

Supplementary Information

Cryogenic Electron Tomography Reveals the Mesoporous Structure Evolution during γ -Al₂O₃ supported Mo and MoNiP Catalyst Formation

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S1. Calculation of corrugation value

Surface characteristics inaccessible to bulk characterization are shape index (SI) and curvedness (CVD). The SI is a measure of the local surface type, whereas the CVD is a measure of the bending degree of the local surface type, as is illustrated in **Figure S2.1**. For each individual reconstructed particle, the SI and CVD are calculated at each triangular patch of the isosurface, forming a distribution of both. Together, these descriptors can be used to describe the total corrugation of a single reconstructed particle.

Here, the corrugation is defined as the fluctuation in different surface types. There are two relevant fluctuations: (1) the shape type variation; and (2) the strength of the curvature variation. A high corrugation is caused by a broad SI distribution spread (i.e., variance) and/or a broad CVD distribution spread (i.e., variance). The corrugation can be calculated based on equation 1, where both the SI and CVD are treated as orthogonal contributions to the corrugation (i.e., they do not influence or interact with each other). The variance of the shape index and curvedness can be calculated with equation 2. To have equal contributions of both fluctuation types, it is important to scale the SI and CVD to [0 1]. The average SI and CVD can be calculated with equation 3, where i is the bin centre of the distribution.

$$\text{Equation 1} \quad \text{Corrugation} = \sqrt{\sigma_{SI}^2 + \sigma_{CVD}^2}$$

$$\text{Equation 2} \quad \text{Variance shape index: } \sigma_{SI}^2 = \frac{\sum_i (n_{counts,i} (SI_i - \mu_{SI})^2)}{\sum_i n_{counts,i}}$$

$$\text{Equation 3} \quad \text{Average shape index: } \mu_{SI} = \frac{\sum_i (n_{counts,i} \times SI_i)}{\sum_i (n_{counts,i})}$$

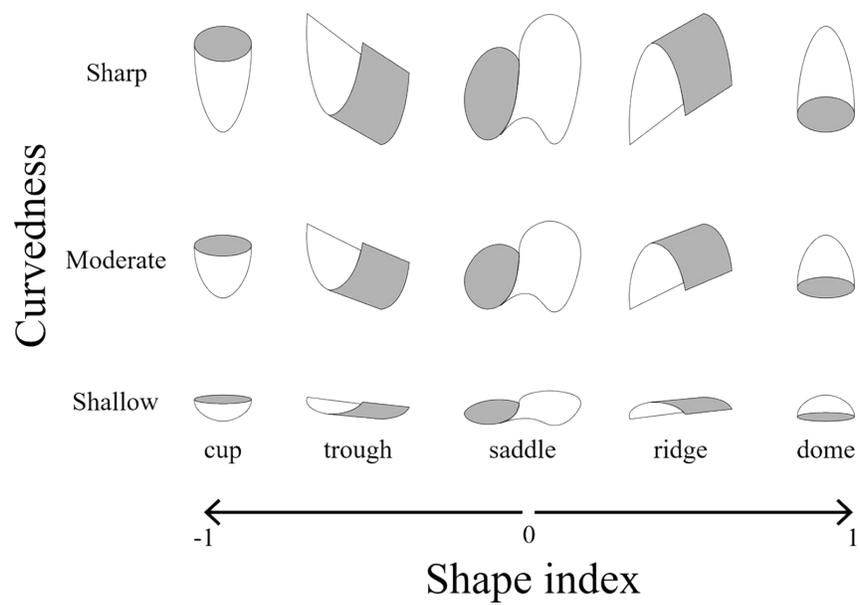


Figure S1.1 Terminology of the different local surface type (i.e., shape index) and bending degree of the local surface type (i.e., curvedness).

S2. Untreated, calcined, and sulfided $\gamma\text{-Al}_2\text{O}_3$ – cross sections, segmentation of Figure 1 (a – c), and pore size distribution

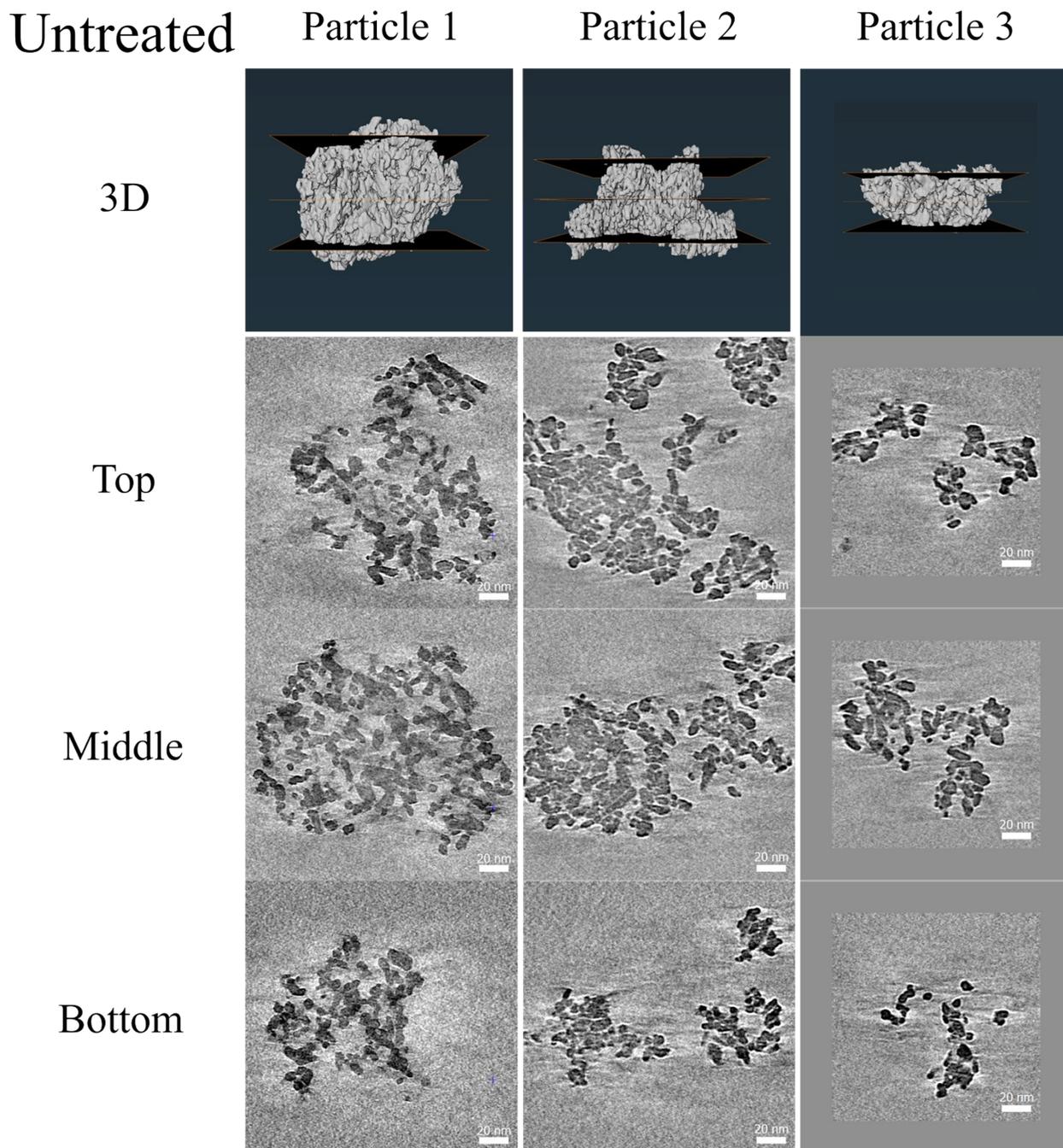
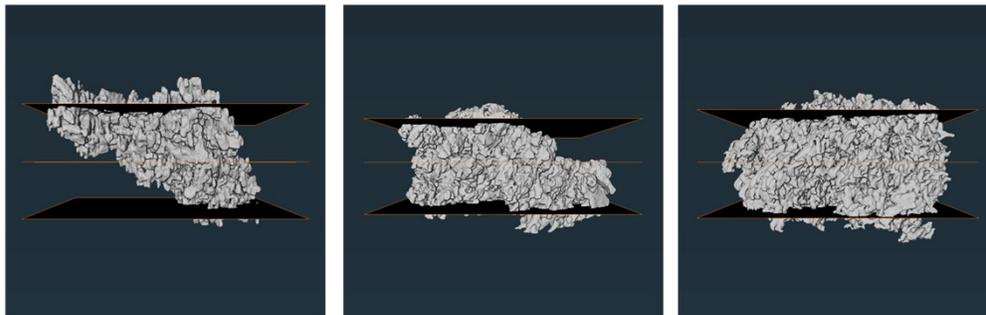


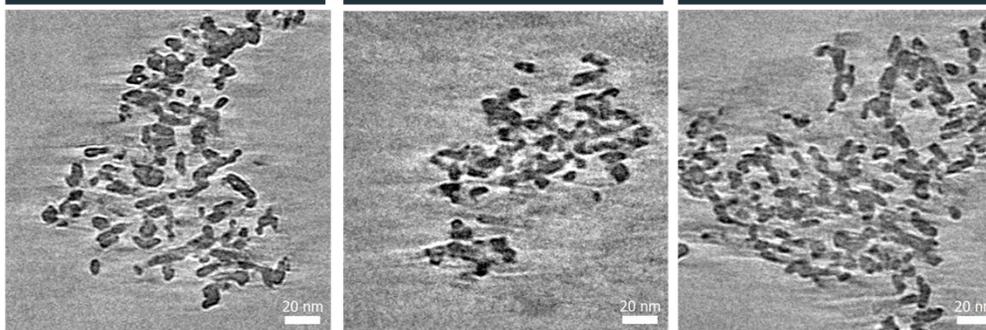
Figure S2.1 Numerical cross sections (thickness = 0.31 nm) through cryo-ET reconstructions of three untreated bare $\gamma\text{-Al}_2\text{O}_3$ particles used for qualitative and quantitative analysis. A 3D rendering of each particle is used to illustrate to height of the top, middle, and bottom numerical cross section.

Calcined Particle 1 Particle 2 Particle 3

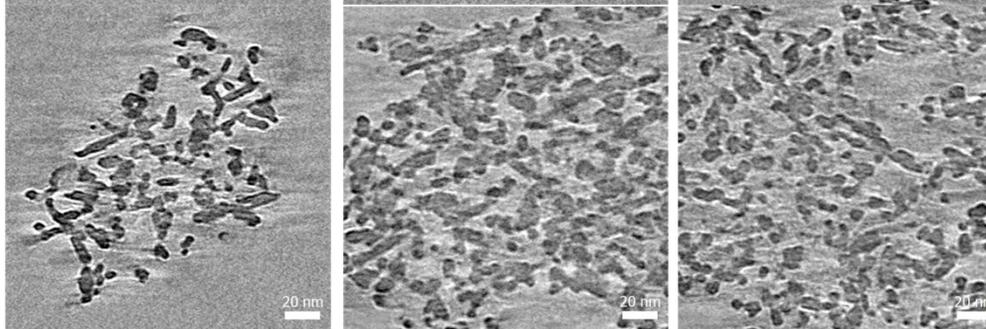
3D



Top



Middle



Bottom

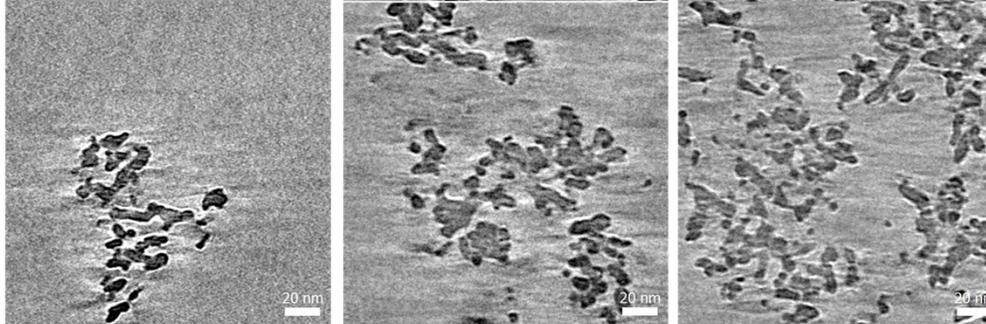


Figure S2.2 Numerical cross sections (thickness = 0.31 nm) through cryo-ET reconstructions of three calcined bare γ - Al_2O_3 particles used for qualitative and quantitative analysis. A 3D rendering of each particle is used to illustrate to height of the top, middle, and bottom numerical cross section.

