

## Supplementary materials

**Table S1.** Formulas for calculation of MoS<sub>2</sub> cluster parameters.

Notation	Definition	Formula
$\bar{L}$	Average length of MoS <sub>2</sub> particles ( $l_i$ – MoS <sub>2</sub> $i$ -crystallite length; $n$ – total number of MoS <sub>2</sub> crystallites) (slab length)	$\bar{L} = \sum l_i/n$
$\bar{N}$	Average number of layers in MoS <sub>2</sub> cluster ( $n_i$ – number of particles with $N_i$ layers) (stacking number)	$\bar{N} = \sum n_i \cdot N_i/n$
$n_i$	Number of Mo atoms along one side of MoS <sub>2</sub> crystallite	$n_i = (10 \cdot \bar{L}/3.2 + 1)/2$
$Mo_T$	Total number of Mo atoms in the average MoS <sub>2</sub> cluster	$Mo_T = (3 \cdot n_i^2 - 3 \cdot n_i + 1) \cdot \bar{N}$
$Mo_{edge}$	Number Mo atoms corresponding to edge-sites in MoS <sub>2</sub> cluster	$Mo_{edge} = (6 \cdot n_i - 6) \cdot (\bar{N} - 2)$
$Mo_{rim}$	Number Mo atoms corresponding to rim-sites in MoS <sub>2</sub> cluster	$Mo_{rim} = Mo_T - Mo_{edge}$
$D$	Dispersion of MoS <sub>2</sub> active sites (based on rim-edge Mo sites)	$D = 100 \cdot (Mo_{edge} + Mo_{rim}) / Mo_T$

**Table S2.** Geometrical parameters of catalyst active phase (MoS<sub>2</sub>) in polycondensation products

Test #	Average cluster						$D, \%$	$f_{edge}$	$f_{rim}$
	$\bar{L}, \text{nm}$	$\bar{N}$	$n_i, \text{atomic.}$	$Mo_T \text{ atomic.}$	$Mo_{edge} \text{ atomic.}$	$Mo_{rim} \text{ atomic.}$			
1	11.9	1.5	19,1	1556,1	0	162,8	10.5	0	0.10
2	6.7	4.7	10,9	1546,4	161,5	119,6	18.2	0.10	0.08
3	6.0	1.7	9,8	448,7	0	90,5	20.2	0	0.20
4	5.0	1.8	8,3	330,0	0	78,9	23.9	0	0.24
2	6.7	4.7	10,9	1546,4	161,5	119,6	18.2	0.10	0.08
5	6.0	2.5	9,8	659,8	26,6	106,5	20.1	0.04	0.16

