Ultradispersed sulfide catalysts: how many atoms for an active site?

Abstract While sulfide nanoparticles have been extensively studied for hydrotreatment catalysis, the role of few-atom sulfide clusters or single atoms in catalysts has received far less attention. Although these small entities are often present in conventional catalysts, their contribution has largely been overlooked. To date, their structure remains unclear, and it is unknown whether they can compete with sulfide nanoparticles in terms of catalytic performance. In this work, we aim to shed light onto these questions and determine the minimum number of atoms required to define the active site for three industrially relevant catalytic reactions.

Keywords **Ultradispersed catalysts, sulfide, hydrodesulfurization, hydrogen evolution, oxygen reduction, X-ray absorption.**

Résumé **Catalyseurs sulfures ultradispersés : combien d'atomes pour un site actif ?**
Alors que les nanoparticules de sulfures ont été largement étudiées pour la catalyse d'hydrotraitement, les catalyseurs contenant des amas de sulfures non cristallins, voire des atomes isolés, ont été beaucoup moins explorés. Bien que ces petites entités soient souvent présentes dans les catalyseurs conventionnels, leur rôle a été largement négligé. À ce jour, leur structure reste floue, et la façon dont elles peuvent rivaliser avec les nanoparticules de sulfures en termes de performance catalytique demeure inconnue. Dans ce travail, nous avons cherché à éclaircir ces questions et à déterminer le nombre minimal d'atomes requis pour définir le site actif pour trois réactions catalytiques d'intérêt industriel.

Mots-clés **Catalyseurs ultradispersés, sulfure, hydrodésulfuration, production d'hydrogène, réduction de l'oxygène, absorption des rayons X.**

Catalysis by transition metal sulfides: the state-of-the-art

Transition metal sulfides are widely used in catalytic reactions that require the activation of hydrogen. For instance, molybdenum sulfide MoS_2 is the main component of the industrial catalysts utilized in the hydrodesulfurization (HDS) of petroleum fractions [1], that is, the reaction by which sulfur is removed from aromatic molecules present in these fractions. Recently, MoS_2-based sulfide catalysts have also shown potential to replace highly active but expensive noble metal-based catalysts in photocatalytic/electrocatalytic hydrogen production (HER) [2-3]. ReS_2 is analogous to MoS_2 in terms of hydrogen activation, with its catalytic performance surpassing that of MoS_2 in HDS [4], and comparable in HER [5].

The functionality of $Mo(Re)S_2$-based systems is directly linked to the number of active sites located at the edges of the layered sulfide nanoparticles (*figure 1*). In order to obtain