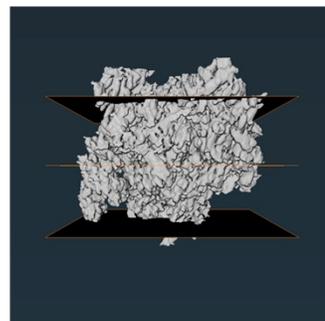
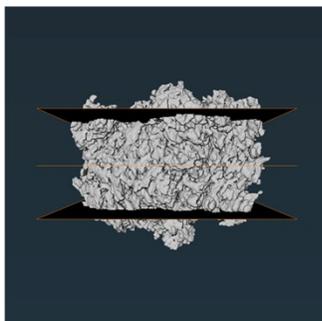
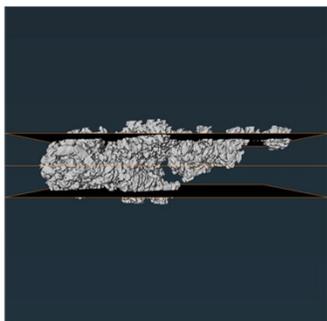
Sulfided

Particle 1

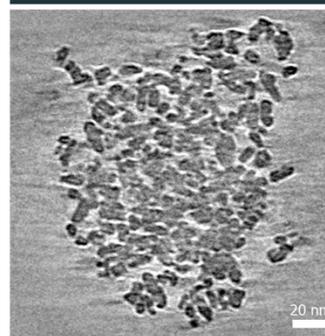
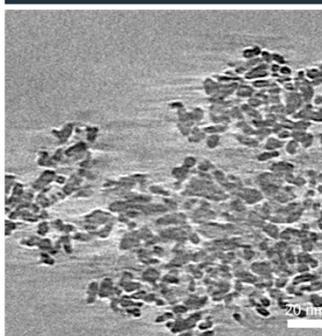
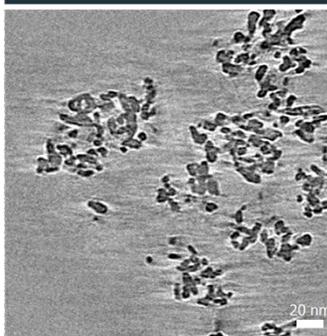
Particle 2

Particle 3

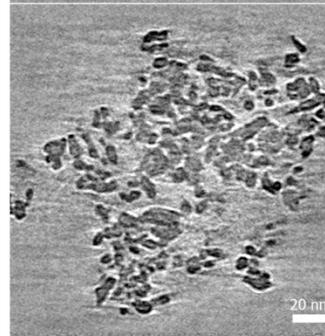
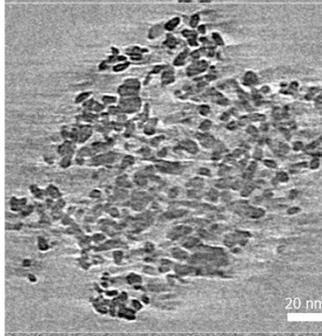
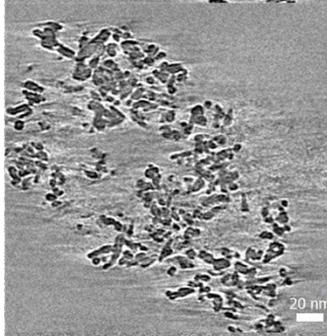
3D



Top



Middle



Bottom

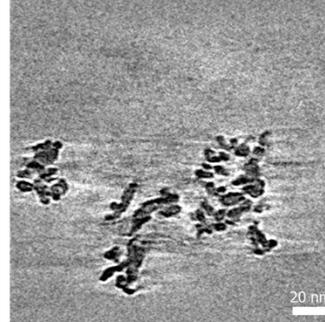
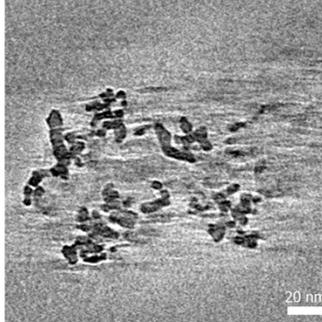
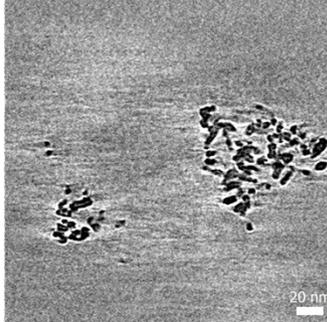


Figure S2.3 Numerical cross sections (thickness = 0.31 nm) through cryo-ET reconstructions of three sulfided bare γ - Al_2O_3 particles used for qualitative and quantitative analysis. A 3D rendering of each particle is used to illustrate to height of the top, middle, and bottom numerical cross section.

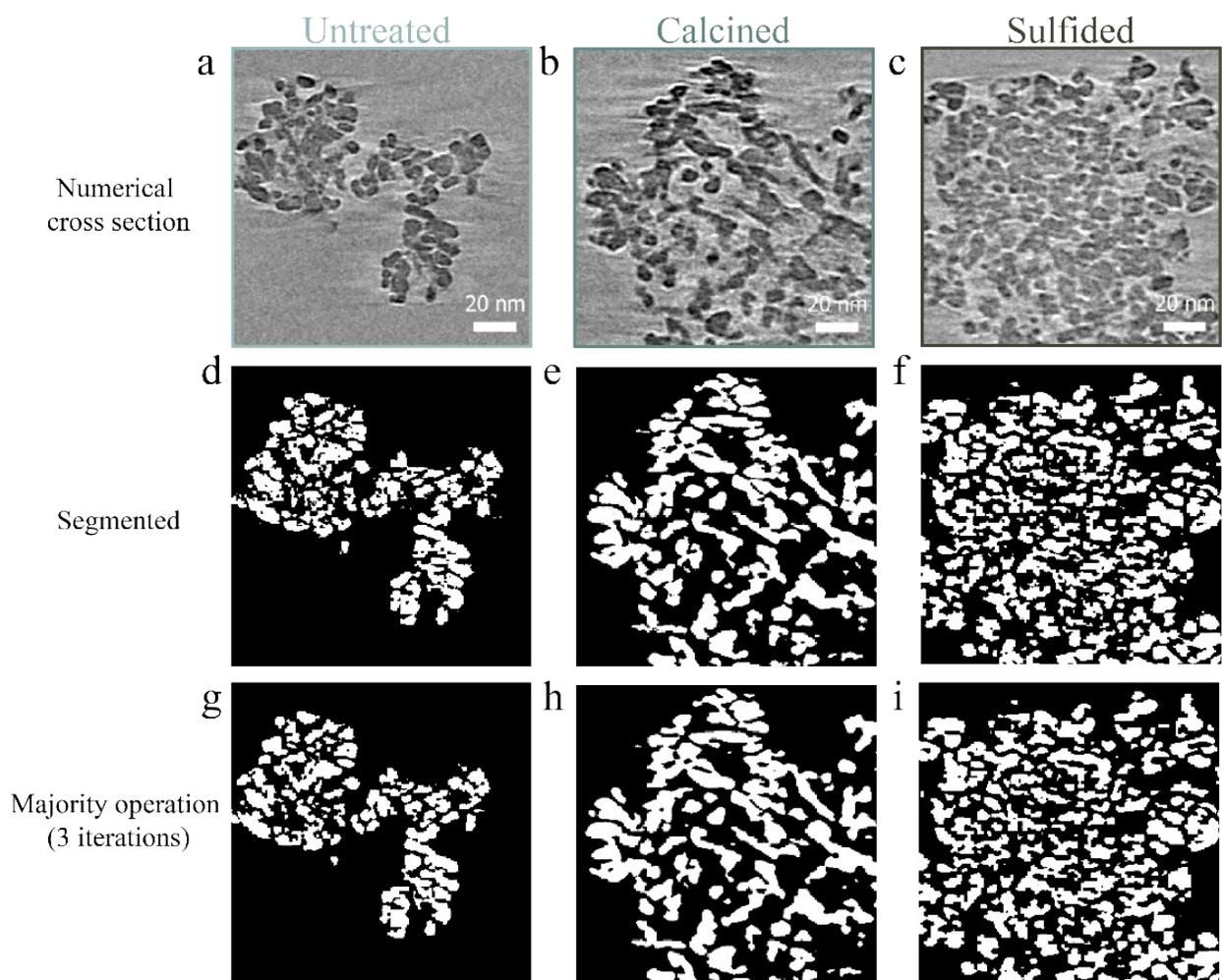


Figure S2.4 Example of the image processing performed on cryo-ET reconstructions of the bare $\gamma\text{-Al}_2\text{O}_3$ particles: (a – c) show the median filtered (kernel size: $3 \times 3 \times 3$) numerical cross sections through cryo-ET reconstructions (thickness = 0.31 nm) of bare, calcined, and sulfided bare $\gamma\text{-Al}_2\text{O}_3$ particles; (d – f) and (g – i) show the segmented slices, corresponding to the numerical slices shown in (a – c), before and after 3 majority iterations, respectively.

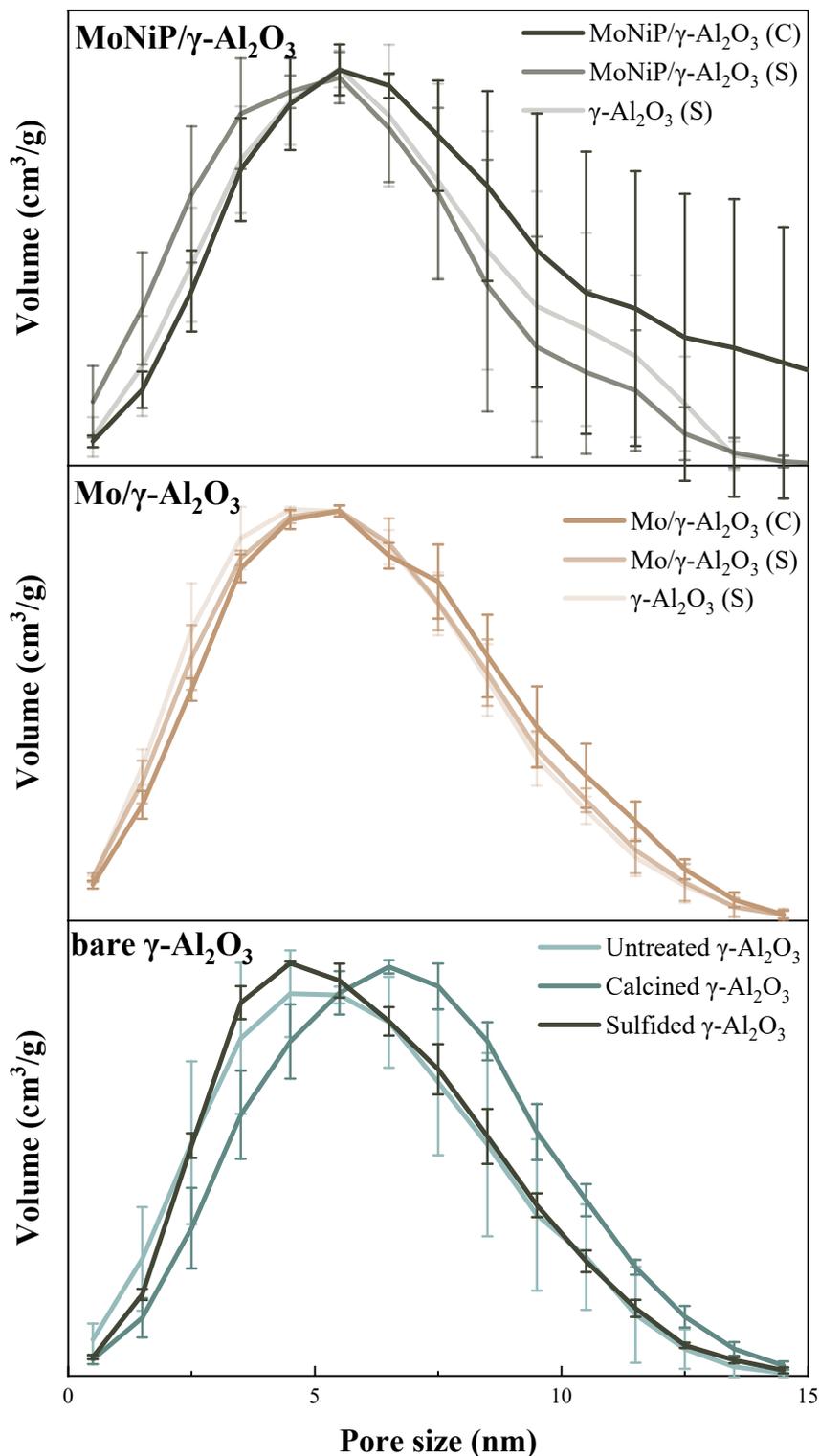


Figure S2.5. Pore size distributions of the 3D reconstructed volumes obtained via cryo-ET. Bottom: bare γ -Al₂O₃ support in its untreated, calcined, and sulfided state. Middle: calcined and sulfided Mo/ γ -Al₂O₃ and the isolated γ -Al₂O₃ in its sulfided state. Top: calcined and sulfided MoNiP/ γ -Al₂O₃ and the isolated γ -Al₂O₃ in its sulfided state.

