



HAL
open science

Direct evidence of the role of Co or Pt,Co single atom promoters on the performance of MoS₂ nanoclusters for hydrogen evolution reaction

Luz Zavala, Kavita Kumar, Vincent Martin, Frédéric Maillard, Françoise Maugé, Xavier Portier, Laetitia Oliviero, Laetitia Dubau

► To cite this version:

Luz Zavala, Kavita Kumar, Vincent Martin, Frédéric Maillard, Françoise Maugé, et al.. Direct evidence of the role of Co or Pt,Co single atom promoters on the performance of MoS₂ nanoclusters for hydrogen evolution reaction. *ACS Catalysis*, 2023, 13, pp.1221-1229. 10.1021/acscatal.2c05432 . hal-03912300

HAL Id: hal-03912300

<https://hal.science/hal-03912300v1>

Submitted on 23 Dec 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Direct evidence of the role of Co or Pt,Co single atom promoters on the performance of MoS₂ nanoclusters for hydrogen evolution reaction

Luz A. Zavala¹, Kavita Kumar³, Vincent Martin³, Frédéric Maillard³, Françoise Maugé¹, Xavier Portier², Laetitia Oliviero^{,1}, Laetitia Dubau^{*,3}*

¹Laboratoire Catalyse et Spectrochimie, Normandie Université, ENSICAEN, UNICAEN, 6, bd du Maréchal Juin, 14050 Caen, France.

²Centre de recherche sur les Ions, les Matériaux et la Photonique, CEA, UMR CNRS 6252, Normandie Université, ENSICAEN, UNICAEN, CNRS, 6, bd du Maréchal Juin, 14050 Caen, France.

³Univ. Grenoble Alpes, CNRS, Grenoble INP, Univ. Savoie Mont Blanc, LEPMI, 38000 Grenoble, France

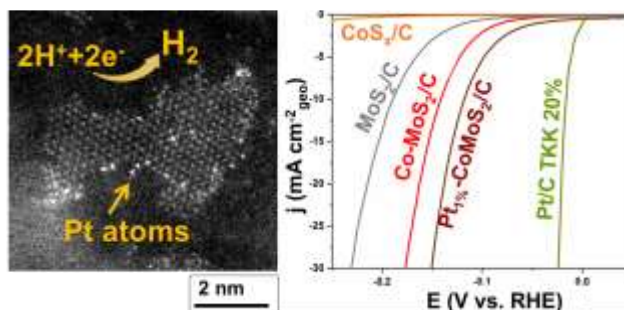
*Corresponding authors

KEYWORDS. Proton Exchange Membrane Water Electrolyzer (PEMWE), Non-noble electrocatalyst, Hydrogen Evolution Reaction (HER), Single Atom Promoted Molybdenum Sulfides, Durability.

ABSTRACT.

Developing alternatives to platinum (Pt) and iridium (Ir) in proton exchange membrane water electrolyzers is crucial on the way to **viable** energy provision schemes. However, although it seems difficult to substitute Ir, alternatives exist for Pt at the PEMWE cathode. Here, we report on the synthesis and the characterization of efficient and durable hydrogen evolution reaction (HER) nanocatalysts based on MoS₂ supported on high surface area carbon. Citric acid was used as a chelating agent to control the size of the crystallites (1.4 nm) and thus the density of active sites (slab edges). Inspired by successful approaches in catalysis for hydrodesulfurization reactions, conventional 2H MoS₂ was sequentially doped with cobalt (Co) then 1 wt. % of Pt. Overpotentials of 188 mV, 140 and 118 mV at 10 mA cm⁻² are reported for MoS₂/C, Co-MoS₂/C and Pt_{1%}-CoMoS₂/C, respectively. This result is attributed to the weakening of H_{ads} binding energy of the promoted MoS₂ edge active sites (because the promoting atoms are mostly located at the edges). Associated with small metal dissolution rates (monitored *in situ*, during HER), our findings demonstrate that metal promotion (doping) is a promising route to replace platinum by earth-abundant elements in acidic water electrolyzers.

Graphical Abstract.



1. INTRODUCTION.

The deleterious effects of greenhouse gases on the earth's climate trigger an intensive search for environmentally friendly alternative energy resources.¹ In that frame, renewable energies are promising candidates but large-scale energy storage systems are required to counterbalance their intermittency. Electrochemical and photoelectrochemical water electrolyzers are best suited to use the surplus of electrical energy produced from renewables and produce molecular hydrogen (H₂), an energy vector with high energy density and minimal environmental impact. However, at the moment, only proton exchange membrane electrochemical water electrolyzers (PEMWE) can withstand the rapid and large-amplitude variations of power induced by wind turbines or solar photovoltaics. Platinum (Pt) nanoparticles in the range of 2-3 nm supported on high surface carbon are the benchmark catalyst to electrocatalyze the hydrogen evolution reaction (HER) at PEMWE cathodes² but the scarcity and the high price of this metal calls for alternative catalysts based on earth-abundant elements.³

