Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary information

Peroxoniobium(V) catalyzed selective oxidation of sulfides with hydrogen peroxide in water : a sustainable approach

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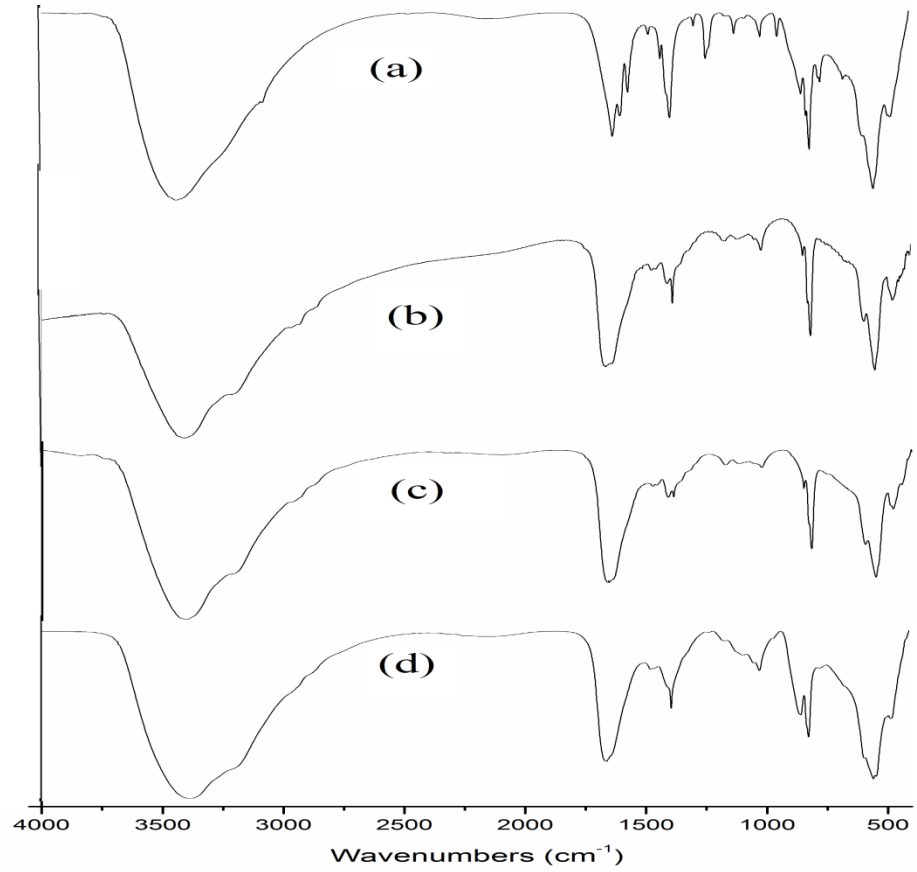


Fig. S1 IR spectra of (a) **NbN,** (b) **NbA,** (c) Regenerated **NbA** after the 2nd cycle of reaction and (d) Diperoxoniobate complex recovered after oxidation of MPS by **NbA**, in absence of H_2O_2.