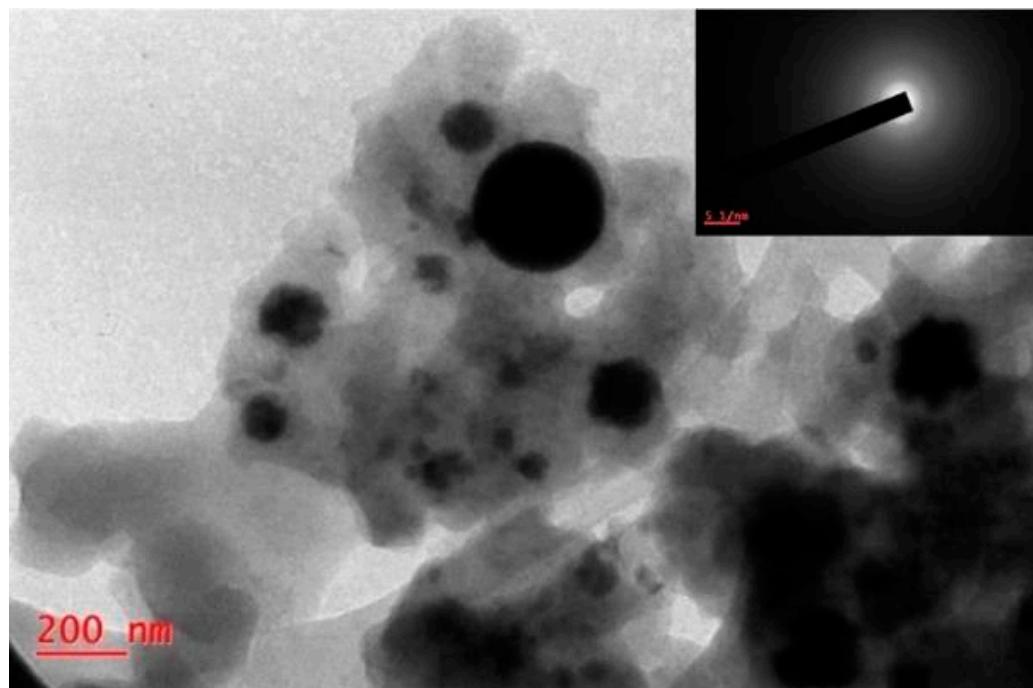


Figure S1. General TEM image of TI-sample (test #4) and corresponding electron-diffraction pattern.

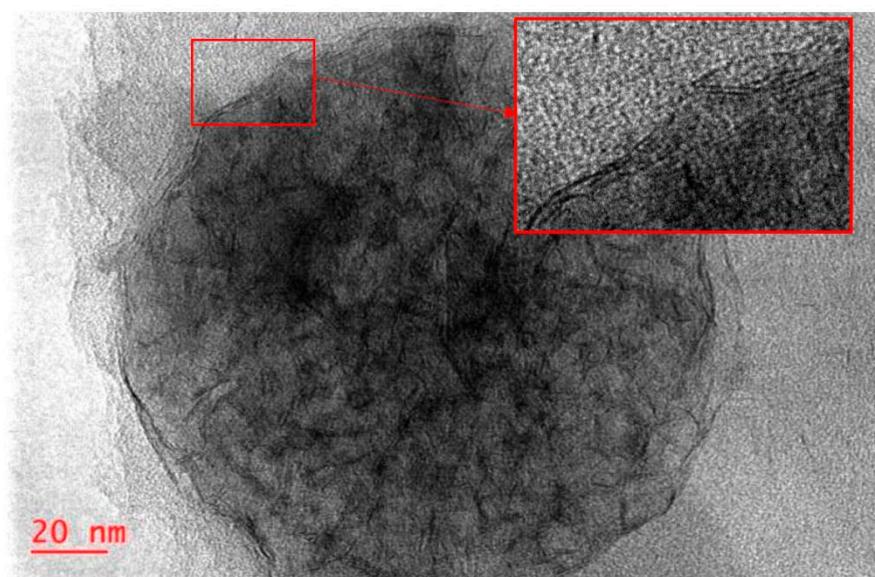


Figure S2. TEM images of openwork formations in TI-sample (test #1, C(Mo)=0.01wt.%).

