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Cryogenic electron tomography reveals the mesoporous structure evolution during γ -Al₂O₃ supported Mo and MoNiP catalyst formation

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Heterogeneous catalysts play a central role in numerous industrially and societally relevant processes. Despite the widespread use, a detailed understanding of the support mesoporosity and its transformation during catalyst preparation remains incomplete. In this study, cryogenic electron tomography (cryo-ET) was utilized to resolve the 3D mesopore structure of γ -Al₂O₃ and to assess structural changes induced by oxidic Mo and MoNiP deposition and sulfidation during the preparation of hydrodesulfurization (HDS) catalysts. The intrinsic γ -Al₂O₃ surface and mesopore structure remained largely stable throughout calcination and sulfidation, although cryo-ET revealed subtle variations inaccessible to bulk characterization techniques. Oxidic Mo deposition introduced slight increases in tortuosity and surface corrugation, whereas oxidic MoNiP deposition induced minimal changes. Compared to the bare support, sulfidation of both Mo and MoNiP supported on γ -Al₂O₃ resulted in more tortuous mesopores and a more corrugated surface. Careful segmentation enabled separate analysis of γ -Al₂O₃ and MoS₂ slabs, revealing that, for both catalysts, the γ -Al₂O₃ exhibited similar surface and mesopore modifications, and there were no significant differences in MoS₂ slab morphology. Corrected Mo loadings derived from cryo-ET aligned with bulk measurements, validating the approach. These findings provide a comprehensive 3D perspective on mesopore stability during catalyst preparation and highlight the need for higher-resolution imaging and advanced 3D analysis to establish robust structure–function correlations.

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Introduction

Ceramic high-surface area mesoporous materials are extensively utilized as support materials in heterogeneous catalysts, which makes them one of the most important classes of industrially employed materials. Heterogeneous catalysts consist of active particles, which are dispersed across and supported on a porous high-surface-area support material. The pore structure and topology of the support material significantly affect the distribution, shape, and accessibility of the deposited active constituents. Consequently, these

support properties directly affect the performance of the active catalyst, including reactivity, selectivity, or stability.¹

Prominent examples of industrial supports are high-surface-area variations of alumina, titania, zirconia, and silica, which can be optimized regarding porosity and other key properties, such as swelling or mechanical and thermal stability.¹ The stability of support materials under operating conditions, such as high temperature and pressure, has been a subject of research interest since the 1990s.^{2,3} These research outcomes have largely contributed to the development of industrial catalysts with support pore structures and topologies engineered to the needs of the catalytic reaction. However, a detailed understanding of the mesopore-level structure and how it evolves during support manufacturing and catalyst preparation remains incomplete. Filling this gap would enable catalyst manufacturers to further optimize catalyst design and performance.

A typical method to prepare heterogeneous catalysts is incipient wetness impregnation (IWI). Here, a porous support material is impregnated with a solution that contains active constituents, followed by drying. Depending on the type of catalyst, subsequent heat-treatment steps under different gas compositions may follow. During drying, the dissolved

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visualized using cryo-ET and to relate these nanoscale observations to established structural models.

Our results reveal that the intrinsic structural and electronic features of bare γ -Al₂O₃ are preserved after calcination and sulfidation, establishing a baseline for comparison of bare and Mo or MoNiP-filled γ -Al₂O₃. Initial observations indicate differences between Mo and MoNiP-filled γ -Al₂O₃ in terms of surface and pore structure descriptors, but notably, sulfidation results in similar surfaces, pores, and active phase descriptors.

Experimental

Catalyst preparation

A γ -Al₂O₃ support (Ketjen, CK300) was used for catalyst preparation. This material contains a disordered network of mesopores and has a H₂O pore volume of 0.62 cm³ g⁻¹. It is supplied as cylindrical extrudates with a diameter of 1 mm and a length of 3–10 mm. This support is produced commercially using a proprietary process that involves acid-peptization of pseudo-boehmite, extrusion of the resulting paste, followed by controlled drying, and calcination at intermediate temperatures. Catalysts were prepared by incipient wetness impregnation (IWI) on the γ -Al₂O₃ extrudates (Table 1). MoNiP/ γ -Al₂O₃ was prepared using a metal salt solution obtained by mixing H₃PO₄ (85%) and MilliQ water (3 mL), followed by the addition and dissolution of MoO₃ and NiCO₃. Next, the solution was heated to 100 °C until a transparent green solution was obtained. To prepare Mo/ γ -Al₂O₃, a metal salt solution was prepared by dissolving MoO₃ in ammonium hydroxide (32% NH₃ in H₂O). MilliQ water was added to both precursor solutions to reach a total volume of 5 mL. These solutions were then used to impregnate the γ -Al₂O₃ extrudates. The impregnated extrudates were rotated on a roller bank in a sealed vial for ~2 h, after which they were transferred to a ceramic crucible covered with perforated aluminium foil to allow drying in air at ambient temperature. The crucible was then placed in an oven overnight at 120 °C to ensure complete solvent removal. The crucible was then placed in a calcination oven, where the material was heated to 400 °C for 2 h ($\Delta T = 6$ °C min⁻¹). Single-stage sulfidation was performed according to traditional model conditions to ensure simplicity, reproducibility and consistency with previously reported structural studies on similar catalysts.^{20,22,73–75} Sulfidation was performed in a stainless-steel reactor with an inner diameter of 4 mm. In detail, ~75 mg of a crushed sieved fraction (75–125 μ m) mixed with 200 mg SiC were loaded in the middle of the reactor and sulfided at ambient pressure

for 2 h at 350 °C ($\Delta T = 6$ °C min⁻¹) in a 50 mL min⁻¹ flow of 10 vol% H₂S in H₂. After sulfidation, the sample was transferred to a glovebox without air exposure until further characterization.

