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Heterogenous Viologen Catalysts for Metal-free and Selective Oxidations

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Chemicals:

Chemicals involved in the material synthesis are use directly without further purification if no specification. Hexakis(bromomethyl)benzene, (>98%, TCI Chemicals), 1,3,5-Tris(bromomethyl)benzene (98%, TCI Chemicals), 4,4′− Dipyridyl (98%,Sigma-Aldrich Chemical), Pyridine (99.9%, Fisher Chemical), Hydrogen peroxide (30%, Fisher chemicals), Thioanisole (99%, Acros organics), 4-Fluorothioanisole (98.0%, TCI Chemicals), 4-Chlorothioanisole (95%, TCI Chemicals), 4-Bromothioanisole (99.0%, TCI Chemicals), 4-Methylthioanisole (98.0%, TCI Chemicals), 4-Methoxythioanisole (98.0%, TCI Chemicals), Benzyl alcohol (99%, Acros organics), 4-Methylbenzyl alcohol (98.0%, Acros organics), 4-methoxybenzyl alcohol (98%, Acros organics), 4-Chlorobenzyl alcohol (99%, Acros organics), 4-Bromobenzyl alcohol (98.0%, Acros Chemical).

Synthesis of PIN-1 and PIN-2

The synthetic routes followed our previous methods (*Advanced Materials*, 2015, 27, 8088-8094). Detailly, to a two neck round bottle flask, 100mL N,N-Dimethylformamide were added, followed by adding Hexakis(bromomethyl)benzene (1.27 g, 2 mmol) and 4,4′−Dipyridyl (1.09 g, 6 mmol). Flask was flowed with N_2 for 10 minutes. Keep reaction solution stirring at room temperature for 6 h and then heated to 80℃ for 20 h under an inert

atmosphere (N_2). The resulting black mixture was filtrated and yield black PIN-1-Br sample. PIN-1 was dried at 80 ℃ in vacuum overnight in prior to use, and was named PIN-1. PIN-2 was prepared via a similar route except that the starting compound was (1, 3, 5-Tris (bromomethyl) benzene).

Synthesis of PIN-1-M1

To a two neck round bottle flask, 20 mL of pyridine was added, followed by adding 1, 4-bis (bromoethyl) benzene (264 mg, 1 mmol). Stirring under N_2 flow for 10 mins. Then reaction mixture was heated to flux for 6 h. Resulting black mixture was poured into 100 mL ethyl acetate, product was collected by filtrated. Obtained black powder was dried at 80 ℃ in vacuum overnight. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.98 (s, 12H), 8.63 (tt, J = 8 Hz, 1.4Hz, 6H), 8.10 (t, J = 7 Hz, 12H), 4.44 (br., 12H).

Synthesis of PIN-1-M2

Synthesis procedure of PIN-1-M2 was followed literature 1. To a two neck round bottle flask, 8 mL of N, N-dimethylformamide was added. Followed by adding 4, 4'-dipyridyl (0.625 g, 4 mmol) and benzyl bromide (1.710 g, 10 mmol) and stirred at 90 °C for 12 hours. The formed precipitate was filtered and washed with chloroform and diethyl ether yielding the product PIN-1-M2.

Synthesis of PIN-1-M3

Synthesis procedure of PIN-1-M3 was followed literature 2. To a two neck round bottle flask, 10 mL of acetone was added. Followed by adding 4, 4'-dipyridyl (0.625 g, 4 mmol). Benzyl bromide (0.68 g, 4 mmol) was added in a drop-wise over 30 minutes and the resulting mixture was stirred at 60 ºC for 7 hours, after the reaction mixture was cooled, mixture filtered and washed with excess acetone to yield monobenzylviologen.