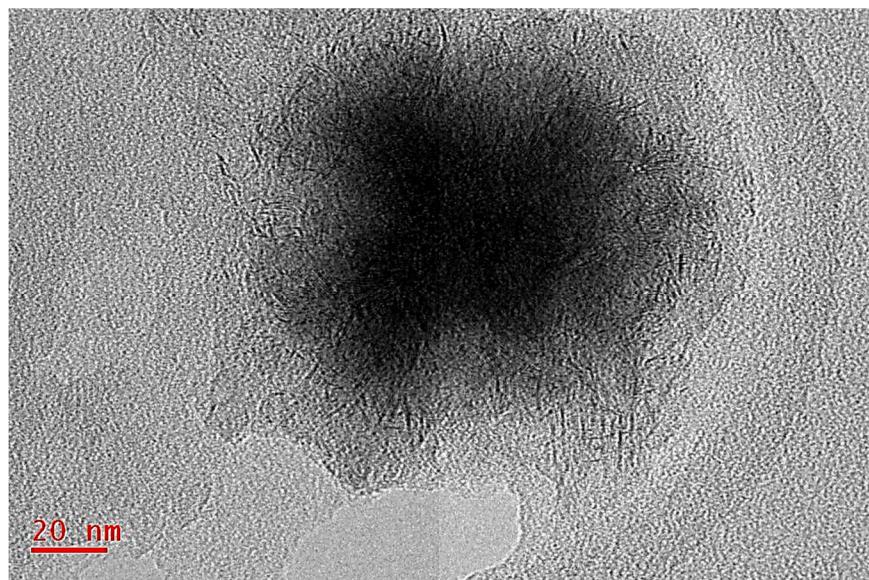


Figure S3. TEM images of irregular shape particles in TI-sample (test #1, C(Mo)=0.01wt.%).

