Supporting Information

Magneli-Type Tungsten Oxide Nanorods as Catalysts for the Selective Oxidation of Organic Sulfides

René Dören, Jens Hartmann, Benjamin Leibauer, Martin Panthöfer, Mihail Mondeshki, and Wolfgang Tremel*

These authors contributed equally to this work.
Department Chemie, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, D-55128 Mainz, Germany
Table of Contents

TABLE S1. PRODUCT COMPOSITION WITH ADDITIONAL WATER TO STANDARD IN SITU EXPERIMENT (0.85 MG WO₃₋ₓ NANOORTDS, 0.04 MMOL THIOANISOLE, 0.06 MMOL H₂O₂ (60%) IN 0.6 ML METHANOL-D₄).............S6

TABLE S2. FIT PARAMETERS FOR WATER CURVES ACCORDING TO THE EQUATION ABOVE.............................................S6

TABLE S3. PRODUCT COMPOSITION AFTER ANNEALING AT DIFFERENT TEMPERATURES FOR STANDARD IN SITU EXPERIMENT (0.85 MG WO₃₋ₓ NANOORTDS, 0.04 MMOL THIOANISOLE, 0.06 MMOL H₂O₂ (60%) IN 0.6 ML METHANOL-D₄)............................................................................................................................................S7

TABLE S4. BET SURFACE AREA AND Ζ–POTENTIAL OF NANOPARTICLES USED FOR SULFIDE OXIDATION..........S8

FIG. S1. PAWLEY REFINEMENTS OF WO₃₋ₓ NRS ANNEALED AT 300°C USING SPACE GROUP P2₁/M AND A QUADRATIC FORM TO COMPENSATE THE ANISOTROPY. Refined parameters are: R_wp: 2.23, GOF: 1.08, CRYSTAL SIZE (A*B*C): 4.1*72.6*4.3 NM. LATTICE PARAMETERS: A=18.196 Å, B=3.794 Å AND C= 14.000 Å. .....................................................................................................................................................................S9

FIG. S2. TEM IMAGES OF WO₃₋ₓ NANOORTDS ANNEALED AT (A) 300 °C, (B) 400 °C, (C) 500 °C AND (D) AFTER SIX REACTION CYCLES. (E) P-XRD PATTERNS OF ANNEALED WO₃₋ₓ NANOORTDS UP TO 500 °C AND (F) AFTER FIVE REACTION CYCLES. REFERENCES: W₁₈O₄₉ (WO₂.72, COD, ENTRY NO.: 96-152-8167), WO₃ (MONOCLINIC, COD, ENTRY NO.: 96-152-8916). .......................................................................................................................S10

FIG. S3. (A) TEM IMAGE AND (B) P-XRD PATTERN OF CEO₂ NANOPARTICLES. REFERENCE: CERIANITE (CEO₂), COD, ENTRY NO.: 96-900-9009)..........................................................................................................................S11

FIG. S4. (A) ¹H-NMR SPECTRA OF A STANDARD CATALYSIS (0.04 MMOL THIOANISOLE, 0.06 MMOL H₂O₂ (60 %), 0.85 MG WO₃₋ₓ NANOORTDS IN 0.6 ML OF METHANOL-D₄) AFTER 10 AND 30 MIN, X MARKING THE PEAKS USED FOR INTEGRATION. (B) TIME DEPENDENT COMPOSITION DURING THE CATALYSIS BASED ON ¹H-NMR DATA..........................................................................................................................................................S13

FIG. S5. (A) ¹H-NMR SPECTRA OF A CATALYSIS WITH DOUBLE AMOUNTS (0.08 MMOL THIOANISOLE, 0.12 MMOL H₂O₂ (60 %), 1.7 MG WO₃₋ₓ NANOORTDS IN 0.6 ML OF METHANOL-D₄) AFTER 10 AND 30 MIN, X MARKING THE PEAKS USED FOR INTEGRATION. (B) TIME DEPENDENT COMPOSITION DURING THE CATALYSIS BASED ON ¹H-NMR DATA.............................................................................................................................................S14

FIG. S6. (A) ¹H-NMR SPECTRA OF A CATALYSIS WITH WATER INFLUENCE (0.04 MMOL THIOANISOLE, 0.06 MMOL H₂O₂ (60 %), 0.85 MG WO₃₋ₓ NANOORTDS IN 0.4 ML OF METHANOL-D₄ AND 0.2 ML D₂O) AFTER 10 AND 30 MIN, X MARKING THE PEAKS USED FOR INTEGRATION. (B) TIME-DEPENDENT COMPOSITION DURING THE CATALYSIS BASED ON ¹H-NMR DATA. .............................................................................................................................................S15

FIG. S7. ¹H-NMR SPECTRA OF A STANDARD CATALYSIS (0.04 MMOL THIOANISOLE, 0.12 MMOL H₂O₂ (60 %), 0.85 MG WO₃₋ₓ NANOORTDS IN 0.6 ML OF METHANOL-D₄) AFTER 10 MIN, 30 MIN, 22H AND 13 D, X MARKING THE PEAKS USED FOR INTEGRATION. ......................................................................................................................................S16

FIG. S8. (A) ¹H-NMR SPECTRA OF AN OXIDATION CATALYSIS USING SULFOXIDES (0.04 MMOL MP-SULFONE, 0.06 MMOL H₂O₂ (60 %), 0.85 MG WO₃₋ₓ NANOORTDS IN 0.6 ML OF METHANOL-D₄) AFTER 10 AND 30 MIN,
FIG. S9. (A) ¹H-NMR SPECTRA OF A STANDARD OXIDATION CATALYSIS (0.04 MMOL THIOANISOLE, 0.06 MMOL H₂O₂ (60 %), 0.85 MG NA₂WO₄ * 2H₂O IN 0.6 ML OF METHANOL-D₄) AFTER 10 AND 30 MIN, X MARKING THE PEAKS USED FOR INTEGRATION. (B) TIME-DEPENDENT COMPOSITION DURING THE CATALYSIS BASED ON ¹H-NMR DATA. ............................................................................................................................................S17