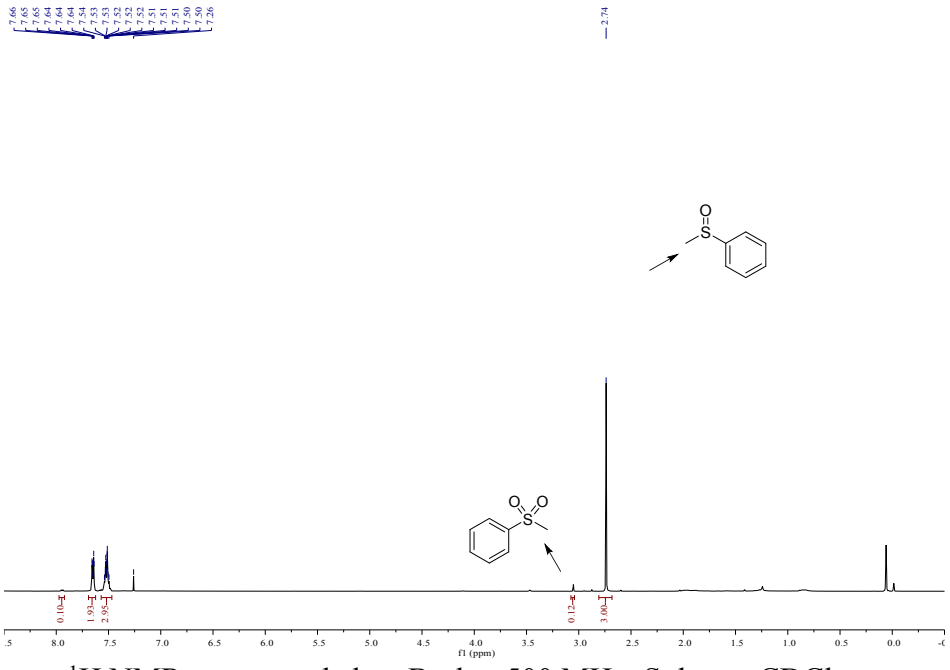
Oxidation of Sulfides

In a typical oxidation, 1 mmol substrate, catalysts used as described in the manuscript, 30%H_2O_2 and 4 mL solvent were added into a 10 mL round bottom glass reactor, which was fitted with a magnetic stirrer. The reaction was performed at 30-60 °C in a water bath with magnetic stirring. After completion of the reaction, anisole (1 mmol) was added to the

mixture as the internal standard. The solid catalyst was recovered by filtration, and the products were analysed by gas chromatography (GC). The structure of products was identified using Perkin Elmer GC–MS (Clarus 680-Clarus SQ 8C) spectrometer by comparing retention times and fragmentation patterns with authentic samples. Selectivities and conversions were calculated from the equations: selectivity (%) = [sulfoxides]/[consumed sulfides] × 100; conversion (%) = [consumed sulfides]/[initial sulfides] × 100, respectively.

The kinetic curves of sulfide oxidation catalyzed with different pre-treatment temperatures were studied. The ln(Co/Ct) vs. reaction time (t) curves are according to the first-order reaction with an equation of $\ln(C_0/Ct) = kt$, and the slope of the liner relationship is used to determine the rate constant. C_0 and Ct are the concentrations of sulfide before the reaction and at a reaction of time t, respectively.