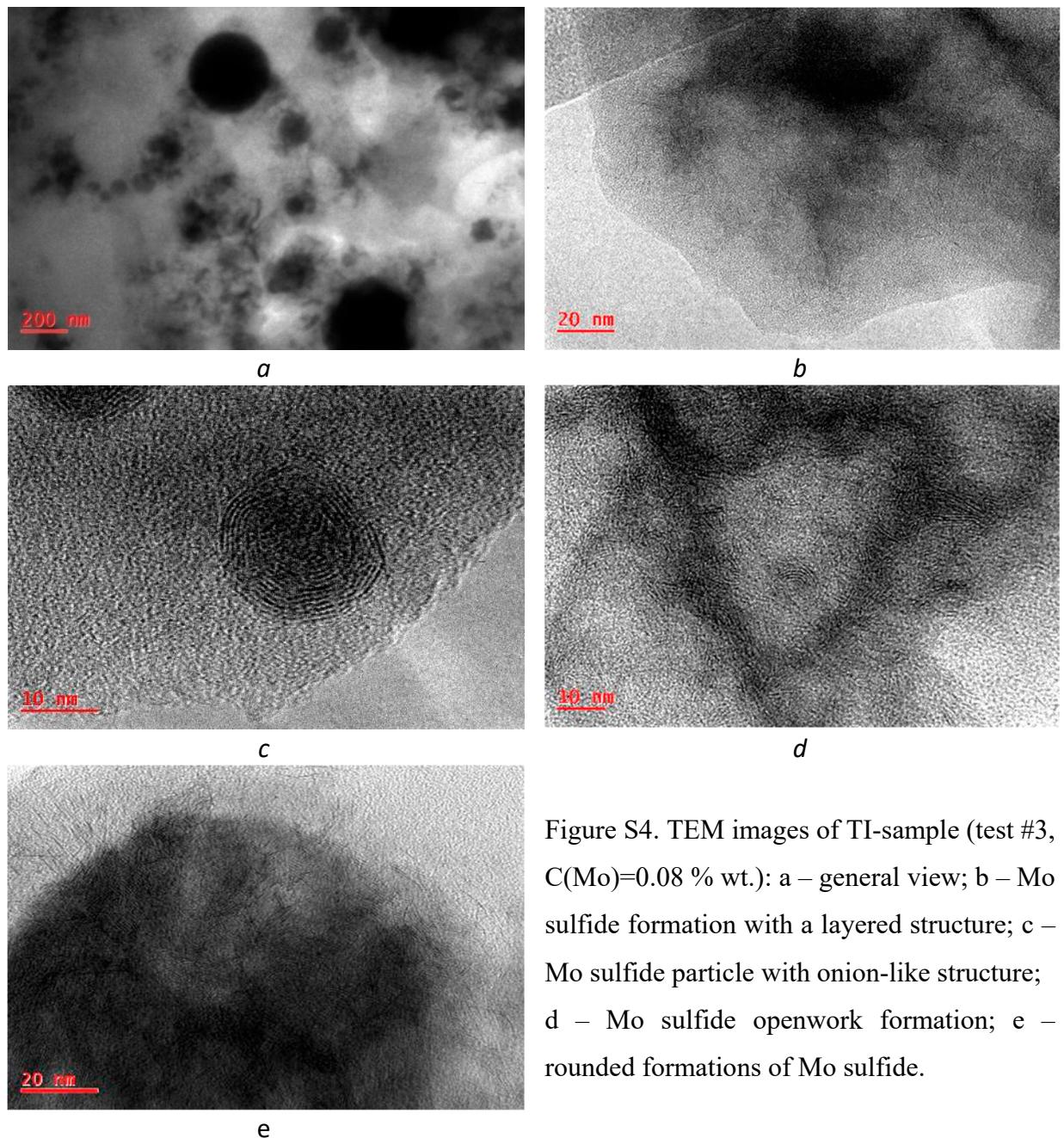


Figure S4. TEM images of TI-sample (test #3, C(Mo)=0.08 % wt.): a – general view; b – Mo sulfide formation with a layered structure; c – Mo sulfide particle with onion-like structure; d – Mo sulfide openwork formation; e – rounded formations of Mo sulfide.

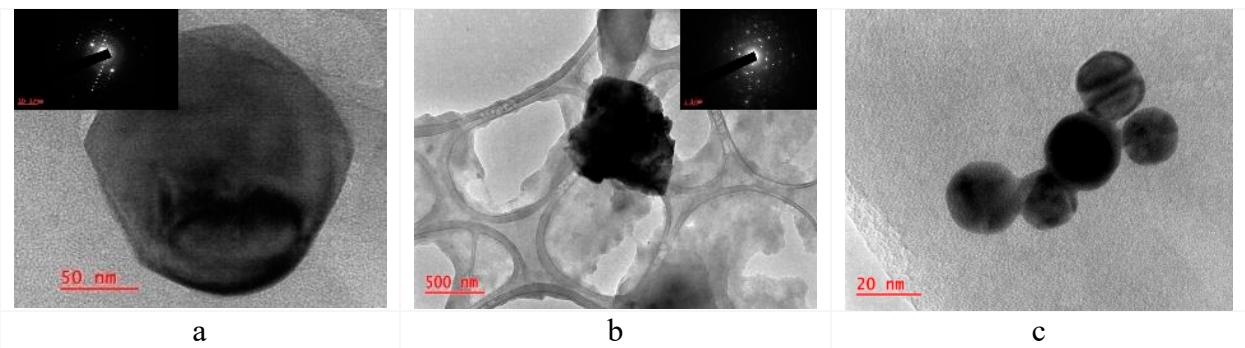


Figure S5. TEM images of Mo particles in Ti-sample (test #2, C(Mo)=0.05wt.%): a – monocrystalline Mo particle and corresponding diffraction pattern; b – polycrystalline Mo<sup>0</sup> particle and corresponding diffraction pattern; c – ultrafine Mo particle.