FIG. S10. (A) ¹H-NMR SPECTRA OF A STANDARD CATALYSIS (0.04 MMOL THIOANISOLE, 0.06 MMOL H₂O₂ (60 %), 0.85 MG CEO₂ NANOPARTICLES IN 0.6 ML OF METHANOL-D₄) AFTER 10 AND 30 MIN, X MARKING THE PEAKS USED FOR INTEGRATION. (B) TIME-DEPENDENT COMPOSITION DURING THE CATALYSIS BASED ON ¹H-NMR DATA. ............................................................................................................................................S18

FIG. S11. (A) ¹H-NMR SPECTRA OF A CATALYSIS USING SULFOXIDE (0.04 MMOL MP-SULFOXIDE, 0.06 MMOL H₂O₂ (60 %), 0.85 MG CEO₂ NANOPARTICLES IN 0.6 ML OF METHANOL-D₄) AFTER 10 AND 30 MIN, X MARKING THE PEAKS USED FOR INTEGRATION. (B) TIME-DEPENDENT COMPOSITION DURING THE CATALYSIS BASED ON ¹H-NMR DATA. ............................................................................................................................................S19

FIG. S12. (A) ¹H-NMR SPECTRA OF A STANDARD CATALYSIS (0.04 MMOL DI-N-PROPYL SULFIDE, 0.06 MMOL H₂O₂ (60 %), 0.85 MG WO₃ₓ NANORODS IN 0.6 ML OF METHANOL-D₄) AFTER 10 AND 30 MIN, X MARKING THE PEAKS USED FOR INTEGRATION. (B) TIME-DEPENDENT COMPOSITION DURING THE CATALYSIS BASED ON ¹H-NMR DATA. ............................................................................................................................................S20

FIG. S13. (A) ¹H-NMR SPECTRA OF A STANDARD CATALYSIS (0.04 MMOL DI-TERT-BUTYL SULFIDE, 0.06 MMOL H₂O₂ (60 %), 0.85 MG WO₃ₓ NANORODS IN 0.6 ML OF METHANOL-D₄) AFTER 10 AND 30 MIN, X MARKING THE PEAKS USED FOR INTEGRATION. (B) TIME-DEPENDENT COMPOSITION DURING THE CATALYSIS BASED ON ¹H-NMR DATA. ............................................................................................................................................S22

FIG. S14. (A) ¹H-NMR SPECTRA OF A STANDARD CATALYSIS (0.04 MMOL DIPHENYL SULFIDE, 0.06 MMOL H₂O₂ (60 %), 0.85 MG WO₃ₓ NANORODS IN 0.6 ML OF METHANOL-D₄) AFTER 10 AND 30 MIN, X MARKING THE PEAKS USED FOR INTEGRATION. (B) TIME-DEPENDENT COMPOSITION DURING THE CATALYSIS BASED ON ¹H-NMR DATA. ............................................................................................................................................S24

FIG. S15. (A) ¹H-NMR SPECTRA OF A STANDARD CATALYSIS (0.04 MMOL DIBENZYL SULFIDE, 0.06 MMOL H₂O₂ (60 %), 0.85 MG WO₃ₓ NANORODS IN 0.6 ML OF METHANOL-D₄) AFTER 10 AND 30 MIN, X MARKING THE PEAKS USED FOR INTEGRATION. (B) TIME-DEPENDENT COMPOSITION DURING THE CATALYSIS BASED ON ¹H-NMR DATA. ............................................................................................................................................S26

FIG. S16. (A) ¹H-NMR SPECTRA OF A STANDARD CATALYSIS (0.04 MMOL 4-NITROPHENYL METHYL SULFIDE, 0.06 MMOL H₂O₂ (60 %), 0.85 MG WO₃ₓ NANORODS IN 0.6 ML OF METHANOL-D₄) AFTER 10 AND 30 MIN, X MARKING THE PEAKS USED FOR INTEGRATION. (B) TIME-DEPENDENT COMPOSITION DURING THE CATALYSIS BASED ON ¹H-NMR DATA. ............................................................................................................................................S28

FIG. S17. (A) ¹H-NMR SPECTRA OF A STANDARD CATALYSIS (0.04 MMOL 4-METHOXYPHENYL METHYL SULFIDE, 0.06 MMOL H₂O₂ (60 %), 0.85 MG WO₃ₓ NANORODS IN 0.6 ML OF METHANOL-D₄) AFTER 10 AND 30 MIN, X MARKING THE PEAKS USED FOR INTEGRATION. (B) TIME-DEPENDENT COMPOSITION DURING THE CATALYSIS BASED ON ¹H-NMR DATA. ............................................................................................................................................S30

FIG. S18. (A) ¹H-NMR SPECTRA OF A STANDARD CATALYSIS (0.04 MMOL 4-METHOXYPHENYL METHYL SULFIDE, 0.06 MMOL H₂O₂ (60 %), 0.85 MG WO₃ₓ NANORODS IN 0.6 ML OF METHANOL-D₄) AFTER 10 AND 30 MIN, X MARKING THE PEAKS USED FOR INTEGRATION. (B) TIME-DEPENDENT COMPOSITION DURING THE CATALYSIS BASED ON ¹H-NMR DATA. ............................................................................................................................................S32
FIG. S18. (A) $^1$H-NMR SPECTRA OF A STANDARD CATALYSIS (0.04 MMOL 4-AMINOPHENYL METHYL SULFIDE, 0.06 MMOL H$_2$O$_2$ (60 %), 0.85 MG WO$_{3-x}$ NANORODS IN 0.6 ML OF METHANOL-D$_4$) AFTER 10 AND 30 MIN, X MARKING THE PEAKS USED FOR INTEGRATION. (B) TIME-DEPENDENT COMPOSITION DURING THE CATALYSIS BASED ON $^1$H-NMR DATA. ...........................................................................................................................................S34