(cryo-)TEM and ET sample preparation

TEM grids of 200 mesh Cu with a 6 nm thick continuous carbon layer were used for all measurements. Sample preparation involved gently crushing the catalyst extrudates into a fine powder, which was then dispersed in absolute ethanol. A small aliquot of the suspension was drop-cast onto a Au back-labelled TEM grid and allowed to dry, enabling the particles to adhere to the carbon layer. As a result, the particles remain attached to the carbon layer and thus ensuring stable imaging conditions.⁷⁶ Preparation of sulfided TEM samples was performed entirely inside the glovebox to prevent exposure to air.

(cryo-)TEM, ET, and STEM-EDX data acquisition

TEM images and tilt series were acquired on a Glacios cryo-TEM (TFS, Thermo Fisher Scientific) operated at 200 kV, equipped with a direct electron detector (FALCON 4i). For best results in (cryo-)TEM and (cryo-)ET, particles were selected with a thickness and width in the 100–300 nm range. 4 K tilt series, were acquired at a magnification of 92 k \times (pixel size = 0.1535 nm) or 150 k \times (pixel size = 0.0942 nm) within an angular range of -68° to 68° at increments of 1° and a nominal defocus of -1.0 μ m (at 92 k \times) or -0.2 μ m (at 150 k \times). At 92 k \times , the dose rate was ~ 5.1 e⁻ \AA^{-2} image and the exposure time 0.3 s. At 150 k \times , the dose rate was ~ 9.0 e⁻ \AA^{-2} image and the exposure time 1.18 s. Potential beam damage was evaluated by acquiring images before and after the tilt series. No detrimental beam effects were observed at the used total dose.

STEM-EDX mapping was performed on a Titan Themis (FEI/TFS) operated at 300 kV and equipped with an XFlash 6 T|60 (Bruker) EDS detector. Elemental EDX maps were acquired at 40 k \times with a beam convergence angle of 9.5 mrad and a camera length of 160 mm. Frames of approximately 450 \times 450 pixels with a dwell time of 32 μ s were recorded for 20 minutes. STEM-EDX maps were averaged by a [3 3] kernel prior to further analysis. K-edge quantification was performed with the Cliff-Lorimer method on Al, O, Mo, Ni, P, and S.

3D reconstruction and 3D quantitative analysis

Tilt-series alignment and tomographic reconstructions were performed in IMOD.^{77–79} In general, the aligned stacks (137

Table 1 Details regarding the IWI preparation of γ -Al₂O₃ supported Mo and MoNiP catalysts

Catalyst	MoO ₃ (g)	NiCO ₃ (g)	H ₃ PO ₄ (g)	γ -Al ₂ O ₃ (g)	Intended loading (wt%)		
					Mo	Ni	P
Mo/ γ -Al ₂ O ₃	1.42	—	—	8.06	10	—	—
MoNiP/ γ -Al ₂ O ₃	1.53	0.50	0.51	8.06	10	2.4	1.3



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)).

Raman spectroscopy was employed to assess the structure, crystallinity, and coordination environment of the metal oxide precursor. Spectra were recorded using a Witec alpha 300 R confocal Raman microscope equipped with a 532 nm diode excitation source, a 1200 lines per mm grating (BLZ = 500 nm), and a charge-coupled device (CCD) was used. A ZEISS LD EC Epiplan-Neofluar Dic 50×/0.55 objective was used. Spectra of the powder samples were collected using 1200 accumulations with an integration time of 1 s per accumulation.

Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) was used to investigate the coordination and aggregation states of the supported metal oxide phases. Spectra were collected from calcined powder samples (<75 μm) using a Thermo Scientific Evolution Pro UV-vis spectrophotometer. A spectral bandwidth of 1.5 nm, a measurement interval of 0.5 nm, and an integration time of 0.5 s were applied. BaSO₄ served as the reflectance standard. The electronic edge energy (E_g) of ligand-to-metal charge transfer transitions was determined from the intercept of the energy-axis and the tangent line of $[F(R_{\infty})/hv]^2$ vs. hv plot, where $F(R_{\infty})$ is the Kubelka–Munk function and hv is the photon energy.

Temperature-programmed reduction (TPR) was performed to study the reducibility of the samples. Experiments were performed on a Micromeritics AutoChem II instrument by loading 100 mg of powder (75–125 μm fraction) into a quartz U-tube reactor, positioned between two layers of quartz wool. Prior to analysis, the samples were pretreated at 200 °C for 1 h in a flow of 50 mL min⁻¹ He. TPR profiles were recorded by heating the sample from 40 °C to 900 °C at a 5 °C min⁻¹ rate in a 50 mL min⁻¹ flow of 4 vol% H₂ in N₂. H₂ consumption was monitored by a thermal conductivity detector (TCD), which was calibrated with an AgO reference.

Results and discussion

Bare γ -Al₂O₃ supports (untreated, calcined, and sulfided)

To determine whether the pore structure of the γ -Al₂O₃ support changes during catalyst preparation, it is essential to investigate the bare support prior to and after each synthesis step, namely the untreated, calcined, and sulfided states. Over years of storage and handling, untreated γ -Al₂O₃ is exposed to air and humidity, resulting in re-hydroxylation of the surface and equilibration with ambient conditions. To refresh the support surface and thereby remove physisorbed water, regenerate hydroxyl groups, and eliminate contaminants, the untreated γ -Al₂O₃ was calcined prior to use. Accordingly, we deemed it necessary to evaluate the stability of the γ -Al₂O₃ mesopore structure at the nanoscale after both the calcination and sulfidation steps. Ideally, many datasets would be averaged to yield a statistically robust distribution of quantitative pore structure descriptors.

However, such extensive data collection is currently impractical with cryo-ET due to substantial time required for acquisition, processing, and analysis. To balance experimental feasibility with statistical relevance, each sample state was therefore imaged in triplicate.