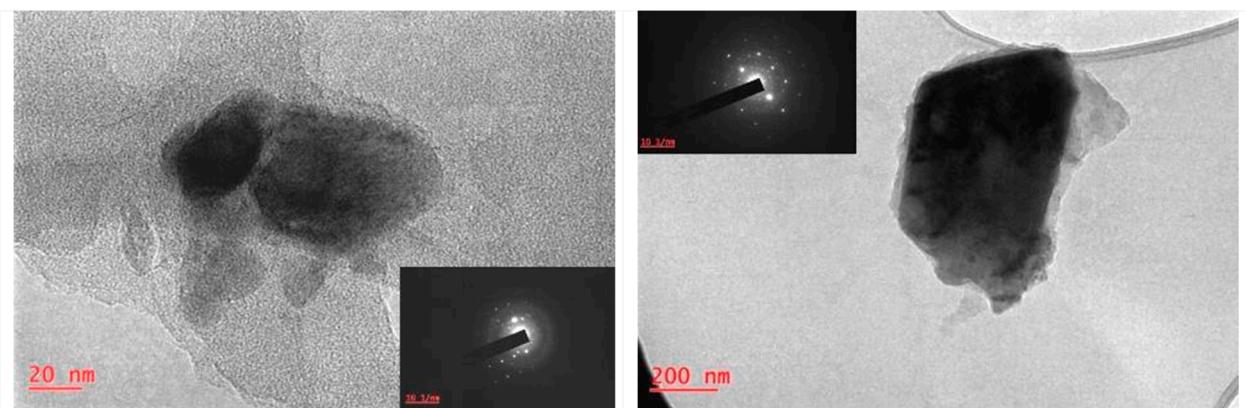


Figure S6. TEM images of Mo<sup>0</sup> particles in Ti-sample (test #1, C(Mo)=0.01wt.%) and corresponding