S3. Bulk characterization of empty γ -Al₂O₃, Mo/ γ -Al₂O₃, and MoNiP γ -Al₂O₃

N₂ physisorption

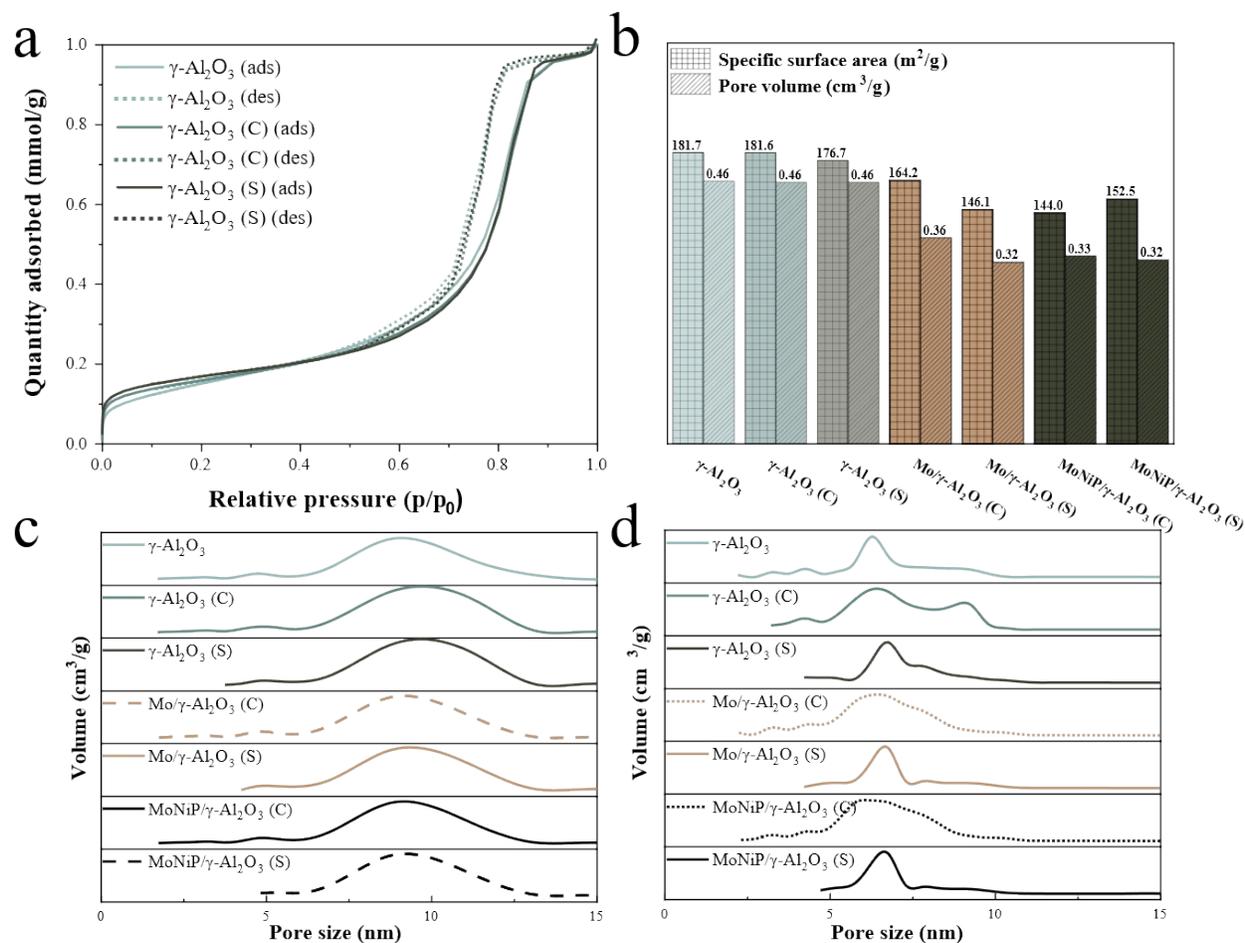


Figure S3.1 N₂ physisorption results of bare γ -Al₂O₃, Mo/ γ -Al₂O₃, and MoNiP/ γ -Al₂O₃ after calcination and sulfidation: (a) adsorption and desorption isotherm of untreated (γ -Al₂O₃), calcined (γ -Al₂O₃ (C)), and sulfided (γ -Al₂O₃ (S)) bare γ -Al₂O₃; (b) specific surface area (m²/g) and pore volume (cm³/g) obtained for each system; (c) the adsorption BJH PSD and (d) the desorption BJH PSD shown as the volumetric contribution (cm³/g) per pore width range.

Table S3.1 PV and SSA obtained through cryo-ET and N₂ physisorption. The change in percentage, relative to the bare γ -Al₂O₃ is calculated for both techniques.

	PV (cm ³ /g)		SSA (m ² /g)	
	Cryo-ET	N ₂ physisorption	Cryo-ET	N ₂ physisorption
γ -Al ₂ O ₃	0.28 (ref)	0.46 (ref)	176 (ref)	180 (ref)
Mo/ γ -Al ₂ O ₃ - calcined	0.22 (-21 %)	0.36 (-22 %)	163 (-7 %)	164 (-9 %)
Mo/ γ -Al ₂ O ₃ - sulfided	0.17 (-39 %)	0.32 (-30 %)	153 (-13 %)	146 (-19 %)
MoNiP/ γ -Al ₂ O ₃ - calcined	0.21 (-25 %)	0.33 (-28 %)	145 (-18 %)	144 (-20 %)
MoNiP/ γ -Al ₂ O ₃ - sulfided	0.16 (-43 %)	0.32 (-30 %)	160 (-9 %)	153 (-15 %)

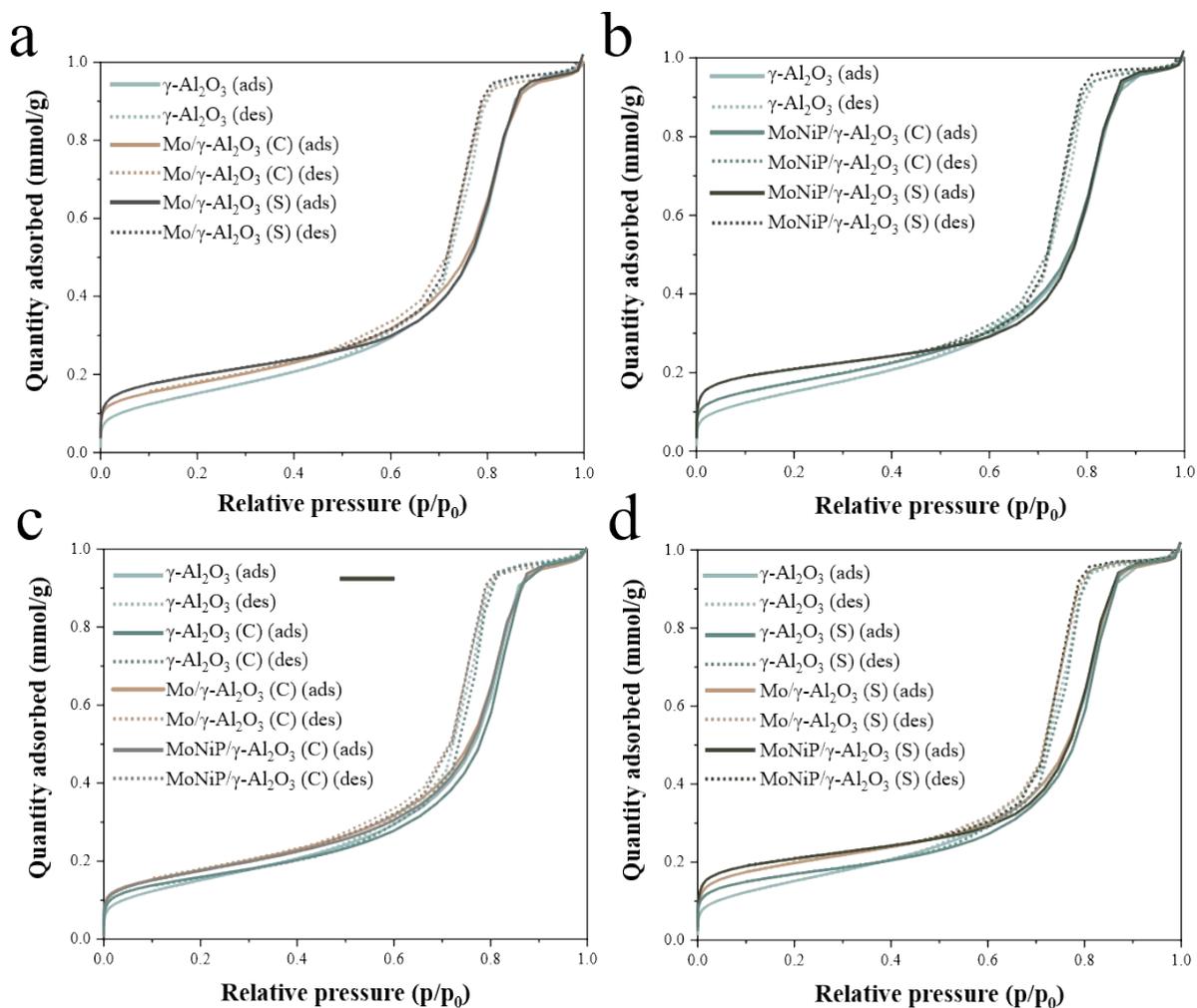


Figure S3.2 N₂ physisorption adsorption and desorption isotherms of bare γ -Al₂O₃, Mo/ γ -Al₂O₃, and MoNiP/ γ -Al₂O₃ after calcination and sulfidation: (a) untreated bare γ -Al₂O₃, calcined Mo/ γ -Al₂O₃, and sulfided Mo/ γ -Al₂O₃; (b) untreated bare γ -Al₂O₃, calcined MoNiP/ γ -Al₂O₃, and sulfided MoNiP/ γ -Al₂O₃; (c) untreated bare γ -Al₂O₃, calcined bare γ -Al₂O₃, calcined Mo/ γ -Al₂O₃, and calcined MoNiP/ γ -Al₂O₃; (d) untreated bare γ -Al₂O₃, sulfided bare γ -Al₂O₃, sulfided Mo/ γ -Al₂O₃, and sulfided MoNiP/ γ -Al₂O₃;

Synchrotron X-Ray Diffraction (XRD)

