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## **Supplementary Information**

## Deep oxidative desulfurization of model fuel catalyzed by polyoxometalates anchored on amine-functionalized ceria doped MCM-41 under molecular oxygen

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Catalyst	W <sup>a</sup> (wt%)	V <sup>a</sup> (wt%)	W/V	POM <sup>b</sup>
			(mol ratio)	(wt%)
10 wt% PW <sub>9</sub> V <sub>3</sub> /APTES-CeM-50	5.35	0.49	3.03	8.91
20 wt% PW <sub>9</sub> V <sub>3</sub> /APTES-CeM-50	11.47	1.06	3.00	19.12
30 wt% PW <sub>9</sub> V <sub>3</sub> /APTES-CeM-50	17.12	1.58	2.99	28.53
40 wt% PW <sub>9</sub> V <sub>3</sub> /APTES-CeM-50	23.25	2.15	3.00	38.75
50 wt% PW <sub>9</sub> V <sub>3</sub> /APTES-CeM-50	27.94	2.58	2.99	46.57
30 wt% PW <sub>9</sub> V <sub>3</sub> /CeM-50	10.11	0.94	3.00	16.83
After used 8 times	12.98	1.20	3.00	21.63

Table S1. ICP results of different catalysts.

<sup>a</sup> As tested by ICP-AES analysis.

<sup>b</sup> As calculated from the ICP-AES results.

 Table S2. APTES amounts of different catalysts.

Sample	Amine <sup>a</sup> (mmol/g)
CeM-50	0
APTES-CeM-50	4.2
30 wt% PW <sub>9</sub> V <sub>3</sub> /APTES-CeM-50	4.2

<sup>a</sup> As obtained according to TG method. The unit of amine amount is mmol amine/g CeM.



Fig. S1. FT-IR spectra of POM/APTES-SiM and PW<sub>9</sub>V<sub>3</sub>/APTES-CeM.



Fig. S2. XRD spectra of POM/APTES-SiM and PW<sub>9</sub>V<sub>3</sub>/APTES-CeM.



Fig. S3. Nitrogen adsorption-desorption isotherms of POM/APTES-SiM and  $PW_9V_3/APTES-CeM$ .

Sample	$S_{BET} \left( m^2/g \right)$	$V_P (cm^{3/g})$	$D_{P}(nm)$
PW <sub>12</sub> /APTES-SiM	297	0.415	2.88
$PW_{11}V_1/APTES-SiM$	292	0.399	2.89
PW10V2/APTES-SiM	286	0.381	2.84
PW <sub>9</sub> V <sub>3</sub> /APTES-SiM	274	0.362	2.81
PW <sub>8</sub> V <sub>4</sub> /APTES-SiM	283	0.374	2.85
PW <sub>9</sub> V <sub>3</sub> /APTES-CeM-100	258	0.358	2.80
PW9V3/APTES-CeM-75	245	0.341	2.76
PW <sub>9</sub> V <sub>3</sub> /APTES-CeM-50	233	0.328	2.74
PW <sub>9</sub> V <sub>3</sub> /APTES-CeM-25	186	0.293	2.67

Table S3. Textural properties of POM/APTES-SiM and PW<sub>9</sub>V<sub>3</sub>/APTES-CeM.



**Fig. S4.** Nitrogen adsorption-desorption isotherms of the 10-50 wt% PW<sub>9</sub>V<sub>3</sub>/APTES-CeM-50 catalysts.

Table 54.	Textural	properties	of the	10-50	Wt% P	W9V3/A	PIES-	CeM-50	catalysts.

Sample	$S_{BET} \left( m^2/g \right)$	$V_P (cm^{3/g})$	$D_{P}(nm)$
10 wt% PW <sub>9</sub> V <sub>3</sub> /APTES-CeM-50	536	0.476	2.90
20 wt% PW <sub>9</sub> V <sub>3</sub> /APTES-CeM-50	374	0.391	2.83
30 wt% PW <sub>9</sub> V <sub>3</sub> /APTES-CeM-50	233	0.328	2.74
40 wt% PW <sub>9</sub> V <sub>3</sub> /APTES-CeM-50	108	0.249	2.68
50 wt% PW <sub>9</sub> V <sub>3</sub> /APTES-CeM-50	67	0.195	2.63



Fig. S5. FT-IR spectra of the fresh and after used 8 times catalyst.