Molybdenum sulfide (MoS₂) has been identified as a promising material to electrocatalyze the HER due to its high catalytic activity and its stability over a wide potential and pH range.^{4,5} The molybdenum disulfide structure (MoS₂) consists of two-dimensional layered materials whose S-Mo-S layers are held together by Van der Waals interactions and are separated by 6.5 Å (trigonal coordinated structure 2H). Each layer is composed of two hexagonal planes of sulphur (S) atoms and an intermediate hexagonal plane of molybdenum (Mo) atoms. MoS₂ slabs mainly exhibit two types of edges: Mo-terminated edge (M-edge) and S-terminated edge (S-edge).^{6,7} By linearly correlating the HER activity with the density of edge sites on model gold (111) supported MoS₂ nanoparticles, Hellstern *et al.* evidenced that M-terminated edges are active sites for the HER.⁸ Therefore, a first approach to enhance the catalytic performance of these materials consists in controlling the morphology and the dispersion of MoS₂ slabs (*i.e.* the HER activity per geometric

surface area). Pushed to the limit, this strategy has led to the design of active $[\text{Mo}_3\text{S}_{13}]^{2-}$ clusters although their stability is questionable.⁸

Another strategy to enhance the intrinsic HER activity of MoS_2 consists in using promoter metals.^{9,10} Indeed, the addition of Co or nickel (Ni) promoters to the MoS_2 structure has been shown to enhance the catalytic activity for the widely studied hydrotreating reaction (HDT) by one order of magnitude.¹¹ The incorporation of promoter atoms takes place exclusively at the edges and modifies the S-metal bond energy leading to a reduction of the S coverage on the active metal sites that weakened H_{ads} binding energy.¹² On the other hand, faster HER kinetics has been reported of MoS_2 upon doping with single metal atoms. For example, Zhang *et al.* reported higher HER performance through doping the basal plane of the MoS_2 slab with Ru single atoms, which they rationalized by combined synergistic effects of single atom Ru doping and generation of S vacancies.¹³ Similarly, other metals like Cu, Pt and Pd have been employed, and it was reported that the doping metal integration boosts the catalytic performance through the activation of the basal plane.^{10,14,15} However, active sites are located on the edges of MoS_2 and local atomic doping essentially takes place at the edges. For example, Weise *et al.* reported a catalyst with Pt integrated at the edges that resulted substantially better in HDS catalytic performance.¹⁶ Consequently, the role of doping is still unclear.

The present work aims at disentangling whether the beneficial effect in activity is due to the doping itself or to an indirect effect impacting the density of edge sites by synthetically designing high surface area carbon-supported MoS_2 and Co- MoS_2 with similar morphology, size and dispersion. Besides Co, Ni, rhodium (Rh), Ir and Pt-Co- MoS_2 trimetallic catalysts have been also reported to outperform Co- MoS_2 for the HDT.^{16,17} Inspired by these studies and owing to the

parallel existing between HER and HDT, both reactions involving H adsorption, we thus extend our synthetic approach to Co-MoS₂/C doped with 1 wt. % Pt (Pt_{1%}-CoMoS₂/C).

2. EXPERIMENTAL SECTION.

2.1. Catalysts Preparation.

The three studied catalysts: MoS₂/C, Co-MoS₂/C and Pt_{1%}-CoMoS₂/C were prepared by incipient wetness impregnation method following a previously reported method.¹⁸ The carbon black support (Vulcan XC 72 Cabot Corp., specific surface area of 223 m².g⁻¹ and pore volume of 0.41 mL g⁻¹) was used as-received. The aqueous impregnation solutions were prepared with a defined amount of ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, Merck) as well as a defined amount of citric acid (C₆H₈O₇·H₂O, Prolabo) in order to obtain CA/(M) = 2, (M=Mo, Co, Pt). *In previous work, we have shown that citric acid forms complex with Mo and thus decreases the rate of MoS₂ formation during the sulfidation step leading to small slab length. In this work, we took benefit from these findings by adjusting the amount of citric acid to the total molar concentration of metal but the variation was limited to achieve a constant pH of the impregnation solution.*¹⁸ For the Co-promoted MoS₂ sample, (Co (NO₃)₂·6H₂O, Alfa Aesar) was used with an atomic ratio equal to Co/Co+Mo= 0.3. For the Pt_{1%}-CoMoS₂/C sample, ammonium hexachloroplatinate (IV) (NH₄)₂PtCl₆ Merck) was used. The content of Mo, Co was fixed to typical values used in representative industrial catalysts (11 wt. % Mo, ~3 wt. % Co and 1 wt.% Pt).¹⁶ Finally, to obtain the catalyst in their sulfide form, a sulfidation procedure was performed at 623 K with a heating rate of 3 K min⁻¹ at 0.1 MPa for 2 h under a 30 cm³ min⁻¹ flow of 10% H₂S/H₂.