FIG. S19. (A) $^1$H-NMR SPECTRA OF A CATALYSIS USING SULFOXIDES (0.04 MMOL DMSO, 0.06 MMOL H$_2$O$_2$ (60 %), 0.85 MG WO$_{3-x}$ NANORODS IN 0.6 ML OF METHANOL-D$_4$) AFTER 10 AND 30 MIN, X MARKING THE PEAKS USED FOR INTEGRATION. (B) TIME-DEPENDENT COMPOSITION DURING THE CATALYSIS BASED ON $^1$H-NMR DATA..........................................................................................................................................................S36

FIG. S20. (A) $^1$H-NMR SPECTRA OF A STANDARD CATALYSIS (0.04 MMOL DIBENZOTHIOPHEN, 0.06 MMOL H$_2$O$_2$ (60 %), 0.85 MG WO$_{3-x}$ NANORODS IN 0.6 ML OF METHANOL-D$_4$) AFTER 10 AND 30 MIN. (B) $^1$H-NMR SPECTRA OF AN EX SITU CATALYSIS (0.04 MMOL DIBENZOTHIOPHEN, 0.06 MMOL H$_2$O$_2$ (60 %), 8.5 MG WO$_{3-x}$ NANORODS IN 1 ML OF METHANOL-D$_4$) AFTER 10 AND 30 MIN. X MARKING THE PEAKS USED FOR INTEGRATION. ...........................................................................................................................................S38
Materials. All chemicals were used as received without further purification. Choline chloride (≥ 98 %) and cerium(III) nitrate hexahydrate (99.5 %, REacton) was purchased from Alfa Aesar, urea (99.5 %, analytical grade) was bought from Acros organics.

Tungsten oxide nanoparticle synthesis. $\text{WO}_3\text{-x}$ nanorods (conditions NR-1) and ammonium tungsten bronze ($\text{(NH}_4\text{)}_{0.2}\text{WO}_3$) nanoparticles (conditions ATB-15c) were synthesized according to our previous publication.\(^1\)

CeO$_2$ nanoparticle synthesis. CeO$_2$ nanoparticles were synthesized based on a synthesis of Hammond et. al.\(^2\) Choline chloride and urea were mixed in molar ratio of 2:1 and heated to 80 °C for 14 h to gain the deep eutectic solvent reline. The reline was dried at 70 °C under reduced pressure for 6 h. Ce(NO$_3$)$_3$·6H$_2$O (750 mg; 1.7 mmol) was dissolved in reline (40 mL), transferred into a stainless steel autoclave (total volume: 50 mL) and heated to 100 °C for 10 h. The highly viscous gel-like reaction mixture was poured into Milli-Q-water (140 mL). The purple product was separated from the suspension by centrifugation (6000-9000 rpm, 10 min), washed three times with Milli-Q-water and three times with ethanol and dried at 80 °C for 14 h. The nanoparticles were calcined at 300 °C for 5 h bevor being used in catalytic experiments.

TiO$_2$ nanoparticles. Anatase TiO$_2$ nanoparticles were synthesized according our previous study,\(^3\) based on a synthesis published by Dinh et. al.\(^4\)

General Considerations. We attribute slight variations for the different standard in situ reactions mainly to residual moisture in the different methanol-d$_4$ batches, water adsorbed to the particles from air, as well as small weighing/pipetting errors.
Table S1. Product composition with additional water to standard in situ experiment (0.85 mg WO$_{3-x}$ nanorods, 0.04 mmol thioanisole, 0.06 mmol H$_2$O$_2$ (60%) in 0.6 ml methanol-d$_4$).

<table>
<thead>
<tr>
<th>Addition of water / µl</th>
<th>Ratio sulfide:sulfoxide:sulfone (10 min)</th>
<th>Ratio sulfide:sulfoxide:sulfone (30 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>39:60:1</td>
<td>8:91:2</td>
</tr>
<tr>
<td>2.34$^a$</td>
<td>50:50:0</td>
<td>14:85:1</td>
</tr>
<tr>
<td>2.34$^b$</td>
<td>48:52:0</td>
<td>12:87:1</td>
</tr>
<tr>
<td>10$^a$</td>
<td>73:26:1</td>
<td>36:62:2</td>
</tr>
<tr>
<td>10$^b$</td>
<td>75:25:0</td>
<td>39:61:0</td>
</tr>
<tr>
<td>50$^{a,c}$</td>
<td>92:8:0</td>
<td>72:28:0</td>
</tr>
<tr>
<td>50$^{b,c}$</td>
<td>92:8:0</td>
<td>74:26:0</td>
</tr>
<tr>
<td>200$^{a,c}$</td>
<td>92:7:1</td>
<td>79:21:0</td>
</tr>
<tr>
<td>200$^{b,c}$</td>
<td>93:7:0</td>
<td>79:21:0</td>
</tr>
</tbody>
</table>

a. addition of H$_2$O. b. addition of D$_2$O. c. total volume fixed to 600 µl.

$r = a * e^{-b*V} + c$

$r =$ conversion / %

V = added volume of H$_2$O / D$_2$O

Table S2. Fit parameters for water curves according to the equation above.

<table>
<thead>
<tr>
<th>Curve</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_2$O 10 min</td>
<td>55.059</td>
<td>0.108</td>
<td>7.256</td>
</tr>
<tr>
<td>H$_2$O 10 min</td>
<td>53.252</td>
<td>0.100</td>
<td>7.775</td>
</tr>
<tr>
<td>D$_2$O 30 min</td>
<td>72.944</td>
<td>0.057</td>
<td>21.365</td>
</tr>
<tr>
<td>H$_2$O 30 min</td>
<td>71.523</td>
<td>0.051</td>
<td>21.457</td>
</tr>
</tbody>
</table>
Table S3. Product composition after annealing at different temperatures for standard *in situ* experiment (0.85 mg WO$_{3-x}$ nanorods, 0.04 mmol thioanisole, 0.06 mmol H$_2$O$_2$ (60%) in 0.6 ml methanol-d$_4$).

