Supporting Information for

Constructing superior Co-Mo HDS catalyst from a crystalline precursor separated from the impregnating solution

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Table S1. Crystal data and structure refinement for Co4Mo12

Empirical formula	$Mo_{12}Co_4O_{52}H_{36}$
CCDC	1003735
Formula weight	2256
Crystal system	triclinic
Space group	P -1(2)
a (Å)	12.0949(19)
b (Å)	12.1400(19)
c (Å)	18.184(3)
α	90.011(16)
β	90.030(14)
γ	93.206(9)
V (Å^3)	2665.82(80)
Z	2
D_{calc} (g cm^{-3})	2.7643

Crystal size	0.18×0.13×0.10 mm
Absorption coefficient (mm^{-1})	2.690
F(000)	2056
Theta range for data collection (°)	2.71-25.00
Limiting indices	-13≤ h ≤12
	-17≤ k ≤18
	-22≤ l ≤24
Data/restraints/parameters	11686/42/983
Goodness-of-fit on F^2	1.018
T (K)	293
λ (Å)	0.71073
R_1[a], wR_2[b] ($I > 2\sigma(I)$)	0.0483, 0.0822
R_1[a] ,wR_2[b] (all data)	0.0893, 0.1027

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

Table S2 Bond valence sum calculations

Mo1 and Mo2

Mo(1)-O(22)	2.01	Mo(2)-O(36)	2.04
Mo(1)-O(16)	1.05	Mo(2)-O(4)	0.95
Mo(1)-O(21)	0.93	Mo(2)-O(5)	0.72
Mo(1)-O(10)	0.54	Mo(2)-O(25)	0.47
Mo(1)-O(17)	0.37	Mo(2)-O(45)	0.40
Mo(1)-O(8)	0.33	Mo(2)-O(20)	0.40
∑	5.24	∑	4.98

Mo3 and Mo4

Mo(3)-O(15)	1.64	Mo(4)-O(42)	1.65
Mo(3)-O(12)	0.94	Mo(4)-O4)	1.00
Mo(3)-O(13)	0.87	Mo(4)-O(5)	0.79
Mo(3)-O(6)	0.53	Mo(4)-O(49)	0.64
Mo(3)-O(33)	0.41	Mo(4)-O(11)	0.45
Mo(3)-O(49)	0.31	Mo(4)-O(6)	0.31

∑	4.70	∑	4.84

Mo5 and Mo6

Mo(5)-O(41)	1.00	Mo(6)-O(43)	1.09
Mo(5)-O(23)	0.99	Mo(6)-O(2)	0.97
Mo(5)-O(2)	0.63	Mo(6)-O(3)	0.92
Mo(5)-O(3)	0.61	Mo(6)-O(28)	0.49
Mo(5)-O(8)	0.50	Mo(6)-O(25)	0.46
Mo(5)-O(10)	0.36	Mo(6)-O(20)	0.37
∑	4.08	∑	4.30

Mo7 and Mo8

Mo(7)-O(37)	1.43	Mo(8)-O(31)	1.56
Mo(7)-O(1)	0.89	Mo(8)-O(1)	0.86
Mo(7)-O(7)	0.85	Mo(8)-O(7)	0.80
Mo(7)-O(11)	0.42	Mo(8)-O(23)	0.64
Mo(7)-O(49)	0.37	Mo(8)-O(8)	0.56
Mo(7)-O(33)	0.36	Mo(8)-O(17)	0.57
∑	4.32	∑	4.99

Mo9 and Mo10

Mo(9)-O(40)	1.49	Mo(10)-O(39)	2.25
Mo(9)-O(13)	0.96	Mo(10)-O(16)	0.68
Mo(9)-O(27)	0.73	Mo(10)-O(21)	0.59
Mo(9)-O(12)	0.70	Mo(10)-O(34)	0.50
Mo(9)-O(9)	0.48	Mo(10)-O(14)	0.44
Mo(9)-O(14)	0.45	Mo(10)-O(9)	0.23
∑	4.79	∑	4.68

Mo11 and Mo12

Mo(11)-O(24)	1.84	Mo(12)-O(46)	1.92
Mo(11)-O(45)	1.02	Mo(12)-O(34)	1.06

Mo(11)-O(28)	0.91	Mo(12)-O(27)	0.83
Mo(11)-O(35)	0.88	Mo(12)-O(35)	0.74
Mo(11)-O(18)	0.80	Mo(12)-O(18)	0.54
Mo(11)-O(20)	0.20	Mo(12)-O(9)	0.21
∑	5.64	∑	5.29

