Supplementary Information (SI) for New Journal of Chemistry. This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2024

Supporting Information

Synthesis of Heterogeneous Nano Catalysts Comprising of Polyoxometalates Ionic Liquids Based Magnetic Nanocomposites for Oxidation of Thiobenzoic acid and 2,2'-Dinitro-5,5'dithiodibenzoic acid

Tariq Aziz,^a Areej S. Alqarni,^b Hameed Ullah,^a Farooq Khurrum Shehzad,^c Muhammad Sohail,^d Muhammad Tariq,^a Khalid Ali Khan,^e Hafiz Muhammad Asif,^{a*}

- a. Inorganic Research Laboratory, Institute of Chemical Sciences, Bahauddin Zakariya University Multan, 60800, Punjab, IR. Pakistan.
- b. Department of Physics, College of Science, Princess Nourah Bint Abdulrahman University, P.O. Box 84428, Rivadh, 11671, Saudi Arabia.
- c. Department of chemistry, Emerson university Multan, Pakistan.
- d. Yangtze Delta Region Institute (Huzhou), University of Electronic Science and Technology of China, Huzhou 313001. China.
- e. Applied College, Center of Bee Research and its Products (CBRP), King Khalid University, P.O. Box 9004, Abha, 61413, Saudi Arabia

Instruments and Measurements

Fourier transform infrared (FTIR) was performed with Shimadzu 8400S having wavenumber range 4000-400 cm⁻¹ using KBr pellets at room temperature. Based on peak intensity FTIR peaks are shortened as w (weak), vs (very sharp), s (sharp), bo (broad), br (branched), and m (medium). UV/visible spectrum was obtained with UV-1800 Shimadzu spectrophotometer having wavelength range 200-800 The F-7000 nm. FL spectrophotometer, equipped with an emission spectrum display having scan speed of 1200 nm min⁻¹ Ex and Em slits of 6 nm and PMT 300 V was used to measure fluorescence. Thermogravimetric analysis was performed with SDT Q600 V20.9 Build 20 with a flow rate of 100 ml min⁻¹ and heat flow of 20°Cmin⁻¹. Temperature was kept from 20°C to 950°C under N2 atmosphere. A vibrating sample magnetometer was used to study the magnetic properties. Scanning electron microscope (SEM) was performed using JSM5910 (JEOL, Japan) for determining porosity percentage, pore distribution and fibre thickness of compounds. Oxidative desulfurization was confirmed using reverse phase high performance liquid chromatography(RP-HPLC) with Shimadzu 10A having Welchrom C-18 column (4.6 ×250 mm) at wavelength 254nm and flow rate of 1 mL min⁻¹. C, H, N

elemental % was confirmed using Thermo-Finnigan FLASH EA 1112 Series. PXRD of synthesized compound was performed with X-ray diffractometer (D8 Advance Bruker) with a scan rate of 0.1° per second. GC-MS was performed with GC6890N-MS5973 to confirm the oxidation of thiobenzoic acid into dibenzoyl sulphone. Bruker Avance III HD 400 MHz was used for ¹HNMR and ¹³CNMR for the confirmation of successful oxidation of thiobenzoic acid.



Figure S1. FT-IR spectrum of MoVPOM-IL, MoVPOM-IL@Fe₃O₄@SiO₂, WPOM-IL and WPOM-IL@Fe₃O₄@SiO₂ using KBr pellet and ambient temperature condition confirming the formation of nanocomposite from POM-ILs

Table S1.	FT-IR	data o	f MoVPON	1-IL,	MoVPO	M-IL@F	$e_3O_4@S$	SiO ₂ ,	WPOM-IL	and	WPO	M-
IL@Fe ₃ O ₄	a SiO ₂	with s	pecific assig	gnme	nts							

MoVPOM-IL	WPOM-IL	MoVPOM-	WPOM-	Assignment
		IL@		
			IL@Fe ₃ O ₄ @SiO	
		Fe ₃ O ₄ @SiO ₂	2	

2058 2028 285	2056 2028 285	2061 2020 205	2062 2028 2854	СЦ
2938,2928,283	2930,2928,283 0	2901,2928,283	2903,2928,2834	С-п
1631	1627	1620	1623	О-Н
1034	_	1062	_	S=O
_	1038	_	1062	Р-О
943	_	949	_	Mo=O
_	935	_	943	W=O
_	885,814	_	872,803	W-O-W
782	_	792	_	Mo-O-Mo
672		681		V-O-V
_	_	587	574	Fe-O
_		995	1015	Fe-O-Si
		1230	1233	O-Si-O
			716	Co-O



Figure S2. UV/Vis spectroscopy graph of MoVPOM-IL(a) and WPOM-IL(b) recorded with quartz cuvette having 1 cm path length using ethanol as reference solvent at wavelength 200-800 nm. Molarity of solution was 10^{-6} M. Tauc plot also drawn for measuring energy band gap. Table S₂. %weight, K value and % atomic weight of each element present in MoVPOM-IL@Fe₃O₄@SiO₂ calculated from EDX graph of MoVPOM-IL@Fe₃O₄@SiO₂.

Element	% weight of element	K value	% atomic weight
С	0.6383	0.0531	1.6675
Ν	2.1926	0.1565	4.9147
V	8.0488	0.1580	4.9618
0	12.1010	0.7563	23.7509
Fe	29.3366	0.5253	16.4965
Мо	5.6064	0.0584	1.8339
Si	37.3022	1.3279	41.7014
S	4.7737	0.1488	4.6729

Element	% weight of element	K value	% atomic weight
С	0.4992	0.0415	1.7572
Ν	0.6294	0.0449	1.9011
0	9.4638	0.5915	25.0455
Fe	22.8565	0.4092	17.3265
Si	29.1729	1.0385	43.9725
W	35.7716	0.1946	8.2398
Р	0.9333	0.0301	1.2745
Со	0.6728	0.0114	0.4827

Table S3 %weight, K value and % atomic weight of each element present in WPOM-IL@Fe₃O₄@SiO₂ obtained EDX plot of WPOM-IL@Fe₃O₄@SiO₂.



(a)







(c)



(d)



(g)

Figure S3. Chromatograms showing oxidation of thiobenzoic acid before reaction(a), after 20 minutes reaction(b), after 40 minutes reaction(c), after 60 minutes reaction(d) after 80 minutes reaction(e), after 100 minutes reaction(f) and stack graph(g).



(c)



Figure S4. Chromatograms showing oxidation of 2,2-dinitro 5,5-dithiobenzoic acid after 20 minutes reaction(a), after 40 minutes reaction(b), after 60 minutes reaction(c), after 80 minutes reaction(d), after 100 minutes reaction(e) and stack graph(f).



Figure S5(a). FTIR spectrum of dibenzoyl sulfone formed as a result of oxidation of thiobenzoic acid. Analysis was performed at ambient conditions.



Figure S5(b): Uv/vis spectrum of dibenzoyl sulfone taken at 200-800 nm wavelength range



Figure S5(c): ¹HNMR spectra of dibenzoyl sulfone of oxidation of thiobenzoic acid taken with methanol as reference solvent.



Figure S5(d): GC graph of dibenzoyl sulphone performed at room temperature.



Figure S5(d): Mass spectrum of dibenzoyl sulphone showing possible fragment formation



Figure S5(e): ¹³C-NMR spectrum performed in CDCl₃ as reference solvent.