Previous work has shown that the untreated bare γ -Al₂O₃ used in this study exhibits regions with different pore structures.⁸³ Fig. 1(a–c) displays numerical cross sections through the reconstructions of untreated, calcined, and sulfided γ -Al₂O₃ support particles. Additionally, numerical cross sections from the top, middle, and bottom regions of all reconstructed particles are shown in SI section S2. Among the states, the observed particles varied in size, which can be attributed to the crushing of the extrudates during TEM sample preparation. Variations in the packing density and size of the fused γ -Al₂O₃ primary particles were observed, which are expected to lead to differences in pore structure descriptors. These variations are not attributed to calcination or sulfidation, as they were observed in the pristine material too (Fig. S2.1). No other visual differences were observed between the states, while quantifying the cryo-ET data can provide a much more detailed description of the mesopore network and possible effects of calcination and sulfidation.

To obtain quantitative insights into the γ -Al₂O₃ pore structure, the support structure was isolated (segmented) from the reconstructed cryo-ET data, resulting in a binary 3D dataset for detailed analysis (Fig. S2.4). For each state, surface and pore structure descriptors of three unique segmented 3D datasets, representing individual γ -Al₂O₃ support particles, were quantified and averaged to assess the preservation of the support. Additionally, bulk characterization techniques were employed to determine the preservation of the main physicochemical properties of the γ -Al₂O₃ throughout the preparation process.

The bulk pore structure was estimated by N₂ physisorption. As shown in Fig. S3.1(a), the untreated, calcined, and sulfided γ -Al₂O₃ samples exhibit a type IV(a) isotherm, characteristic of mesoporous materials.⁵⁰ The adsorption–desorption branches and the associated hysteresis loops indicate that the overall pore structures of the three γ -Al₂O₃ states appear very similar. In contrast, the averaged cryo-ET data, shown in Fig. 1(d and e), reveal pronounced differences in pore volume (PV), pore size (distribution in Fig. S2.5), specific surface area (SSA), and strut width among the states. These variations corroborate the qualitative differences evident from visual inspection of the reconstructions.

For each state, the PV derived from cryo-ET (Fig. 1(d)) is significantly smaller than the PV derived from N₂ physisorption analysis (Fig. S3.1(b)). This discrepancy likely arises from fracturing of the structure along the largest pores during sample preparation, where grinding may preferentially open wide pores. As a result, these larger pores are no longer enclosed volumes and are therefore not captured in the PV determination by cryo-ET. The PV measured by cryo-ET remains essentially constant following



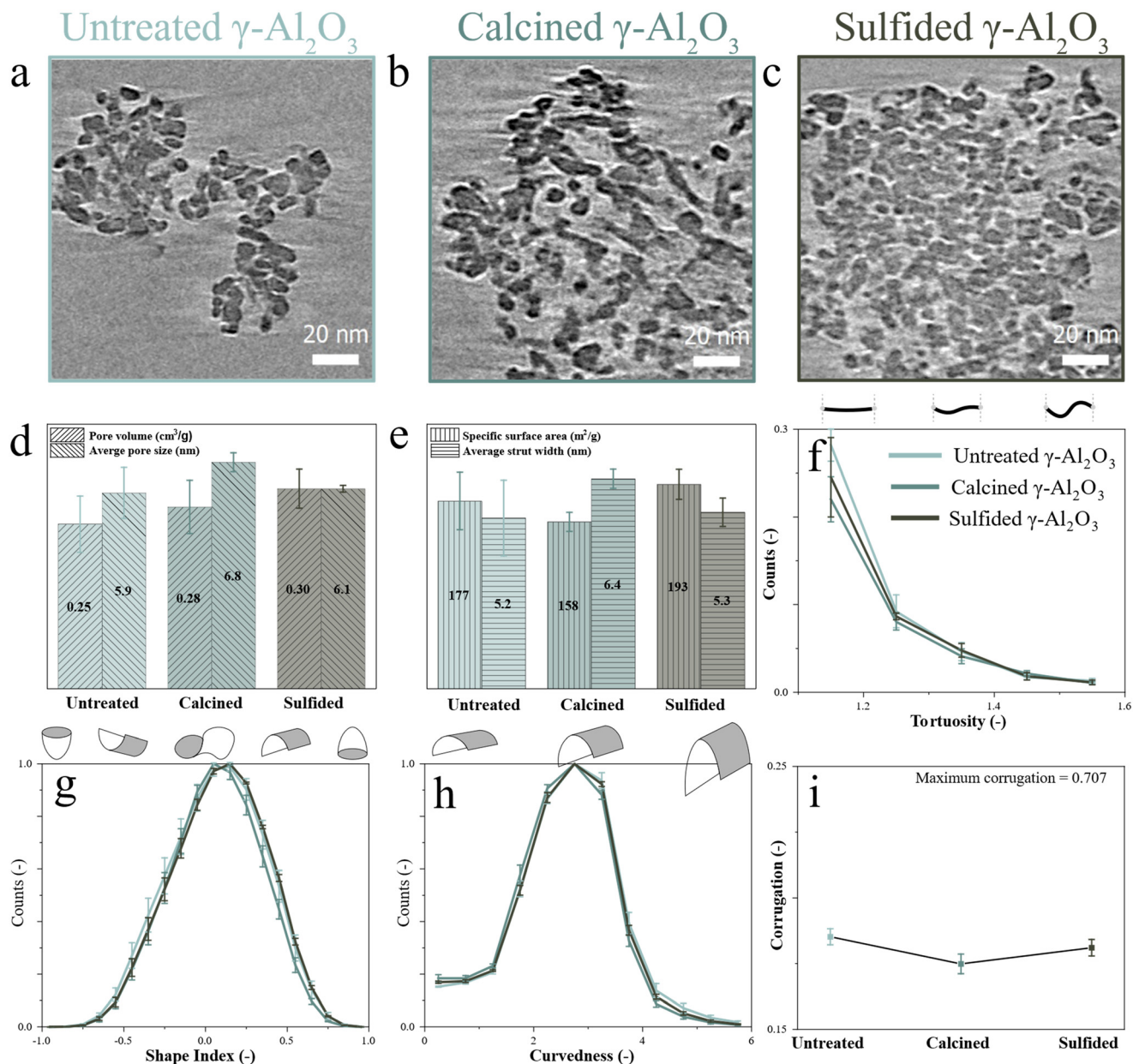


Fig. 1 Quantitative ET showing numerical cross sections (thickness = 0.31 nm) through cryo-ET reconstructions of bare γ -Al₂O₃ supports in (a) untreated, (b) calcined, and (c) sulfided state (each triplo). Quantitative analysis of the surface and pore network showing the averaged values for: (d) PV and average pore size; (e) SSA and average strut width; (f) tortuosity; (g) shape index, (h) curvedness, and (i) corrugation.

