDCl₃) δ: 148.8, 144.5, 134.8, 134.3, 131.9, 129.8, 129.6, 125.4, 124.1, 122.8, 120.6.

(d) 4, 4'-Dichloroazoxybenzene: ¹H-NMR (500 MHz, CDCl3): δ 8.26 (2H, d), 8.24 (2H, d), 7.49 (4H, dd); ¹³C NMR (CDCl₃) δ: 146.5, 142.1, 138.0, 135.2, 129.5, 129.0, 128.9, 127.0, 124.9, 123.6.

(e) 4, 4'-Dimethoxyazoxybenzene: ¹H-NMR (500 MHz, CDCl₃): δ 8.2 (4H, dd). 6.9 (4 H, dd), 3.85 (6H, s, OMe). ¹³C NMR (CDCl₃) δ 161.8, 160.2, 141.7, 138.0, 127.8, 123.7, 113.6, 55.7, 55.5.

(f) 4,4'-dinitroazoxybenzene: ¹H-NMR (500 MHz, CDCl₃): 8.54 (2H, d), 8.44-8.36 (4H, m), 8.30 (2H, d); ¹³C NMR (CDCl₃): δ 151.3, 149.8, 147.7, 147.4, 126.3, 124.5, 124.3, 123.8.

(g) 4, 4'-Dichloroazoxybenzene: ¹H-NMR (500 MHz, CDCl₃): 8.36–8.29 (2H, m), 8.28–8.22 (2H, m), 7.23–7.13 (4H, m). ¹³C NMR (CDCl₃): δ 165.1, 147.4, 161.8, 147.0, 144.2, 140.3, 128.0, 127.9, 124.5, 124.4, 115.8, 115.7, 115.5, 115.4.



Figure S8. ¹H NMR spectrum in CDCl₃



Figure S9. ¹³C NMR spectrum in CDCl₃



Figure S10. ¹H NMR spectrum in CDCl₃



Figure S11. ¹³C NMR spectrum in CDCl₃



Figure S12. ¹H NMR spectrum in CDCl₃



Figure S13. ¹³C NMR spectrum in CDCl₃



Figure S14. ¹H NMR spectrum in CDCl₃



Figure S15. ¹³C NMR spectrum in CDCl₃



Figure S16. ¹H NMR spectrum in CDCl₃



Figure S17. ¹³C NMR spectrum in CDCl₃

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