2.2. HER (Hydrogen Evolution Reaction) Activity Measurements.

Homogenous catalytic inks were prepared by mixing the catalyst powder, a Nafion[®] suspension (5 wt. % in *n*-propanol), isopropanol, and ultrapure water (Millipore, 18.2 M Ω cm at $T = 293$ K, total organic compounds < 3 ppb). An aliquot of this ink was then deposited onto the working electrode, a glassy carbon disk of 5 mm diameter. Then, the Nafion[®] and other solvents were evaporated. The catalyst loading was 300 $\mu\text{g}_{\text{powder}} \text{cm}^{-2}$ for the HER activity measurements. All electrochemical measurements were carried out using a bi-potentiostat (Autolab PGSTAT302N) operated with NOVA 2.0 software. All glassware used in this work was cleaned using a H₂SO₄/H₂O₂ (50 % v/v) solution before use. We used a four-electrode electrochemical cell thermostated at $T = 298$ K. A carbon plate and a freshly prepared home-made reversible hydrogen electrode (RHE) were used as counter-electrode and reference electrode, respectively. The electrochemical experiments were carried out using a rotating disk electrode. For each sample, 10 HER cyclic voltammograms (CVs) were recorded between 0.1 and -0.3 V vs. RHE at $\nu = 10$ mV s⁻¹ in Ar-saturated 0.5 M H₂SO₄ electrolyte at $T = 298$ K and at 1600 rpm. The metric used to compare the different electrocatalysts was the value of the overpotential reported at a current density of 10 mA cm⁻² (η_{10}). All electrochemical data were dynamically iR corrected, where the solution resistance was determined by electrochemical impedance spectroscopy.

2.3. Microscopy Observation by HR STEM-HAADF.

The images of the catalysts after sulfidation shown in this work were obtained using a double corrected JEOL ARM 200F cold FEG microscope operated at 200 kV. The nanostructure and morphology of the MoS₂ and Co-MoS₂/C or Pt_{1%}-CoMoS₂/C slabs were analyzed by high resolution scanning transmission electron microscopy (HR STEM) using a high angle annular dark field (HAADF) detector. The particle length was considered as the longest distance measured in each particle. The length distributions of sulfide slabs were determined statistically by measuring

at least 100 slabs per sample. Only those particles that present 2H symmetry are considered, that is, isolated atoms or groups of few atoms in which it cannot be concluded with certainty that they correspond to the MoS₂ phase (present in a very low fraction) are excluded. The image treatment was performed using the commercial software GMS3 from GATAN Inc. DigitalMicrograph[®]. The average length (\bar{L}) were calculated according to previous methodology described in Refs. ^{19,20}.

2.4. MoS₂ Phase characterization: X Ray Diffraction and Raman spectroscopy.

The X-ray powder diffraction (XRD) patterns were obtained on a XPERT-PRO diffractometer (Cu α radiation $\lambda = 1.5401$) in the 2θ range of 5-75° at a scanning rate of 1° min⁻¹, analyzing the samples in their sulfide form. Raman spectroscopy was performed on the sulfide catalysts using a Jobin Yvon Labram 300 Raman spectrometer equipped with a confocal microscope, an Nd-YAG laser ($\lambda=532$ nm) and a charge coupled device detector.

2.5. Inductively coupled plasma mass spectroscopy (ICP-MS) coupled to electrochemical flow cell.

The metal ions (⁹⁴Mo, ⁵⁹Co and ¹⁹⁵Pt) were detected online with a PerkinElmer NexION 2000c inductively coupled plasma mass spectrometer coupled with a home-made electrochemical flow cell. These analyses are referred to *in situ* FC-ICP-MS measurements in the work. Prior to the *in-situ* FC-ICP-MS measurements, calibration curves were determined with daily prepared calibration solutions of ⁹⁴Mo, ⁵⁹Co and ¹⁹⁵Pt at 0, 5, 10 and 20 $\mu\text{g L}^{-1}$. We used standard solutions (Carl Roth GmbH & Co.) diluted with 0.05 mol L⁻¹ H₂SO₄ (Suprapur[®] 96 %, Merck) in ultrapure water (MilliQ, 18.2 M Ω cm, TOC < 3 ppb) for calibration. Calibrations were made before and after each FC-ICP-MS experiment to check the apparatus drift (inferior at 3 %). A three-electrode configuration and an Autolab potentiostat (PGSTAT302N) were used for the FC-ICP-MS measurements. A commercial microelectrode Ag/AgCl/3.4 M Cl⁻ (ET072, eDAQ) and a glassy

carbon rod (SIGRADUR[®], HTW) were used as the reference and counter electrode, respectively. The working electrode was a glassy carbon disk (5 mm diameter) embedded into a Teflon cylinder. The catalytic suspensions were prepared by mixing 16 mg of catalytic powder with 54 μL of a 5.0 wt. % Nafion[®] solution (Electrochem. Inc.), 1125 μL of isopropanol and 700 μL of ultrapure water. 5 μL of the ultrasonically homogenized suspension was deposited into the working electrode, resulting in a catalyst loading of 20 $\mu\text{g}_{\text{Mo}} \text{cm}^{-2}$. The electrolyte consisted of a 0.05 mol L⁻¹ H₂SO₄ solution de-aerated with argon (Ar, 99.999%, Messer) was pumped through the flow cell with a constant flow of 430 $\mu\text{L min}^{-1}$ using a peristaltic pump. For the metal detection, the flow cell outlet was connected to the ICP-MS nebulizer. The dwell time used was 100 ms with 1 replicate by reading. During the FC-ICP-MS measurements, the delay time between the Autolab and the ICP-MS signal was experimentally synchronized. Practically speaking, one potential pulse was applied, resulting in high intensity ICP-MS signal and providing the response time (usually inferior to 4 s). Twenty cyclic voltammograms (CVs) between 0.1 and -0.2 V vs. RHE at $\nu = 10 \text{ mV s}^{-1}$ were performed. The experiments were performed at room temperature ($T = 295 + 2 \text{ K}^\circ$) and all potentials are referred vs. the RHE. All *in situ* FC-ICP-MS measurements were performed at least two times and average values of the metal dissolution are shown. Error bars correspond to the standard deviation.