calcination and sulfidation. For each state, the average pore size estimated by cryo-ET (Fig. 1(d)) is in good agreement with the desorption BJH pore size distributions (Fig. S3.1(d)). Additionally, the SSA calculated from cryo-ET (Fig. 1(e)) matches well the BET results (Fig. S3.1(b)). Finally, for each state, the average strut width, measured by cryo-ET (Fig. 1(e)), showed variations from 4.0 to 6.7 nm. This aligns with the presence of a range of primary γ -Al₂O₃ platelet sizes at every state. The application of the Scherrer equation to the synchrotron XRD data revealed crystallite sizes ranging from 4.2 to 8.4 nm for the untreated and calcined γ -Al₂O₃ and 4.0 to 8.4 nm for the sulfided γ -Al₂O₃ (Fig. S3.3 and Table S3.2). These results suggest that the

primary γ -Al₂O₃ platelets remain stable during calcination and sulfidation.

In addition, cryo-ET enabled a more detailed analysis of structural features that were not directly accessible by bulk characterization. In Fig. 1(f–i), the tortuosity, shape index, curvedness, and corrugation of untreated, calcined, and sulfided γ -Al₂O₃ are shown. These descriptors exhibit only minor variations with overlapping error ranges. Therefore, the structural features of bare γ -Al₂O₃ appear to be preserved following calcination and sulfidation.

Based on the combined assessment of the cryo-ET data and bulk characterization results, γ -Al₂O₃ appears structurally stable after both calcination and sulfidation.



The observed variations in surface and pore descriptors are therefore more attributed to intrinsic local heterogeneity of the support, heterogeneity that cryo-ET is uniquely sensitive to, rather than from systematic modification of the γ - Al_2O_3 framework. Moreover, the combined set of descriptors obtained for each particle can be used to construct a structural model of the pore architecture, which can be used to illustrate the relation among individual descriptors (SI section S4). To establish a reference for the intrinsic structural heterogeneity of the bare γ - Al_2O_3 , the average values from the untreated, calcined, and sulfided datasets, comprising a total of 9 reconstructed particles, are used as a baseline for

comparison with Mo or MoNiP-containing γ - Al_2O_3 samples, which will be discussed in the next section.

γ - Al_2O_3 supported Mo or MoNiP after calcination and sulfidation

This section examines the changes in surface and pore structure following the deposition of oxidic Mo or MoNiP on γ - Al_2O_3 supports and subsequent sulfidation. To ensure a fair comparison, the intended Mo weight loading for both Mo/ γ - Al_2O_3 and MoNiP/ γ - Al_2O_3 is 10 wt%. The actual Mo loadings of the calcined samples were characterized using ICP-OES, XPS, and STEM-EDX, with results shown