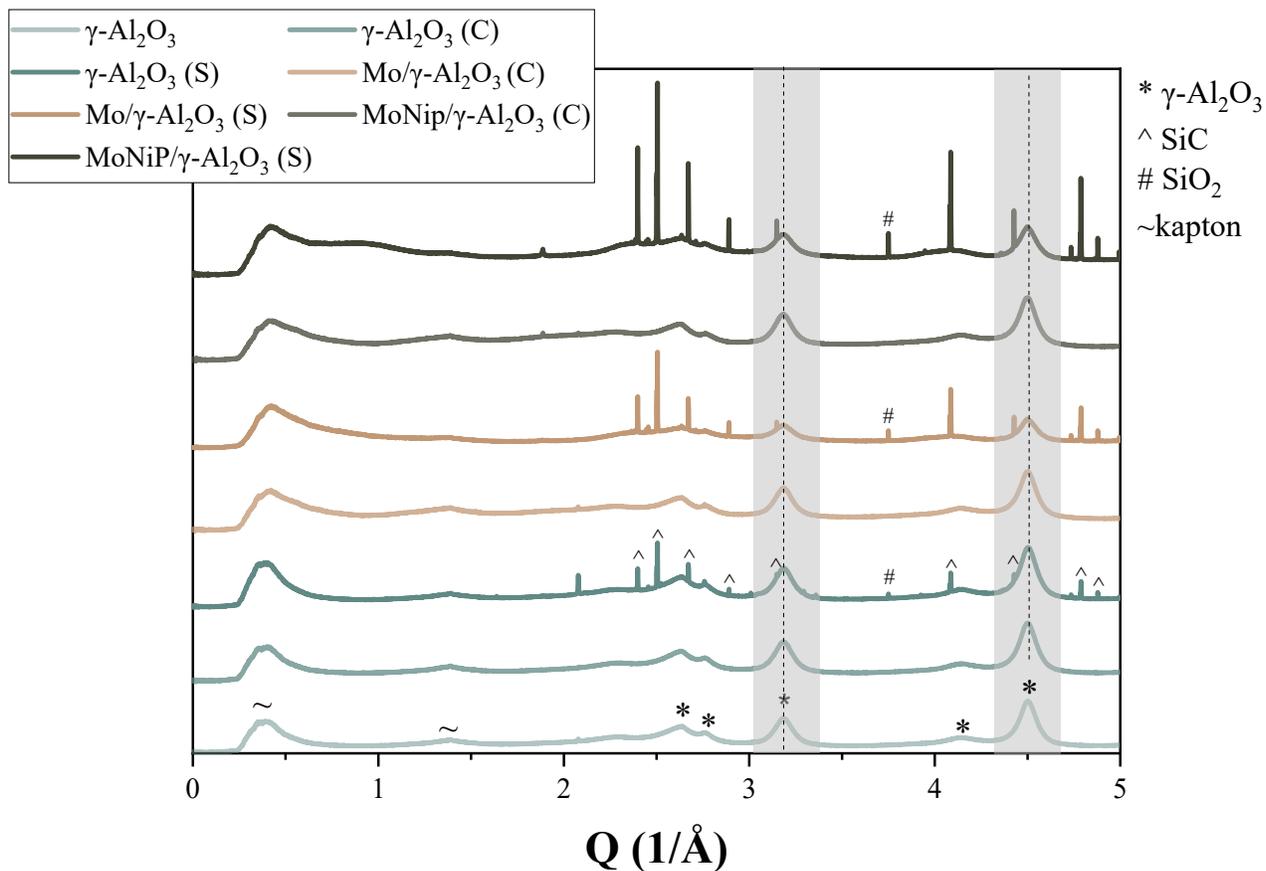


Figure S3.3 Synchrotron XRD patterns.

Table S3.2. Scherrer equation. Peak fitting was done in Origin.

Q (1/Å) (hkl)	γ-Al ₂ O ₃	γ-Al ₂ O ₃ (C)	γ-Al ₂ O ₃ (S)	Mo/γ-Al ₂ O ₃ (C)	Mo/γ-Al ₂ O ₃ (S)	MoNiP/γ-Al ₂ O ₃ (C)	MoNiP/γ-Al ₂ O ₃ (S)
	Crystallite size (nm)						
2.6 (311)	4.2	4.2	4.0	4.1	5.2	5.2	5.4
2.8 (222)	8.4	8.4	8.4	7.9	8.9	9.5	9.4
3.2 (400)	5.4	5.3	5.2	5.4	5.4	5.4	5.5
4.1 (511)	4.4	4.6	4.3	4.3	3.9	4.3	2.7
4.5 (440)	5.9	5.7	5.9	5.9	5.8	5.7	5.5
Average	5.7	5.6	5.6	5.5	5.8	5.8	5.7
Std	1.5	1.5	1.6	1.4	1.7	1.9	2.1

X-ray Photoelectron Spectroscopy (XPS)

By means of the software CasaXPS, a standard procedure involving calibration towards the Al 2p signal (74.1 eV) and Shirley background subtraction was performed on all spectral data. Fitting was performed with a symmetric pseudo-Voigt function (GL(30)). Al 2p spectra were deconvoluted into $2p_{3/2}$ and $2p_{1/2}$ doublets and were used for the determination of the total Al 2p area. O 1s spectra were deconvoluted into three peaks to measure the total area. These peaks possibly originate from (a combination of) Al_2O_3 , MoO_3 , NiO, and P_2O_5 . However, further specification was out-of-scope. Mo 3d spectra were deconvoluted into Mo^{4+} (as in MoS_2), Mo^{5+} (as in MoS_xO_y), and Mo^{6+} (as in MoO_3) doublets with splitting energy of 3.15 eV.¹⁻⁵ Ni 2p spectra were deconvoluted into Ni^{2+} with a satellite peak at around + 6 eV (as in NiO, NiS, or NiMoS).^{2,5} NiS and NiMoS could not be distinguished and were deconvoluted as one. P 2p spectra were deconvoluted into $2p_{3/2}$ and $2p_{1/2}$ doublets. S 2p spectra were deconvoluted into two doublets, terminal disulfide and/or sulfide (S^{2-}) ligands and bridging disulfide ligands (S_2^{2-}).³⁻⁵

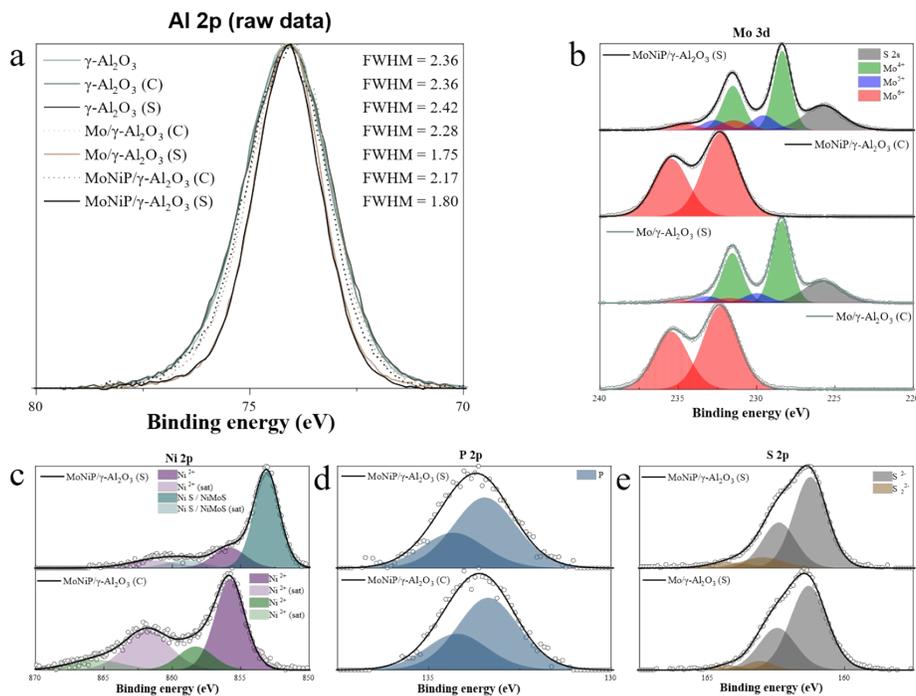


Figure S3.4 XPS results after calcination and sulfidation: (a) raw spectra of the Al 2p in bare $\gamma\text{-Al}_2\text{O}_3$, $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$, and $\text{MoNiP}/\gamma\text{-Al}_2\text{O}_3$; (b) fitting of Mo 3d spectra of $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ and $\text{MoNiP}/\gamma\text{-Al}_2\text{O}_3$; fitting of Ni 2p spectra (c), P 2p spectra (d), and S 2p spectra (d) of $\text{MoNiP}/\gamma\text{-Al}_2\text{O}_3$.

XPS spectra in **Figure S3.4 (b)** revealed that, after deposition and calcination, only oxidic Mo^{VI} species, as in MoO_3 , are present in both the $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ and $\text{MoNiP}/\gamma\text{-Al}_2\text{O}_3$. After sulfidation, XPS (**Figure S3.4**) reveals a mixture of Mo^{IV} species as in MoS_2 , Mo^{V} species as in intermediate oxysulfidic Mo, and Mo^{VI} species as in residual MoO_3 are detected, with sulfidation degrees of approximately 73% for $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ and 74% for $\text{MoNiP}/\gamma\text{-Al}_2\text{O}_3$.^{2,6} No differences in sulfur speciation are observed between the two catalysts.

For MoNiP/ γ -Al₂O₃, Ni exists predominantly as NiO_x after deposition and calcination, and as NiS_x, NiMo_xS_x, and NiO_x species after sulfidation. The speciation of P remains unchanged throughout the process.

The degree of sulfidation, at% and wt% were calculated by the following equation:

$$\text{Degree of sulfidation} = \frac{[Mo^{4+}]}{[Mo^{4+}] + [Mo^{5+}] + [Mo^{6+}]}$$

$$\text{at}\%_X = \frac{\frac{[X]}{SF_X}}{\sum_i \frac{[X_i]}{SF_i}} \times 100\%,$$

where SF = Sensitivity factor according to CasaXPS library for K-Alpha instrument (Al 2p = 0.5371; O 1s = 2.93; Mo 3d = 9.5; Ni 2p = 14.61; P 2p = 1.192; S 2p = 1.677)

$$\text{wt}\%_X = \frac{\text{at}\%_X \cdot M_X}{\sum_i \text{at}\%_i \cdot M_i}, \text{ where M is the molar mass of X}$$

Table S3.3 Peak locations found through XPS. Each sample was measured in triplo for wt% quantification.

	S1_cp_10Mo	S1_sp_10Mo	S1_cp_10MoNiP	S1_sp_10MoNiP
	<i>B.E. (eV)</i>	<i>B.E. (eV)</i>	<i>B.E. (eV)</i>	<i>B.E. (eV)</i>
Mo ⁴⁺ 3d _{5/2}	-	228.44 ± 0.04	-	228.50 ± 0.09
Mo ⁴⁺ 3d _{3/2}	-	231.59 ± 0.04	-	231.65 ± 0.09
Mo ⁵⁺ 3d _{5/2}	-	229.93 ± 0.05	-	230.60 ± 0.62
Mo ⁵⁺ 3d _{3/2}	-	233.08 ± 0.05	-	233.72 ± 0.62
Mo ⁶⁺ 3d _{5/2}	232.39 ± 0.06	231.85 ± 0.09	232.29 ± 0.04	231.24 ± 1.18
Mo ⁶⁺ 3d _{3/2}	235.54 ± 0.06	235.00 ± 0.09	235.54 ± 0.04	234.39 ± 1.18
S 2s	-	225.87 ± 0.05	-	225.84 ± 0.05
NiO _x	-	-	855.87 ± 0.05	853.27 ± 0.12
NiO _x (sat)	-	-	861.89 ± 0.17	860.28 ± 0.84
NiO _x	-	-	857.98 ± 0.48	-
NiO _x (sat)	-	-	864.31 ± 1.65	-
NiS / NiMoS	-	-	-	855.73 ± 0.12
NiS / NiMoS (sat)	-	-	-	863.50 ± 1.41
P 2p _{3/2}	-	-	133.42 ± 0.04	133.43 ± 0.02
P 2p _{1/2}	-	-	134.28 ± 0.04	134.29 ± 0.02
S ²⁻ 2p _{3/2}	-	161.35 ± 0.04	-	161.36 ± 0.08
S ²⁻ 2p _{1/2}	-	162.50 ± 0.04	-	162.51 ± 0.08
S ₂ ²⁻ 2p _{3/2}	-	163.14 ± 0.11	-	163.06 ± 0.08
S ₂ ²⁻ 2p _{1/2}	-	164.29 ± 0.11	-	164.21 ± 0.08
Al 2p ¹	74.10 ± 0.00	74.10 ± 0.00	74.10 ± 0.00	74.10 ± 0.00
O 1s ²	530.76 ± 0.04	530.84 ± 0.03	530.87 ± 0.04	530.88 ± 0.04

¹ fit of Al 2p by doublet for total area; ² fit of O 1s by three peaks for total area.

Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-VIS DRS)

UV-VIS DRS spectra of Mo/ γ -Al₂O₃ and MoNiP/ γ -Al₂O₃ are shown in **Figure S3.5**. The adsorption bands between 200 and 400 nm correspond to the ligand-to-metal charge transfer O²⁻ \rightarrow Mo⁶⁺.⁹ In line with RAMAN, UV VIS DRS shows a highly dispersed mixture of isolated tetrahedral (band around 230 to 260 nm) molybdate species and octahedral (band around 280 to 320 nm) coordinated polymolybdate species.¹⁰ The slight absorption increases in the range of 550 to 800 nm, which indicates the presence of octahedral Ni oxide species. Finally, the larger band-gap energy (E_g) for MoNiP/ γ -Al₂O₃ suggests smaller particles compared to Mo/ γ -Al₂O₃.

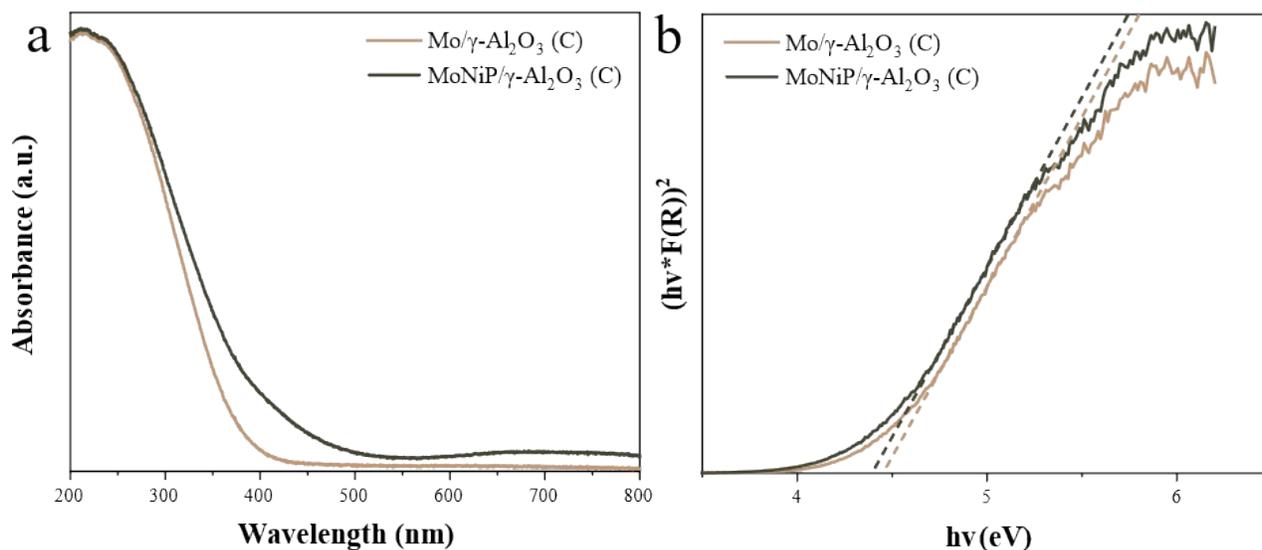


Figure S3.5 UV VIS DRS results of Mo/ γ -Al₂O₃ and MoNiP/ γ -Al₂O₃. (a)

Table S3.4 The electronic edge energy (E_g) of Mo/ γ -Al₂O₃ and MoNiP/ γ -Al₂O₃ found at the intercept between the x-axis and the tangent line of $[F(R_{\infty}hv)]^2$ versus hv .

	E_g (eV)
Mo/ γ -Al ₂ O ₃	4.40
MoNiP/ γ -Al ₂ O ₃	4.45

Raman spectroscopy

Raman spectra of Mo/ γ -Al₂O₃ and MoNiP/ γ -Al₂O₃ (**Figure S3.6**) revealed adsorption peaks at 955 cm⁻¹, 910 cm⁻¹, 840 cm⁻¹, 566 cm⁻¹, 355 cm⁻¹, and 220 cm⁻¹. The bands at around 955 cm⁻¹, 910 cm⁻¹, 355 cm⁻¹, and 220 cm⁻¹ are characteristic of vibrations within octahedrally coordinated polymolybdate species.^{7,8} The broad band at around 840 cm⁻¹ is characteristic of vibrations within isolated tetrahedrally coordinated molybdate. The band at 566 cm⁻¹ is attributed to the Al-O stretching mode.⁸ Both samples consist of a mixture of octahedral and tetrahedral coordinate molybdate species. However, the intensity differences observed in the bands at 840 cm⁻¹ and 910 cm⁻¹ suggest there are more tetrahedrally coordinated molybdate species in Mo/ γ -Al₂O₃, exhibiting a stronger interaction with γ -Al₂O₃.⁸

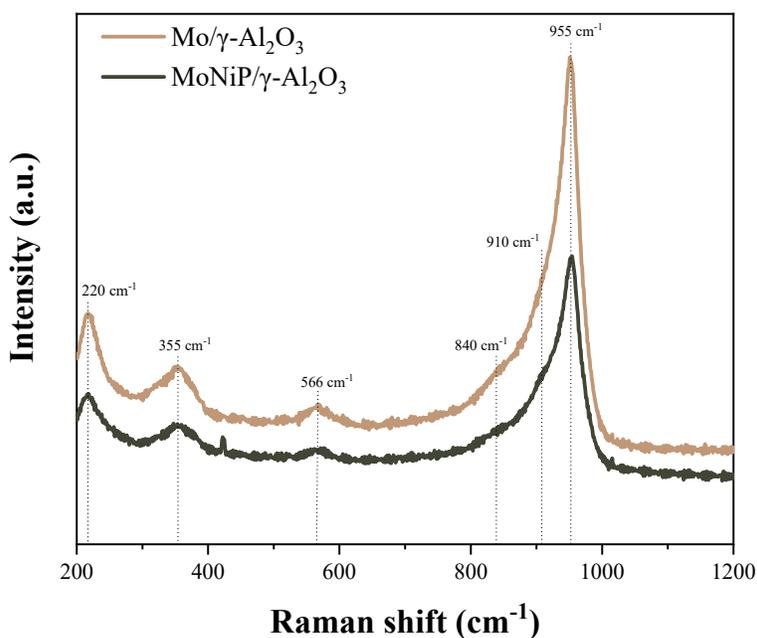


Figure S3.6 RAMAN spectra of Mo/ γ -Al₂O₃ and MoNiP/ γ -Al₂O₃.

H₂ – temperature programmed reduction (TPR)

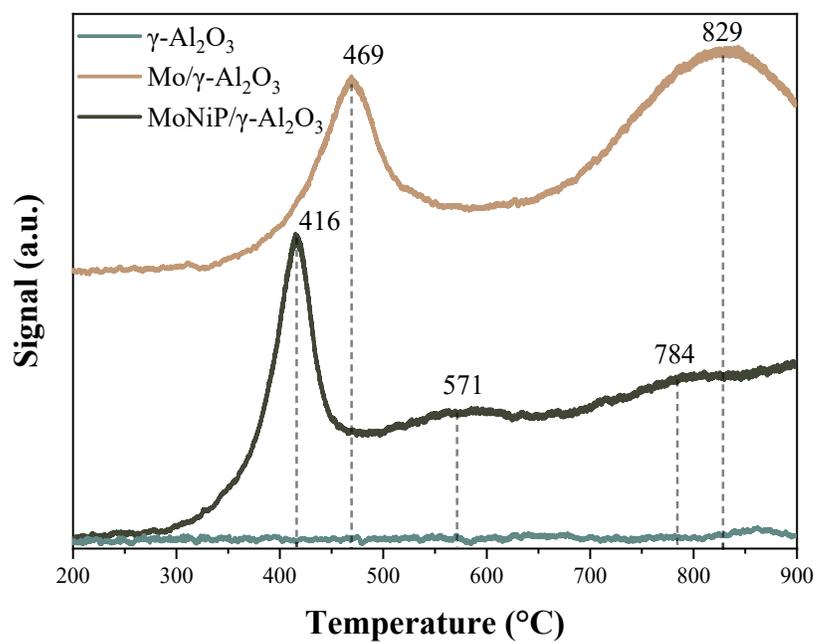


Figure S3.7 TPR of bare γ -Al₂O₃, Mo/ γ -Al₂O₃ and MoNiP/ γ -Al₂O₃.

Weight loading and atom percentage by ICP-OES, XPS and STEM-EDX

Table S3.5 Weight loadings according to ICP-OES, XPS and STEM-EDX.

<i>Weight loading (wt%)</i>	Mo (10 wt%¹)			Ni (2.4 wt%¹)			P (1.3 wt%¹)			S		
	ICP-OES	XPS	STEM-EDX ²	ICP-OES	XPS	STEM-EDX ²	ICP-OES	XPS	STEM-EDX ²	ICP-OES	XPS	STEM-EDX ²
Calcined Mo/γ-Al₂O₃	11.08 ± 0.00	12.68 ± 0.45	12.02 ± 1.37	-	-	-	-	-	-	-	-	-
Sulfided Mo/γ-Al₂O₃	-	9.68 ± 0.37	12.00 ± 0.85	-	-	-	-	-	-	-	6.45 ± 0.37	6.65 ± 0.39
Calcined MoNiP/γ-Al₂O₃	10.96 ± 0.04	11.97 ± 0.27	10.34 ± 0.82	2.51 ± 0.02	2.19 ± 0.26	2.05 ± 0.19	1.65 ± 0.02	1.61 ± 0.13	1.17 ± 0.26	-	-	-
Sulfided MoNiP/γ-Al₂O₃	-	9.53 ± 0.20	10.93 ± 0.50	-	2.49 ± 0.07	2.08 ± 0.11	-	1.67 ± 0.18	1.29 ± 0.17	-	6.78 ± 0.28	6.59 ± 0.44

¹ intended weight loading; ² STEM-EDX is averaged over 5 individual particles

Table S3.6 Atom percent according to ICP-OES, XPS and STEM-EDX

<i>Atom percent (%)</i>	Mo (2.2 at%¹)			Ni (0.9 at%¹)			P (0.9 at%¹)			S		
	ICP-OES	XPS	STEM-EDX ²	ICP-OES	XPS	STEM-EDX ²	ICP-OES	XPS	STEM-EDX ²	ICP-OES	XPS	STEM-EDX ²
Calcined Mo/γ-Al₂O₃		2.97 ± 0.11	2.87 ± 0.40	-	-	-	-	-	-	-	-	-
Sulfided Mo/γ-Al₂O₃	-	2.29 ± 0.07	2.99 ± 0.26	-	-	-	-	-	-	-	4.53 ± 0.37	4.96 ± 0.37
Calcined MoNiP/γ-Al₂O₃		2.82 ± 0.08	2.43 ± 0.23		0.85 ± 0.10	0.79 ± 0.07		1.18 ± 0.10	0.86 ± 0.20	-	-	-
Sulfided MoNiP/γ-Al₂O₃	-	2.30 ± 0.07	2.66 ± 0.16	-	0.98 ± 0.03	0.83 ± 0.05	-	1.24 ± 0.14	0.98 ± 0.14	-	4.89 ± 0.24	4.89 ± 0.24