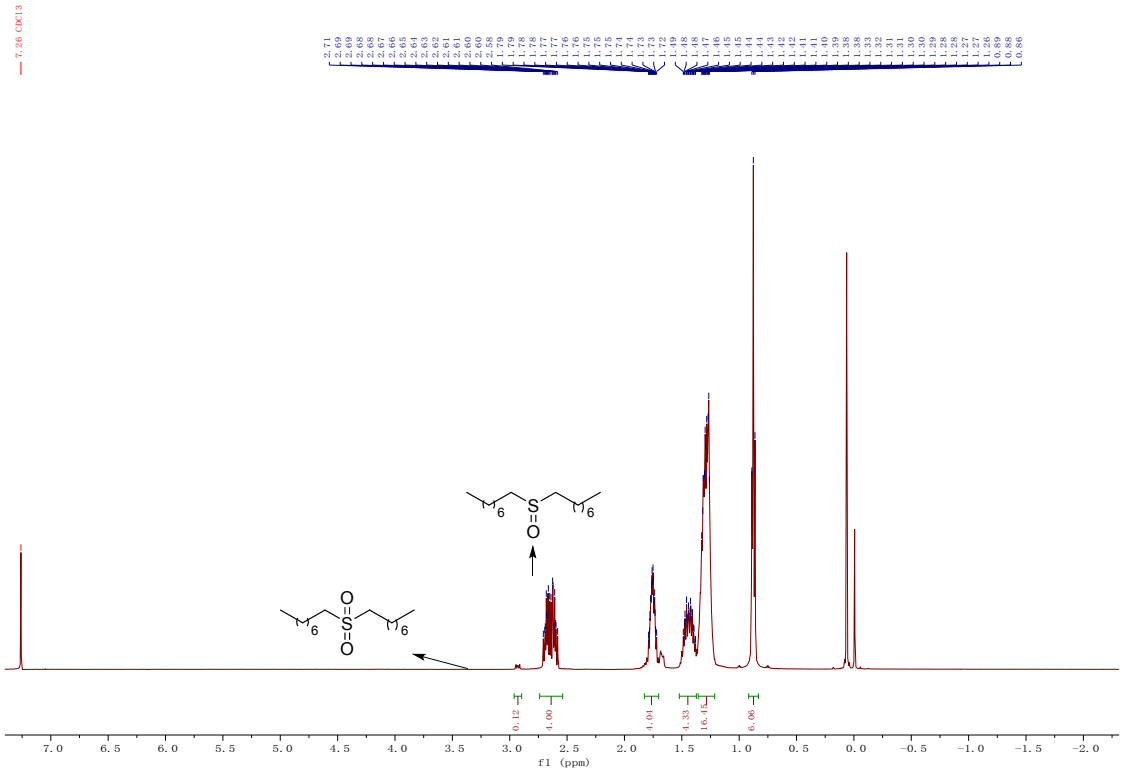
A gram-scale preparation of (methylsulfinyl)benzene was then investigated. The oxidation of thioanisole (1.24-gram scale) carried out in the presence of PIN (100 mg) and H_2O_2 (20 mmol) in MeOH (30 mL) at 60 ^oC for 2 h gained (methylsulfinyl) benzene in 95% isolated yield (1.39 g), as a colorless oil. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.69 – 7.62 (m, 2H), 7.57 – 7.47 (m, 3H), 2.74 (s, 3H)



^1H NMR was recorded on Bruker 500 MHz; Solvent: $CDCl_3$

When the dioctyl sulfide was used as the substrate we also separate the sulfoxide product

in 92% yield as a white solid. ^{1}H NMR (500 MHz, Chloroform-d) 2.74 – 2.56 (m, 4H), 1.70 – 1.80 (m, 4H), 1.54 – 1.39 (m, 4H), 1.37 – 1.21 (m, 16H), 0.88 (t, J = 6.9 Hz, 6H).



^{1}H NMR was recorded on Bruker 500 MHz; Solvent: $CDCl_3$

General Methods:

The materials were characterized by N_2 adsorption (TriStar, Micromeritics) at 77 K, powder XRD (Panalytical Empyrean diffractometer with Cu Ka radiation operating at 45 kV and 40 mA), thermogravimetric analysis (TGA 2950, TA Instruments), Fourier-transform infrared spectrum (PerkinElmer Frontier FTIR spectrometer), Elemental Analysis (Vario EL Cube) and NMR (AVANCE III HD 500, Bruker).