Co1 and Co2

Co(1)-O(52)	0.39	Co(2)-O(30)	0.39
Co(1)-O(21)	0.38	Co(2)-O(5)	0.39
Co(1)-O(12)	0.37	Co(2)-O(18)	0.37
Co(1)-O(32)	0.35	Co(2)-O(13)	0.33
Co(1)-O(7)	0.33	Co(2)-O(47)	0.32
Co(1)-O(44)	0.28	Co(2)-O(26)	0.31
∑	2.10	∑	2.10

Co3 and Co4

Co(3)-O(29)	0.36	Co(4)-O(3)	0.38
Co(3)-O(51)	0.35	Co(4)-O(38)	0.35
Co(3)-O(1)	0.34	Co(4)-O(16)	0.34
Co(3)-O(4)	0.31	Co(4)-O(50)	0.32
Co(3)-O(2)	0.29	Co(4)-O(35)	0.28
Co(3)-O(48)	0.29	Co(4)-O(19)	0.25
∑	1.95	∑	1.92

Table S3 The bond length (Å) of Mo-O in Co4Mo12.

Mo1-Oa	1.678	Mo1-Ob	2.057	Mo1-Oc	1.895
Mo2-Oa	1.670	Mo2-Ob	2.094	Mo2-Oc	1.897
Mo3-Oa	1.730	Mo3-Ob	2.142	Mo3-Oc	1.922
Mo4-Oa	1.743	Mo4-Ob	2.193	Mo4-Oc	1.948
Mo5-Oa	1.881	Mo5-Ob	2.017	Mo5-Oc	1.980
Mo6-Oa	1.846	Mo6-Ob	2.083	Mo6-Oc	1.883

Mo7-Oa	1.765	Mo7-Ob	2.120	Mo7-Oc	1.906
Mo8-Oa	1.734	Mo8-Ob	2.003	Mo8-Oc	1.941
Mo9-Oa	1.734	Mo9-Ob	2.124	Mo9-Oc	1.973
Mo10-Oa	1.646	Mo10-Ob	2.072	Mo10-Oc	1.975
Mo11-Oa	1.677	Mo11-Ob	1.953	Mo11-Oc	1.975
Mo12-Oa	1.682	Mo12-Ob	2.032	Mo12-Oc	1.983
∑	1.732	∑	2.074	∑	1.940