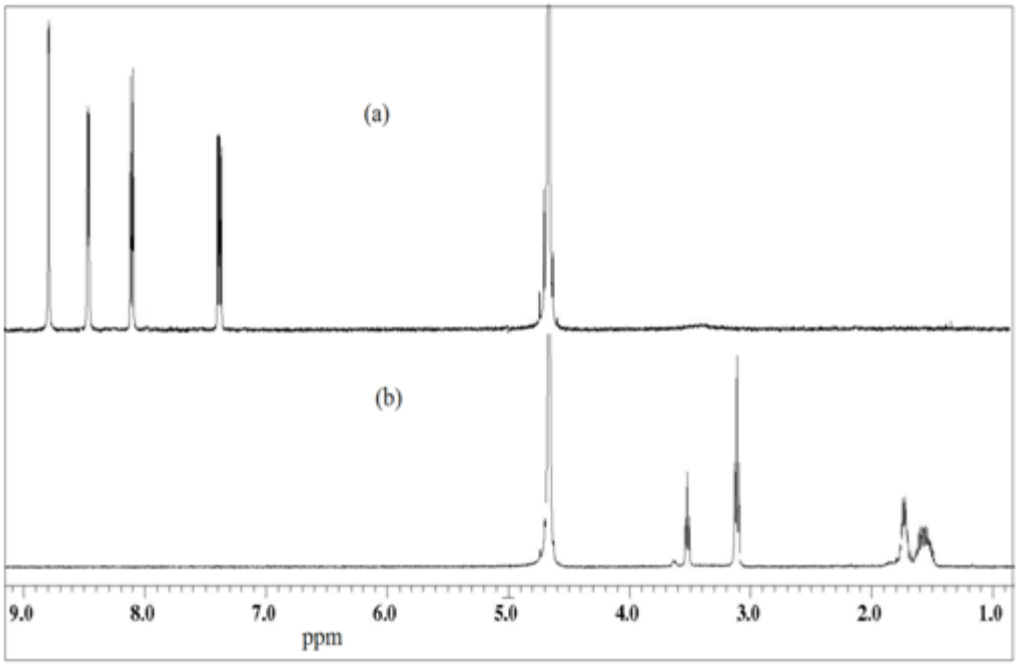
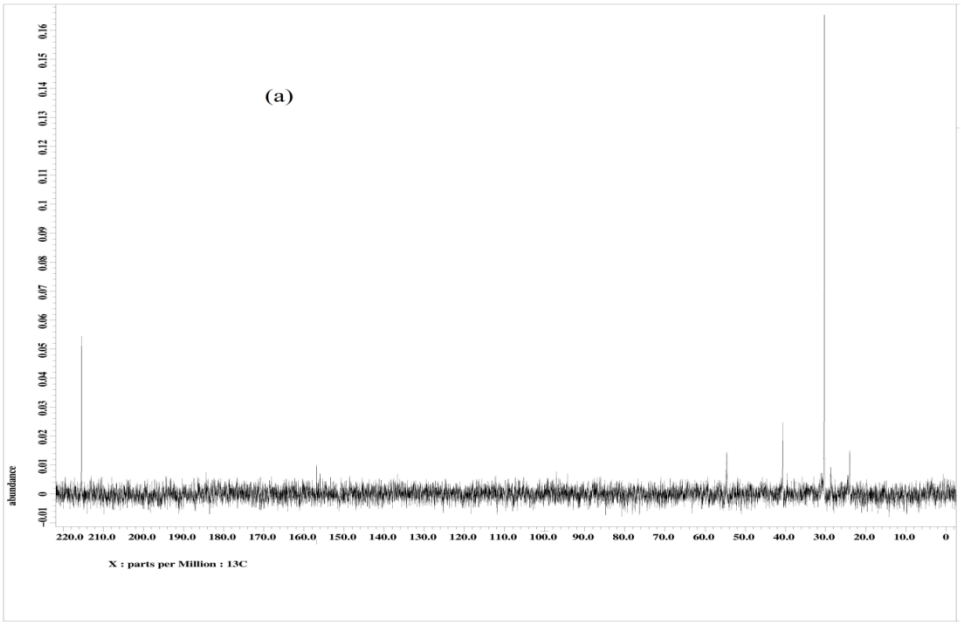


