Supporting Information for

A new approach to construct a hydrodesulfurization catalyst from a crystalline precursor: ligand-induced self-assembly, sulfidation and hydrodesulfurization

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Table S1 Crystal Data and Structure Refinement for Mo_2Ni and $PMo_{11}Ni$.[1, 2]

Items	$PMo_{11}Ni$	Mo_2Ni
Empirical formula	$C_{40}H_{47}Ni_2Mo_{11}N_8O_{45}P$	$C_{30}H_{24}Mo_4N_6Ni_2O_{14}$
CCDC	943445	943446
Formula weight	2563.59	1194
Crystal system	triclinic	triclinic
Space group	P-1(2)	P-1(2)
a (Å)	11.4548(7)	7.1747(5)
b (Å)	15.2635(11)	11.1258(13)
c (Å)	20.3065(13)	11.4017(8)
α	92.623(5)	98.021(8)
β	91.039(5)	90.098(6)
γ	110.491(6)	106.227(8)
V ($Å^3$)	3320.1(4)	864.53(13)
Z	2	2
D_{calc} (g cm^{-3})	2.564	2.293
Crystal size (mm)	0.18×0.13×0.10	0.12×0.11×0.15
Absorption coefficient (mm^{-1})	2.690	2.690
F(000)	2472	2472
Theta range for data collection (°)	2.71-25.00	2.71-25.00
Limiting indices	-13≤h≤12	-13≤h≤12
	-17≤k≤18	-17≤k≤18
	-22≤l≤24	-22≤l≤24
Data/restraints/parameters	11686/42/983	11686/42/983
Goodness-of-fit on F^2	1.018	1.018
T (K)	293	293
λ (Å)	0.71073	0.71073
R_1[a], wR_2[b] (I>2σ(I))	0.0483, 0.0822	0.0537, 0.0822
R_1[a], wR_2[b] (all data)	0.0893, 0.1027	0.0893, 0.0925

[a]$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$. [b]$wR_2 = \sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$

Crystal Data: CCDC 943445 and 943446 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

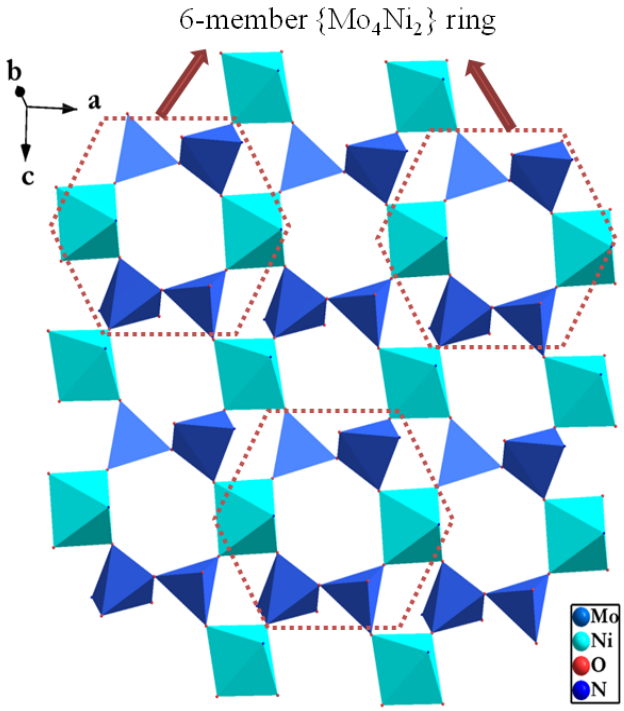

Fig. S1 Two-dimensional layered structure consisting of 6-member $\{Mo_4Ni_2\}$ rings viewed along the *ac* plane in Mo_2Ni.[1]

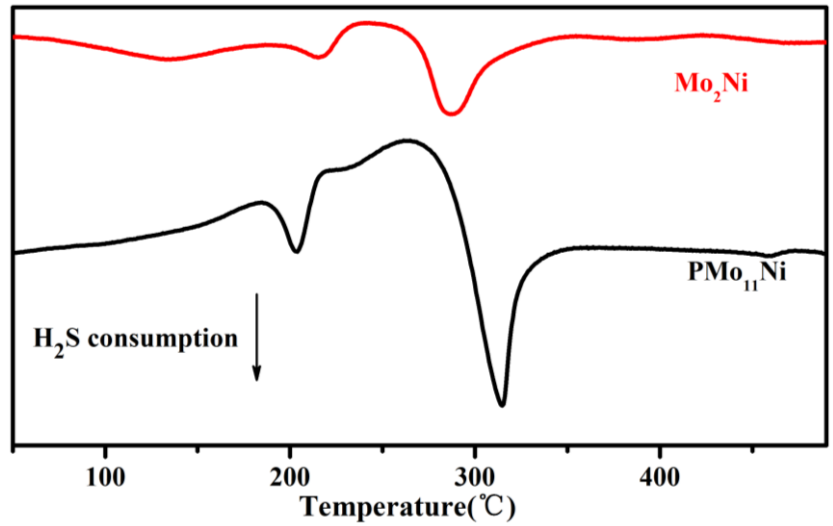

Fig. S2 TPS profiles of bulk Mo_2Ni and $PMo_{11}Ni$.