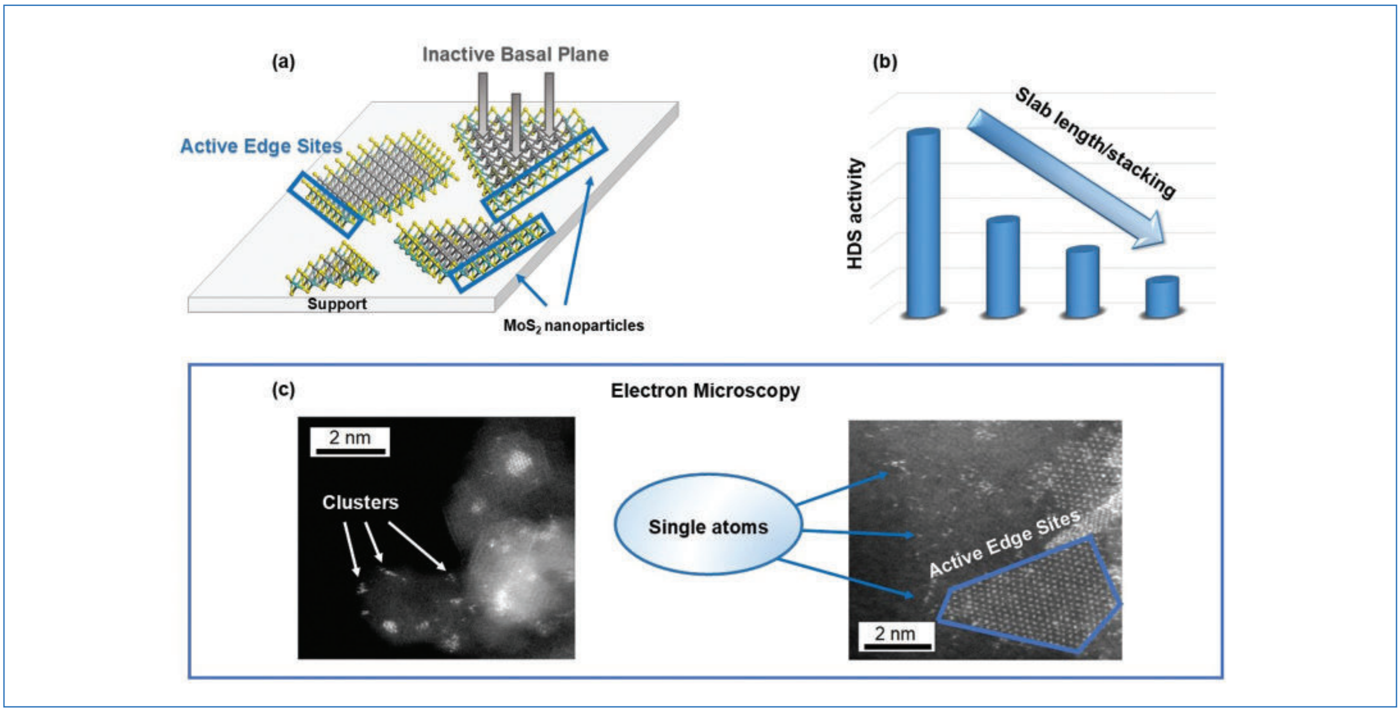


Figure 1 - (a) Model structure of supported MoS_2 showing the location of active sites. (b) Correlation between hydrodesulfurization activity and the increase of slab length/stacking. (c) HAADF-STEM microscopy images revealing small clusters and single atoms.

smaller nanoparticles exhibiting a large number of edge sites, Mo(Re)S_2 is usually dispersed over a support, for instance, carbon, silica, alumina or titania. The higher the dispersion, the shorter are the sulfide slabs, meaning that more active sites are available [1]. Numerous studies have been conducted to improve the catalytic activity of these systems through various approaches, such as different synthesis routes, modification of sulfides with other metals, and the synthesis of MoS_2 polymorphs. While major discoveries in this field have been already made (see for instance [6]), it has recently become possible to study MoS_2 catalysts at the atomic scale owing to the development of advanced characterization methods, mainly of HAADF-STEM (High Angle Annular Dark Field – Scanning Transmission Electron Microscopy) and *operando* XAS (X-ray absorption spectroscopy). In addition to the known MoS_2 sulfide slabs, it was found that disordered atomic clusters and even single atoms were present on the catalyst surface (*figure 1*) [7-8]. Yet their role in catalysis has remained unknown.

What ultradispersion is, and how it impacts catalytic activity

Catalytic phases are termed "ultradispersed", or "atomically dispersed", when the active site consists of one or a few transition metal atoms, all accessible to reactants [9]. Single-atom catalysts, a specific category of ultradispersed catalysts, have recently emerged. With near-100% atomic efficiency, these systems require minimal metal quantities and, in some cases, exhibit higher activity and selectivity than nanoparticle counterparts [10]. Most research in this field focuses on noble metal atoms grafted onto or incorporated into the support through coordination with light elements, such as oxygen or nitrogen [11]. In contrast, publications dedicated to sulfided Mo single atoms/clusters are scarce and none address rhenium [12-13]. The boundary between ultradispersed catalysts and transition metal sulfide nanoparticles remains unexplored, yet it could lead to the discovery of novel, highly active systems. Furthermore, investigating this boundary may reveal the minimum number of atoms needed to define an active site, depending on the reaction mechanism. Three model reactions are discussed here (*insert 1*): thiophene hydrodesulfurization (HDS), hydrogen evolution reaction (HER), and oxygen reduction reaction (ORR).

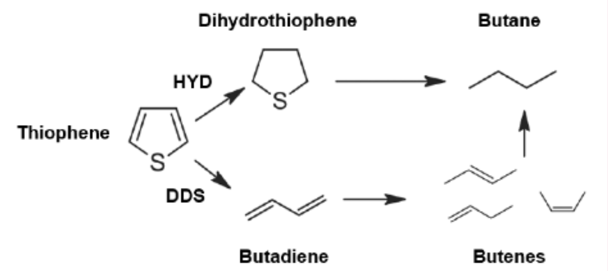
Synthesizing supported ultradispersed sulfide catalysts

The most common methods for preparing ultradispersed catalysts involve impregnation or adsorption of molecular precursors onto a suitable support. For example, adsorbing ammonium thiomolybdate $(NH_4)_2MoS_4$ onto a highly porous carbonaceous support, followed by thermal decomposition/reduction at 350 °C in H_2S/H_2, yields highly dispersed sulfidic Mo sites. At low metal loadings (0.5 wt.% Mo), adsorption under equilibrium conditions has produced catalysts containing only disordered, sulfidic Mo clusters with a few atoms, or single atoms [14]. A similar approach was used for Re catalysts: the impregnation of the same carbonaceous support with a solution of NH_4ReO_4, followed by sulfidation in H_2S/N_2 at 350 °C, has resulted in highly dispersed Re sulfidic species. However, a major challenge arises when characterizing these systems *ex situ* (under ambient conditions): while nanoparticulate sulfides oxidize over days or months, small clusters and single atoms oxidize and lose their sulfidic coordination within hours. Thus, a comprehensive characterization of sulfidic ultradispersed catalysts requires an *operando* approach (under controlled atmosphere).