Fig. S2 ^{1}H NMR spectra of (a) **NbN** and (b) **NbA.**



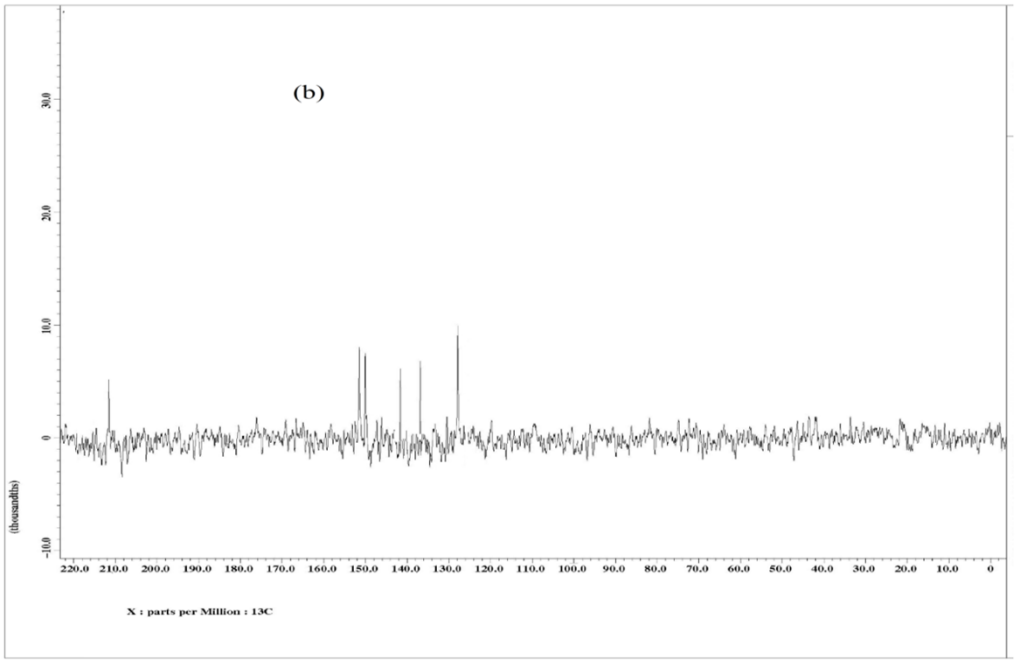


Fig. S3 ^{13}C NMR spectra of (a) **NbA** and (b) **NbN.**

Text S4 Determination of H_2O_2 efficiency or effective use of H_2O_2 in the sulfoxidation reaction

The calculations are shown with oxidation of methyl phenyl sulfide (MPS) to methyl phenyl sulfoxide as a representative example.

H_2O_2 efficiency (%) = 100 × [mole of H_2O_2 consumed in the formation of oxyfunctionalized products / mole of H_2O_2 converted]

(a) Assuming that one mole of oxidant reacts with one mole of substrate, H_2O_2 (mole) consumed in the formation of sulfoxide (yield: 96%) from 5 mmol sulfides = **4.80 mmol**

(b) The spent catalyst was isolated from the aqueous extract of the reaction mixture by precipitation with acetone followed by centrifugation. The H_2O_2 left was estimated by titration with standard cerium (IV) solution. The value was found to be: **4.79 mmol**

Since 10 mmol H_2O_2 has been originally used for the reaction,

Therefore, total mole of H_2O_2 converted = (10.0 – 4.79) mmol = **5.21 mmol**

Thus, **H_2O_2 efficiency = 100 × [4.80 / 5.21]**

= 92.13 %

Text S5 Characterization of Sulfoxides and Sulfones:

(a) Methylphenylsulfoxide: Isolated as light yellow solid; mp 28-29^{o}C; ν (KBr)/cm^{-1} 1047;

^{1}H NMR (400MHz; $CDCl_3$, δ): 2.73(s, 3H); 7.30-7.36(m, 1H); 7.40-7.49(m, 2H); 7.61-7.69(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 43.92; 123.52; 128.68; 130.98; 145.49

(b) Methylphenylsulfone: Isolated as white solid; mp 85-86^{o}C; ν (KBr)/cm^{-1} 1320, 1164;

^{1}H NMR (400MHz; $CDCl_3$, δ): 3.01(s, 3H); 7.52-7.58(m, 1H); 7.61-7.69(m, 2H); 7.91-7.95(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 44.82; 126.21; 128.52; 133.24; 137.42

(c) Methyl-p-tolylsulfoxide: Isolated as pale yellow liquid; mp 43-45 ^{o}C; ν (KBr)/cm^{-1} 1036

^{1}H NMR (400MHz; $CDCl_3$, δ): 7.53 (d, 2H), 7.32 (d, 2H), 2.70 (s, 3H), 2.42 (s, 3H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 142.58, 141.57, 129.99, 123.61, 44.00, 21.41

(d) Methyl-p-tolylsulfone: Isolated as white solid; mp 85-87^{o}C; ν (KBr)/cm^{-1} 1293, 1146

^{1}H NMR (400 MHz, CDCl3) δ (ppm): 7.84 (d, 2H), 7.38 (d, 2H), 3.04 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, CDCl3) δ (ppm): 144.69, 137.63, 129.96, 127.38, 44.63, 21.64

(e) Allylphenylsulfoxide: Isolated as pale yellow liquid; ν (KBr)/cm^{-1} 1044;

^{1}H NMR (400MHz; $CDCl_3$, δ): 3.41(dt, 2H, J=7.11, 1.12Hz); 5.00(dq, 1H, J=1.42, 17.10Hz); 5.15(dq, 1H, J=1.12, 10.22Hz); 5.45(ddt, 1H, J=7.11, 10.22, 17.10 Hz); 7.26-7.30(m, 1H); 7.37-7.39(m, 2H); 7.60-7.63(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 60.38; 117.99; 124.70; 125.08; 129.09; 131.24; 142.19

(f) Allylphenylsulfone: Isolated as pale yellow liquid; ν (KBr)/cm^{-1} 1319, 1147;

^{1}H NMR (400MHz; $CDCl_3$, δ): 3.94(dt, 2H, J= 7.19, 1.22Hz); 5.00(dq, 1H, J= 1.48, 17.21Hz); 5.17(dq,1H, J= 1.22, 10.31Hz); 5.62(ddt, 1H, J= 7.19, 10.31, 17.21Hz); 7.38-7.41(m, 1H); 7.63-7.69(m, 2H); 7.90-7.93(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 60.66; 117.56; 124.66; 128.87; 129.07; 133.79; 138.25