Fig. S6. SEM images of the (a) fresh and (b) after used 8 times catalyst.



Fig. S7. Low angel XRD patterns of the fresh and after used 8 times catalyst.



Fig. S8. Wide angel XRD patterns of the fresh and after used 8 times catalyst.



**Fig. S9.** Nitrogen adsorption-desorption isotherms and BJH pore size distribution curves of the fresh and after used 8 times catalyst.





Fig. S10. The GC-MS analysis of the product after ODS. (a) oil phase, (b) CH<sub>3</sub>CN phase.

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Temperature/°C	Rate constant k/min <sup>-1</sup>	Correlation factor R <sup>2</sup>
50	0.00905	0.99132
60	0.01208	0.98763
70	0.01596	0.99221
80	0.02481	0.99732

Table S5. The kinetic data of different reaction temperature.

<b>Table S6.</b> The comparison between ODS results of different POM based cataly	ysts
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Catalyst	Oxidant	Temperature/ DBT		Reference
		°C	conversion/%	
Ag-POM/SWNTs	H <sub>2</sub> O <sub>2</sub>	20	98.9	S1
$K_6 P_2 W_{18} O_{62}/GO$	Air	60	96.10	S2
HPMo/C	$H_2O_2$	60	100	<b>S</b> 3
HPW@MOFs	$O_2$	90	90	S4
HPW/MgAl-LDH-DBS <sup>a</sup>	$H_2O_2$	60	99.81	S5
H <sub>8</sub> PV <sub>5</sub> Mo <sub>7</sub> O <sub>40</sub>	$O_2$	120	99	<b>S</b> 6
(TBA) <sub>4</sub> PW <sub>11</sub> Fe@PbO <sup>b</sup>	CH <sub>3</sub> COOH/H <sub>2</sub> O <sub>2</sub>	60	97	S7
CNTs@MOF-Mo <sub>16</sub> V <sub>2</sub>	$O_2$	80	98.30	<b>S</b> 8
PW <sub>9</sub> V <sub>3</sub> /APTES-CeM-50	$O_2$	80	99.26	This work

<sup>a</sup> This catalyst represents the phosphotungstic acid (HPW) supported the sodium dodecyl benzene sulfonate (SDBS) modified layered double hydroxides (LDH).

<sup>b</sup> This catalyst means a tetra(n-butyl)ammonium salt of iron-substituted phosphotungstate@lead oxide composite.

## Reference

- S1 H. Zhang, X. Xu, H. Lin, Din, A. U. M, H. Wang and X. Wang, *Nanoscale*, 2017, 9, 13334-13340.
- S2 S. Dou and R. Wang, New J. Chem., 2019, 43, 3226-3235
- S3 R. Ghubayra, C. Nuttall, S. Hodgkiss, M. Craven, E. F. Kozhevnikova and I. V. Kozhevnikov, *Appl. Catal., B*, 2019, **253**, 309-316.

- S4 J. W. Ding and R. Wang, Chin. Chem. Lett., 2016, 27(5), 655-658.
- S5 P. Huang, A. Liu, L. Kang, M. Zhu and B. Dai, New J. Chem., 2018, 42, 12830-12837.
- S6 B. Bertleff, J. Claußnitzer, W. Korth, P. Wasserscheid, A. Jess and J. Albert, ACS Sustainable Chem. Eng., 2017, 5(5), 4110-4118.
- S7 M. A. Rezvani, S. Khandan and N. Sabahi, *Energy Fuels*, 2017, **31**, 5472-5481.
- S8 Y. Gao, Z. Lv, R. Gao, G. Zhang, Y. Zheng and J. Zhao, J. Hazard. Mater., 2018, 359, 258–265.