electron-diffraction patterns.

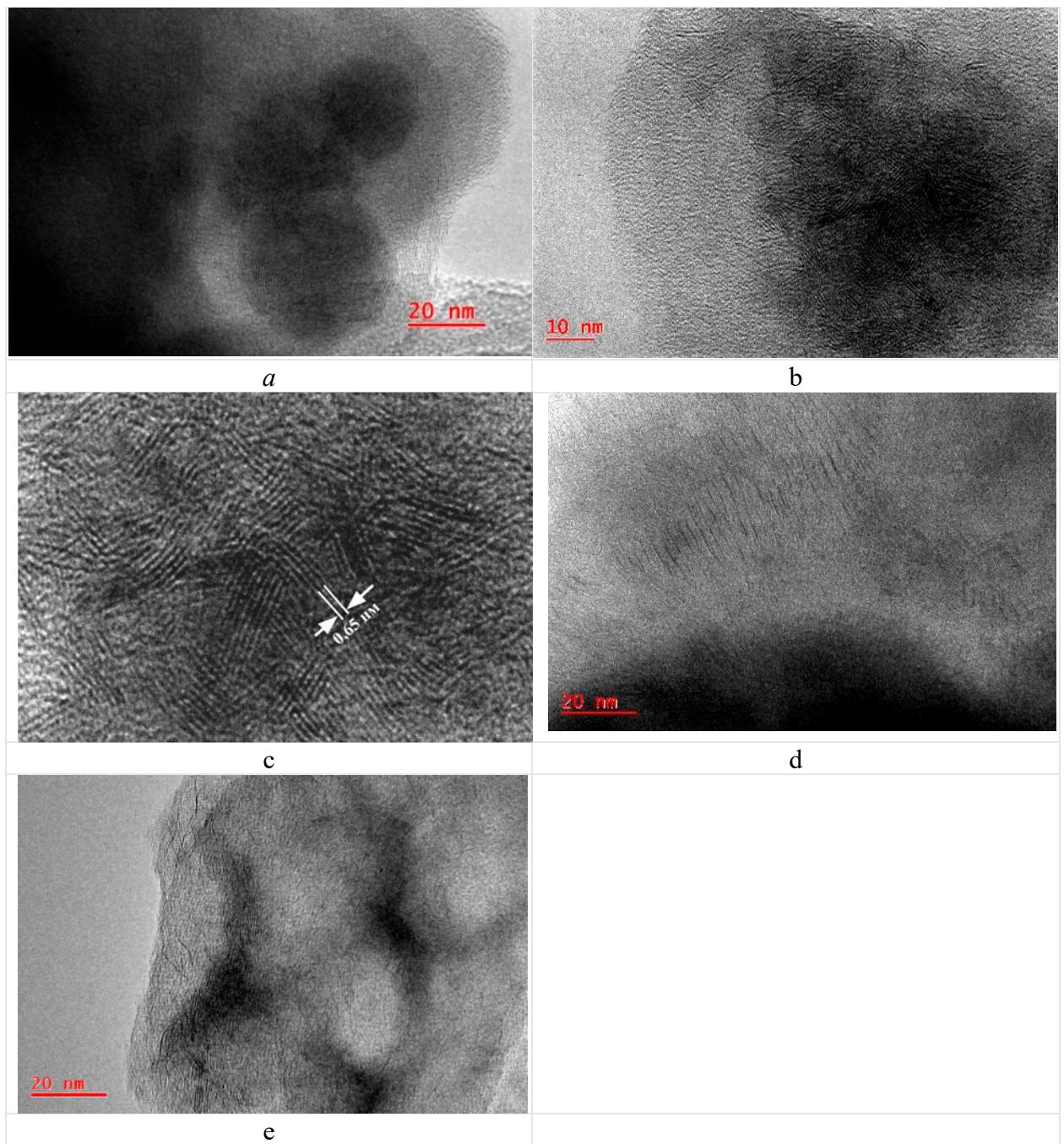
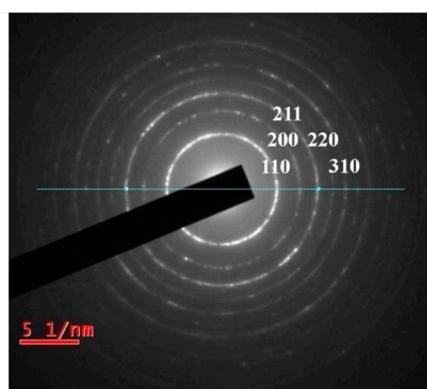
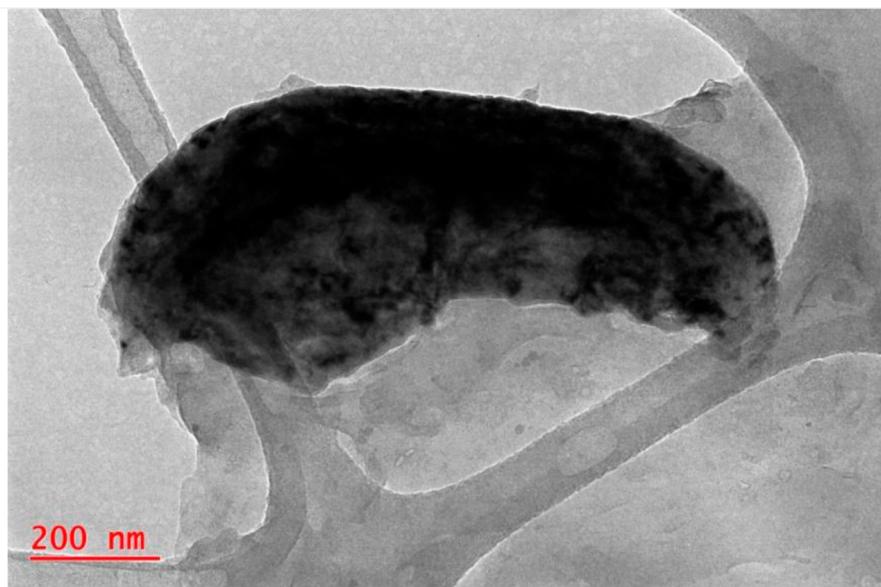


