The catalytic efficiency of Fe-porphyrins supported onto multiwalled carbon nanotubes in the oxidation of olefins and sulfides with molecular oxygen

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S-1:

Characterization of porphyrin

5,10,15,20-Tetrakis(4-hydroxyphenyl)porphyrin: Dark violet solid; m.p. >320 °C: ¹H NMR: (MeOD, 500 MHz, δ (ppm)): 8.88 (s, 8H, β pyrrole), 7.99–8.02 (d, 8, *o*-phenyl), 7.19–7.22 (d, 8H, *m*-phenyl).; FT-IR (KBr), cm⁻¹: 1271 (*v* C–O–H), 1349 (*v* C–N), 1445 (*v* C=N), 1484 (*v* C=C_{Pyrrol}), 1591 (*v* C=C_{Pyrrol}), 3425 (*v* N–H); UV–Vis, DMF (λ_{max}): 422, 517, 555, 594, 647; Anal. Calcd for C₄₄H₃₀N₄O₄: C, 77.85; H, 4.46; N, 8.25. Found: C, 77.93; H, 4.51; N, 8.32%.

5,10,15,20-Tetrakis(4-hydroxyphenyl)porphinatoiron(III) chloride: dark red solid, m.p. >300 °C; FT-IR (KBr, cm–1): 1005 (v C–N _{Pyrrole}), 1078 and 1167 (δ C–H _{Ph}), 1340 (v C-N), 1439 (v C=N), 1587 (v C=C _{Ph}), 3061 (v C–H _{Ph}). UV–Vis, EtOH (λ_{max}): 421 (Soret), 560;

S-2:

The preparation of [Fe(THPP)Cl@MWCNT]

The Fe-porphyrin was anchored covalently onto the surface of modified MWCNTs by the following procedure: to a mixture of 500mg of MWCNT-OH in 50 mL DMF, 360 mg of Fe(THPP)Cl, 400 mg of 2-(1Hbenzotriazole-1-yl)-1,1,3,3-tetramethyluronium tetrafluoroborate(TBTU) and 300mg of N,N-diisopropylamine (DIPEA) were added and the mixture was stirred for about 48 h at room temperature. The dark solid product was filtered and washed several times with DMF and dried by vacuum pump for removing the weakly adsorbed metalloporphyrins and also to remove adsorbed DMF.

S3:

Characterization of [Fe(THPP)Cl@MWCNT]

FTIR

The FTIR spectra of the catalyst confirmed the presence of metalloporphyrins on the surface of nenotube.



SEM

The image of scanning electron microscopy (SEM) of Fe(THPP)Cl@MWCNT shows that the structure of nanotubes remains unchanged after Fe-porphyrin immobilization on the surface of nanotube



TGA:

Thermo-gravimetric analysis (TGA) exhibits the thermal stability of the heterogenized catalyst up to \sim 350 °C. The 15% mass loose below 300 °C could be related to adsorbed water and deprotonation of COOH groups.





TGA curves of the [Fe(THPP)CI@MWCNT] (a) and Fe(THPP)CI (b)

TEM



Transmission electron microscopy (TEM) of Fe(THPP)Cl@MWCNT

S-4:

Oxidation of various sulfides:

Oxidation of various organic sulfides were investigated with O2/IBA in the presence of Fe(THPP)Cl@MWCNT in the mild conditions.



Oxidation of various sulfides in CH₃CN catalyzed by [Fe(THPP)Cl@MWCNT], Reaction condition: the molar ratio of Cat:Sulfide:IBA is (1:30:450) and O₂ (balloon), reaction time:90 min.

FT-IR spectra of the catalyst before and after 5 catalytic cycles



FI-IR spectra of (A) Fe(THPP)Cl@MWCNT and (B) recovered Fe(THPP)Cl@MWCNT after 5 catalytic cycle.