3. RESULTS AND DISCUSSION.

3.1. 2H MoS₂ Phase characterization.

Figure 1a shows the XRD patterns of the three synthesized MoS₂ catalysts. The broad peaks detected are an evidence of small particle size nevertheless it is possible to observe reflections that correspond to MoS₂ hexagonal structure (molybdenite, ICSD card No. 98-002-1880). The two

bands centered at 379 (E_{2g}^1 mode) and 403 (A_{1g} mode) cm^{-1} characteristic of a hexagonal MoS_2 symmetry provide further evidence that the 2H structure of MoS_2 was synthesized (**Figure 1b**).

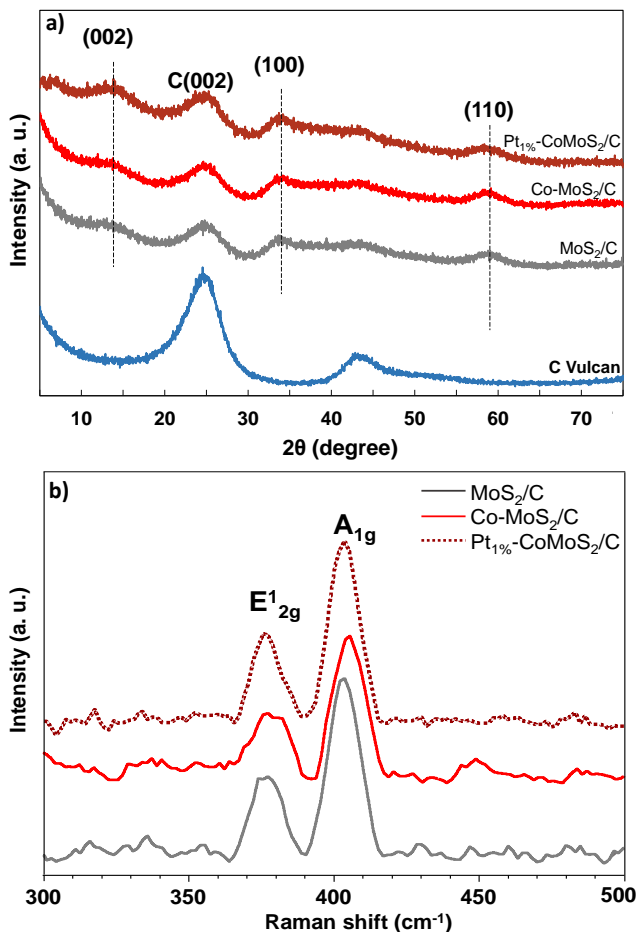


Figure 1. Structural characterization of the 2H MoS_2 phase. (a) XRD patterns of MoS_2/C , $\text{Co-MoS}_2/\text{C}$ and $\text{Pt}_{1\%}\text{-CoMoS}_2/\text{C}$ and of the high surface area carbon support (Vulcan XC 72) used as support. (b) Raman spectra of MoS_2/C , $\text{Co-MoS}_2/\text{C}$ and $\text{Pt}_{1\%}\text{-CoMoS}_2/\text{C}$ supported on carbon catalysts showing the corresponding signals of 2H- MoS_2 structure.

3.2. Electron Microscopy by HR STEM HAADF.

Figure 2 shows representative STEM-HAADF images with atomic resolution to get insights on the morphology of the MoS_2/C , $\text{Co-MoS}_2/\text{C}$ and $\text{Pt}_{1\%}\text{-CoMoS}_2/\text{C}$ catalysts. The typical morphology of the three catalysts consists of extended MoS_2 plates, as previously observed for

Al₂O₃ supported catalysts.²⁰ The formation of the thermodynamically stable trigonal prismatic 2H MoS₂ lattice structure is revealed by the typical separation of about 0.63 nm detected on stacked slabs.²¹ When observed in detail with greater magnification, it appears that the plates consist of very tiny particles with a mean size of 1.4 ± 0.2 nm for MoS₂, 1.4 ± 0.2 nm for Co-MoS₂/C and 1.5 ± 0.2 nm for Pt_{1%}-CoMoS₂/C. These small mean lengths are in line with the observed broad diffraction peaks (**Figure 1a**). Note that these values were obtained by measuring the longest transverse distance detected in the particle, from the enhanced contrast HAADF images rather than from traditional TEM images. Indeed, TEM images feature a poor contrast between the carbon support and the MoS₂ slabs. Furthermore, the fringes of the carbon support can be confused with MoS₂ slabs, adding additional error in the estimation of the particle size. Hence, only advanced HAADF images allows to rigorously monitor the size and shape of sulfide materials supported on carbon. The formation of tiny single layer particles of less than one nanometer as well as clusters of few atoms were also detected (**Figure 2 b, e, h**). The obtained images evidenced that Co and Pt addition had neither changed the size nor the shape of the slabs. In HAADF mode, the intensities of the contrast are directly proportional to the atomic number (*Z*) of the elements at the power 1.7,⁷ leading to contrast variations between the Pt (*Z* = 78) and the Mo (*Z* = 42) or Co (*Z* = 27) atoms, as shown in **Figure 2(g-h)**. The atoms located in the bulk of the slabs present homogeneous brightness while some of the atoms at the edges appear brighter, with intense contrast.

