Electronic Supplementary Information

Room Temperature Selective Oxidation of Aniline to Azoxybenzene over Silver supported Tungsten Oxide Nanostructured Catalyst †

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Experimental:

Azoxybenzene : ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.40–7.56 (6H, m), 8.16–8.32 (4H, m); IR, υ (KBr disc): 1473, 1435, 1327, 763, 684 cm^{-1}.

4, 4'-Dichloroazoxybenzene: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.5 (4H, dd, J=6 and 3 Hz), 8.20 (2H, d J=3 Hz), 8.26 (2H, d, J=7 Hz); IR, υ (KBr disc): 1573, 1480, 1399, 1310, 821 cm^{-1}.

3, 3'-Dichloroazoxybenzene: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.3-7.6 (4H, m), 7.90-8.43 (4H, m); IR, υ (KBr disc): 1571, 1471, 1190, 1010, 780, 675 cm^{-1}.

4, 4'-Dimethoxyazoxybenzene: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.85 (6H, s, OMe), 6.9 (4 H, dd, J=9.5 and 3 Hz), 8.2 (4H, dd, J= 9 and 9 Hz); IR, υ (KBr disc): 1594, 1492, 1300, 1020, 837 cm^{-1}.

4, 4'-Dinitroazoxybenzene: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.4(4 H, dd, J= 5 and 2 Hz), 8.6 (4H, dd, J= 5 and 3 Hz); IR, υ (KBr disc): 1514, 1472, 1365, 1078, 847, 719 cm^{-1}.

2, 2'-Diethylazoxybenzene: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.5 (4H, m), 1.5 (6 H), 7.4-7.6 (6H, m), 7.9 (1H, d, J= 3 Hz), 8.3 (1H, d, J = 2.5 Hz) ; IR, υ (KBr disc): 1597, 1491, 1335, 1120, 827 cm^{-1}.

3, 3'-Dimethylazoxybenzene: ^{1}HNMR (500 MHz, $CDCl_3$): δ 2.34 (6H,s), 7.3–7.5 (4H, m), 7.95–8.2 (4H, m); IR, υ (KBr disc): 1597, 1496, 1448, 1336, 780 cm^{-1}.

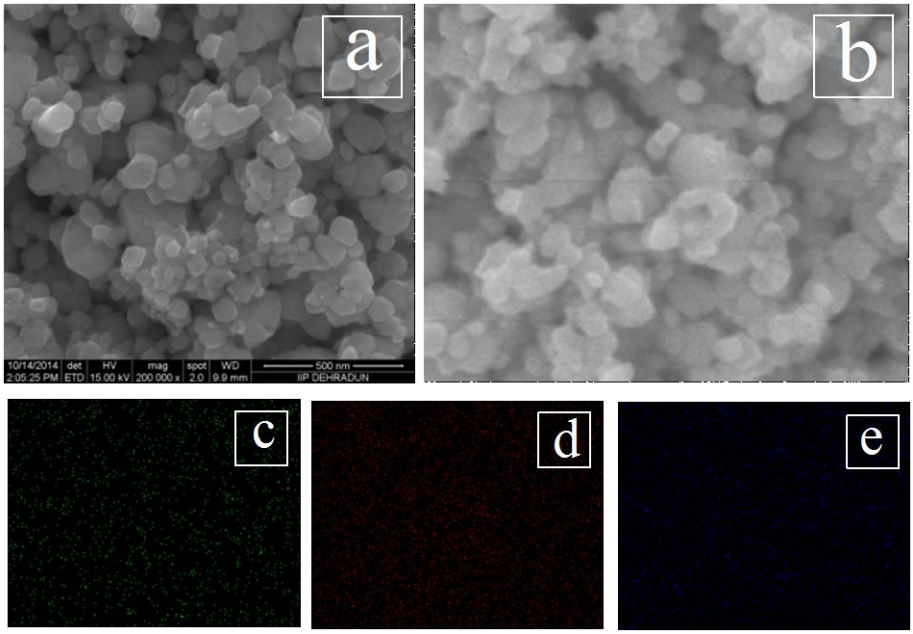


Figure S1. Elemental mapping of Ag/WO_3 catalyst a), b) SEM image, c) position of silver, d) position of oxygen and e) position of tungsten.