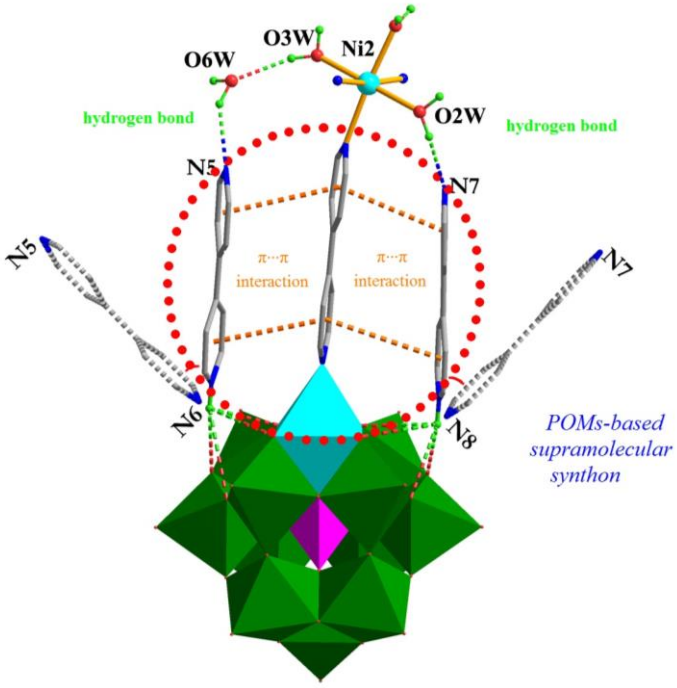

Fig. S3 POMs-based supramolecular synthon in $PMo_{11}Ni$.[2]

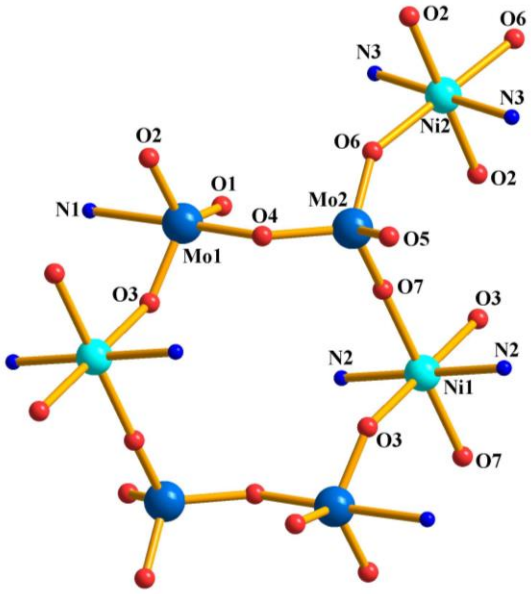

Fig. S4 The coordination environment of Mo-O in Mo_2Ni.

Table S2 The bond length (Å) of Mo-O in Mo_2Ni.

Mo1-Oa	1.729	Mo1-Ob	1.853
Mo2-Oa	1.721	Mo2-Ob	1.953
∑	1.725	∑	1.903

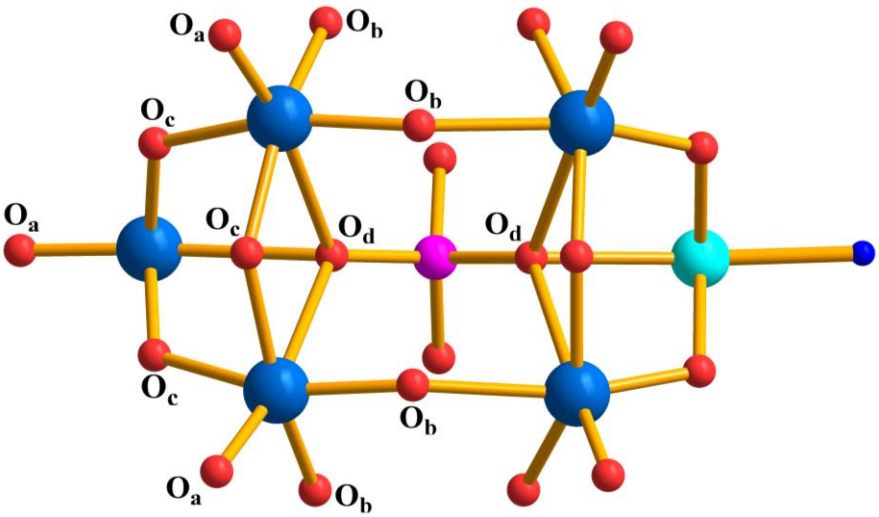

Fig. S5 The coordination environment of Mo-O in $PMo_{11}Ni$.