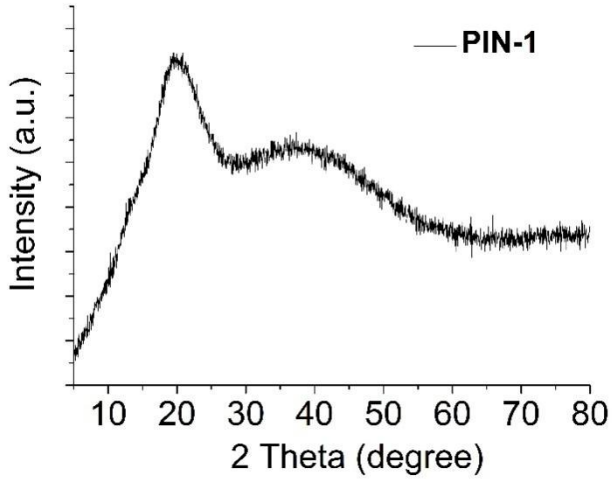


Figure S1. The XRD pattern of PIN-1 catalyst.

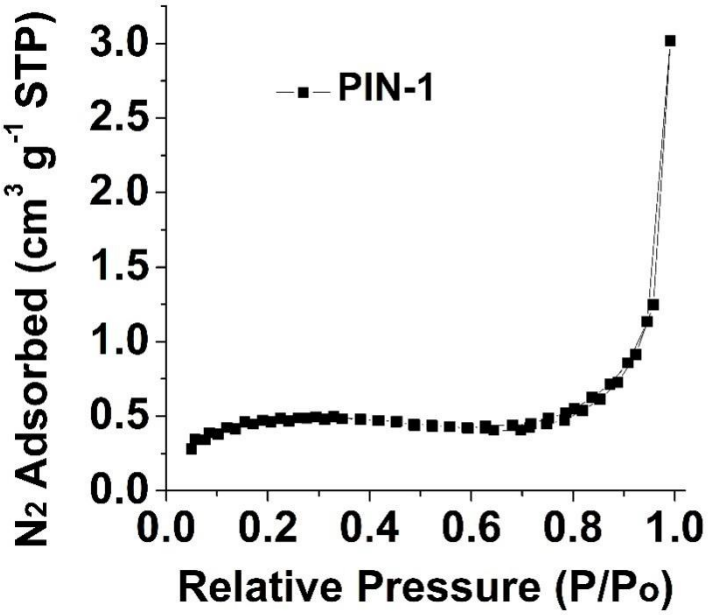


Figure S2. The N_2 sorption isotherm (77K) of PIN-1 material.