Few *operando* techniques can provide insights into the state of Mo (or Re) in these clusters or single atoms, such as the number and nature of their nearest neighbors, and the formation mechanism of the species. The most powerful technique is X-ray absorption spectroscopy (XAS).

Insert 1

Some information about the reactions under study



Thiophene hydrodesulfurization (HDS) is an exothermic reaction which may proceed via two pathways:

(1) hydrogenation to tetrahydrothiophene, and subsequent desulfurization to form butane,

(2) desulfurization to butadiene, and hydrogenation to butenes (butene-1, cis-2-butene and trans-2-butene).

Hydrogen must be dissociatively adsorbed on the surface of the active phase for HDS to occur.

In the electrochemical water splitting, the **hydrogen evolution reaction (HER)** takes place on the cathode, while the oxygen evolution reaction (OER) occurs at the anode. The sulfide catalyst on the working electrode acts as the cathode, and the auxiliary electrode (graphite) works as the anode.

Hydrogen evolution reaction (HER) $4H^+ + 4e^- \rightarrow 2H_2$ ($E^0 = 0$ V)
Oxygen evolution reaction (OER) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ ($E^0 = -1.23$ V)

where E^0 are the standard potentials of the half-reactions (potentials that are needed to be reached in standard conditions for the reaction to occur, on a thermodynamic basis).

Finally, the **oxygen reduction reaction (ORR)** in alkaline medium can proceed *via* two-electron or four-electron processes:

Four-electrons $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ ($E^0 = 1.23$ V)
Two-electrons $O_2 + H_2O + 2e^- \rightarrow H_2O^- + OH^-$ ($E^0 = 0.695$ V)

Due to the low solubility of oxygen in water, the kinetics of ORR is slow, and the ORR currents observed are usually much smaller than those resulting from HER.

X-ray absorption spectroscopy and Multivariate Curve Resolution: a chemometric approach to study the formation of low-nuclearity species

XAS relies on the interaction of X-rays within a specific energy range with the electrons of the absorbing metal. When X-rays are absorbed, a core electron is ejected, and the resulting wave is scattered by the absorber's nearest neighbors. The region of the XAS spectrum within 50-100 eV of the edge jump (where electron ejection probability is highest) is called XANES (X-ray Absorption Near Edge Structure); it reveals the geometry and oxidation state of the absorbing atom. The EXAFS (Extended X-ray Absorption Fine Structure) region, at higher energies, consists of oscillations that reflect the nature, number, and distances of the nearest neighbors to the absorber. Due to the high penetration of X-rays, XAS spectra can be recorded under *operando* conditions, such as during sulfidation and catalytic reactions.

When using Quick-XAS rocking monochromators at the ROCK beamline of synchrotron SOLEIL, the state of the metal can be probed every few seconds. However, a one-hour sulfidation treatment generates hundreds of spectra, requiring extensive post-processing. To address this, the Multivariate Curve Resolution – Alternate Least Squares procedure (MCR-ALS, *figure 2*) offers a chemometric solution, significantly reducing processing effort. First, Principal Component Analysis (PCA) determines the minimum number of pure components needed to explain spectral evolution. Second, the spectra in the dataset (matrix D) are reconstructed as the product of the pure component spectra matrix (matrix ST) and a time-dependent concentration matrix (matrix C). This approach identifies the number of components present during the process and the changes of their relative concentration with temperature [15]. Only the pure component spectra require detailed analysis to identify the successive species.

We will examine the sulfidation of a sample prepared by adsorbing ammonium thiomolybdate on carbon (*figures 2-3*). After adsorption, the precursor undergoes significant changes: sulfur atoms are partially replaced by oxygen, and instead of isolated single sites, a mixture of oligomeric structures and single sites forms (Component 1). In these structures, Mo sites are primarily surrounded by oxygen atoms, with sulfur present as sulfate rather than S^{2-}. As sulfidation begins, oxygen is gradually replaced by sulfur, and Mo atoms migrate across the support surface. The initial oxidic oligomers can transform into oxysulfide species (MoO_xS_y, Component 2) and into sulfur-rich MoS_x structures (Component 3). By around 150 °C, the final fully sulfided Component 4 emerges: tetrahedral sulfidic Mo species, present as oligomers and single sites. This component further participates in the catalytic reaction. The transformation of the components does not necessarily follow the linear pathway ($1 \rightarrow 2 \rightarrow 3 \rightarrow 4$), as Component 4 can be formed from Component 2 and Component 3 from Component 1 (*figure 3*). Interestingly, while the overall sulfidation mechanism remains the same for other supports like silica, titania, or alumina, the formation temperatures of the components shift slightly. The key role of the support lies in influencing the dispersion of the final sulfidic Mo (Component 4): fully ultradispersed MoS_x species form on carbon and titania, whereas on silica and alumina, a mixture of ultradispersed species and MoS_2 nanoparticles is formed [16].