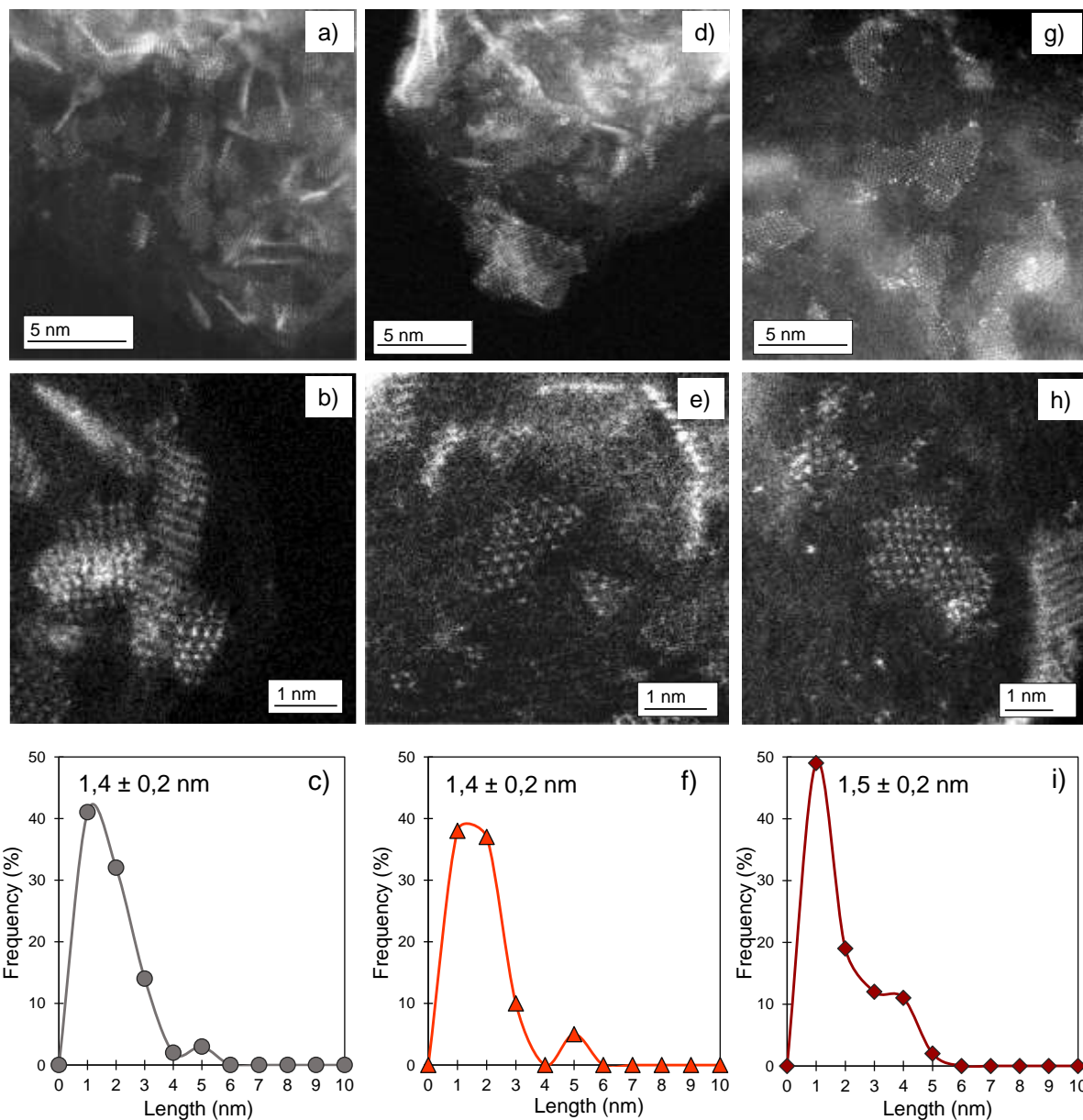


Figure 2. High-resolution STEM-HAADF micrographs of particles and length frequency histograms of (a-c) MoS_2/C , (d-f) $\text{Co-MoS}_2/\text{C}$, (g-i) $\text{Pt}_1\%-\text{CoMoS}_2/\text{C}$ catalysts.

These variations in contrast can be ascribed to Pt atoms being located at the edges while Mo atoms are in the bulk, and they provide atomic-scale evidences of the promotion of the MoS_2 edges with Pt atoms. On the contrary, the location of Co atoms on the edges of MoS_2 slab is not as

easily observed by contrast variations despite the far difference in atomic numbers between Co and Mo atoms. This may be due to the depth variations typical of a material supported on a 3D architecture such as carbon black. Nevertheless, the improvement of catalytic performance for HDS agrees with the decoration effect of Co, as previously reported for CoMoS slabs.²⁰