<table>
<thead>
<tr>
<th>Annealing temperature / °C</th>
<th>Crystallographic phase</th>
<th>Ratio sulfide:sulfoxide:sulfoxone (10 min)</th>
<th>Ratio sulfide:sulfoxide:sulfoxone (30 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70$^a$</td>
<td>WO$_{3-x}$</td>
<td>96:4:0</td>
<td>90:10:0</td>
</tr>
<tr>
<td>200</td>
<td>WO$_{3-x}$</td>
<td>92:8:0</td>
<td>88:12:0</td>
</tr>
<tr>
<td>250</td>
<td>WO$_{3-x}$</td>
<td>51:49:0</td>
<td>17:82:1</td>
</tr>
<tr>
<td>300</td>
<td>WO$_{3-x}$</td>
<td>39:60:1</td>
<td>8:90:2</td>
</tr>
<tr>
<td>350</td>
<td>WO$_{3-x}$</td>
<td>70:30:0</td>
<td>41:58:0</td>
</tr>
<tr>
<td>400</td>
<td>WO$_{3-x}$</td>
<td>77:23:0</td>
<td>55:45:0</td>
</tr>
<tr>
<td>500</td>
<td>WO$_3$ (monoclinic)</td>
<td>97:3:0</td>
<td>97:3:0</td>
</tr>
</tbody>
</table>

$^a$ Particles additionally dried @ 40 °C under reduced pressure (~1*10$^{-2}$ mbar), 1.7 mg particles in 0.6 ml methanol-d$_4$, 0.2 mmol thioanisole, 0.3 mmol H$_2$O$_2$ (60%).
Table S4. BET surface area and ζ – potential of nanoparticles used for sulfide oxidation.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>Specific surface area / m$^2$g$^{-1}$</th>
<th>ζ – potential / mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO$_{3-x}$ nanorods</td>
<td>47.0</td>
<td>-39.7</td>
</tr>
<tr>
<td>(NH$_4$)$_2$WO$_3$ nanoparticles</td>
<td>22.8</td>
<td>-36.8</td>
</tr>
<tr>
<td>WO$_3$ reference (monoclinic)</td>
<td>2.7</td>
<td>-39.3</td>
</tr>
<tr>
<td>CeO$_2$ nanoparticles</td>
<td>133.9</td>
<td>23.8</td>
</tr>
<tr>
<td>TiO$_2$ nanoparticles</td>
<td>151.7</td>
<td>-9.1</td>
</tr>
<tr>
<td>TiO$_2$ P25</td>
<td>49.7</td>
<td>17.7</td>
</tr>
</tbody>
</table>
Fig. S1. Pawley refinements of WO$_{3-x}$ NRs annealed at 300°C using space group $P2/m$ and a quadratic form to compensate the anisotropy. Refined parameters are: $R_{wp}$: 2.23, GOF: 1.08, crystal size $(a*b*c)$: 4.1*72.6*4.3 nm. Lattice parameters: $a=18.196$ Å, $b=3.794$ Å and $c=14.000$ Å.
Fig. S2. TEM images of WO$_{3-x}$ nanorods annealed at (a) 300 °C, (b) 400 °C, (c) 500 °C and (d) after six reaction cycles. (e) P-XRD patterns of annealed WO$_{3-x}$ nanorods up to 500 °C and (f) after five reaction cycles. References: W$_{18}$O$_{49}$ (WO$_{2.72}$, COD, Entry No.: 96-152-8167), WO$_3$ (monoclinic, COD, Entry No.: 96-152-8916).
Fig. S3. (a) TEM image and (b) P-XRD pattern of CeO\textsubscript{2} nanoparticles. Reference: Cerianite (CeO\textsubscript{2}), COD, Entry No.: 96-900-9009).
\textbf{\textsuperscript{1}H-NMR characterization}

Thioanisole (methyl phenyl sulfide)

\begin{center}
\includegraphics[width=0.2\textwidth]{thioanisole.png}
\end{center}

\textsuperscript{1}H-NMR (400 MHz, d\textsubscript{4}-MeOD) \(\delta\) (ppm): 7.29-7.26 (m, 4H), 7.15-7.12 (m, 1H) 2.48 (s, 3H).

Published elsewhere\textsuperscript{5}: \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm): 7.32-7.20 (m, 4H), 7.17-7.07 (m, 1H), 2.47 (s, 3H).

Methyl phenyl sulfoxide

\begin{center}
\includegraphics[width=0.2\textwidth]{methylphenylsulfoxide.png}
\end{center}

\textsuperscript{1}H-NMR (400 MHz, d\textsubscript{4}-MeOD) \(\delta\) (ppm): 7.74-7.61 (m, 5H), 2.81 (s, 3H).

Published elsewhere\textsuperscript{6}: \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm): 7.62-7.60 (m, 2H), 7.51-7.44 (m, 3H), 2.68 (s, 3H).

Methyl phenyl sulfone

\begin{center}
\includegraphics[width=0.2\textwidth]{methylphenylsulfone.png}
\end{center}

\textsuperscript{1}H-NMR (400 MHz, d\textsubscript{4}-MeOD) \(\delta\) (ppm): 7.99-7.95 (m, 2H), ~7.66-7.54 (m, 3H), 3.13 (s, 3H).

Published elsewhere\textsuperscript{6}: \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm): 7.92 (d, \(J = 7.5\) Hz, 2H), 7.66-7.54 (m, 3H), 3.04 (s, 3H).