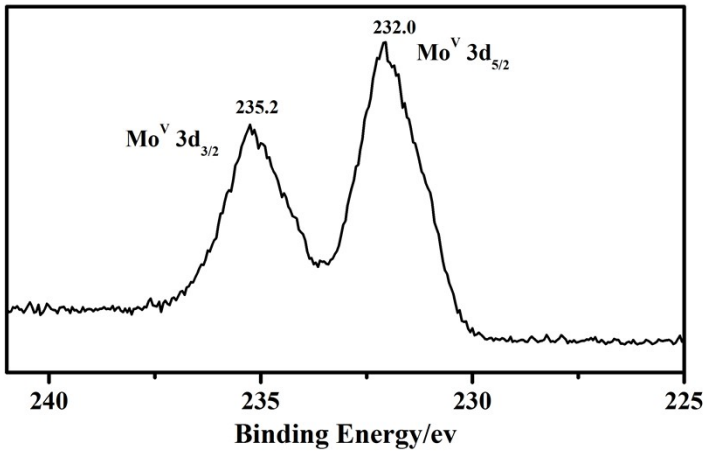

Fig. S1 XPS spectrum for Mo in Co4Mo12

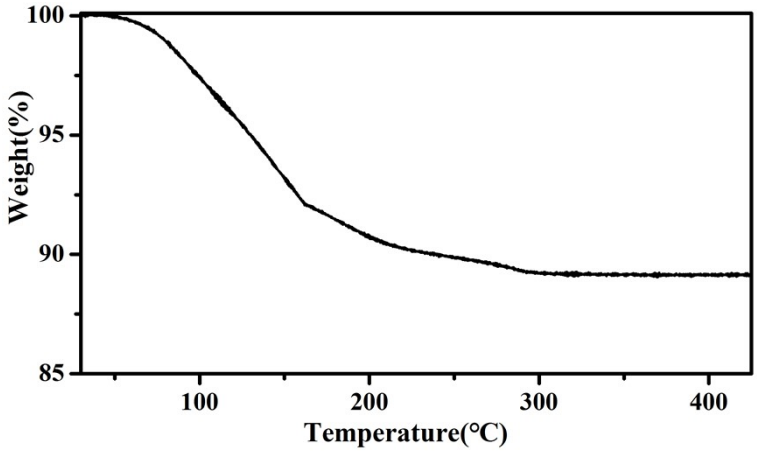

Fig. S2 TGA of the synthesized Co4Mo12

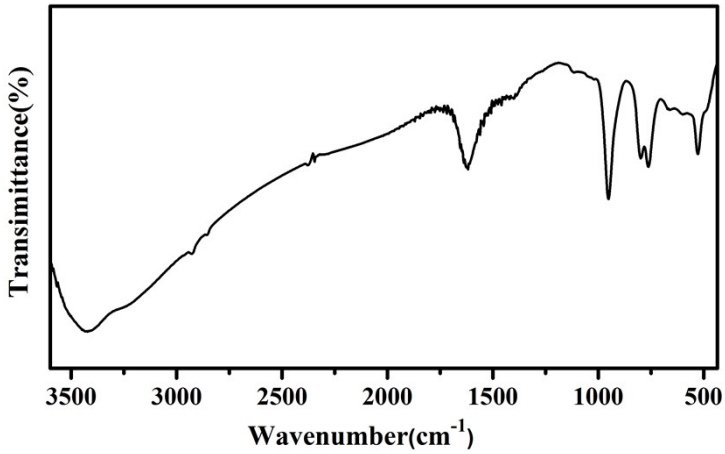

Fig. S3 FT-IR spectrum of the synthesized Co4Mo12

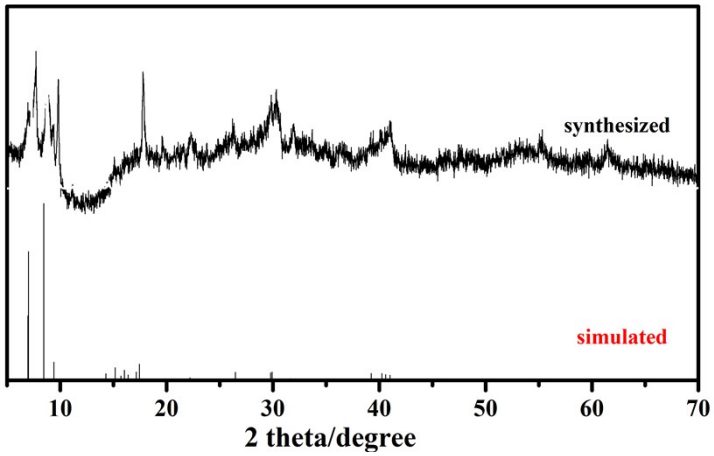

Fig. S4 The synthesized and simulated powder X-ray diffraction patterns of Co4Mo12

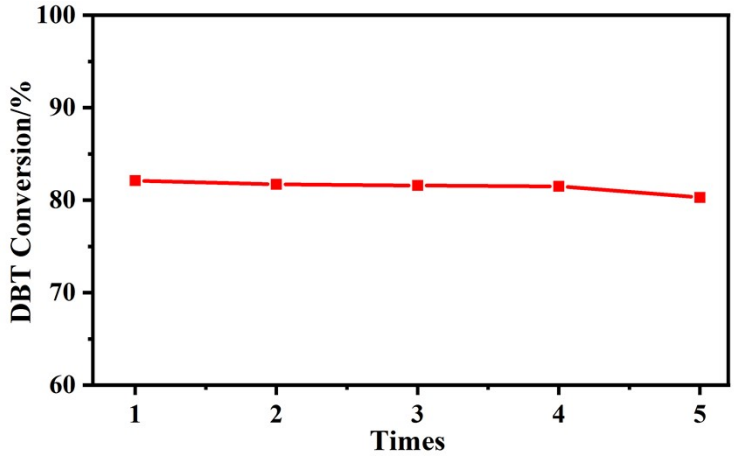

Fig. S5 Catalytic stability of crystalline Co4Mo12 sulfided at 400 °C.