3.3. HER Electrocatalytic activity of sulfides-based materials.

Figure 3 displays the HER performance of the three MoS₂-based catalysts and of carbon black supported Pt nanoparticles (Pt/C) as a reference. The best performance was observed for the commercial Pt/C catalyst, and the MoS₂-based/C materials ranked as Pt_{1%}-CoMoS₂/C > Co-MoS₂/C > MoS₂/C. The overpotential required to reach a geometrical current density of 10 mA cm⁻²_{geo} (η_{10}) was used as a metric to compare the HER activity of the MoS₂-based materials. An overpotential of 188 mV was reported for MoS₂/C, consistent with previous reports for nanostructured MoS₂, in particular for [Mo₃S₁₃]²⁻ nanoclusters anchored on N-doped carbon nanotubes (**Figure 3b**).²² Promotion by Co atoms at the edges of MoS₂ clusters led to a 48 mV decrease of the η_{10} value. Doping with single Pt atoms further decreased the η_{10} value by 22 mV, **slightly moving towards** the performance of the reference Pt/C.^{10,23} As the crystallite size, and thus the density of active sites, was identical for the three catalysts, we ascribed this performance to an electronic effect induced by the promoter Co and Pt atoms. Moreover, a cobalt sulfide supported on carbon black, CoS_x/C, synthesized using the same approach poorly performed towards the HER (**Figure 1a**, orange curve), confirming that the HER activity enhancement observed in Co-MoS₂/C is not due to added activities between two separated phases. **On the Pt side, former findings from Chia et al. have revealed that PtS₂ is active towards HER in acidic media.**²⁴ However, the overpotential required to reach a current density of 10 mA cm⁻² amounts to 862 mV for the PtS₂ catalyst compared to 118 mV for Pt_{1%}-CoMoS₂/C. The Tafel slope observed for the PtS₂ material

is also 3 times higher (216 mV dec⁻¹) in comparison to Pt_{1%}-CoMoS₂/C (68 mV dec⁻¹). For these reasons, should PtS_x species be formed during the synthesis, they would poorly contribute to the HER activity. Rather, we argue that the intimate contact between Co/Pt atoms and the MoS₂ slabs is responsible for HER activity enhancement. Our results evidenced that Pt and Co doping enhances the HER activity suggesting that different active sites may have formed. Evidence has been provided from the HDT reaction that Mo and S atoms located at the proximity of the Co atoms are involved in the catalytic cycle.²⁵ We thus propose that similar synergy could take place in the HER. Furthermore, as shown by DFT calculations, Co doping can lead to activation of S_{edge} for H adsorption as H binding energy is decreased on these sites.²⁶ To gain insights into the HER mechanism, Tafel slopes were determined (**Figure 3c**). In acidic conditions, the HER is known to proceed according to three steps (i) the adsorption of the first proton: $\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O}$ (Volmer step) followed by either (ii) the proton desorption $\text{H}_{\text{ads}} + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2 + \text{H}_2\text{O}$ (Heyrovsky step) or (iii) the recombination of two H_{ads} to form the H_2 molecule $\text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2$ (Tafel step). Hence, the value of the Tafel slope depends on which of these three steps is rate determining, and 120, 40 and 30 mV decade⁻¹ are theoretical values for limitation by Volmer, Heyrovsky and Tafel step, respectively. On Pt/C, a value of 30 mV decade⁻¹ indicates that the Tafel step is the rate-limiting step at low overpotential.²⁷ Higher values of Tafel slopes measured on MoS₂-based catalysts suggest different rate determining steps. Several factors can account for that: (i) a lower electronic conductivity due to the semi-conducting nature of the 2H phase, (ii) a more sluggish discharge of H_3O^+ ions or, (ii) a more sluggish electrochemical desorption of H_{ads} atoms from the electrode surface. Importantly, the Co-MoS₂/C phase synthesized in this study exhibits a lower Tafel slope compared to MoS₂/C: this actually suggests that Co atoms may modify the H_{ads} binding energy, in line with the results of former DFT calculations.²⁶ This effect was less pronounced in the case of Pt_{1%}-CoMoS₂/C. Moreover, in HDT reaction Co promotion is ascribed to the increase

of S electron density (basicity) and thus to an increase in S-H formation which could favor an activation of edge sites for HER.