¹ intended atom percent; ² STEM-EDX is averaged over 5 individual particles

STEM-EDX mapping

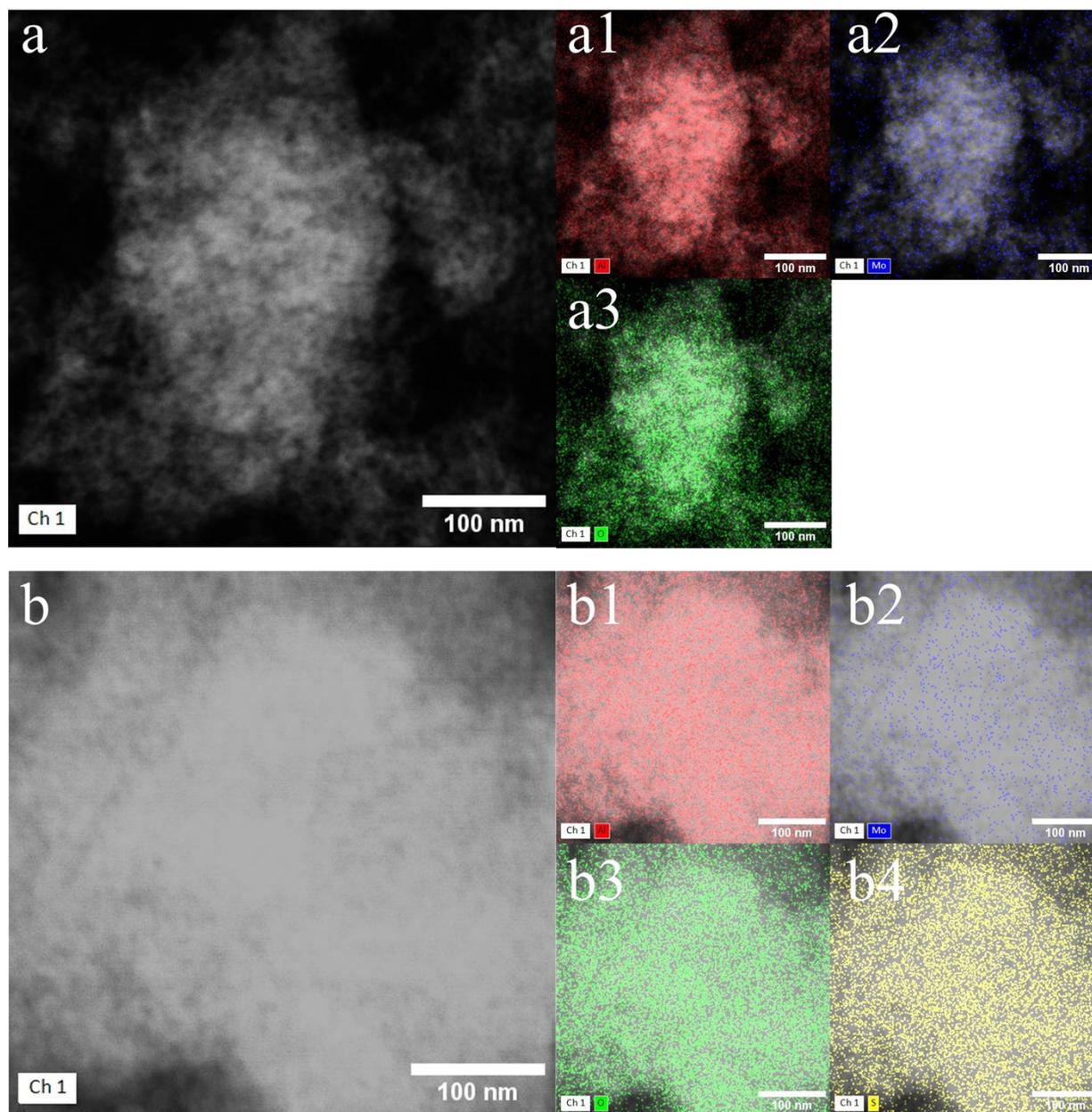


Figure S3.8 STEM-EDX mapping of calcined (a) and sulfided (b) Mo/ γ -Al₂O₃.

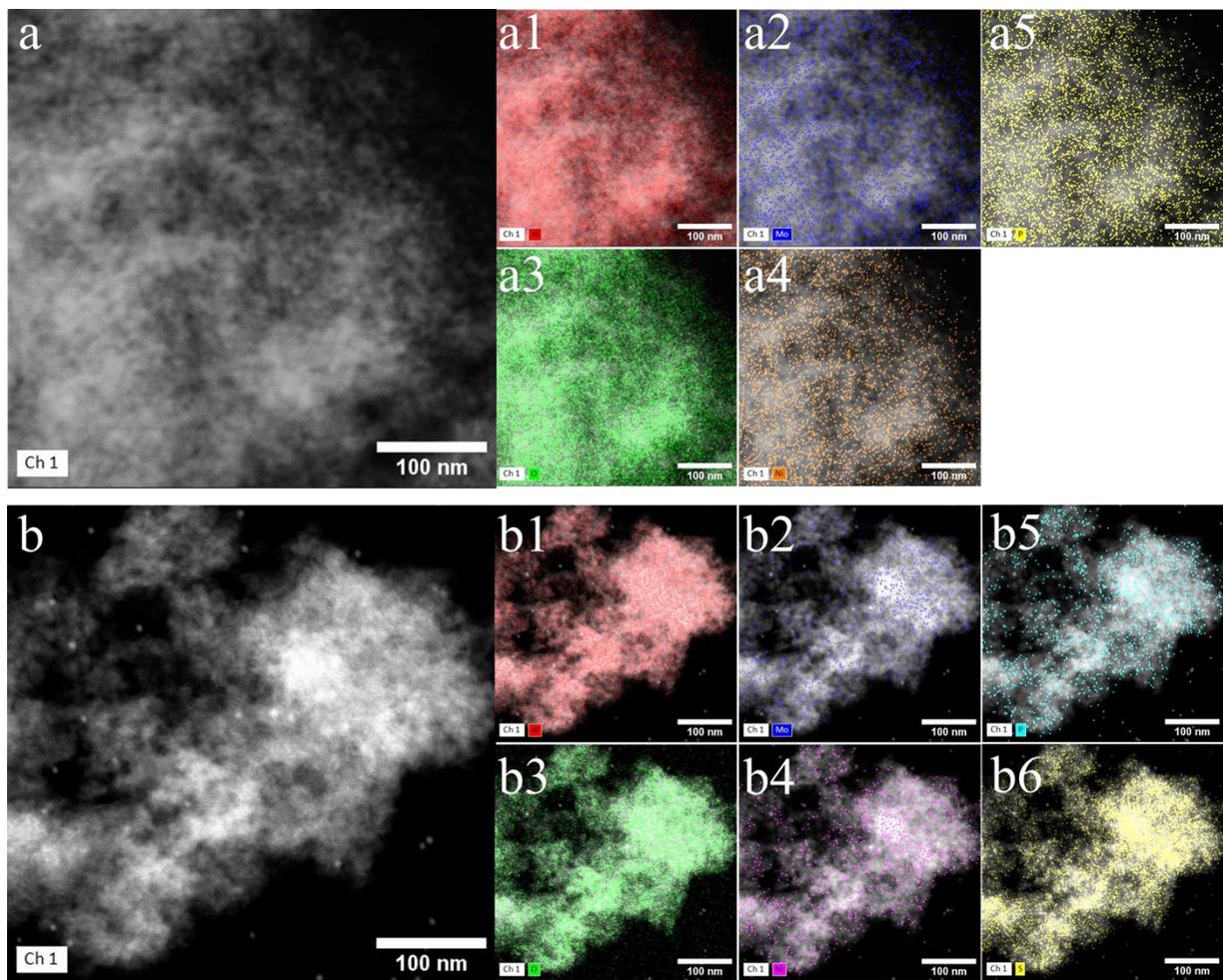


Figure S3.9 STEM-EDX mapping of calcined (a) and sulfided (b) MoNiP/ γ -Al₂O₃.

S4. Cryo-ET descriptor ranking of empty γ -Al₂O₃, Mo/ γ -Al₂O₃, and MoNiP γ -Al₂O₃

The combined set of descriptors obtained for each particle can be used to construct a structural model of the pore architecture that illustrates the relation among descriptors. This requires an overview of the descriptors for each state of bare γ -Al₂O₃ (Table S3.1), including a ranking from highest to lowest value for each descriptor. The structural model of the untreated γ -Al₂O₃ is as follows. It has the broadest distribution of shape index and curvedness, which implies a highly corrugated surface. This surface corrugation originates from its lowest average strut width, corresponding to the smallest primary particles. At last, a high surface corrugation leads to a high tortuosity.

Table S4.1 Ranking of the descriptors. (1) highest / broadest; (2) middle; (3) smallest / narrowest

	Untreated	Calcined	Sulfided
Shape index	1	3	2
Curvedness	1	3	2
SSA	2	3	1
Average struct width	3	1	2
Tortuosity	1	3	2
Pore volume	3	2	1
Average pore size	3	1	2

S5. Calcined & sulfided Mo(NiP)/ γ -Al₂O₃ – zoom, cross sections & segmentation of Figure 2 (a – d)

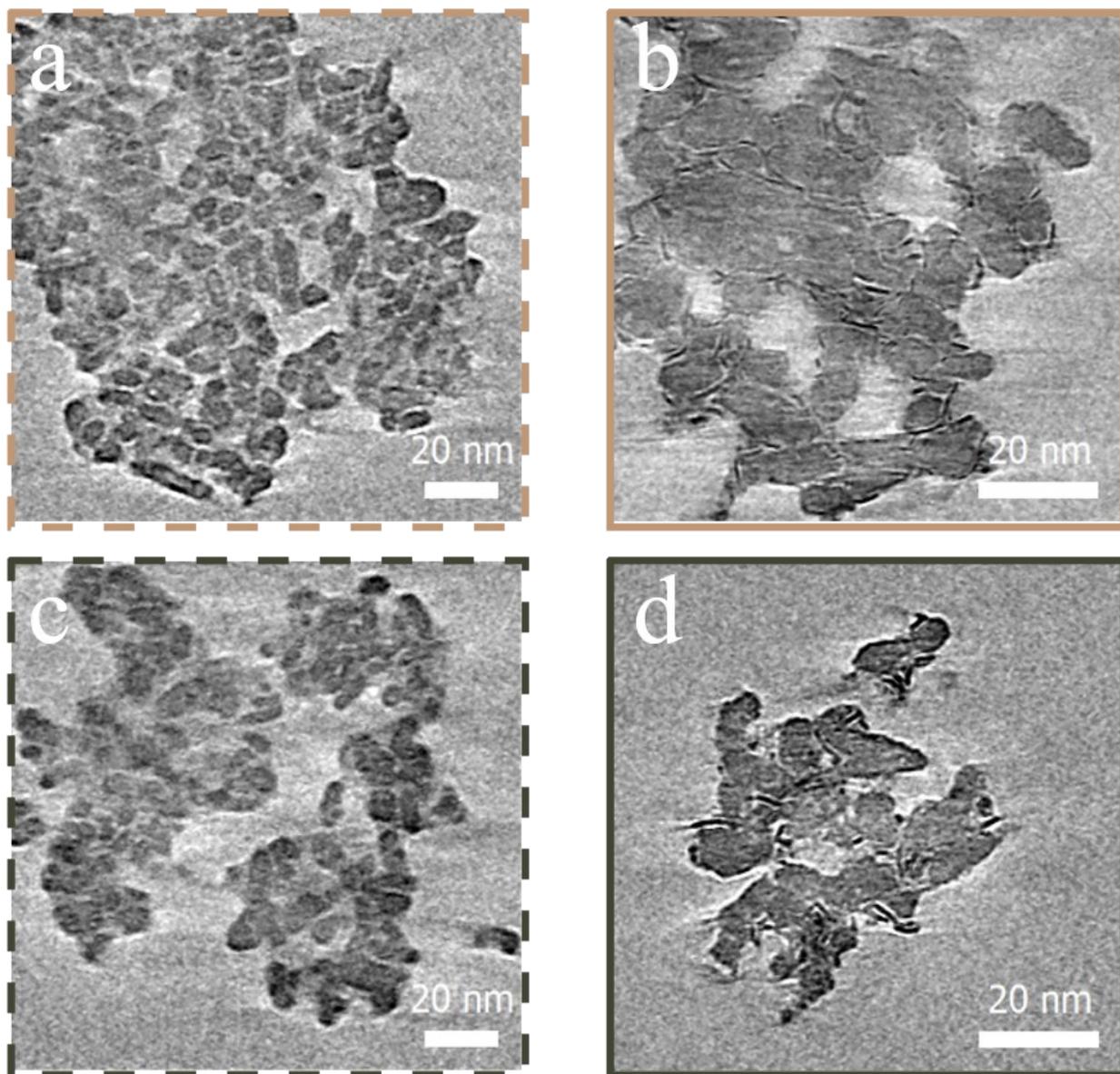


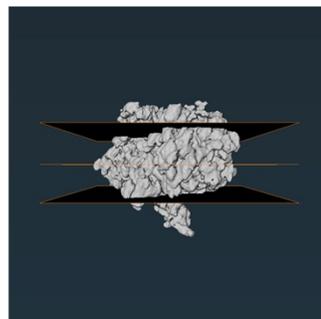
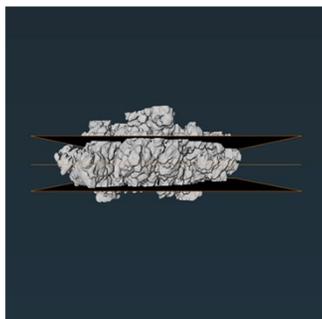
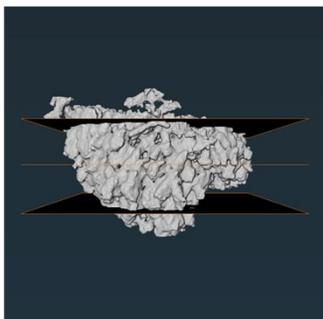
Figure S5.1 Numerical cross sections ((a and c) thickness = 0.31 nm; (b and d) thickness = 0.19 nm) through cryo-ET reconstruction of calcined (a and c) and sulfided (b and d) Mo/ γ -Al₂O₃ and MoNiP/ γ -Al₂O₃. Enlarged view of **Figure 2** in the main text.