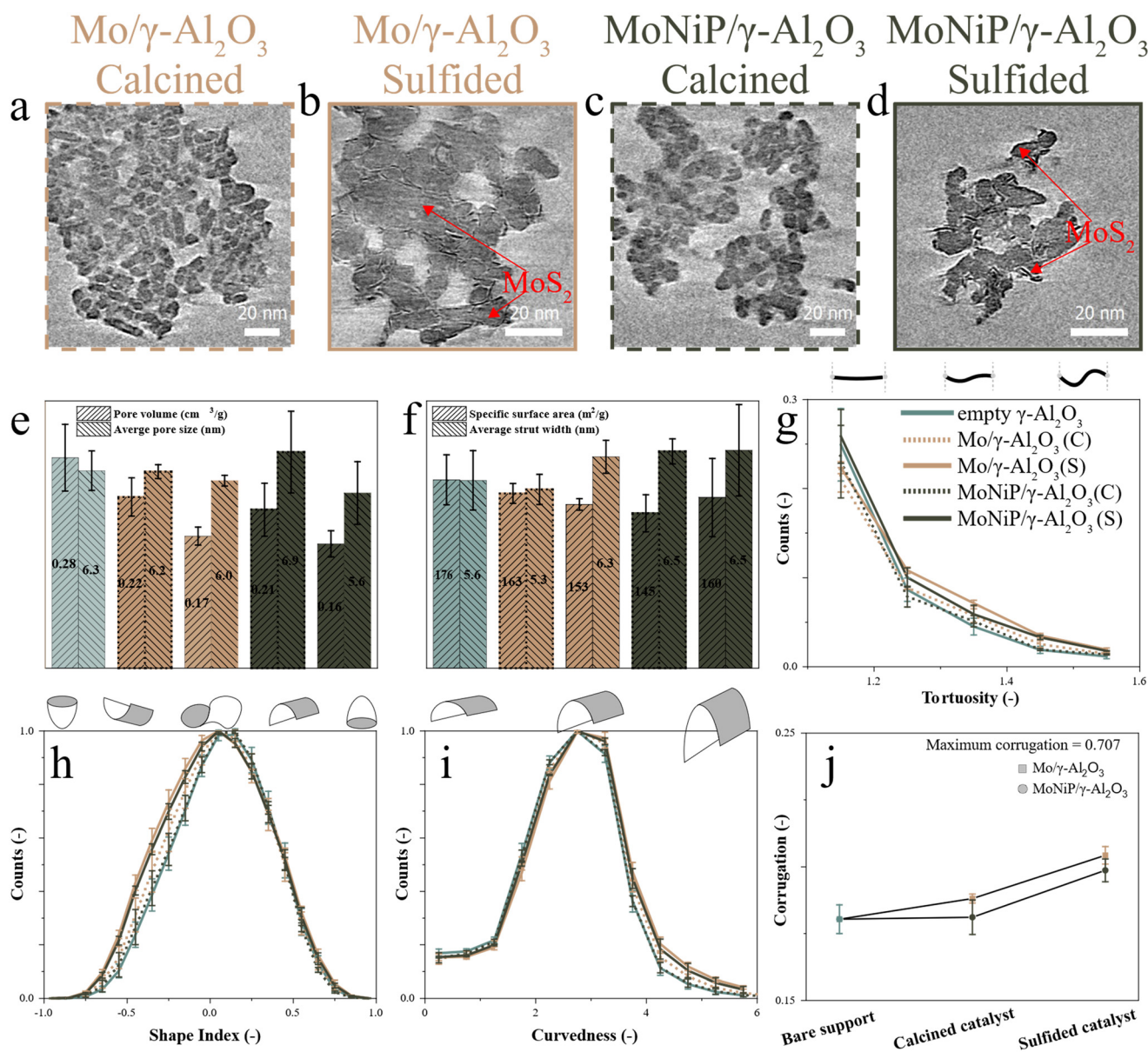


Fig. 2 Quantitative ET showing numerical cross sections ((a and c) thickness = 0.31 nm; (b and d) thickness = 0.19 nm) through cryo-ET reconstruction of calcined (a and c) and sulfided (b and d) Mo/ γ - Al_2O_3 and MoNiP/ γ - Al_2O_3 . An enlarged image of (a-d) is shown in Fig. S5.1(a-d). The formed MoS_2 particles are indicated by red arrows. Quantitative analysis of the surface and pore network showing: (e) PV and average pore size; (f) SSA and average strut width; (g) tortuosity; (h) shape index, (i) curvedness; and (j) surface corrugation.



in the SI (Tables S3.5 and S3.6). Moreover, as shown in Fig. S3.7(a) and S3.8(a), STEM-EDX reveals a uniform sub-micron-level distribution of the calcined Mo in Mo/ γ -Al₂O₃ and of calcined Mo, Ni, P in MoNiP/ γ -Al₂O₃.

Numerical cross sections of calcined and sulfided Mo/ γ -Al₂O₃ are shown in Fig. 2(a and b), with an enlarged view in Fig. S5.1(a and b). Cross sections from the top, middle, and bottom regions of all reconstructed Mo/ γ -Al₂O₃ particles are shown in Fig. S5.2 and S5.3. The calcined Mo/ γ -Al₂O₃ particles exhibit a similar structure to the bare γ -Al₂O₃, where the fused primary particles form the porous backbone. The absence of features that could be associated with segregated Mo oxide particles indicates that oxidic Mo is uniformly dispersed at the nanometer scale across the γ -Al₂O₃ surface. Due to this uniform distribution, insufficient contrast existed between the two materials for the oxidic Mo to be identified. After sulfidation, the structure of the primary γ -Al₂O₃ particles changed, and oxidic Mo transformed into MoS₂ slabs visible on the surface of the γ -Al₂O₃ (Fig. 2(a and c)). A variety of basal and edge plane connections between the slabs and γ -Al₂O₃, combined with minimal slab stacking, were observed. Similar observations were made for the numerical cross sections of calcined and sulfided MoNiP/ γ -Al₂O₃, shown in Fig. 2(c and d), with an enlarged view in Fig. S5.1(c and d) and cross sections from the top, middle, and bottom regions of all reconstructed MoNiP/ γ -Al₂O₃ particles in Fig. S5.4 and S5.5. How and to what extent the deposition of calcined Mo or MoNiP and subsequent sulfidation change the pore structure with respect to the bare γ -Al₂O₃ will be discussed in the next section.

To extract surface and mesopore structure descriptors inaccessible through visual interpretation alone, the solid material depicted in Fig. 2(a–d) was segmented. Slices of the segmented volumes are shown in Fig. S5.6. Descriptors were extracted for three distinct Mo/ γ -Al₂O₃ and MoNiP/ γ -Al₂O₃ particles, with results averaged for the calcined and sulfided states, and compared to initially bare γ -Al₂O₃. Bulk characterization techniques were employed to assess the primary physicochemical properties following solids deposition and sulfidation.

The effect of deposition of both oxidic Mo and MoNiP (*i.e.*, the calcined state) on the γ -Al₂O₃ surface, as well as the following sulfidation, resulted in different surface and mesopore structures compared to the initially bare γ -Al₂O₃. As shown in Fig. 2(e), a similar decrease in PV occurred after the deposition of oxidic Mo or MoNiP and sulfidation. Additionally, the bulk PV decreased similarly after solids deposition (Fig. S3.1 and Table S3.1), suggesting preferential deposition of solids in pores ranging from 2 to 15 nm, which are more prevalent in cryo-ET specimens than in the bulk powder. Notably, cryo-ET suggests that after Mo or MoNiP deposition and sulfidation, the average pore size remained within the initial range determined for bare γ -Al₂O₃. This is also observed in the bulk, as BJH analysis of the adsorption and desorption branches, shown in Fig. S3.1(c and d), does

not reveal a significant decrease in the PSD after solids deposition or sulfidation.

In Fig. 2(f), the SSA and average strut width after solids deposition and subsequent sulfidation are depicted. The subtle trends in SSA resemble those observed in bulk (Fig. S3.1 and Table S3.1), suggesting that the SSA is primarily determined by the mesopores. Moreover, both cryo-ET and bulk show a sequential SSA decrease after solids deposition and sulfidation for Mo/ γ -Al₂O₃. In contrast, for MoNiP/ γ -Al₂O₃, the SSA decreases after solids deposition but shows a slight increase after sulfidation. In this study, it is not possible to unambiguously assign the observed increase in SSA for Mo/ γ -Al₂O₃ and the decrease for MoNiP/ γ -Al₂O₃ to specific molecular-level mechanisms. Nevertheless, these trends are likely linked to the broader structural and compositional changes occurring during sulfidation. Formation of MoS₂ involves replacement of O by S, which occupies a larger atomic volume than O in the oxidic Mo species, and visual inspection reveals accompanying changes to the γ -Al₂O₃ framework, altering its pore and surface structure. The presence of Ni and P is expected to influence MoS₂ morphology and may also affect the γ -Al₂O₃ surface after sulfidation compared with Mo-only catalysts. The average strut width, found through cryo-ET, remains within the range observed for the bare γ -Al₂O₃, implying that deposition of Mo or MoNiP does not substantially change the average strut width.