Rhenium-based systems behave similarly. However, during the sulfidation step, the sulfur-rich intermediate is skipped, and the sulfidation of oxysulfidic ReO_xS_y proceeds directly to the final sulfidic component, containing sulfidic rhenium clusters.

Toward the control of nuclearity

Overall, adsorption/impregnation methods enable the synthesis of ultradispersed species. However, these methods lack precise nuclearity control: regardless of the support or loading, the metal always exists as a mixture of different species.

Homogeneous single-atomicity can potentially be achieved through one-pot methods, leading to incorporated metal atoms. In this approach, a metal precursor (Mo, Re) is mixed with a carbon source (possibly including N, O, or S) and heated to elevated temperatures. Heteroatoms (N, O, S) can act as anchoring sites for the metal atoms, resulting in single atomic

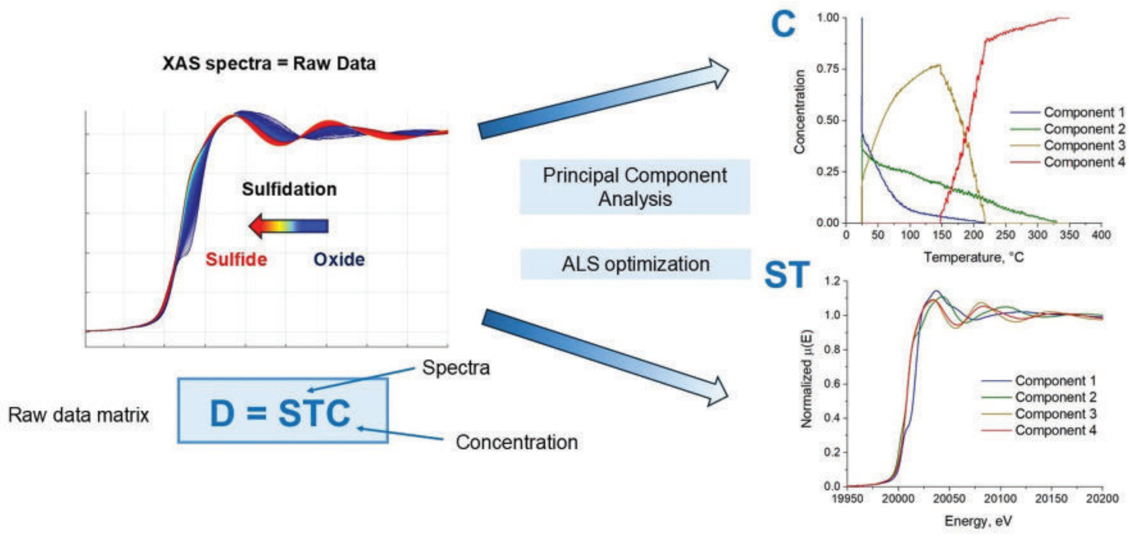


Figure 2 - A simplified scheme of the utilization of the MCR-ALS approach during sulfidation, providing XAS spectra of the pure components (ST), and their concentration profiles with increasing temperature (C).