Figure S7. TEM images of TI-sample after test #4 ( $P=60$  atm); a-e – Mo sulfide particles of different morphology; f –  $\text{Mo}^0$  polycrystalline particle and corresponding electron-diffraction pattern.

**42-1120 Mo**

Molybdenum

Sys: Cubic

S.G.: Im3m (229)

a: 3.1472

b:

c:

A:

C:

d,A	int	hkl	d,A	int	hkl
2.225	100	1 1 0			
1.5738	16	2 0 0			
1.2847	31	2 1 1			
1.1129	9	2 2 0			
0.9953	14	3 1 0			
0.9085	3	2 2 2			
0.8411	24	3 2 1			

Figure S8. TEM images of TI-sample after test #4 (P=60 atm): Mo<sup>0</sup> polycrystalline particle and corresponding electron-diffraction pattern.

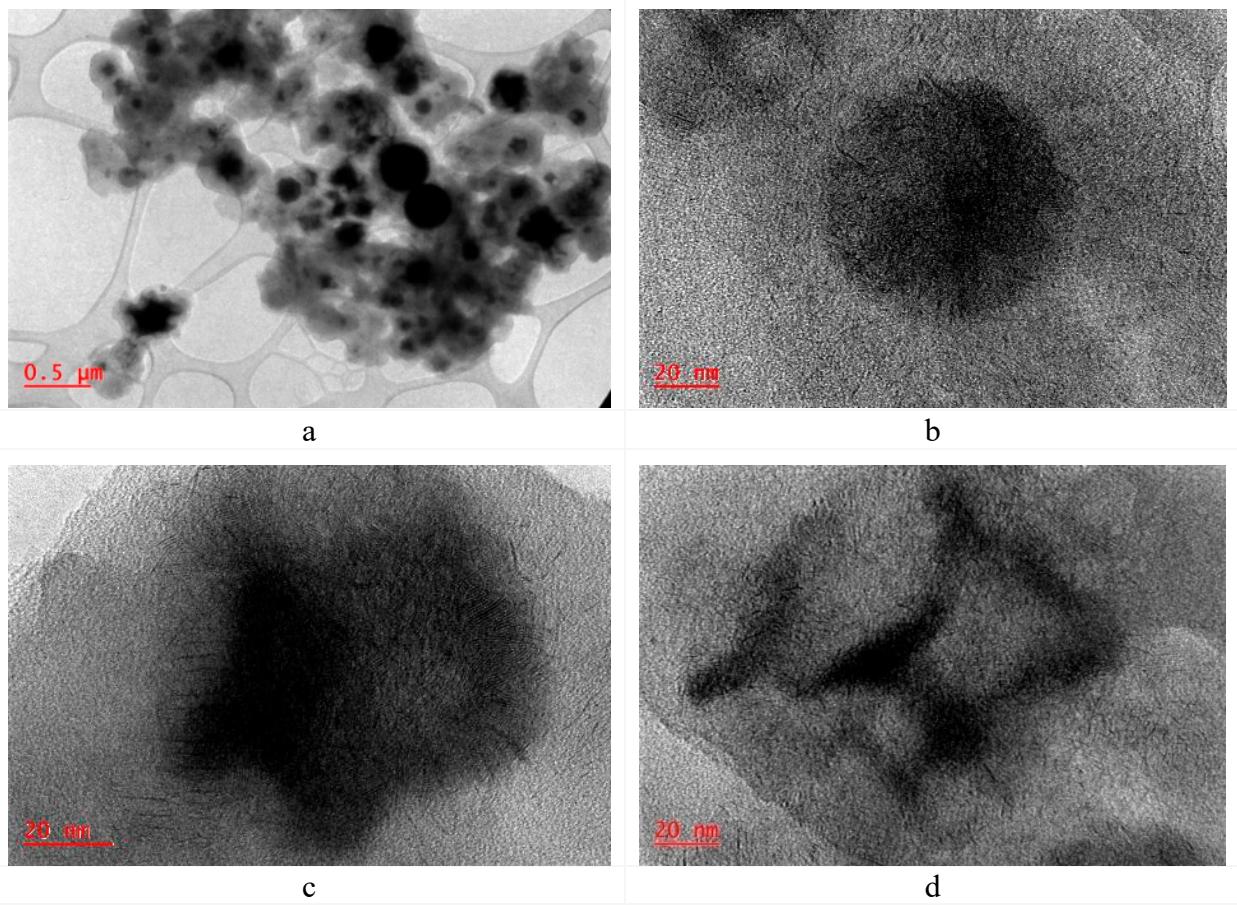
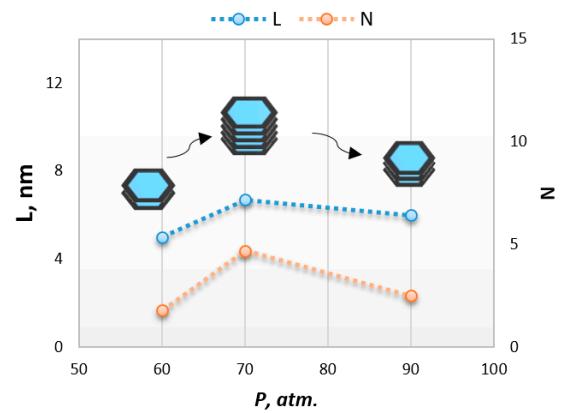
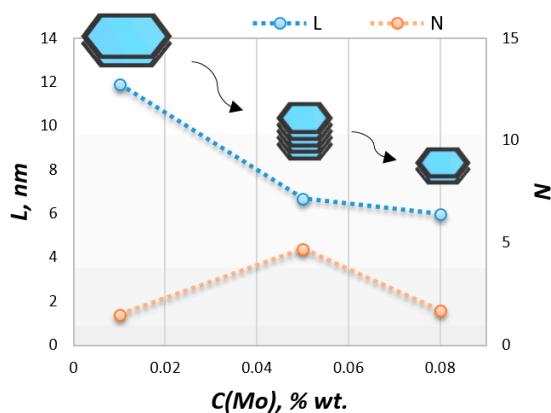