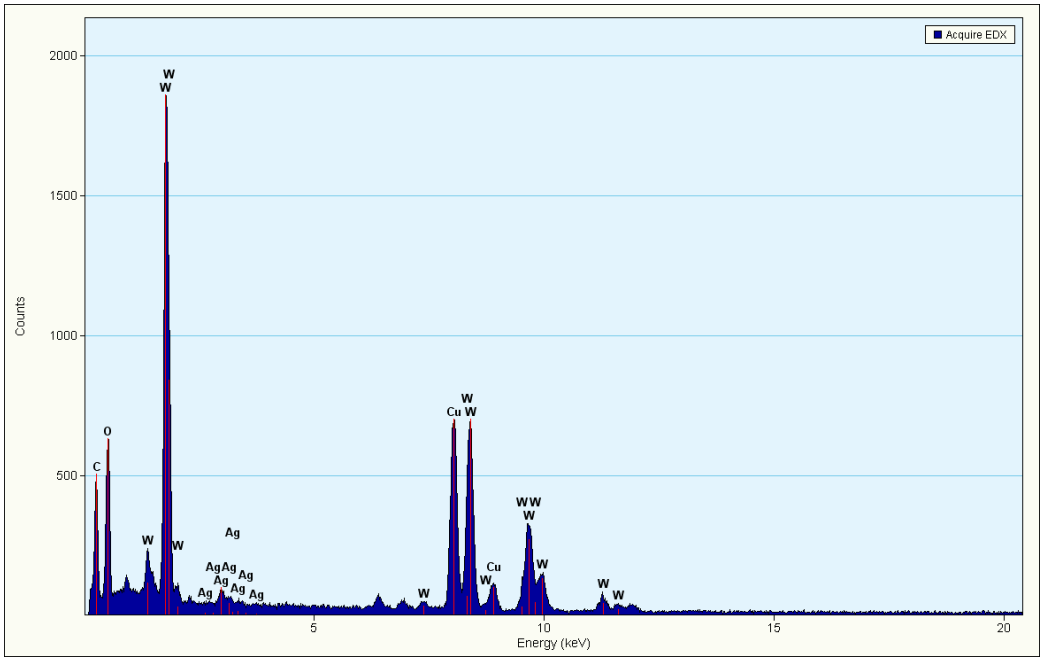


Figure S2. TEM-EDX of Ag/WO_3 catalyst.

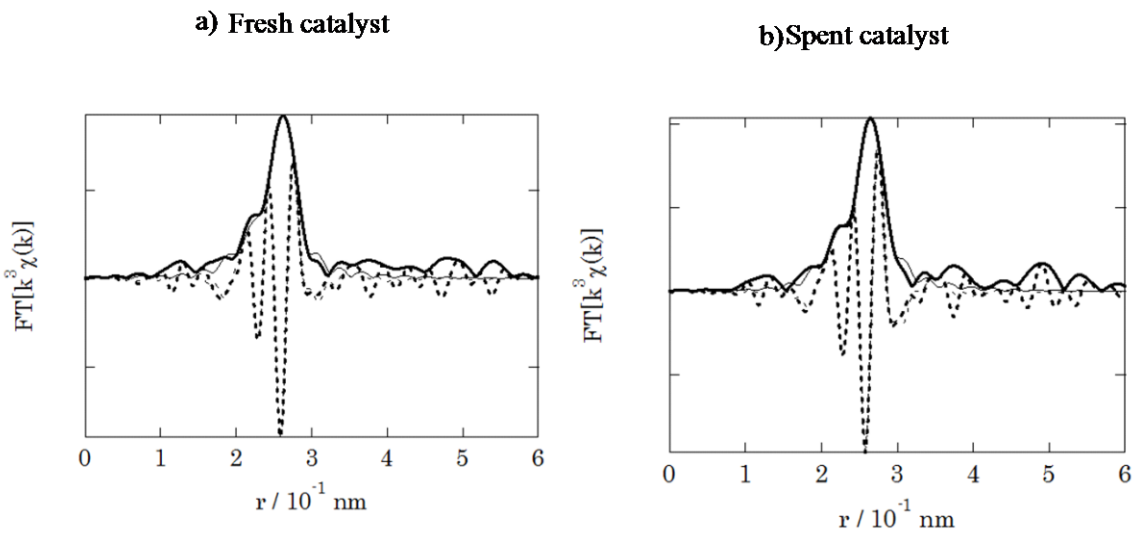


Fig. S3 EXAFS spectra of Ag/ WO_3 catalyst a) fresh catalyst and b) spent catalyst.

Dissociation of H_2O_2

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$H_2O_2 + OH^- \rightleftharpoons HO_2^- + H_2O$$