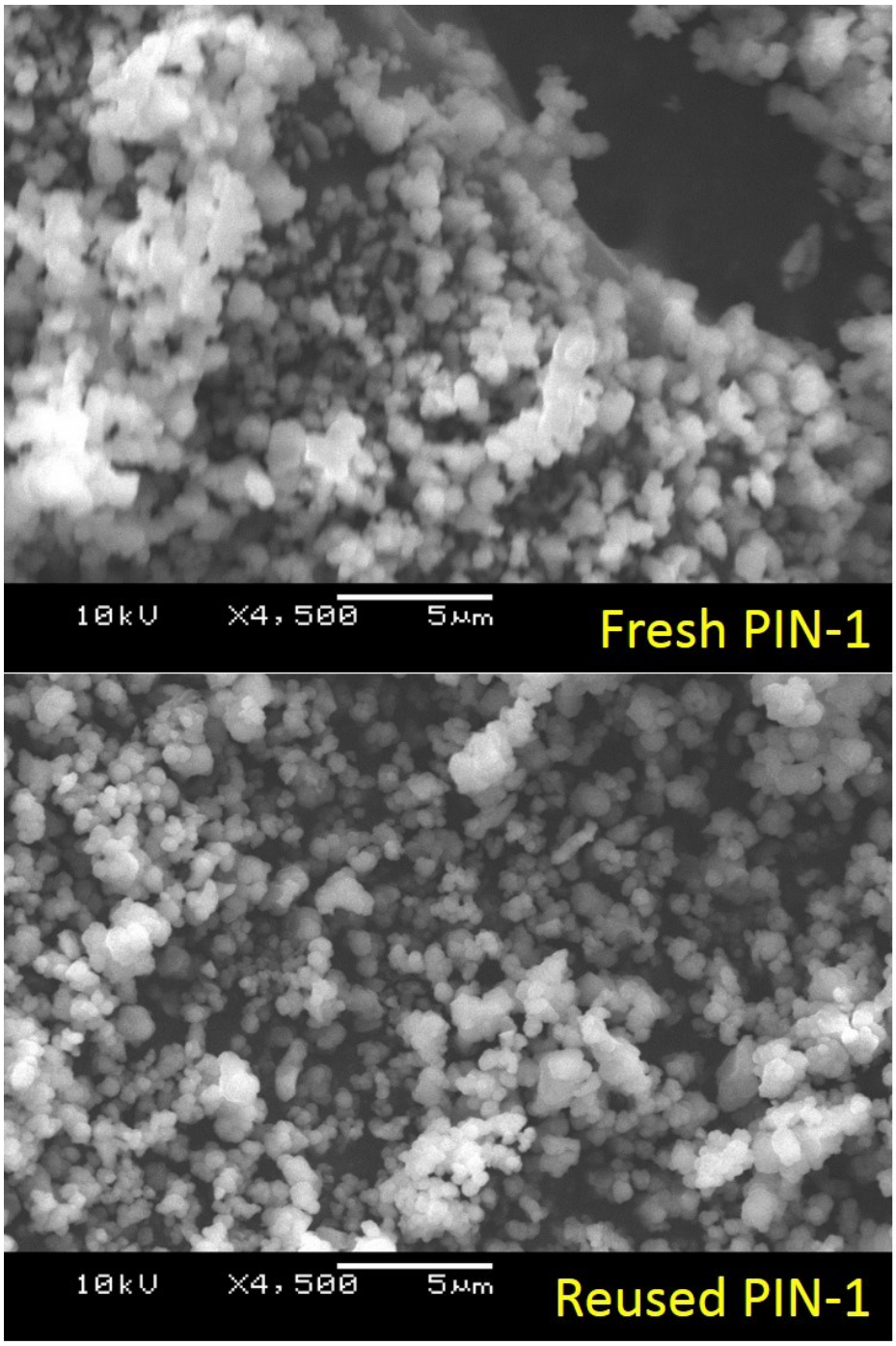
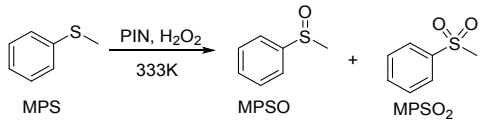


Figure S3. SEM images of Fresh and Recycled PIN-1 catalyst.

Table S1. Selective oxidation of methyl phenyl sulfide in different catalyst amount [a].



Entry	Cat. (mg)	Conv.	selectivity	
			MPSO	$MPSO_2$
1	1	12.4	97%	2%
2	2.5	24.4	97%	2%
3	3.5	23.8	98%	2%
4	5	26.3	98%	1%
5	7.5	52.9	99%	1%
6	10	58.7	98%	1%
7	15	63.9	98%	1%

[a] Reaction conditions: methyl phenyl sulfide 1 mmol, $CNCH_3$ 4 mL, 30% H_2O_2 2 mmol, 60 °C, 1 h.

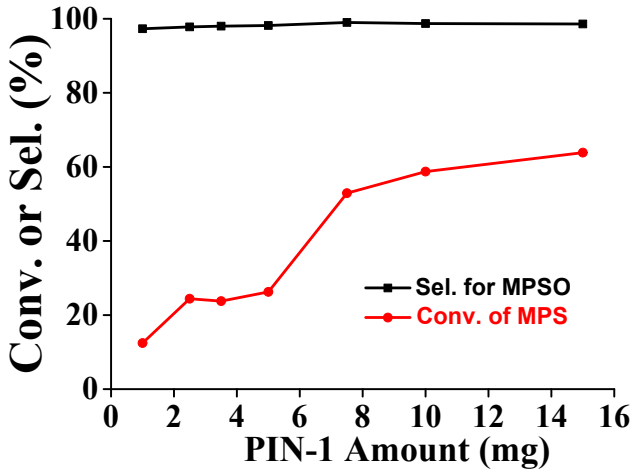


Figure S4. The effect of catalyst amount on the catalytic oxidation of methyl phenyl sulfide. Reaction conditions: methyl phenyl sulfide 1 mmol, catalyst amount as described in the **Table S1**, CH_3CN 4 mL, 30% H_2O_2 2 mmol, 60 °C, 1 h.