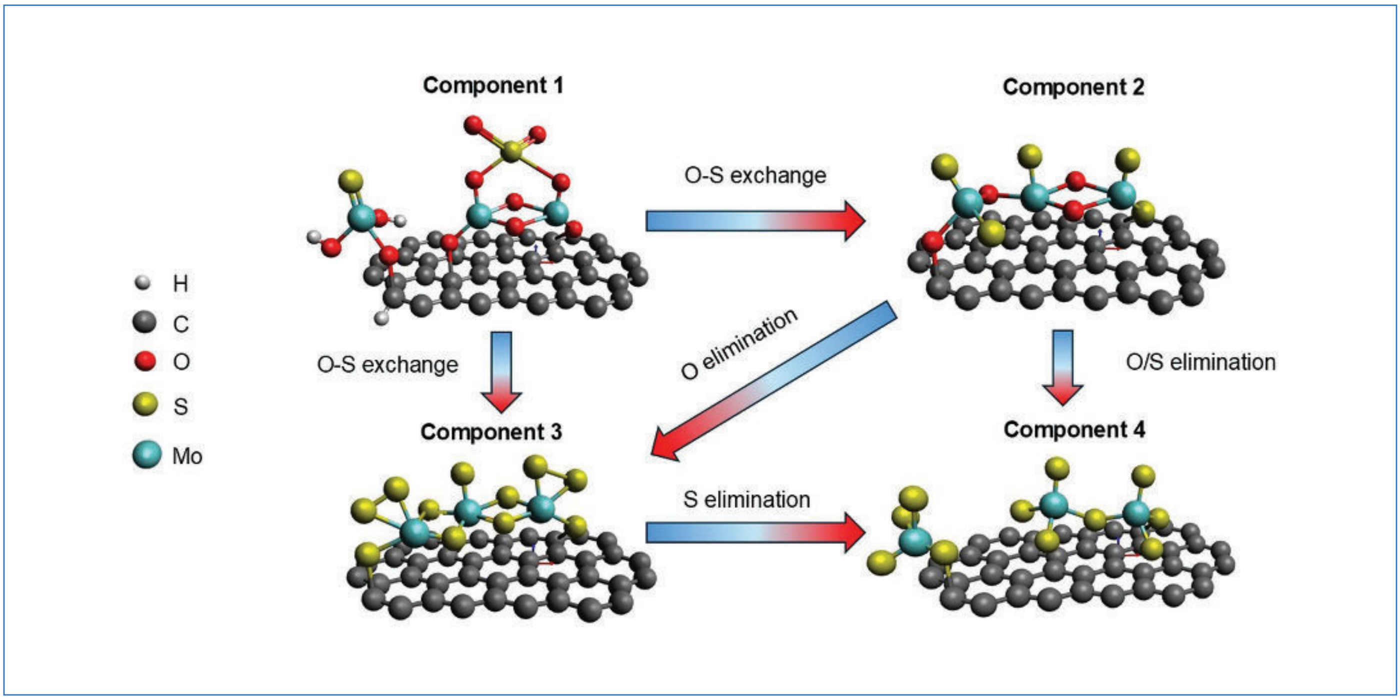


Figure 3 - Scheme illustrating the formation of supported sulfidic Mo clusters. The arrows indicate the transformations between the components.

metal sites incorporated into a carbonaceous network doped with the light elements. Since sulfur introduction is always a goal, we tested two routes: (1) mixing sulfur-containing precursors and heating in Ar at 550 °C, and (2) mixing sulfur-free precursors, heating in Ar at 550 °C, and then introducing sulfur via a sulfidation step. The first route yields variable results, highly dependent on the nature of the Mo, C, and S precursors. For example, mixing ammonium thiomolybdate with urea or thiourea produces MoS_2 slabs on carbon nitride (C_3N_4), which exhibit high activity in HDS and photocatalytic HER [17]. Mixing thiomolybdate with thioacetamide gives single atomic inactive Mo species. However, if ammonium heptamolybdate is used as a metal precursor and mixed with sulfur powder and urea, the final solids contain a high amount of metal (more than 40 wt.%) and ultradispersed Mo sites in mixed coordination of light elements (C, N, O and S), active in electrochemical HER [18].

In a second approach, phthalocyanine molecules, widely used in homogeneous catalysis, were chosen as the building block. A mixture of molybdenyl acetylacetonate (Mo precursor), urea, and pyromellitic anhydride (C and N sources) was heated to 550 °C in an Ar atmosphere. Microscopy and XAS confirmed a homogeneous distribution of Mo sites, with Mo coordinated to four in-plane nitrogen atoms (as in phthalocyanines) and two out-of-plane oxygens. During sulfidation in H_2S/H_2, sulfur replaced the out-of-plane oxygens in the Mo coordination environment (*figure 4*). Notably, these MoN_4S_2 species remain stable as single-atom sites up to 600 °C, collapsing only above 700 °C to form MoS_2.

This phthalocyanine-based approach can also be applied to rhenium. Replacing molybdenyl acetylacetonate with ammonium perrhenate yields similar single-atomic ReN_4O_2 sites. After sulfidation, ReN_4S_2 single-atom sites form, which, like Mo, collapse at temperatures above 600 °C.

The choice of precursors and carbon, nitrogen, and sulfur sources significantly influences the reaction pathway and the resulting metal sites. The phthalocyanine strategy produces homogeneous single-atom sites in mixed N, S coordination, while other methods yield diverse outcomes, ranging from MoS_2 to non-equivalent ultradispersed sites in mixed coordination.