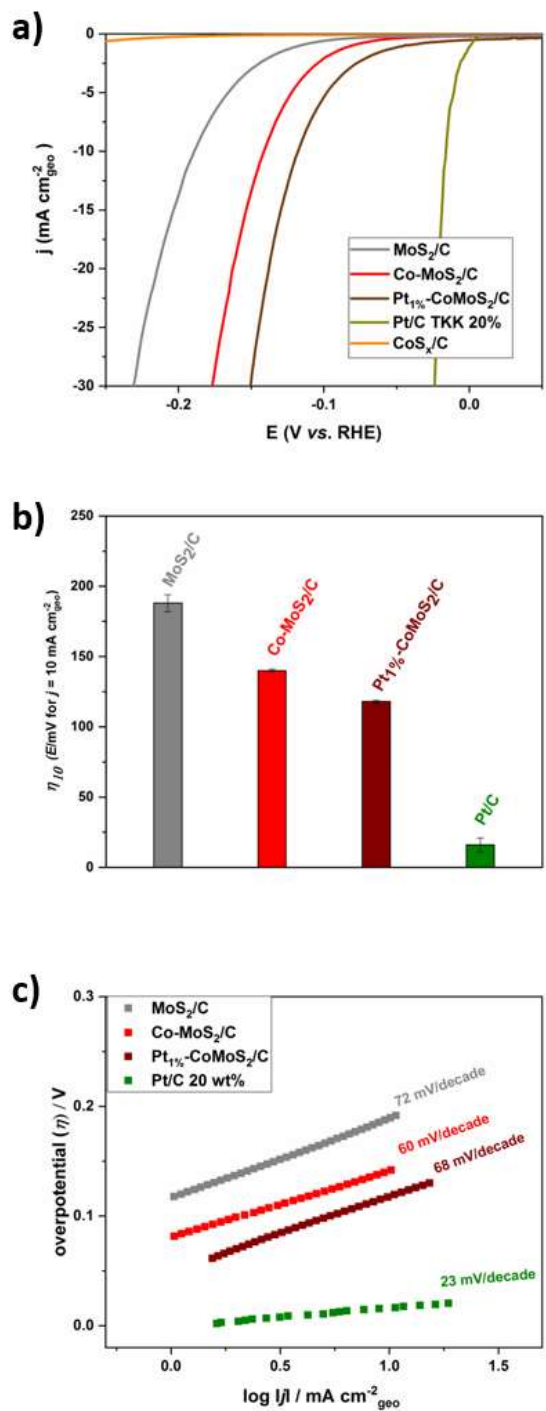


Figure 3. HER activity measurements. (a) polarization curves (b) overpotential measured at 10 mA cm⁻² (η_{10}) and (c) and Tafel plots for MoS₂/C, Co-MoS₂/C, Pt_{1%}-CoMoS₂/C and the commercial Pt/C reference catalysts. The HER polarization curves were performed in Ar-saturated 0.5 M H₂SO₄, $\omega = 1600$ rpm, $\nu = 10$ mV s⁻¹, $T = 298$ K. The catalyst's loading was 300 $\mu\text{g}_{\text{powder}} \text{cm}^{-2}$

Discussing the HER activity in more details, we emphasize that Luo *et al.* reported a very active MoS₂ doped with 1 wt. % of Pd atoms in substitution to Mo atoms. The authors used the octahedral 1T MoS₂, which is intrinsically more active owing to its higher electronic conductivity and to its higher density of active sites (both the edges and the basal planes are reported to be active for HER in the 1T phase).^{15,28} Nevertheless, the 1T phase is metastable and prone to revert to the 2H phase, rendering this strategy not viable for practical PEMWE devices. In contrast, the synthesis method described in this study leads to thermodynamically stable hexagonal 2H MoS₂ materials, as confirmed by the diffraction patterns observed in XRD, by the stacking distance measured in HAADF STEM images and by the two Raman peaks centered at 379 (E_{2g}^1 mode) and 403 (A_{1g} mode) cm⁻¹ characteristic of a hexagonal MoS₂ symmetry (**Figure 1b**). The alternative synthesis approaches described in this work demonstrate that it is possible to enhance the HER activity of the thermodynamically stable 2H phase of MoS₂ with only 1 wt. % Pt.

Additional measurement comparing the HER performance of Pt/C and Pt_{1%}-CoMoS₂/C at identical Pt loading has been performed and are displayed in **Figure S2**. Given the very low Tafel slope of Pt/C and its extremely high intrinsic activity towards the HER, it was no surprise that Pt/C still remains far more active. It should be mentioned that Pt is in very different state in the two electrodes: under the form of metallic Pt nanoparticles 2-3 nm in size in the commercial material vs. single Pt atoms promoting Mo-S edges of MoS₂ nanoclusters in the Pt_{1%}-CoMoS₂/C. Nevertheless, we can just infer that, for a practical point of view, Pt is largely underutilized when dispersed as single atoms onto Pt_{1%}-CoMoS₂/C catalyst as it acts as a doping element. In terms of pure HER performance, doping MoS₂ slabs with Pt is not a relevant strategy. However, this result is interesting from a fundamental point of view on the role of promoters. The choice of the doping elements should be envisioned in the direction of non-noble metal.

3.4. In-situ stability of MoS₂ based catalysts.

To analytically assess the stability of the bare or doped MoS₂ nanocatalysts, the dissolution of Mo, Co and Pt elements was monitored *in situ* using a flow cell connected to an inductively-coupled mass spectrometer. Such set-up was introduced in our former study to dynamically monitor the dissolution of Ir, tin (Sn) and doping elements from IrO_x/doped-SnO₂ catalysts during the OER.²⁹ We simulated the experimental conditions of a PEMWE cathode by applying a triangular cycling protocol between 0.1 and -0.2 V *vs.* RHE. **Figure 4 a), b) and c)** display the potential- and element-resolved dissolution for MoS₂/C, Co-MoS₂/C, Pt_{1%}-CoMoS₂/C, respectively. We first remark that elemental dissolution was always more pronounced during the first 3-5 potential cycles for Mo and for the doping elements. Note also that the scale in Y-axis is different for Mo (0-200 ppb), Co (0-2 ppb) and Pt (0-0.02 ppb) elements. This difference suggests that most of dissolved Mo arise from oxy-sulfides, which were not entirely sulfided during the sulfidation step (presence of oxy-sulfides was already noticed in our former work, see Ref. ³⁰). After these first potential cycles, the quantities of dissolved Mo, Pt or Co decreased, approaching 1 ppb, < 0.5 ppb and < 0.01 ppb, respectively. A closer look at the dissolution profiles shows that Mo, Co and Pt dissolution initiate at -0.15 V *vs.* RHE during the anodic sweep, confirming that the doping elements were intimately linked together with the MoS₂ slabs. Interestingly, the calculated Pourbaix diagram of MoS₂ indicates that this potential corresponds to the transformation of MoS₂ into [MoS₂]¹⁻.³¹ The presence of [MoS₂]¹⁻ thus surely facilitates the adsorption of the H₃O⁺ ions on Mo sites but also seems to destabilize the MoS₂ structure. Further work is ongoing in our group to better understand these complex HER activity – durability relationships.