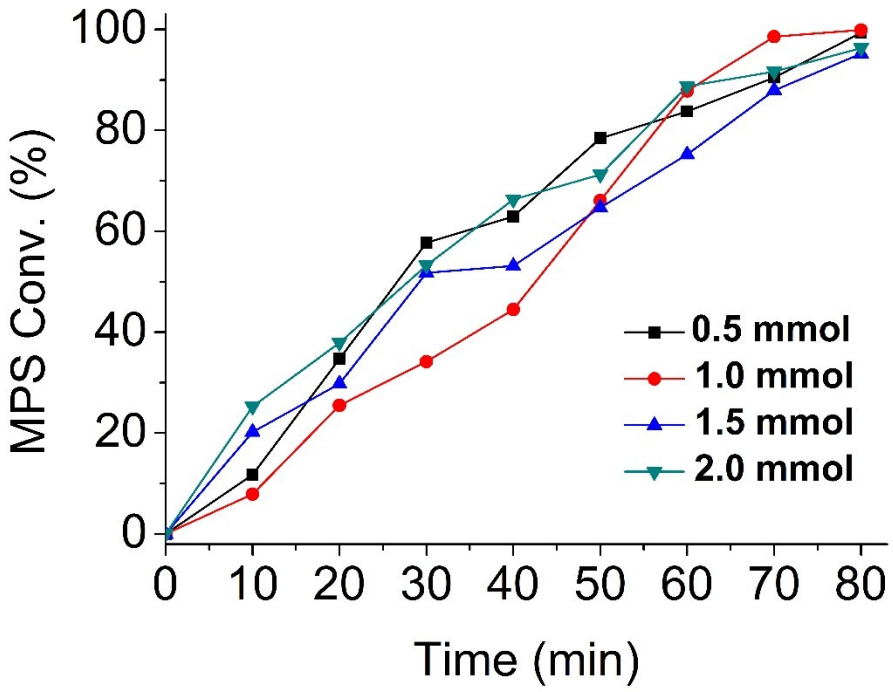


Figure S5. Four control experiments at different primary concentration of the initial substrate concentration (0.5, 1.0, 1.5, 2.0 mmol MPS, 1.0, 2.0, 3.0, 4.0 mmol 30% H_2O_2) to study the reaction order. Reaction conditions: PIN-1 20 mg, CH_3CN 4 mL, 60 °C.