(g) Phenylvinylsulfoxide: Isolated as pale yellow liquid; ν (KBr)/cm^{-1} 1053;

^{1}H NMR (400MHz; $CDCl_3$, δ): 5.93(d, 1H, J=10.13Hz); 6.28(d, 1H, J=15.89Hz); 6.56-6.69(m, 1H); 7.27-7.36(m, 1H); 7.45-7.52(m, 2H); 7.63-7.69(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 120.59; 124.59; 129.35; 131.17; 142.96; 143.40

(h) Phenylvinylsulfone: Isolated as white solid; mp 63-64^{o}C; ν (KBr)/cm^{-1} 1365, 1162;

^{1}H NMR (400MHz; $CDCl_3$, δ): 6.12(d, 1H, J=9.60Hz); 6.44(d, 1H, J=16.42Hz); 6.64-6.77(m, 1H); 7.44-7.52(m, 1H); 7.58-7.67(m, 2H); 7.87-7.91(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 127.85; 129.33; 133.77; 138.51; 139.70

(i) 2-(Phenylsulfinyl)ethanol: Isolated as light brown solid; mp 42-43^{o}C; ν (KBr)/cm^{-1} 1039;

^{1}H NMR (400MHz; $CDCl_3$, δ): 2.41(s, 1H); 3.13(t, 2H, J=5.31Hz); 3.86(t, 2H, J=5.26Hz); 7.28-7.37(m, 1H); 7.48-7.56(m, 2H); 7.64-7.69(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 56.19; 60.94; 125.41; 129.99; 131.24; 144.51

(j) 2-(Phenylsulfonyl)ethanol: Isolated as white solid; mp 96-97^{o}C; ν (KBr)/cm^{-1} 1338, 1155;

^{1}H NMR (400MHz; $CDCl_3$, δ): 2.49(s, 1H); 3.31(t, 2H, J=5.46Hz); 3.96(t, 2H, J=5.26Hz); 7.45-7.52(m, 1H); 7.58-7.67(m, 2H); 7.89-7.96(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 57.39; 61.57; 128.93; 129.54; 134.06; 140.74

(k) Ethylphenylsulfoxide: Isolated as pale yellow liquid; ν (KBr)/cm^{-1} 1054;

^{1}H NMR (400MHz; $CDCl_3$, δ): 1.23(t, 3H, J=6.61Hz); 2.69-2.78(q, 1H, J=6.61Hz); 2.91(q, 1H, J=6.61Hz) 7.13-7.48(m, 3H); 7.49-7.84(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 10.39, 47.19, 125.42, 129.85, 131.47, 145.69

(l) Ethylphenylsulfone: Isolated as white solid; mp > 261 ^{o}C; ν (KBr)/cm^{-1} 1322, 1153;

^{1}H NMR (400MHz; $CDCl_3$, δ): 1.30(t, 3H, J=7.11Hz); 3.09(q, 2H, J=7.11Hz); 7.59(m, 3H); 7.99(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 7.34, 50.28, 127.86, 128.92, 133.47, 138.31

(m) Diphenyl sulfoxide: Isolated as white solid; mp 70 ^{o}C; ν (KBr)/cm^{-1} 1043;

^{1}H NMR(400MHz; $CDCl_3$, δ): 7.63-7.68(m, 4H), 7.43-7.51(m, 6H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 144.71, 129.87, 128.23, 123.71

(n) Diphenyl sulfone: Isolated as pale yellow solid; mp 127^{o}C; ν (KBr)/cm^{-1} 1322, 1155;

^{1}H NMR(400MHz; $CDCl_3$, δ): 7.91-7.99(m, 4H),7.44-7.53(m, 6H)

(o) Dimethylsulfoxide: Isolated as liquid; ν (KBr)/cm^{-1} 1050;

^{1}H NMR (400MHz; $CDCl_3$, δ): 2.61(s, 6H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 40.54

(p) Dimethylsulfone: Isolated as white solid; mp 236-237^{o}C; ν (KBr)/cm^{-1} 1316, 1139;

^{1}H NMR (400MHz; $CDCl_3$, δ): 3.28(s, 6H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 44.61

(q) Dihexylsulfoxide: Isolated as pale yellow liquid; ν (KBr)/cm^{-1} 1042;