Cryo-ET descriptors inaccessible by bulk characterization revealed distinct differences in the surface and mesopore structure after calcination and sulfidation of the bare γ -Al₂O₃, Mo/ γ -Al₂O₃, and MoNiP/ γ -Al₂O₃. During calcination, aggregated molybdate structures are expected to form on the γ -Al₂O₃ surface.⁸⁴ Fig. 2(g–j) show that, compared to the bare γ -Al₂O₃, the Mo/ γ -Al₂O₃ exhibits a more tortuous pore system (*i.e.*, higher tortuosity) and a more corrugated surface (*i.e.*, broadened shape index and curvedness distribution), suggesting the formation of topographically prominent Mo domains. In contrast, the tortuosity and corrugation of MoNiP/ γ -Al₂O₃ are similar to the bare γ -Al₂O₃, suggesting that the oxidic MoNiP is distributed as a thin layer that does not alter the pores and surface. This interpretation is consistent with UV-vis DRS, suggesting smaller and thinner Mo aggregates in MoNiP/ γ -Al₂O₃ (Fig. S3.5), and Raman displaying more tetrahedrally coordinated (isolated) Mo species in Mo/ γ -Al₂O₃ (Fig. S3.6).

H₂-TPR data (Fig. S3.7) reveals that Mo/ γ -Al₂O₃ undergoes reduction at higher temperatures and exhibits a pronounced high-temperature bulk-reduction feature, consistent with strong stabilization of Mo–O–Al species. In contrast, MoNiP/ γ -Al₂O₃ shows a significant shift of the main reduction peak to lower temperatures and the disappearance of the bulk-reduction signal. This behavior reflects a markedly weakened effective metal–support interaction, arising from suppression of strong Mo–O–Al bonding and the formation of thin Mo–O–P networks near Ni. The presence of Ni and P enhances hydrogen accessibility to Mo species and thus facilitates reduction.



In future work, it will be important to gain insights into the exact location of deposited oxidic species. This requires deposits to be distinguished from the support, which was not possible for the combination of Mo and $\gamma\text{-Al}_2\text{O}_3$ in this study. There are various routes to accomplish this, such as four-dimensional (4D) scanning TEM, integrated differential phase contrast (iDPC) - STEM, or segmentation through deep learning.^{70,85,86}

During the sulfidation step, oxidic Mo converts to MoS_2 , which is the active catalyst phase. Interestingly, after sulfidation, the pore morphologies of $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ and $\text{MoNiP}/\gamma\text{-Al}_2\text{O}_3$ are quite similar yet different from the bare

$\gamma\text{-Al}_2\text{O}_3$ (Fig. 2(g-j)). During sulfidation, immobilized MoO_x species are transformed into mobile MoS_x domains, which aggregate and grow into MoS_2 slabs.⁸⁴ The resulting MoS_2 particles affect the pore structure of both $\text{MoNiP}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ similarly, suggesting that the MoS_2 particles occupy comparable positions on the $\gamma\text{-Al}_2\text{O}_3$ surface.

Direct quantification of isolated $\gamma\text{-Al}_2\text{O}_3$ and MoS_2 slabs after sulfidation

The previous section showed that the deposition of oxidic Mo or MoNiP, followed by sulfidation, resulted in a different