\textsuperscript{a} Signals of the aromatic protons partially overlapping with those of MP-sulfoxide. MP-sulfone content calculated as 2.5 times the integral of the signal at 7.99-7.95 ppm. The MP-sulfoxide content was calculated as the integral of the signal at 7.62-7.44 ppm minus the 1.5 times the integral of the signal at 7.99-7.95 ppm.
Fig. S4. (a) $^1$H-NMR spectra of a standard catalysis (0.04 mmol thioanisole, 0.06 mmol $\text{H}_2\text{O}_2$ (60%), 0.85 mg WO$_3$ nanorods in 0.6 mL of methanol-d$_4$) after 10 and 30 min, x marking the peaks used for integration. (b) Time dependent composition during the catalysis based on $^1$H-NMR data.
Fig. S5. (a) $^1$H-NMR spectra of a catalysis with double amounts (0.08 mmol thioanisole, 0.12 mmol H$_2$O$_2$ (60 %), 1.7 mg WO$_{3-x}$ nanorods in 0.6 mL of methanol-d$_4$) after 10 and 30 min, x marking the peaks used for integration. (b) Time dependent composition during the catalysis based on $^1$H-NMR data.
Fig. S6. (a) $^1$H-NMR spectra of a catalysis with water influence (0.04 mmol thioanisole, 0.06 mmol H$_2$O$_2$ (60 %), 0.85 mg WO$_{3-x}$ nanorods in 0.4 mL of methanol-d$_4$ and 0.2 ml D$_2$O) after 10 and 30 min, x marking the peaks used for integration. (b) Time-dependent composition during the catalysis based on $^1$H-NMR data.
Fig. S7. $^1$H-NMR spectra of a standard catalysis (0.04 mmol thioanisole, 0.12 mmol H$_2$O$_2$ (60 %), 0.85 mg WO$_{3-x}$ nanorods in 0.6 mL of methanol-d$_4$) after 10 min, 30 min, 22 h and 13 d, x marking the peaks used for integration.
Fig. S8. (a) $^1$H-NMR spectra of an oxidation catalysis using sulfoxides (0.04 mmol MP-sulfone, 0.06 mmol $\text{H}_2\text{O}_2$ (60 %), 0.85 mg WO$_{3-x}$ nanorods in 0.6 mL of methanol-d$_4$) after 10 and 30 min, x marking the peaks used for integration. (b) Time-dependent composition during the catalysis based on $^1$H-NMR data.
Fig. S9. (a) $^1$H-NMR spectra of a standard oxidation catalysis (0.04 mmol thioanisole, 0.06 mmol H$_2$O$_2$ (60%), 0.85 mg Na$_2$WO$_4$ * 2H$_2$O in 0.6 mL of methanol-d$_4$) after 10 and 30 min, x marking the peaks used for integration. (b) Time-dependent composition during the catalysis based on $^1$H-NMR data.
Fig. S10. (a) $^1$H-NMR spectra of a standard catalysis (0.04 mmol thioanisole, 0.06 mmol H$_2$O$_2$ (60 %), 0.85 mg CeO$_2$ nanoparticles in 0.6 mL of methanol-d$_4$) after 10 and 30 min, x marking the peaks used for integration. (b) Time-dependent composition during the catalysis based on $^1$H-NMR data.
Fig. S11. (a) $^1$H-NMR spectra of a catalysis using sulfoxide (0.04 mmol MP-sulfoxide, 0.06 mmol H$_2$O$_2$ (60 %), 0.85 mg CeO$_2$ nanoparticles in 0.6 mL of methanol-d$_4$) after 10 and 30 min, x marking the peaks used for integration. (b) Time-dependent composition during the catalysis based on $^1$H-NMR data.
Di-n-propyl sulfide

\[
\begin{array}{c}
\text{H}_3\text{C} & \text{S} & \text{CH}_3 \\
\end{array}
\]

\(^1\text{H-}{\text{NMR}}\) (400 MHz, d\(_4\)-MeOD) \(\delta\) (ppm): 2.49 (t, \(J = 7.2\) Hz, 4H), 1.66-1.56 (m, 4H), 1.00 (t, \(J = 7.4\) Hz, 6H).

Published elsewhere\(^7\): \(^1\text{H-}{\text{NMR}}\) (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 2.47 (t, \(J = 7.4\) Hz, 4H), 1.59 (sext, \(J = 7.4\) Hz, 4H), 0.97 (t, \(J = 7.4\) Hz, 6H).

Di-n-propyl sulfoxide

\[
\begin{array}{c}
\text{H}_3\text{C} & \text{S} & \text{CH}_3 \\
\end{array}
\]

\(^1\text{H-}{\text{NMR}}\) (400 MHz, d\(_4\)-MeOD) \(\delta\) (ppm): 2.83-2.72 (m, 4H), 1.87-1.77 (m, 4H), 1.12 (t, \(J = 7.4\) Hz, 6H).

Published elsewhere\(^6\): \(^1\text{H-}{\text{NMR}}\) (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 2.72-2.53 (m, 4H), 1.83-1.73 (m,4H), 1.05 (t, \(J = 7.4\) Hz, 6H).

Di-n-propyl sulfone

\[
\begin{array}{c}
\text{H}_3\text{C} & \text{S} & \text{O} & \text{CH}_3 \\
\end{array}
\]

\(^1\text{H-}{\text{NMR}}\) (400 MHz, d\(_4\)-MeOD) \(\delta\) (ppm): 3.07-3.03 (m, 4H), ~1.88-1.75 (m, 4H)\(^a\), ~1.12 (t, \(J = 7.4\) Hz, 6H)\(^a\).

Published elsewhere\(^6\): \(^1\text{H-}{\text{NMR}}\) (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 2.90-2.86 (m, 4H), 1.86-1.76 (m,4H), 1.02 (t, \(J = 7.4\) Hz, 6H).

\(^a\) Signals of the protons partially overlapping with those of di-n-propyl sulfoxide.
Fig. S12. (a) $^1$H-NMR spectra of a standard catalysis (0.04 mmol di-n-propyl sulfide, 0.06 mmol H$_2$O$_2$ (60 %), 0.85 mg WO$_{3-x}$ nanorods in 0.6 mL of methanol-d$_4$) after 10 and 30 min, x marking the peaks used for integration. (b) Time-dependent composition during the catalysis based on $^1$H-NMR data.
Di-tert-butyl sulfide

\[
\begin{align*}
\text{Published elsewhere}^8: & \quad ^1\text{H-NMR (400 MHz, } \text{d}_4\text{-MeOD) } \delta (\text{ppm}): 1.42 \text{ (s, 18H).}
\end{align*}
\]

Di-tert-butyl sulfoxide

\[
\begin{align*}
\text{Published elsewhere}^9: & \quad ^1\text{H-NMR (400 MHz, } \text{CDCl}_3) \delta (\text{ppm}): 1.12 \text{ (s, 18H).}
\end{align*}
\]