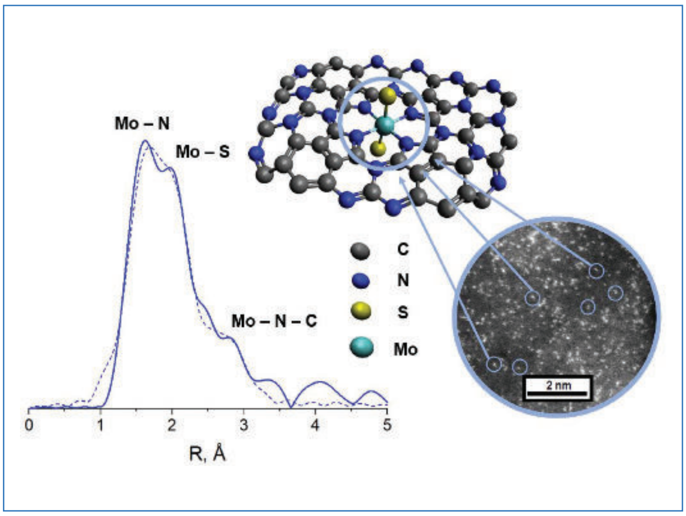


Figure 4 - EXAFS Fourier transform and microscopy image of a single-atom catalyst containing MoN_4S_2 sites in phthalocyanine-type coordination. The full lines represent EXAFS spectra and the dashed lines represent the best fit.

Catalytic activity of supported and incorporated ultradispersed systems

The catalytic systems described above were tested in reactions involving hydrogen: hydrodesulfurization (HDS) and hydrogen evolution reaction (HER), as well as in the oxygen reduction reaction (ORR). The HDS of thiophene was performed in the gas phase at 320 °C, in a hydrogen/thiophene flow. HER and ORR were carried out under electrochemical conditions, using our samples as the working electrodes, in acidic media (0.5 M H_2SO_4) for HER, and basic media (0.1 M KOH) for ORR.

Supported ultradispersed catalysts demonstrated considerable catalytic performances in the HDS of thiophene, with an activity per metal atom of 5.5 and 18 h^{-1} for Mo and Re systems, respectively. This is 5 and 2 times more than the corresponding supported MoS_2 and ReS_2 reference catalysts containing sulfide nanoparticles (*figure 5*). Interestingly, Mo and Re catalysts prepared via the phthalocyanine route were totally unactive, indicating that single atomic species are not suitable for this reaction. It is likely that one metal atom cannot handle both the adsorption of the thiophene molecule and the dissociation of hydrogen, meaning that at least two atoms are required for the increased activity [14, 16].

To compare the performances in HER and ORR, we have used the onset potential (potential that is required to break H_3O^+ or activate O_2) and the Tafel slope which characterizes the reaction rate. The lower these values, the better the catalyst. For comparison, pure Pt catalysts, which are considered to be the best in HER, possess an onset potential close to zero mV, and a Tafel slope of 30 mV/dec.

Results similar to HDS are observed in electrochemical HER. Supported sulfidic Mo and Re clusters demonstrated high activity, with respective onset potentials of 184 and 250 mV, and Tafel slopes of 114 and 186 mV/dec (*figure 5*). For such metal loadings (0.5 and 0.6 wt.%), this is an outstanding catalytic activity. However, the incorporated single-atom systems almost showed no activity, with currents comparable to the bare glassy carbon electrode. Apparently, the fully single MoN_4S_2 or ReN_4S_2 species do not have the required adsorption energy ΔG_H, and either bind the incoming proton too strongly or too weakly for its subsequent reduction.

For ORR performance, the trend was less clear. Both supported and incorporated catalysts exhibited ORR activity via a four-electron process, producing water as the main product. The onset potentials for all systems were similar, ranging from 820 to 840 mV, while the Tafel slopes followed the order: incorporated ReN_4S_2 sites (127 mV/dec) > supported sulfidic Re (96 mV/dec) > incorporated MoN_4S_2 sites (93 mV/dec) > supported sulfidic Mo (84 mV/dec) (*figure 5*).

The catalytic performance is comparable to the best reported ReS_2 and MoS_2 nanoparticulate catalysts. Although incorporated Mo(Re) systems show significant activity, ultradispersed Mo(Re) catalysts are not far behind. Both single-atom sites and small clusters appear to serve as effective adsorption sites for ORR intermediates OOH* and OH*.

Ultradispersed catalysts with few-atom clusters or single-atom systems thus exhibit varying activity depending on the reaction. For less demanding reactions like ORR, single-atom Mo or Re systems can compete with those containing oligomers. However, it seems that reactions involving hydrogen dissociative adsorption or associative desorption require more than one atom to sustain the catalytic cycle.