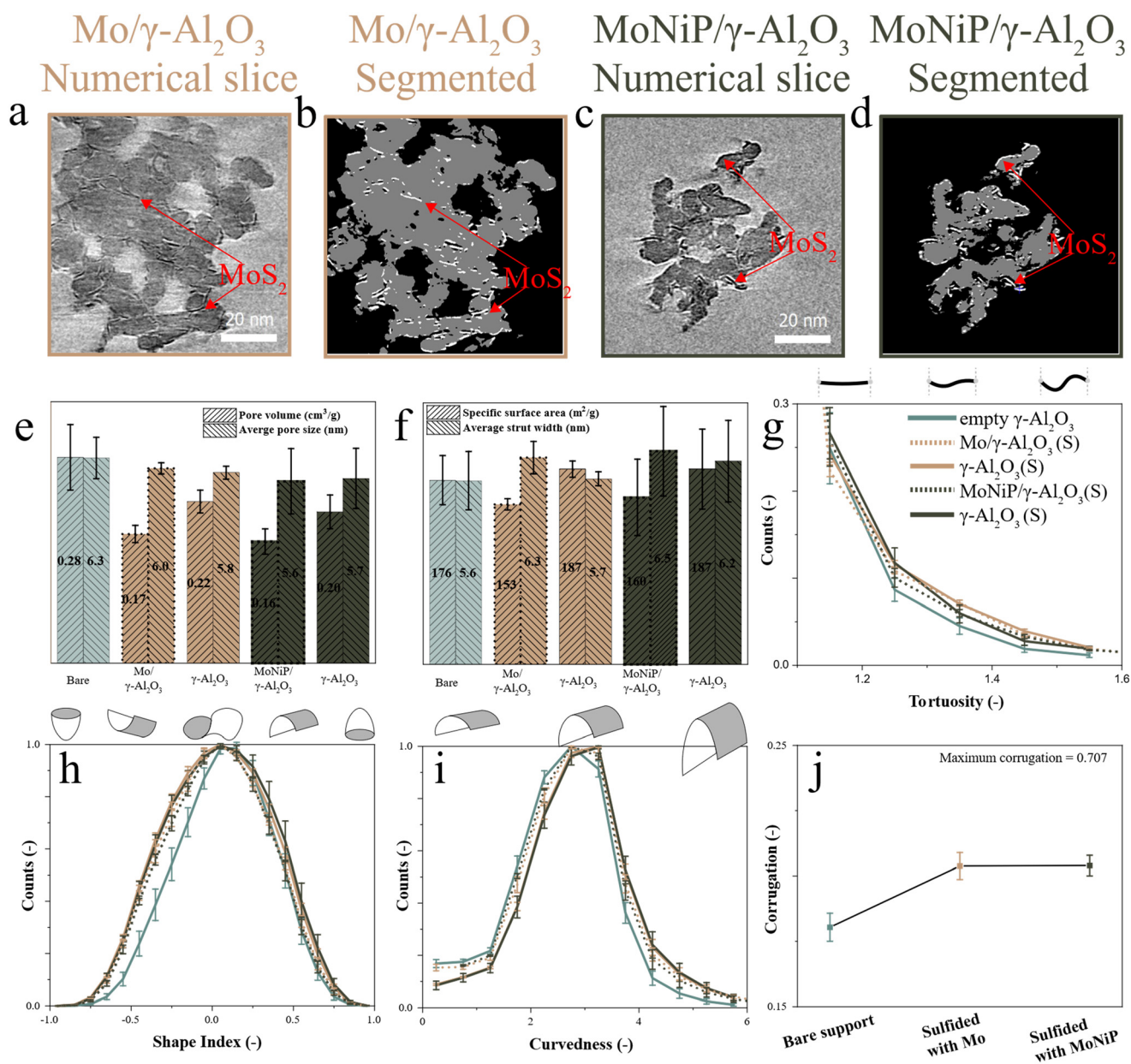


Fig. 3 Quantitative ET showing numerical cross sections (thickness = 0.19 nm) and corresponding segmented cross sections of sulfided $\gamma\text{-Al}_2\text{O}_3$ segmented from the $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ (a and b) and $\text{MoNiP}/\gamma\text{-Al}_2\text{O}_3$ (c and d). The $\gamma\text{-Al}_2\text{O}_3$ is compared to the sulfided full solids $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ and $\text{MoNiP}/\gamma\text{-Al}_2\text{O}_3$. The formed MoS_2 particles are indicated by red arrows. Quantitative analysis of the surface and pore network showing: (e) PV and average pore size; (f) SSA and average strut width; (g) tortuosity; (h) shape index, (i) curvedness; and (j) surface corrugation.



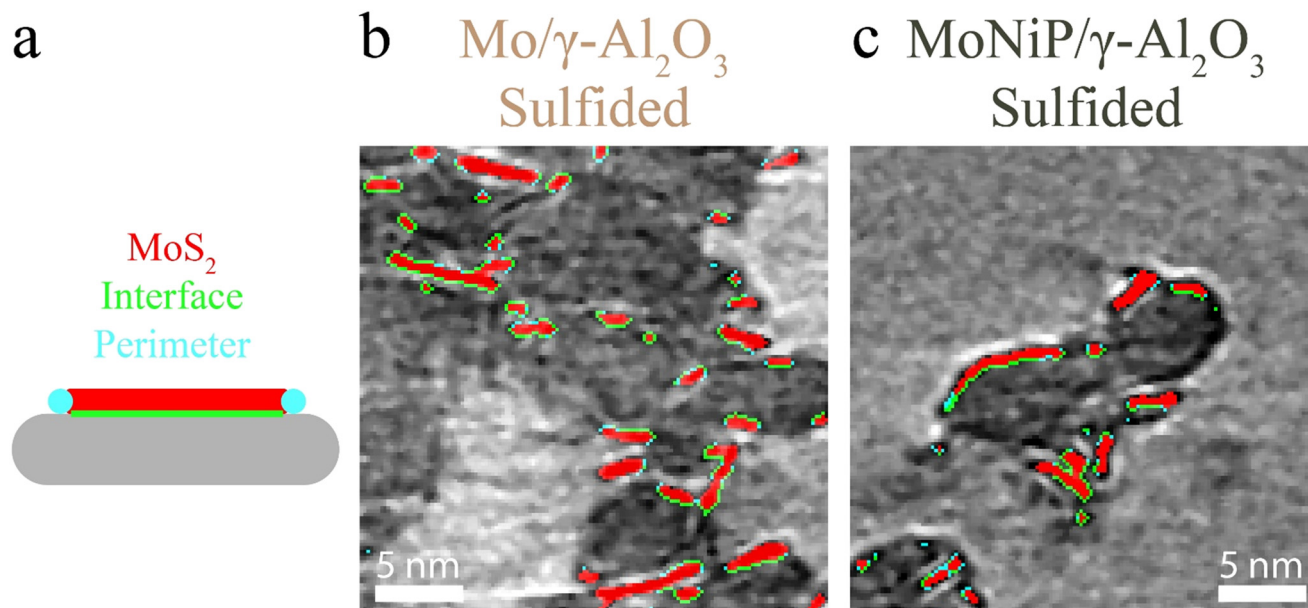


Fig. 4 (a) Schematic of the MoS₂ slab structure on a γ-Al₂O₃ surface. (b) and (c) show a zoom of a numerical slice (thickness = 0.19 nm) through cryo-ET reconstructions of sulfided Mo/γ-Al₂O₃ and MoNiP/γ-Al₂O₃, respectively. The MoS₂ (red), interface (green), and perimeter (cyan) are annotated.