Di-tert-butyl sulfone

\[
\begin{align*}
\text{Not observed.} \quad \text{Published elsewhere}^9: & \quad ^1\text{H-NMR (400 MHz, } \text{CDCl}_3) \delta (\text{ppm}): 1.31 \text{ (s, 18H).}
\end{align*}
\]
Fig. S13. (a) $^1$H-NMR spectra of a standard catalysis (0.04 mmol di-tert-butyl sulfide, 0.06 mmol $\text{H}_2\text{O}_2$ (60 %), 0.85 mg WO$_{3-x}$ nanorods in 0.6 mL of methanol-d$_4$) after 10 and 30 min, x marking the peaks used for integration. (b) Time-dependent composition during the catalysis based on $^1$H-NMR data.
Diphenyl sulfide

\[
\begin{align*}
\text{\textbf{\textsuperscript{1}H-NMR} (400 MHz, d_4-MeOD) } & \delta \text{ (ppm): 7.33-7.24 (m, 10H).} \\
\text{Published elsewhere}^5 & : \text{\textbf{\textsuperscript{1}H-NMR} (400 MHz, CDCl}_3\text{) } \delta \text{ (ppm): 7.39 (d, } J = 7.4 \text{ Hz, 4H), 7.34 (dd, } J = 9.9, 4.8 \text{ Hz, 4H), 7.28 (dd, } J = 7.6, 5.1 \text{ Hz, 2H).}
\end{align*}
\]

Diphenyl sulfoxide

\[
\begin{align*}
\text{\textbf{\textsuperscript{1}H-NMR} (400 MHz, d_4-MeOD) } & \delta \text{ (ppm): 7.72-7.69 (m, 4H), 7.55-7.53 (m, 6H).} \\
\text{Published elsewhere}^6 & : \text{\textbf{\textsuperscript{1}H-NMR} (400 MHz, CDCl}_3\text{) } \delta \text{ (ppm): 7.66-7.64 (m, 4H), 7.49-7.42 (m, 6H).}
\end{align*}
\]

Diphenyl sulfone

\[
\begin{align*}
\text{Not observed.} \\
\text{Published elsewhere}^6 & : \text{\textbf{\textsuperscript{1}H-NMR} (400 MHz, CDCl}_3\text{) } \delta \text{ (ppm): 7.96-7.94 (m, 4H), 7.59-7.49 (m, 6H).}
\end{align*}
\]
Fig. S14. (a) $^1$H-NMR spectra of a standard catalysis (0.04 mmol diphenyl sulfide, 0.06 mmol H$_2$O$_2$ (60 %), 0.85 mg WO$_{3-x}$ nanorods in 0.6 mL of methanol-d$_4$) after 10 and 30 min, x marking the peaks used for integration. (b) Time-dependent composition during the catalysis based on $^1$H-NMR data.
Dibenzyl sulfide

\[\begin{array}{c}
\text{苯} & \text{S} & \text{苯} \\
\end{array}\]

$^1$H-NMR (400 MHz, d$_4$-MeOD) δ (ppm): 7.31-7.23 (m, 10H), 3.61 (s, 4H).
Published elsewhere$^{10}$: $^1$H-NMR (400 MHz, CDCl$_3$) δ (ppm): 7.26-7.14 (m, 10H), 3.55 (s, 4H).

Dibenzyl sulfoxide

\[\begin{array}{c}
\text{苯} & \text{S} & \text{O} & \text{苯} \\
\end{array}\]

$^1$H-NMR (400 MHz, d$_4$-MeOD) δ (ppm): 7.41-7.36 (m, 10H), 4.20 (d, $J$ = 13.0, 2H), 3.98 (d, $J$ = 13.0, 2H).
Published elsewhere$^6$: $^1$H-NMR (400 MHz, CDCl$_3$) δ (ppm): 7.38-7.24 (m, 10H), 3.91 (d, $J$ = 12.0, 2H), 3.86 (d, $J$ = 12.0, 2H).

Dibenzyl sulfone

\[\begin{array}{c}
\text{苯} & \text{S} & \text{O} & \text{O} & \text{苯} \\
\end{array}\]

$^1$H-NMR (400 MHz, d$_4$-MeOD) δ (ppm): 7.60-7.55 (m, 10H), 4.38 (s, 4H).
Published elsewhere$^{11}$: $^1$H-NMR (400 MHz, CDCl$_3$) δ (ppm): 7.40-7.46 (m, 10H), 4.16 (s, 4H).
Fig. S15. a) $^1$H-NMR spectra of a standard catalysis (0.04 mmol dibenzyl sulfide, 0.06 mmol H$_2$O$_2$ (60 %), 0.85 mg WO$_{3-x}$ nanorods in 0.6 mL of methanol-d$_4$) after 10 and 30 min, x marking the peaks used for integration. (b) Time-dependent composition during the catalysis based on $^1$H-NMR data.
4-Nitrothioanisole (4-nitrophenyl methyl sulfide)

\[
\begin{align*}
\text{H-NMR} & \quad (400 \text{ MHz, } \text{d}_4-\text{MeOD}) \quad \delta (\text{ppm}): 8.16 \ (\text{d, } J = 9.0 \text{ Hz, 2H}), \ 7.42 \ (\text{d, } J = 9.0 \text{ Hz, 2H}), \\
& \quad \ 2.59 \ (\text{s, 3H}). \\
\end{align*}
\]

Published elsewhere\textsuperscript{12}: \textbf{H-NMR} (400 MHz, CDCl\textsubscript{3}) \( \delta \) (ppm): 8.24-8.04 (m, 2H), 7.34-7.14 (m, 2H), 2.54 (s, 3H).