Mo/ γ -Al₂O₃ Particle 1
Calcined

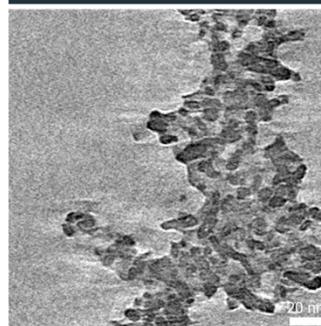
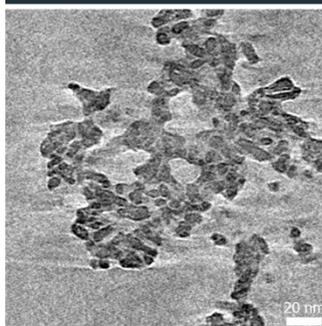
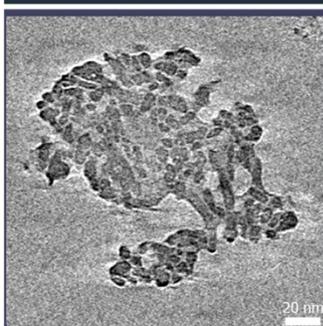
Particle 2

Particle 3

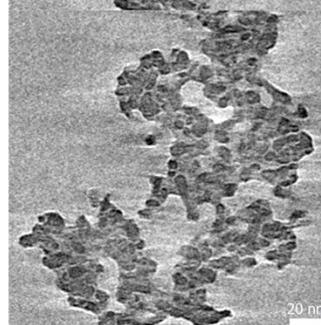
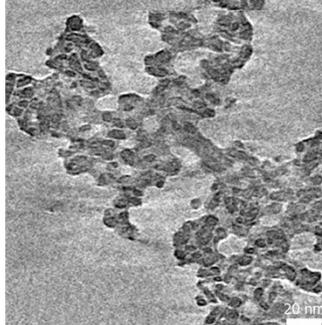
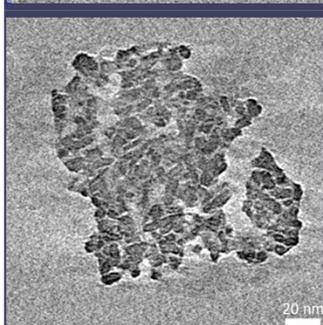
3D



Top



Middle



Bottom

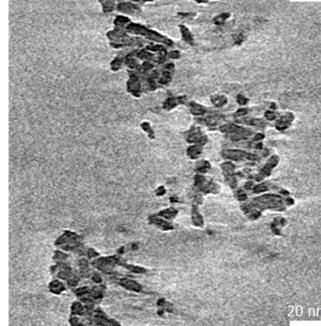
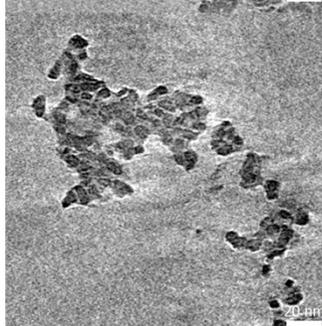
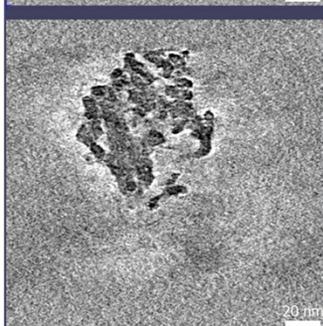


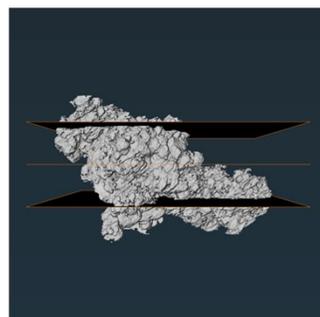
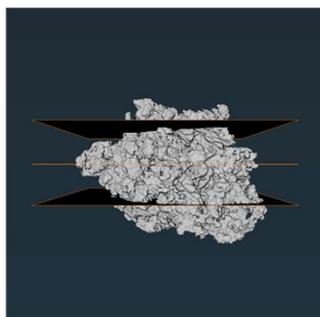
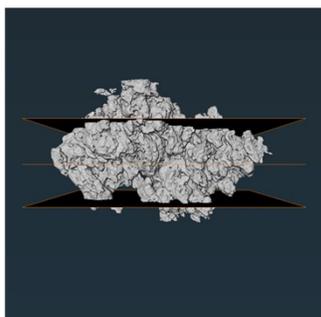
Figure S5.2 Numerical cross sections (thickness = 0.31 nm) through cryo-ET reconstructions of three calcined Mo/ γ -Al₂O₃ particles used for qualitative and quantitative analysis. A 3D rendering of each particle is used to illustrate to height of the top, middle, and bottom numerical cross section.

Mo/ γ -Al₂O₃ Particle 1
Sulfided

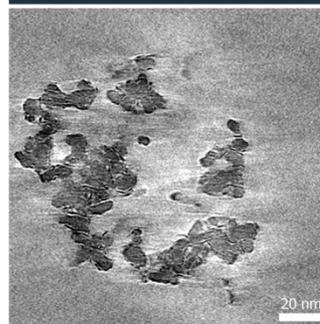
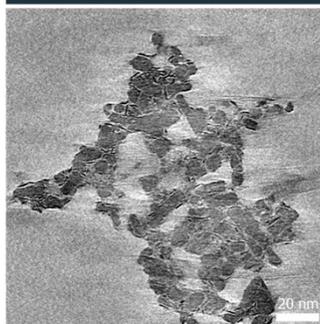
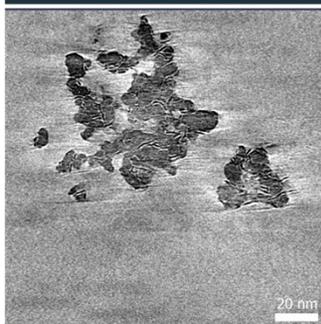
Particle 2

Particle 3

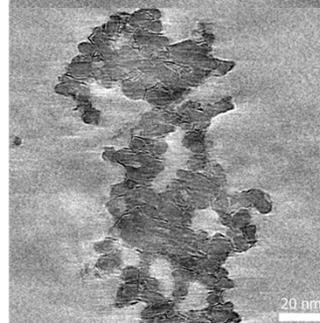
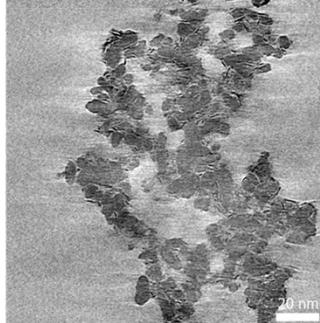
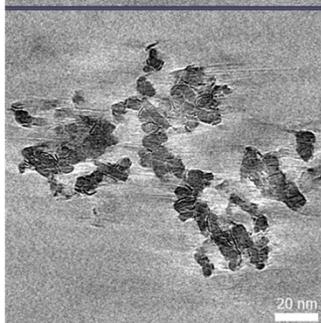
3D



Top



Middle



Bottom

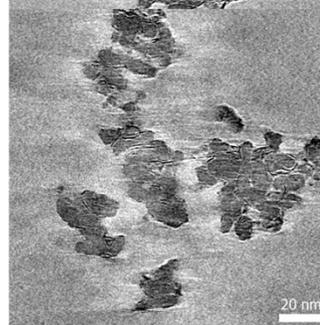
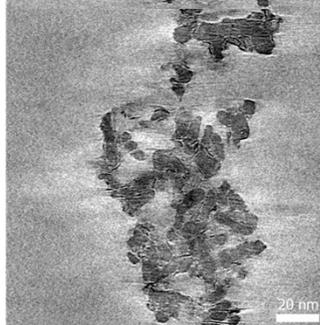
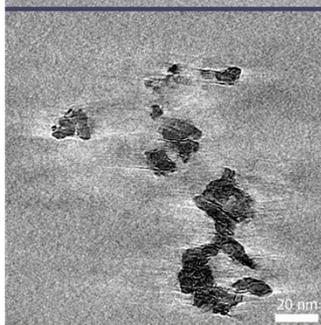


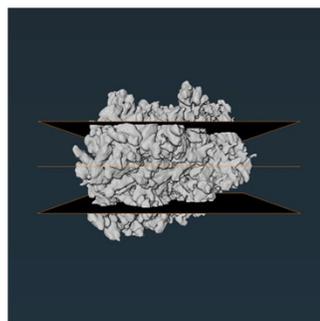
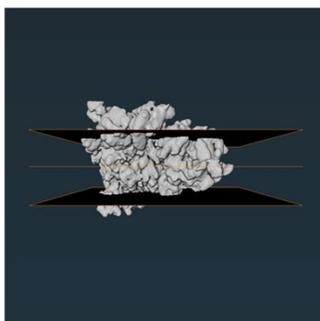
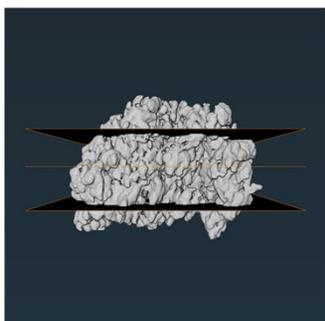
Figure S5.3 Numerical cross sections (thickness = 0.19 nm) through cryo-ET reconstructions of three sulfided Mo/ γ -Al₂O₃ particles used for qualitative and quantitative analysis. A 3D rendering of each particle is used to illustrate to height of the top, middle, and bottom numerical cross section.

MoNiP/ γ -Al₂O₃ Particle 1
Calcined

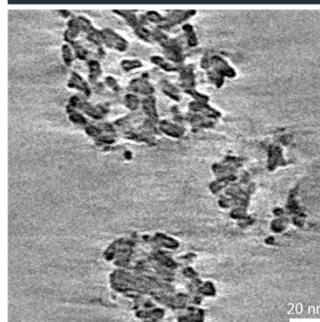
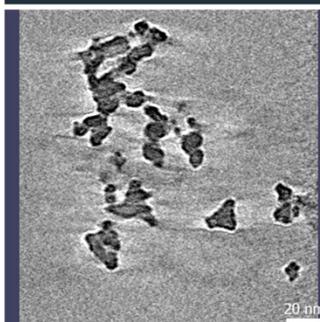
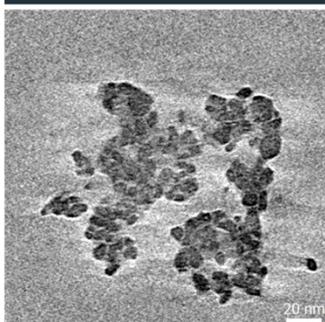
Particle 2

Particle 3

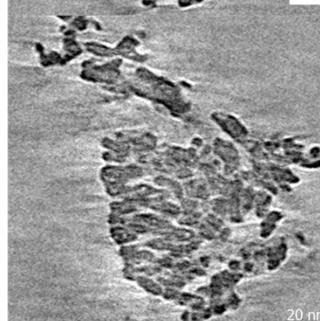
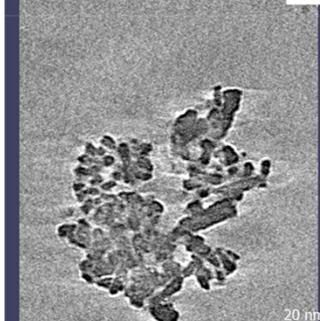
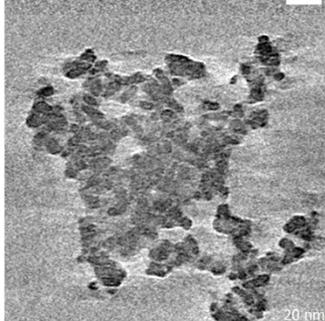
3D