Figure S9. TEM images of TI-sample after test #5 ( $P = 90$  atm): a – general view; b – spherical particle of Mo sulfide; c – Mo sulfide particle of irregular shape; d – openwork formation of Mo sulfide particles.



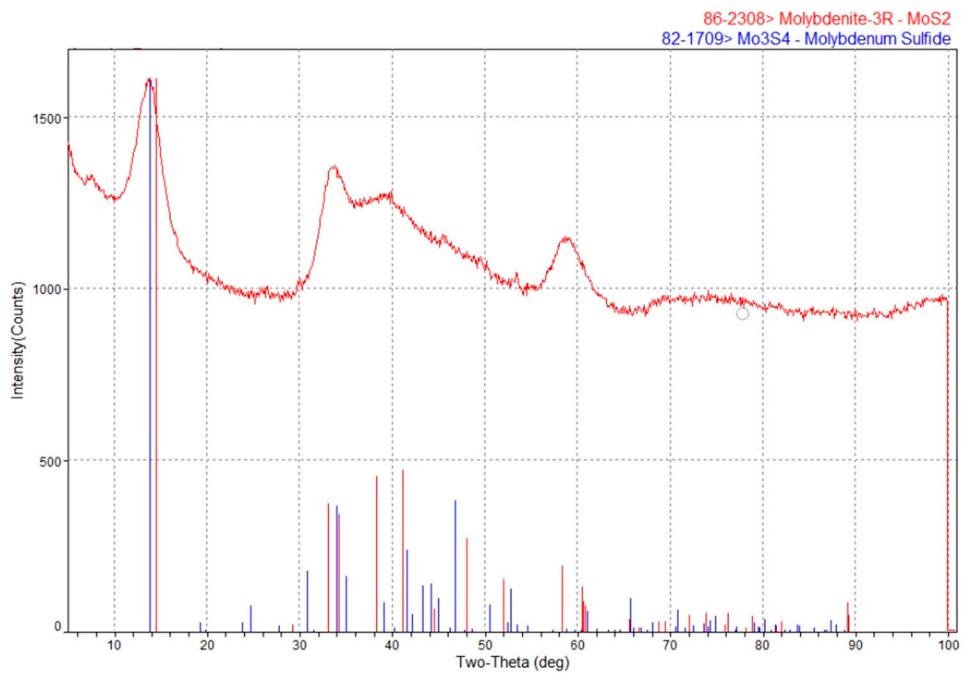


Figure S12. Typical XRD-pattern for Mo-containing solids (T1) extracted from hydroconversion products (XRD device: Rigaku Rotaflex RU-200 X-ray instrument, ICDD PDF-2 diffraction database).