$$OH^- + HO_2^- \rightleftharpoons O_2^{2-} + H_2O$$

$$O_2^{2-} + H_2O_2 \rightleftharpoons O_2^{\bullet -} + OH^- + {}^{\bullet}OH$$

$${}^{\bullet}OH + H_2O_2 \longrightarrow H_2O + OH^-$$

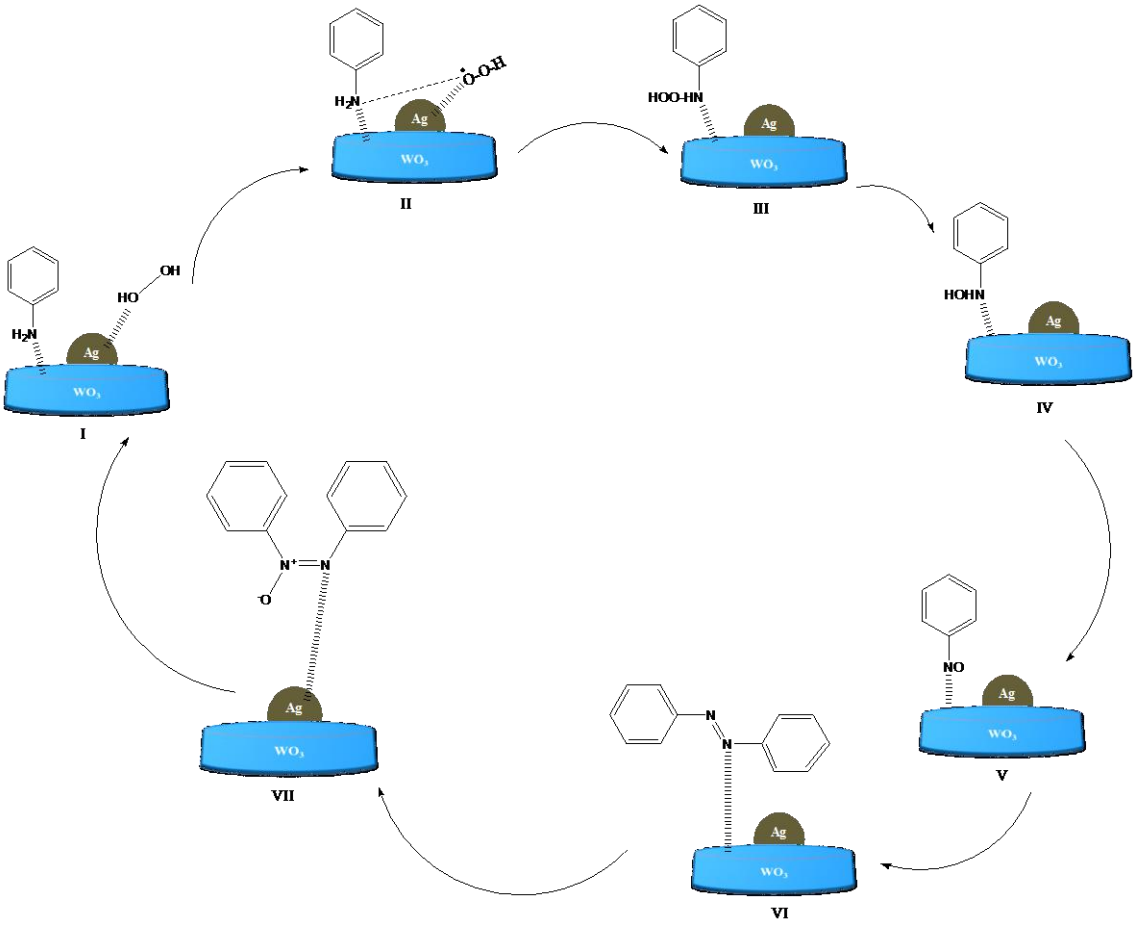
$$O_2^{\bullet -} + H_2O \longrightarrow HO_2^{\bullet} + OH^-$$

$$2HO_2^{\bullet} \longrightarrow H_2O_2 + O_2$$

Scheme S1. Mechanism of oxidative coupling of aniline to azoxybenzene

$$Ag^0 + 2H_2O_2 \longrightarrow Ag^+ + \dot{O}_2^- + 2H_2O \quad \text{(i)}$$

$$\dot{O}_2^- + H_2O \longrightarrow H\dot{O}_2 + OH^- \quad \text{(ii)}$$



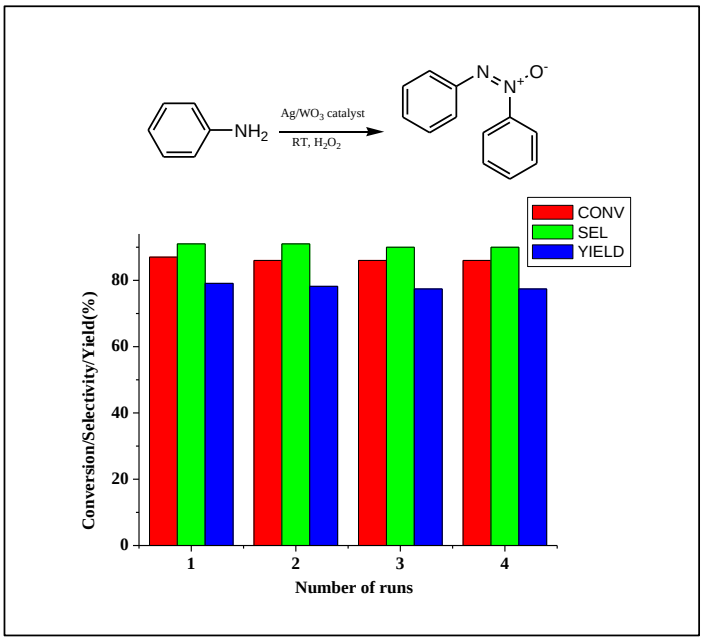


Fig. S4 Recyclability test of Ag/WO_3 nanostructure catalyst for the oxidation of aniline to azoxybenzene.

Reaction Condition: solvent= acetonitrile; aniline =1g; weight of catalyst = 0.10 g; aniline: H_2O_2 mole ratio =1:3; temperature = Room Temperature, time= 24 h.