4-Nitrophenyl methyl sulfoxide

\[
\begin{align*}
\text{H-NMR} & \quad (400 \text{ MHz, } \text{d}_4-\text{MeOD}) \quad \delta (\text{ppm}): 8.45 \ (\text{d, } J = 8.9 \text{ Hz, 2H}), \ 7.96 \ (\text{d, } J = 8.9 \text{ Hz, 2H}), \\
& \quad \ 2.89 \ (\text{s, 3H}). \\
\end{align*}
\]

Published elsewhere\textsuperscript{13}: \textbf{H-NMR} (300 MHz, CDCl\textsubscript{3}) \( \delta \) (ppm): 8.36 (d, \( J = 8.7 \text{ Hz, 2H} \)), 7.82 (d, \( J = 8.7 \text{ Hz, 2H} \)), 2.78 (s, 3H).

4-Nitrophenyl methyl sulfone

Not observed.

Published elsewhere\textsuperscript{13}: \textbf{H-NMR} (300 MHz, CDCl\textsubscript{3}) \( \delta \) (ppm): 8.43 (d, \( J = 8.8 \text{ Hz, 2H} \)), 8.16 (d, \( J = 8.8 \text{ Hz, 2H} \)), 3.12 (s, 3H).
Fig. S16. (a) $^1$H-NMR spectra of a standard catalysis (0.04 mmol 4-nitrophenyl methyl sulfide, 0.06 mmol H$_2$O$_2$ (60 %), 0.85 mg WO$_3 \times$ nanorods in 0.6 mL of methanol-d$_4$) after 10 and 30 min, x marking the peaks used for integration. (b) Time-dependent composition during the catalysis based on $^1$H-NMR data.
4-Methoxythioanisole (4-methoxyphenyl methyl sulfide)

\[
\begin{array}{c}
\text{H}_3\text{C} & \text{O} \\
& \text{S} & \text{CH}_3
\end{array}
\]

\[^1\text{H-NMR}\] (400 MHz, d$_4$-MeOD) $\delta$ (ppm): 7.27 (d, $J = 8.8$ Hz, 2H), 6.88 (d, $J = 8.8$ Hz, 2H), 3.78 (s, 3H), 2.42 (s, 3H).

Published elsewhere$^5$: \[^1\text{H-NMR}\] (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.23 (d, $J = 8.6$ Hz, 2H), 6.81 (d, $J = 8.6$ Hz, 2H), 3.75 (s, 3H), 2.40 (s, 3H).

4-Methoxyphenyl methyl sulfoxide

\[
\begin{array}{c}
\text{H}_3\text{C} & \text{O} \\
& \text{S} & \text{CH}_3
\end{array}
\]

\[^1\text{H-NMR}\] (400 MHz, d$_4$-MeOD) $\delta$ (ppm): 7.68 (d, $J = 8.7$ Hz, 2H), 7.15 (d, $J = 8.7$ Hz, 2H), 3.88 (s, 3H), 2.79 (s, 3H).

Published elsewhere$^{13}$: \[^1\text{H-NMR}\] (300 MHz, CDCl$_3$) $\delta$ (ppm): 7.53-7.58 (m, 2H), 7.01-6.96 (m, 2H), 3.81 (s, 3H), 2.65 (s, 3H).

4-Methoxyphenyl methyl sulfone

\[
\begin{array}{c}
\text{H}_3\text{C} & \text{O} \\
& \text{S} & \text{O} & \text{S} & \text{CH}_3
\end{array}
\]

\[^1\text{H-NMR}\] (400 MHz, d$_4$-MeOD) $\delta$ (ppm): 7.89 (d, $J = 8.4$ Hz, 2H), $\alpha$(2H), $\alpha$(3H), 3.01 (s, 3H).

Published elsewhere$^{13}$: \[^1\text{H-NMR}\] (300 MHz, CDCl$_3$) $\delta$ (ppm): 7.87 (d, $J = 8.8$ Hz, 2H), 7.02 (d, $J = 8.8$ Hz, 2H), 3.89 (s, 3H), 3.03 (s, 3H).

a. Signal intensity partially too low for assignment.
Fig. S17. (a) $^1$H-NMR spectra of a standard catalysis (0.04 mmol 4-methoxyphenyl methyl sulfide, 0.06 mmol $\text{H}_2\text{O}_2$ (60 %), 0.85 mg WO$_{3-x}$ nanorods in 0.6 mL of methanol-d$_4$) after 10 and 30 min, x marking the peaks used for integration. (b) Time-dependent composition during the catalysis based on $^1$H-NMR data.
4-Aminothioanisole (4-aminophenyl methyl sulfide)

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{S} \quad \text{CH}_3 \\
\end{align*}
\]

\[^1\text{H-NMR}\ (400 \text{ MHz, } \text{d}_4\text{-MeOD}) \; \delta \text{ (ppm): } 7.14 \ (d, \ J = 8.6 \text{ Hz}, 2\text{H}), \ 6.68 \ (d, \ J = 8.6 \text{ Hz}, 2\text{H}), \ 2.37 \ (s, 3\text{H}).
\]

Published elsewhere\(^{12}\): \[^1\text{H-NMR}\ (400 \text{ MHz, } \text{CDCl}_3) \; \delta \text{ (ppm): } 7.21-7.11 \ (m, 2\text{H}), \ 6.65-6.60 \ (m, 2\text{H}), \ 3.38 \ (s, 2\text{H}), \ 2.41 \ (s, 3\text{H}).
\]

4-Aminophenyl methyl sulfoxide

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{S} \quad \text{CH}_3 \quad \text{O} \\
\end{align*}
\]

\[^1\text{H-NMR}\ (400 \text{ MHz, } \text{d}_4\text{-MeOD}) \; \delta \text{ (ppm): } 7.46 \ (d, \ J = 8.7 \text{ Hz}, 2\text{H}), \ 6.80 \ (d, \ J = 8.7 \text{ Hz}, 2\text{H}), \ 2.76 \ (s, 3\text{H}).
\]

Published elsewhere\(^{14}\): \[^1\text{H-NMR}\ (400 \text{ MHz, } \text{CDCl}_3) \; \delta \text{ (ppm): } 7.45 \ (d, \ J = 8.8 \text{ Hz}, 2\text{H}), \ 6.76 \ (d, \ J = 8.8 \text{ Hz}, 2\text{H}), \ 3.79 \ (s, 2\text{H}), \ 2.69 \ (s, 3\text{H}).
\]

4-Aminophenyl methyl sulfone

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{S} \quad \text{CH}_3 \quad \text{O} \quad \text{O} \\
\end{align*}
\]

Not observed.