Top



Middle



Bottom

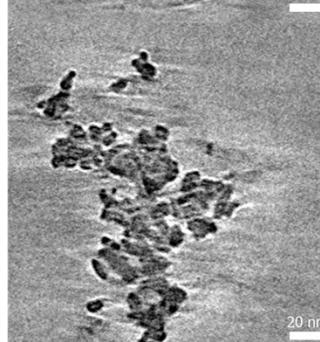
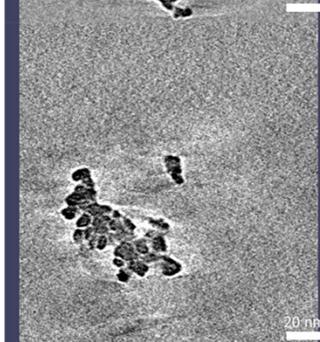
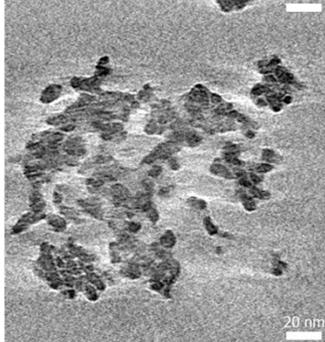


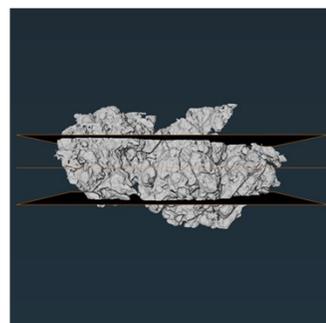
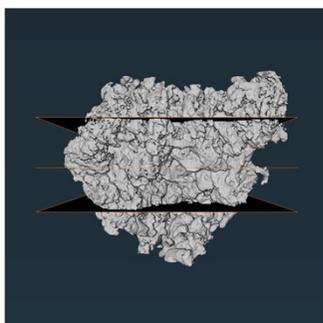
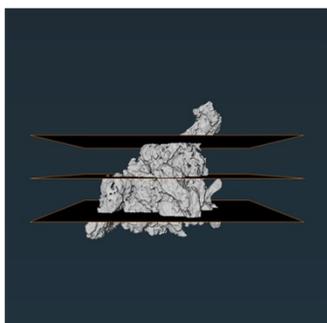
Figure S5.4 Numerical cross sections (thickness = 0.31 nm) through cryo-ET reconstructions of three calcined MoNiP/ γ -Al₂O₃ particles used for qualitative and quantitative analysis. A 3D rendering of each particle is used to illustrate to height of the top, middle, and bottom numerical cross section.

MoNiP/ γ -Al₂O₃ Particle 1
Sulfided

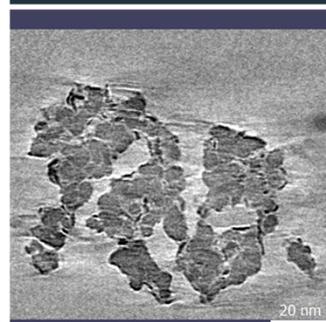
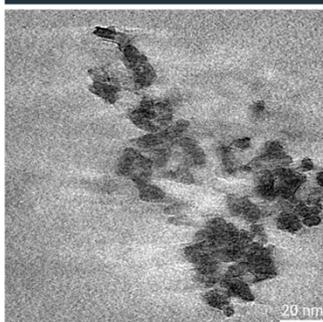
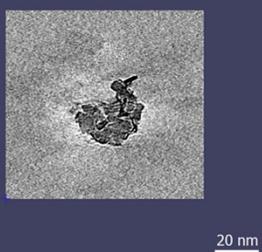
Particle 2

Particle 3

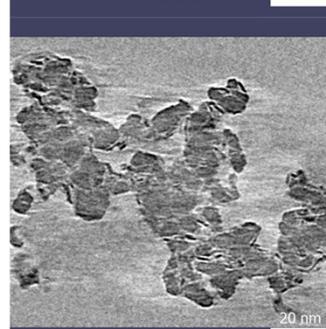
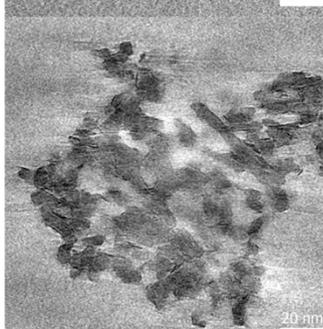
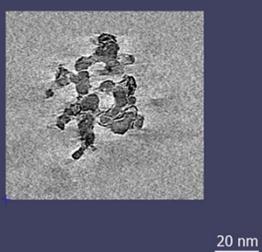
3D



Top



Middle



Bottom

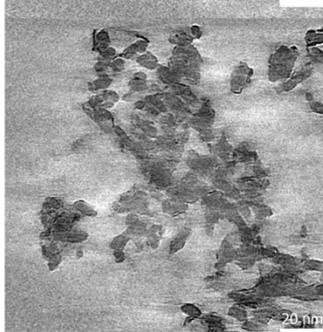
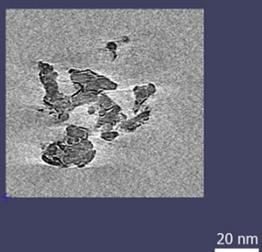


Figure S5.5 Numerical cross sections (thickness = 0.19 nm) through cryo-ET reconstructions of three sulfided MoNiP/ γ -Al₂O₃ particles used for qualitative and quantitative analysis. A 3D rendering of each particle is used to illustrate to height of the top, middle, and bottom numerical cross section.

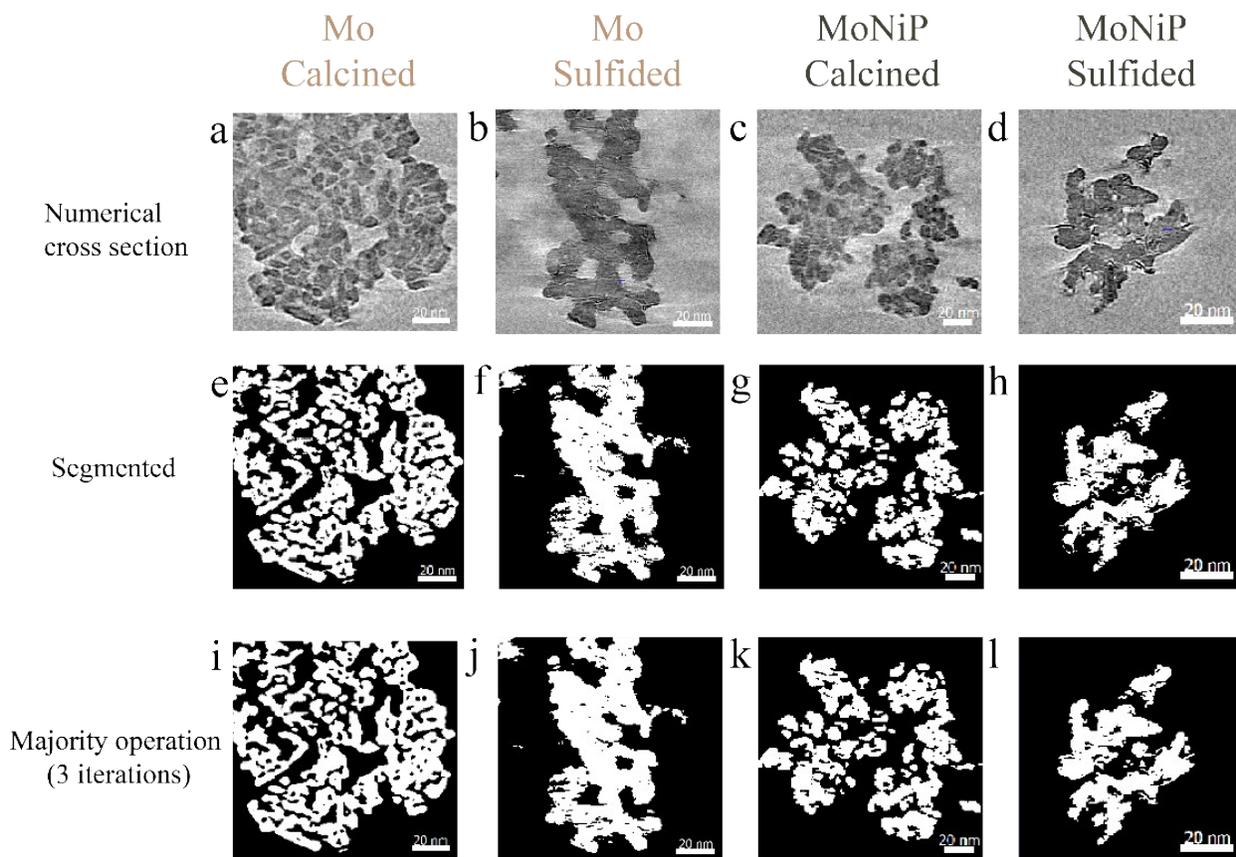


Figure S5.6 Example of the image processing performed on cryo-ET reconstructions of the calcined and sulfided Mo/ γ -Al₂O₃ and MoNiP/ γ -Al₂O₃ particles: (a and c) show the median filtered (kernel size: 3x3x3) numerical cross sections through cryo-ET reconstructions (thickness = 0.31 nm) of calcined Mo/ γ -Al₂O₃ and MoNiP/ γ -Al₂O₃; (b and d) show the median filtered (kernel size: 3x3x3) numerical cross sections through cryo-ET reconstructions (thickness = 0.19 nm) of sulfided Mo/ γ -Al₂O₃ and MoNiP/ γ -Al₂O₃ particles; (e – h) and (i – l) show the segmented slices, corresponding to the numerical slices shown in (a – d), before and after 3 majority iterations, respectively.

S6. Theoretical surface area of MoS₂ and missing wedge correction

Calculation of theoretical maximum MoS₂- γ -Al₂O₃ interface

Assumption: each layer consists out of one layer of Mo sandwiched between two layers of S. The value calculated represents the ideal case where every atom in a hexagonal structure contributes to the surface area and there is perfect exfoliation into monolayers without any stacking or aggregation. The in-plane lattice constant, a , is equal to 3.16 Å.

$$\text{Unit cell area for primitive cell in hexagonal structures} = \frac{\sqrt{3}}{2}a^2 = \frac{\sqrt{3}}{2}3.16^2 = 8.65 \text{ \AA}^2 = 8.65 \times 10^{-20} \text{ m}^2$$

$$\text{Number of MoS}_2 \text{ units per gram} = \frac{N_A}{\text{mass Mo} + 2 \times \text{mass S}} = \frac{6.022 \times 10^{23}}{95.95 + 2 \times 32.06} = 3.76 \times 10^{21} \text{ units/g}$$

$$\text{Theoretical MoS}_2 - \gamma - \text{Al}_2\text{O}_3 \text{ interface} = 3.76 \times 10^{21} \times 8.65 \times 10^{-20} \approx 325 \text{ m}^2/\text{g MoS}_2$$

Missing wedge correction

The missing wedge poses a problem in ET as it leads to an anisotropic resolution in the form of elongation and blurring of the objects in the z-direction.^{11,12} As a consequence, it can be expected that not all MoS₂ slabs will be sufficiently visible for segmentation. Rather complex approaches to suppress the missing information and increase the resolution in the z-direction exist but are out of scope in this study.^{11,12} However, a simple estimate, assuming isotropic orientation of the slabs in the disordered γ -Al₂O₃ matrix, is used to account for the loss in MoS₂.

The tilt range is $\pm 68^\circ$ which gives a missing wedge of $180^\circ - 136^\circ = 44^\circ$. Hence the fraction of Fourier space which is not sampled is $43^\circ/180^\circ = 0.24$. This means that 24% of the slabs are in orientations within the missing wedge. The correction factor is then equal to $1 / (1 - 0.24) = 1.31$. This would indicate that there are about 31% more slabs present than imaged. This value will be used in the final section to correct the weight loading found.

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