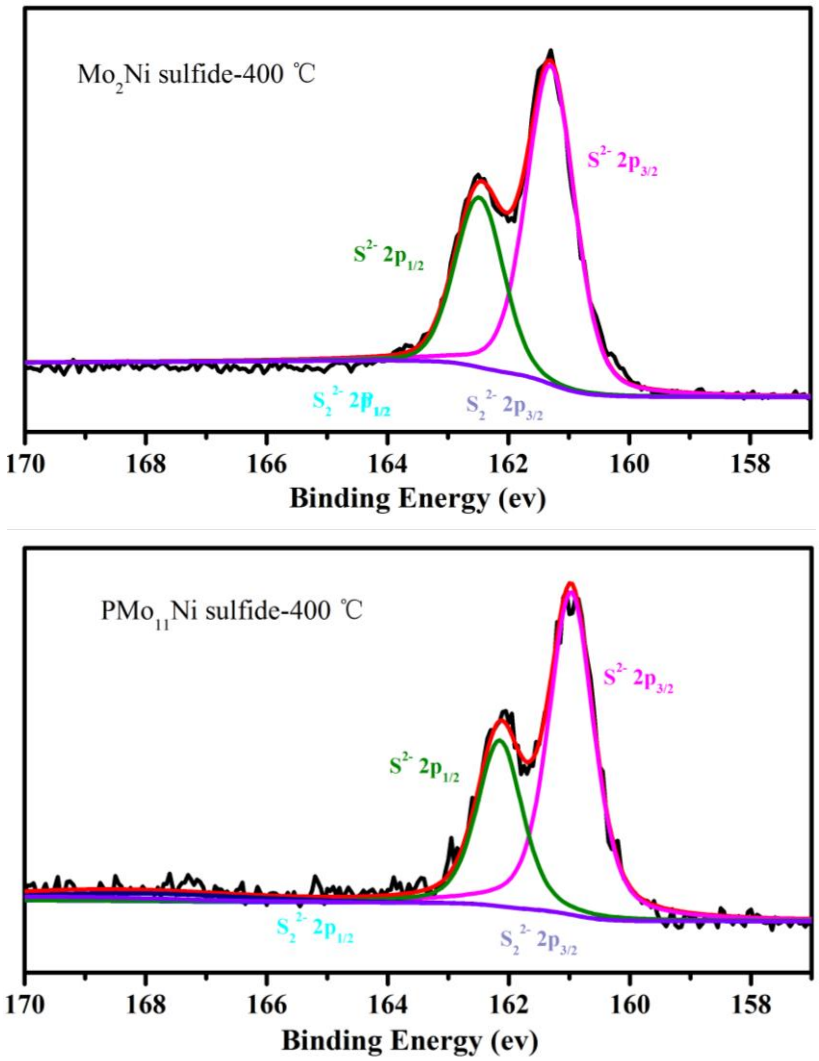

Fig. S6 Deconvolution of S 2p XPS spectra of Mo_2Ni and $PMo_{11}Ni$ sulfides.

Table S3 The bond length (Å) of Mo-O in $PMo_{11}Ni$.

Mo1-Oa	1.677	Mo1-Ob	1.937	Mo1-Oc	1.901
Mo2-Oa	1.681	Mo2-Ob	1.948	Mo2-Oc	1.903
Mo3-Oa	1.681	Mo3-Ob	1.914	Mo3-Oc	2.016
Mo4-Oa	1.681	Mo4-Ob	1.976	Mo4-Oc	1.963
Mo5-Oa	1.689	Mo5-Ob	1.887	Mo5-Oc	1.875
Mo6-Oa	1.681	Mo6-Ob	1.943	Mo6-Oc	1.953
Mo7-Oa	1.682	Mo7-Ob	1.864	Mo7-Oc	1.952
Mo8-Oa	1.696	Mo8-Ob	1.884	Mo8-Oc	1.896
Mo9-Oa	1.679	Mo9-Ob	2.017	Mo9-Oc	2.016
Mo10-Oa	1.677	Mo10-Ob	2.022	Mo10-Oc	1.937
Mo11-Oa	1.682	Mo11-Ob	2.012	Mo11-Oc	1.854
∑	1.682	∑	1.946	∑	1.933

References

1. J. Liang, Y. Lu, J. Zhao, X. Li, Y. Pan, M. Wu, Y. Liu, C. Liu, *RSC Adv.*, 2014, **4**, 27787-27790.

2. J. Liang, H. Zhang, Y. Lu, H. Guo, J. Zhao, M. Wu, Y. Liu, C. Liu, *Inorg. Chem.Commun.*, 2014, **45**, 135-139.