Some finishing strokes

For the first time, we demonstrated the high catalytic activity of ultradispersed Mo (or Re) species in a sulfidic coordination environment. Our results show that at least two metal atoms in a sulfide cluster are needed to form an active site for the reactions that involve hydrogen activation (HER, HDS). These findings hold both fundamental and practical importance.

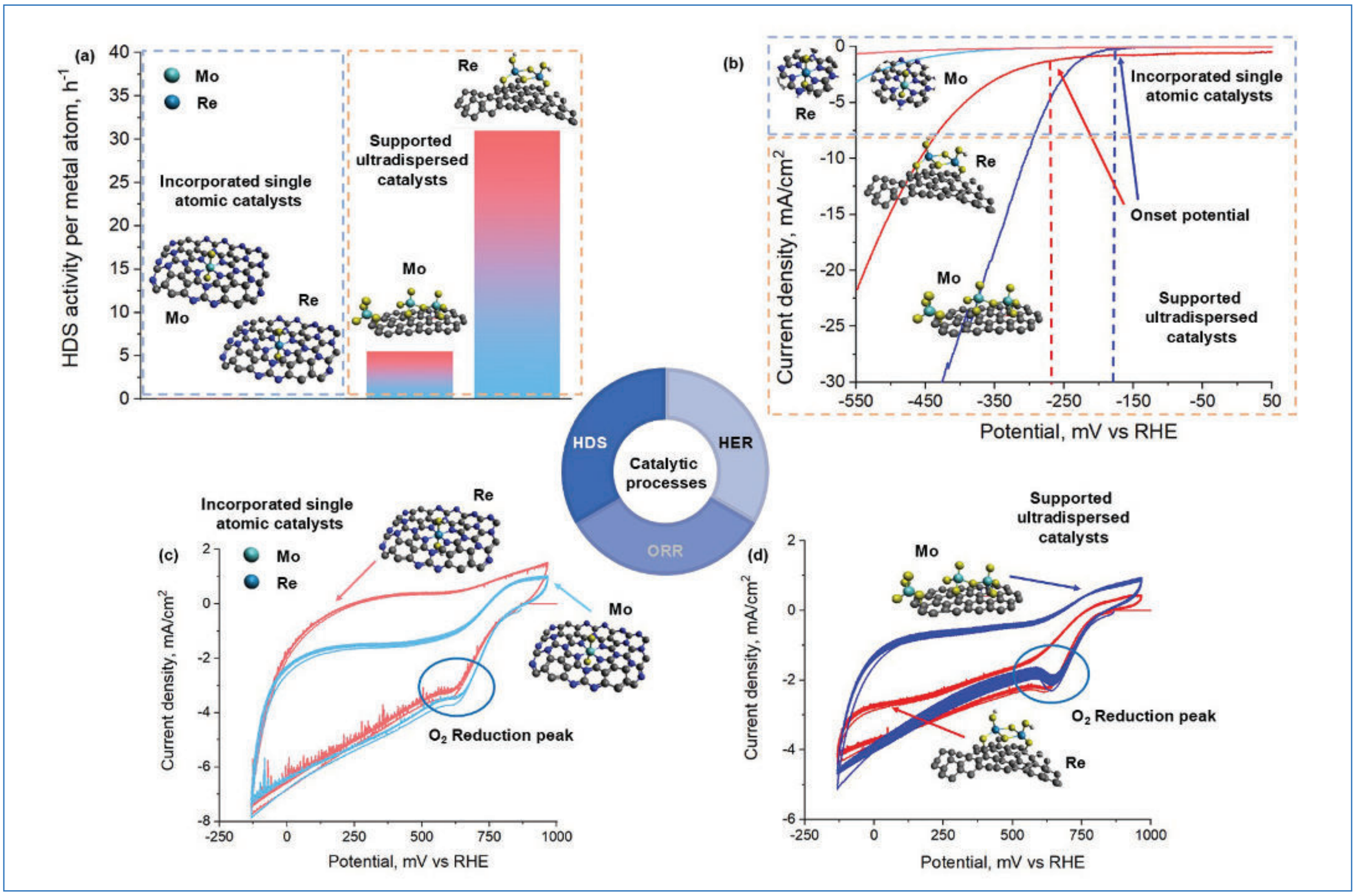


Figure 5 - Catalytic activity of the ultradispersed supported and incorporated single atomic catalysts based on Mo and Re: (a) in HDS, (b) in electrochemical HER, and (c-d) in ORR. For (a) and (b), the dashed rectangles separate the incorporated systems from supported ones.