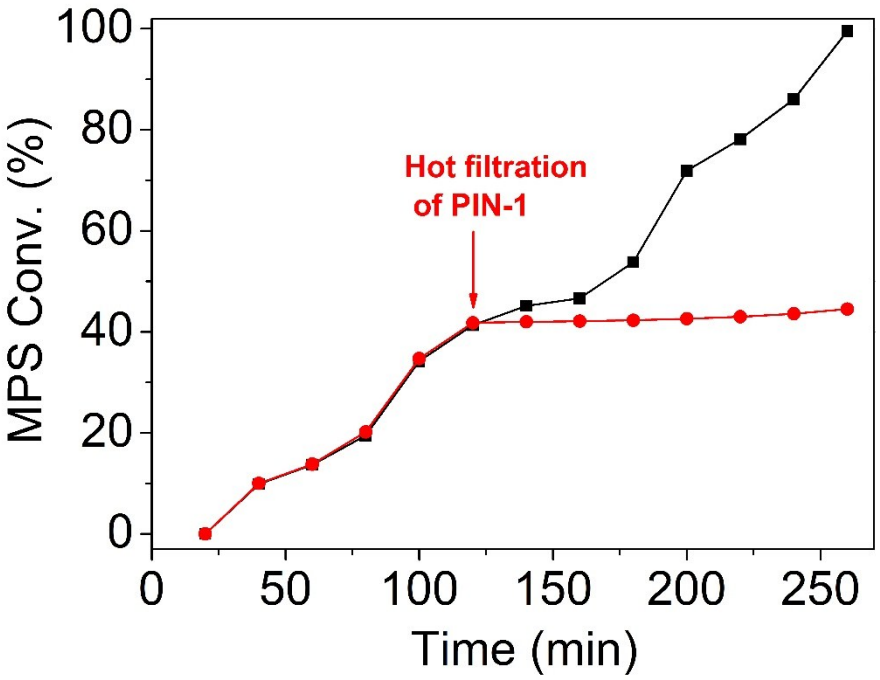


Figure S6. The data of hot filtration test. Red Line: the PIN-1 solid was removed by a hot filtration at 120 min.

Reaction conditions: methyl phenyl sulfide 1 mmol, PIN-1 20 mg, 30% H_2O_2 2 mmol, CH_3CN 4 mL, 40 °C.

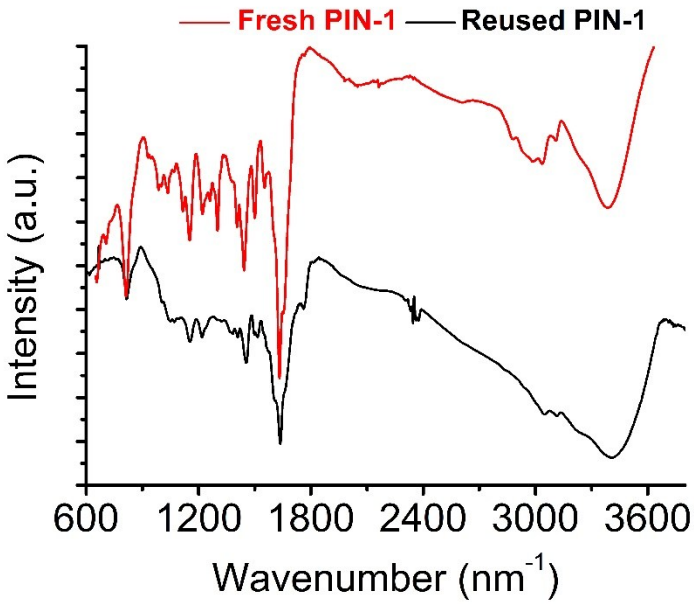
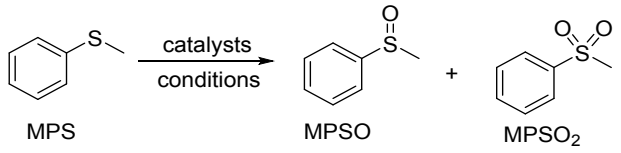


Figure S7. FTIR spectra of Fresh and Recycled PIN-1 catalyst.

Table S2. Catalytic oxidation of methyl phenyl sulfide by various catalysts.