^{1}H NMR (400MHz; $CDCl_3$, δ): 0.95 (t, 6H, J= 7.65 Hz), 1.21-1.37 (m, 12H), 1.68 (m, 4H), 2.71 (t, 4H, J=6.71Hz)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 13.54, 21.91, 32.85, 27.64, 28.53, 52.64

(r) Dihexylsulfone: Isolated as pale yellow liquid; ν (KBr)/cm^{-1} 1323, 1161;

^{1}H NMR (400MHz; $CDCl_3$, δ): 0.95 (t, 6H, J= 7.66 Hz), 1.21-1.38 (m, 12H), 1.91 (m, 4H), 3.36 (t, 4H, J=6.71Hz)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 13.48, 21.78, 32.64, 27.91, 26.45, 53.72

(s) Dibutylsulfoxide: Isolated as white solid; mp 32-33^{o}C; ν (KBr)/cm^{-1} 1061;

^{1}H NMR (400MHz; $CDCl_3$, δ): 0.96(t, 6H, J=7.41Hz); 1.37-1.48(m, 4H); 1.69-1.78(m, 4H); 2.62-2.68(m, 4H)

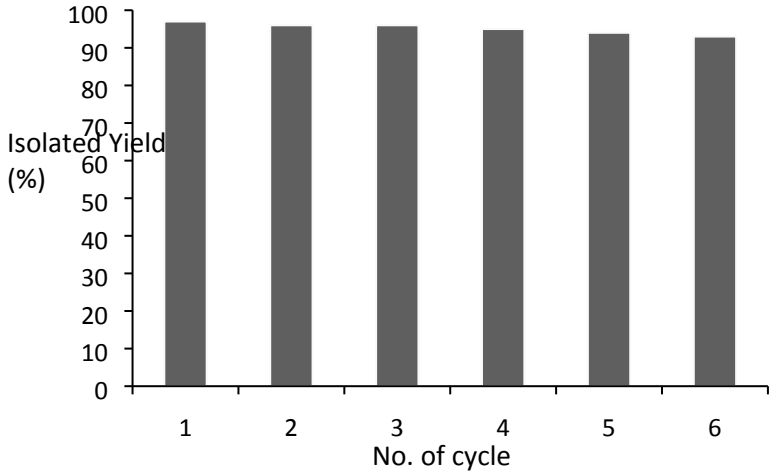
^{13}C NMR (100.5MHz; $CDCl_3$, δ): 13.72; 22.15; 24.50; 51.96

(t) Dibutylsulfone: Isolated as white solid; mp 42-43^{o}C; ν (KBr)/cm^{-1} 1344, 1134;

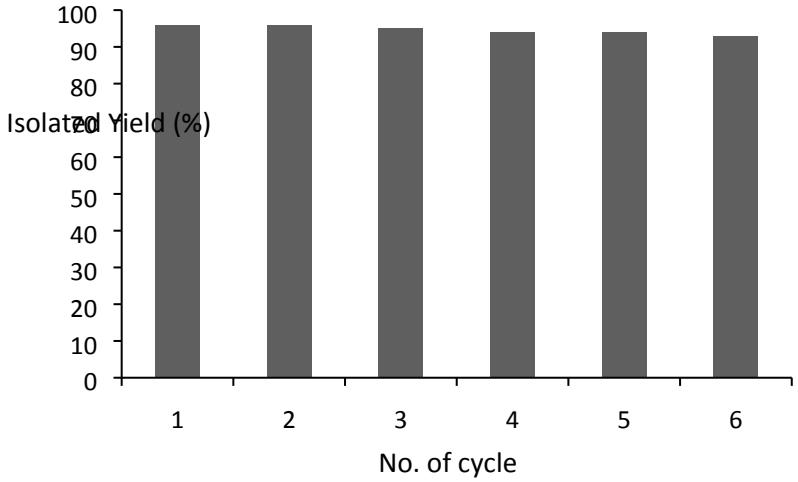
^{1}H NMR (400MHz; $CDCl_3$, δ): 0.96 (t, 6H, J=7.41Hz); 1.39-1.49 (m, 4H); 1.79-1.89(m, 4H); 2.87-2.93(m, 4H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 13.52; 21.76; 23.92; 52.54

Splitting patterns are designated as s (singlet), d (dublet), t (triplet), dt (double triplet), ddt (double-double triplet), q (quartet), dq (double quartet), m (multiplet).



(a)



(b)

Fig. S6 Catalyst regeneration upto 6th reaction cycle. Recyclability of **NbA** (used as representative catalyst) for the selective oxidation of MPS to (a) sulfoxide or (b) sulfone.