Published elsewhere\(^{15}\): \[^1\text{H-NMR}\ (400 \text{ MHz, } \text{CDCl}_3) \; \delta \text{ (ppm): } 7.66 \ (d, \ J = 8.5 \text{ Hz}, 2\text{H}), \ 6.69 \ (d, \ J = 8.5 \text{ Hz}, 2\text{H}), \ 4.26 \ (s, 2\text{H}), \ 2.99 \ (s, 3\text{H}).
\]
Fig. S18. (a) $^1$H-NMR spectra of a standard catalysis (0.04 mmol 4-aminophenyl methyl sulfide, 0.06 mmol $\text{H}_2\text{O}_2$ (60 %), 0.85 mg WO$_{3-x}$ nanorods in 0.6 mL of methanol-d$_4$) after 10 and 30 min, x marking the peaks used for integration. (b) Time-dependent composition during the catalysis based on $^1$H-NMR data.
Dimethyl sulfoxide (DMSO)

\[
\text{H}_3\text{C}\overset{\text{S}}{\text{\text{\text{\text{O}}}}}\text{CH}_3
\]

\[^1\text{H-NMR}\ (400\ \text{MHz},\ \text{d}_4\text{-MeOD})\ \delta\ (\text{ppm}):\ 2.68\ (s,\ 3\text{H}).\]

Published elsewhere\textsuperscript{16}: \[^1\text{H-NMR}\ (400\ \text{MHz},\ \text{CDCl}_3)\ \delta\ (\text{ppm}):\ 2.50\ (s,\ 6\text{H}).\]

Dimethyl sulfone

\[
\text{H}_3\text{C}\overset{\text{S}}{\text{\text{\text{\text{O}}}}}\text{CH}_3
\]

\[^1\text{H-NMR}\ (400\ \text{MHz},\ \text{d}_4\text{-MeOD})\ \delta\ (\text{ppm}):\ 3.03\ (s,\ 3\text{H}).\]

Published elsewhere\textsuperscript{16}: \[^1\text{H-NMR}\ (400\ \text{MHz},\ \text{CDCl}_3)\ \delta\ (\text{ppm}):\ 2.97\ (s,\ 6\text{H}).\]
Fig. S19. (a) $^1$H-NMR spectra of a catalysis using sulfoxides (0.04 mmol DMSO, 0.06 mmol $\text{H}_2\text{O}_2$ (60 %), 0.85 mg WO$_{3-x}$ nanorods in 0.6 mL of methanol-d$_4$) after 10 and 30 min, x marking the peaks used for integration. (b) Time-dependent composition during the catalysis based on $^1$H-NMR data.
Dibenzothiophene (DBT)

\[ \begin{align*}
\text{\textsuperscript{1}H-NMR} (400 \text{ MHz, d}_4-\text{MeOD}) \ & \delta \text{ (ppm)}: \ 8.27-8.24 \ (m, \ 2H), \ 7.91-7.89 \ (m, \ 2H), \ 7.51-7.49 \ (m, \ 4H). \\
\text{Published elsewhere}^{17}: \ & \text{\textsuperscript{1}H-NMR} (400 \text{ MHz, CDCl}_3) \ & \delta \text{ (ppm)}: \ 8.21-8.13 \ (m, \ 2H), \ 7.91-7.82 \ (m, \ 2H), \ 7.51-7.42 \ (m, \ 4H).
\end{align*} \]

Dibenzothiophene sulfoxide

\[ \begin{align*}
\text{\textsuperscript{1}H-NMR} (400 \text{ MHz, d}_4-\text{MeOD}) \ & \delta \text{ (ppm)}: \ 8.05 \ (\text{dd, } J = 7.7, 4.3 \text{ Hz, } 4H), \ 7.75 \ (t, \ J = 7.6 \text{ Hz, } 2H), \ 7.63 \ (t, J = 7.7 \text{ Hz, } 2H). \\
\text{Published elsewhere}^{16}: \ & \text{\textsuperscript{1}H-NMR} (400 \text{ MHz, CDCl}_3) \ & \delta \text{ (ppm)}: \ 7.99 \ (d, \ J = 7.6 \text{ Hz, } 2H), \ 7.82 \ (d, \ J = 7.7 \text{ Hz, } 2H), \ 7.61 \ (t, J = 7.5 \text{ Hz, } 2H), \ 7.51 \ (t, J = 7.5 \text{ Hz, } 2H).
\end{align*} \]

Dibenzothiophene sulfone

\[ \begin{align*}
\text{\textsuperscript{1}H-NMR} (400 \text{ MHz, d}_4-\text{MeOD}) \ & \delta \text{ (ppm)}: \ 8.08-8.03 \ (m, \ 4H), \ 7.80 \ (t, \ J = 8.8 \text{ Hz, } 2H), \ 7.66 \ (t, \ J = 8.4 \text{ Hz, } 2H). \\
\text{Published elsewhere}^{16}: \ & \text{\textsuperscript{1}H-NMR} (400 \text{ MHz, CDCl}_3) \ & \delta \text{ (ppm)}: \ 7.83-7.78 \ (m, \ 4H), \ 7.66-7.62 \ (m, \ 2H), \ 7.55-7.51 \ (m, \ 2H).
\end{align*} \]
Fig. S20. (a) $^1$H-NMR spectra of a standard catalysis (0.04 mmol dibenzothiophen, 0.06 mmol H$_2$O$_2$ (60 %), 0.85 mg WO$_{3-x}$ nanorods in 0.6 mL of methanol-d$_4$) after 10 and 30 min. (b) $^1$H-NMR spectra of an ex situ catalysis (0.04 mmol dibenzothiophen, 0.06 mmol H$_2$O$_2$ (60 %), 8.5 mg WO$_{3-x}$ nanorods in 1 mL of methanol-d$_4$) after 10 and 30 min. x marking the peaks used for integration.
References