Fundamentally, the conventional model, which focuses solely on sulfide slabs and their edge atoms, requires reevaluation, as small clusters – often present alongside sulfide slabs – can also act as active sites. Practically, our systems could be applied to other reactions, such as hydrogenation/dehydrogenation. Further improvements should focus on precise nuclearity control and exploring other transition metals, like Co, Ni, or Cu.

[1] H. Topsøe, B.S. Clausen, Active sites and support effects in hydrodesulfurization catalysts, *Appl. Catal.*, **1986**, *25*, p. 273-93.

[2] R. Li *et al.*, Recent advances in MoS_2-based materials for electrocatalysis, *Chem. Commun.*, **2022**, *58*, p. 2259-78.

[3] Z. Li, X. Meng, Z. Zhang, Recent development on MoS_2-based photocatalysis: A review, *J. Photochem. Photobiol. C: Photochem.*, **2018**, *35*, p. 39-55.

[4] N. Escalona, M. Vrinat, D. Laurenti, F.J. Gil Llambías, Rhenium sulfide in hydrotreating, *Appl. Catal. A: Gen.*, **2007**, *322*, p. 113-20.

[5] Y. Zhou *et al.*, Auto-optimizing hydrogen evolution catalytic activity of ReS_2 through intrinsic charge engineering, *ACS Nano*, **2018**, *12*, p. 4486-93.

[6] P. Afanasiev, Synthetic approaches to the molybdenum sulfide materials, *C.R. Chim.*, **2008**, *11*, p. 159-82.

[7] L. Zavala-Sanchez, X. Portier, F. Maugé, L. Oliviero, Formation and stability of CoMoS nanoclusters by the addition of citric acid: A study by high resolution STEM-HAADF microscopy, *Catal. Today*, **2021**, *377*, p. 127-34.

[8] B. Baubet *et al.*, Quantitative two-dimensional (2D) morphology-selectivity relationship of CoMoS nanolayers: A combined high-resolution high-angle annular dark field scanning transmission electron microscopy (HR HAADF-STEM) and density functional theory (DFT) study, *ACS Catal.*, **2016**, *6*, p. 1081-92.

[9] L. Piccolo, Restructuring effects of the chemical environment in metal nanocatalysis and single-atom catalysis, *Catal. Today*, **2021**, *373*, p. 80-97.

[10] B. Qiao *et al.*, Single-atom catalysis of CO oxidation using Pt_1/FeO_x, *Nat. Chem.*, **2011**, *3*, p. 634-41.

[11] R. Li *et al.*, Single atoms supported on metal oxides for energy catalysis, *J. Mater. Chem. A*, **2022**, *10*, p. 5717-42.

[12] R. Khare *et al.*, Di- and tetrameric molybdenum sulfide clusters activate and stabilize dihydrogen as hydrides, *JACS Au*, **2022**, *2*, p. 613-22.

[13] C. Tang *et al.*, Coordination tunes selectivity: Two-electron oxygen reduction on high-loading molybdenum single-atom catalysts, *Angew. Chem. Int. Ed.*, **2020**, *59*, p. 9171-76.

[14] D. Ryaboshapka *et al.*, Ultradispersed (Co)Mo catalysts with high hydrodesulfurization activity, *Appl. Catal. B: Environ.*, **2022**, *302*, 120831.

[15] A. Rochet, B. Baubet, V. Moizan, C. Pichon, V. Briois, Co-K and Mo-K edges Quick-XAS study of the sulphidation properties of Mo/Al_2O_3 and $CoMo/Al_2O_3$ catalysts, *C.R. Chim.*, **2016**, *19*, p. 1337-51.

[16] D. Ryaboshapka *et al.*, Genesis of active phase and support effect in ultradispersed Mo sulfide catalysts, *ACS Catal.*, **2023**, *13*, p. 10511-26.

[17] D. Ryaboshapka, P. Bargiela, L. Piccolo, P. Afanasiev, On the electronic properties and catalytic activity of MoS_2-C_3N_4 materials prepared by one-pot reaction, *Int. J. Hydrog. Energy*, **2022**, *47*, p. 34012-24.

[18] D. Ryaboshapka, P. Afanasiev, One-pot synthesis of amorphous high entropy Mo–C–N–O–S solids with ultradispersed Mo sites, *J. Mater. Sci.*, **2024**, *59*, p. 20982-96.

Daria RYABOSHAPKA*, postdoctoral researcher, and **Pavel AFANASIEV**, senior researcher, Institut de recherches sur la catalyse et l'environnement (IRCELYON), UMR 5256, CNRS/Université Claude Bernard Lyon 1, Villeurbanne.

*daria.ryaboshapka@ircelyon.univ-lyon1.fr

D. Ryaboshapka

Daria RYABOSHAPKA a reçu le Prix de thèse 2024 de la division Catalyse (DivCat) de la Société Chimique de France.