Table 2 XPS, STEM-EDX, and cryo-ET quantification results of MoS₂ slabs

		MoS ₂	MoS ₂ NiP
Mo sulfidation degree (%)	XPS	73 ± 2	74 ± 5
	STEM-EDX	79 ± 6	89 ± 8
S loading (wt%)	XPS	6.5 ± 0.4	6.8 ± 0.3
	STEM-EDX	6.7 ± 0.4	6.6 ± 0.4
	Cryo-ET (in MoS ₂) ^a	5.8 ± 0.7	5.7 ± 1.6
Mo loading (wt%)	XPS	9.7 ± 0.4	9.5 ± 0.2
	STEM-EDX	12.0 ± 0.9	10.9 ± 0.5
	Cryo-ET (in MoS ₂) ^a	8.7 ± 1.0	8.6 ± 2.4
Structural descriptors found by cryo-ET	Cryo-ET (MoS ₂ + MoO _x) ^b	11.9 ± 1.4	11.6 ± 3.3
	Average MoS ₂ thickness (nm)	0.51 ± 0.13	0.54 ± 0.05
	MoS ₂ -γ-Al ₂ O ₃ (m ² g ⁻¹ cat)	15.2 ± 3.6	16.1 ± 0.9
	MoS ₂ -γ-Al ₂ O ₃ (m ² g ⁻¹ MoS ₂)	170	178
	Total slab perimeter (m ² g ⁻¹ cat)	8.1 ± 0.8	6.6 ± 2.0
	Average NN distance (nm)	2.50 ± 0.05	2.70 ± 0.20

^a Corrected to theoretical thickness and for missing wedge. ^b Corrected to theoretical thickness, for missing wedge, and incomplete sulfidation.

the NiP-promoted catalyst, which, after sulfidation, results in a larger total MoS₂ surface area in contact with the support. A lower interface area suggests a greater proportion of edge-plane connections. Additionally, the total slab perimeter reflects the interface accessible to reactants. The presence of Ni and P results in a smaller average perimeter, although the standard deviation overlaps with the Mo-only system. Finally, the average nearest-neighbor (NN) distance between slabs is comparable for Mo/γ-Al₂O₃ and MoNiP/γ-Al₂O₃.

Establishing correlations between structural descriptors obtained after catalyst preparation and activation, and catalytic performance is crucial in catalysis research. Although no catalytic tests were performed in this study, it is

well established that MoNiP/γ-Al₂O₃ exhibits enhanced HDS activity compared to Mo/γ-Al₂O₃ due to the presence of Ni.^{33,35,36,89,90} Only small structural differences, accompanied by significant variability, are observed between the slabs in the Mo/γ-Al₂O₃ and MoNiP/γ-Al₂O₃ catalyst. This may suggest that cryo-ET lacks the resolution to capture the promotional effects, which are known to arise from the formation of Ni-Mo-S active sites, where Ni is preferentially located at the sulfur-terminated MoS₂ edges.⁹⁰ Moreover, the S-edge/M-edge ratio plays a critical role in catalytic performance and can be tuned through synthesis conditions and additives.¹⁶ Baubert *et al.* demonstrated through high-resolution HAADF-STEM that the 2D shape index of MoS₂ slabs directly correlates with the exposure of M- and S-edges, and thus catalytic activity,⁸⁸



highlighting opportunities for the 3D assessment performed in this study. However, achieving such correlations requires higher imaging resolution and more sophisticated segmentation, followed by quantitative 3D slab analysis (e.g., shape index of individual slabs). Exploring these 3D quantitative structure–function relationships at the nanoscale remains largely unexplored for catalysts in general, providing a promising direction for future research.

Conclusions

This study demonstrates the capability of cryo-ET to resolve the 3D surface and mesopore structure of bare γ -Al₂O₃ supports and γ -Al₂O₃-supported hydrotreating catalysts after calcination and subsequent sulfidation. While bare γ -Al₂O₃ largely retains its structural integrity during calcination and sulfidation, cryo-ET reveals subtle variations in surface and pore descriptors that remain inaccessible to bulk characterization techniques. Deposition of oxidic Mo or MoNiP induces modest restructuring of the intrinsic γ -Al₂O₃ structure. The Mo-only catalyst shows more pronounced surface corrugation and pore tortuosity than the MoNiP catalyst, consistent with thicker Mo deposition in the absence of Ni and P, in line with trends observed in bulk characterization and literature. Following sulfidation, both Mo/ γ -Al₂O₃ and MoNiP/ γ -Al₂O₃ display overall comparable structural characteristics. Visual assessment of the γ -Al₂O₃ and the segmentation of MoS₂ slabs from its surface implies local restructuring of the underlying support. Moreover, slab segmentation indicates that they are preferentially located on sharply curved dome- and cup-like regions of the γ -Al₂O₃ surface. Despite the established influence of P and Ni on MoS₂ morphology and HDS performance, no significant differences in the 3D structural descriptors of the sulfided catalyst were detected. These findings emphasize the need for higher-resolution 3D imaging, more advanced segmentation approaches, and deeper 3D structural analysis to enable robust structure–function correlations capable of establishing a fundamental framework for identifying optimum catalyst configurations beyond the specific catalysts investigated in this study.

Author contributions

J. M. J. J. Heinrichs: conceptualization, data curation, formal analysis, investigation, methodology, project administration, resources, software, validation, visualization, writing – original draft. Th. Weber: conceptualization, funding acquisition, validation, supervision, writing – reviewing & editing. H. Friedrich: conceptualization, validation, supervision, writing – reviewing & editing. J. Zečević: conceptualization, validation, writing – reviewing & editing. A. Evtushkova: formal analysis, investigation, writing – reviewing & editing. E. J. M. Hensen: conceptualization, funding acquisition, validation, supervision, writing – reviewing & editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information (SI): S1. Calculation of corrugation value; S2. Untreated, calcined, and sulfided γ -Al₂O₃ – cross sections & segmentation of Fig. 1(a–c), and pore size distribution; S3. Bulk characterization of empty γ -Al₂O₃, Mo/ γ -Al₂O₃, and MoNiP/ γ -Al₂O₃; S4. Cryo-ET descriptor ranking of empty γ -Al₂O₃, Mo/ γ -Al₂O₃, and MoNiP/ γ -Al₂O₃; S5. Calcined & sulfided Mo(NiP)/ γ -Al₂O₃ – zoom, cross sections & segmentation of Fig. 2(a–d) and S6. Theoretical surface area of MoS₂ and missing wedge correction; S7. References. See DOI: <https://doi.org/10.1039/d5cy01396h>.

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