No.	Catalysts	Reaction conditons	Conv.	selectivity		Ref.
				MPSO	$MPSO_2$	
1	$Mn(OAc)_2@CeO_2$	10 bar O_2, CH_3CN, 105 °C, 23 h	98.3%	44%	53%	1
2	mpg-C_3N_4	1 atm O_2, IBA 300, CH_3CN, isobutyraldehyde, a mercury lamp (150 W) 4 h	100%	5%	92%	2
3	$[MoO_3(2,2'–bipy)]_n$	TBHP, CH_2Cl_2, 20 °C, 4 h	>97%	96%	trace	3
4	$PVPyPS_4PMo_{10}V_2$,	H_2O_2, EtOH, rt,10 min	100%	98%	2%	4
5	PS Mo	H_2O_2, H_2O, rt, 10 min	>98%	98%	-	5
6	$[(Me_3TACN)_2Mn_2^{IV}(l\text{-}O)_3](PF_6)_2$	H_2O_2, CH_3CN, rt, 4 h	58%	25%	23%	6
7	Ru-PVP/γ-Al_2O_3	H_2O_2, CH_3CN, rt, 120 min	100%	98%	2%	7
8	SBA-15/NH_2-FeQ_3	H_2O_2, H_2O, rt, 3 h	-	87%	10%	8
9	$BaRuO_3$	0.1 MPa O_2, *t*-BuOH, 60 °C, 10 h	73%	79%	21%	9
10	VSBC@NS (nano silica)	H_2O_2, MeOH, rt, 2 h	99%	-	-	10
11	Mo-MnO_2	5 atm O_2, *o*-dichlorobenzene, 150 °C, 6 h	82	75%	3	11
12	Co-SiO_2@Ti-Si	1 MPa O_2, CH_3CN, 120 °C, 4 h	95%	32%	68%	12
13	$(Me_3TACN)MnCl_3$	*t*-BuOOH, CH_3CN, 23 °C, 7 h	99%	99%	1%	13
14	MNP@TA-IL/W	H_2O_2, H_2O, 25 °C, 1 h	98	99%	1%	14

1. P.-F. Zhang, H.-F. Lu, S.-Z. Yang, W.-C. Zhan, W.-S. Zhu, X.-G. J, C. Huang, and S Dai, *ChemistrySelect*, 2016, **6**, 1179-1183.
2. P.-F. Zhang, Y. Wang, H.-R. Li and M. Antoniettib, *Green Chem.*, 2012, **14**, 1904-1908
3. I. Tosia, C. Vurchioa, M. Abrantesc, I. Gonçalvesd, M. Pillingerd, F. Cavanib, F. M. Corderoa, A. Brandi, *Catal. Commun.,* 2018, **103**, 60-64
4. E. Rafiee, S. Shahebrahimi, *J. Mol. Struct.*, 2017, **1139**, 255-263
5. J. J. Boruah, K. Ahmed, S. Das, S. R. Gogoi, G.Saikia, M. Sharma, N. S. Islam, *J. Mol. Catal. A Chem.,* 2016, **425**, 21–30
6. J. E. Barker, T. Ren, *Tetrahedron Lett.*, 2004, **45**, 4681–4683
7. P. Veerakumar, Z.-Z. Lu, M. Velayudham, K.-L. Lu, S. Rajagopal, *J. Mol. Catal. A Chem.,* 2010, **332,** 128–137
8. H. G. Hosseini and S. Rostamnia, *New J. Chem.*, 2018, **42**, 619-627
9. K. Kamata, K. Sugahara, Y. Kato, S. Muratsugu, Y. Kumagai, F. Oba, M. Hara, *ACS appl. Mater. Interfaces,* 2018, **10**, 23792-23801.
10. M. Dabiri, M. Koohshari, F. Shafpour, M. Kasmaei, P. Salari, D. MaGee, *J. Iran. Chem. Soc.,* 2016, **13,** 1265–1272
11. T. Uematsu, Y. Miyamoto, Y. Ogasawara, K. Suzuki, K. Yamaguchi and N. Mizuno, *Catal. Sci. Technol.*, 2016, **6**, 222-233
12. M. Liu, S. Shi, L. Zhao, M. Wang, G.-Z. Zhu, X, Zheng, J. Gao, and J. Xu, *ACS Catal.,* 2018, **8**, 683−691
13. J. E. Barker, T. Ren, *Tetrahedron Lett.*, 2005, **46**, 6805–6808
14. S. H. Hosseini, M. Tavakolizadeh, N. Zohreh, R. Soleyman, *Appl. Organometal Chem.*, 2018, **32,** 3953-3963