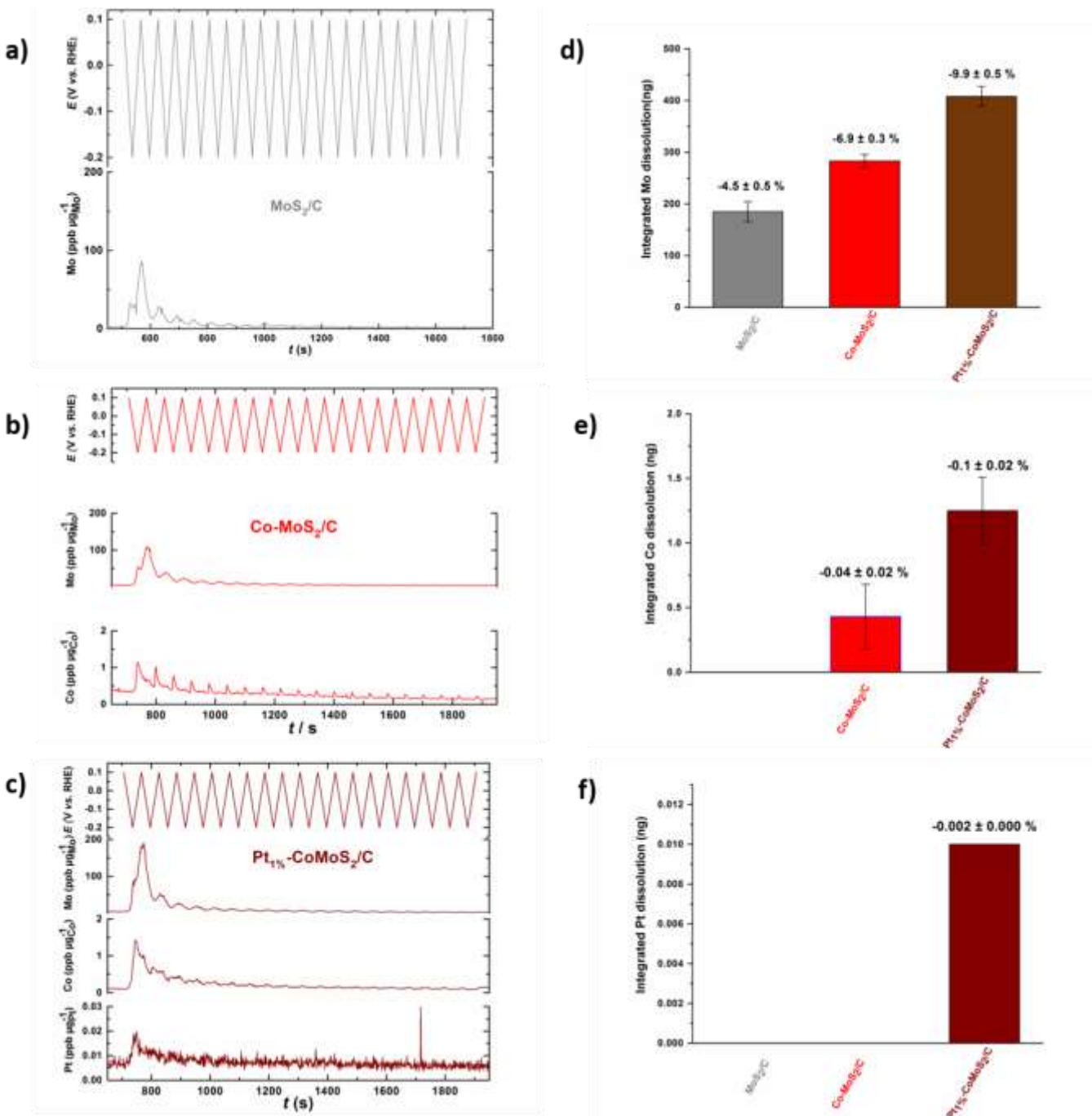


Figure 4. Stability of MoS_2 -based electrocatalysts monitored by *in situ* FC-ICP-MS. Potential- and element-resolved dissolution measured during 20 cycles HER cycles from -0.2 to 0.1 V vs. RHE for (a) MoS_2/C , (b) $\text{Co-MoS}_2/\text{C}$ and (c) $\text{Pt}_{1\%}\text{-CoMoS}_2/\text{C}$. The quantities of dissolved elements during the protocol are represented in (d), (e) and (f) for Mo, Co and Pt, respectively.

Finally, the quantities of Mo, Co and Pt dissolved during the experiments were integrated and normalized to the amount initially loaded onto the backing electrode (**Figure 4 d-f**). We found that at least 5 % of the Mo atoms contained in the 2H MoS₂/C structures dissolved during the electrochemical protocol. In contrast, the quantities of dissolved promoters were extremely low: only 0.04% and 0.002 % of the initial amount of Co and Pt was dissolved in the same conditions. Here again, we emphasize that the lack of stability essentially arises from partially sulfided MoS₂/C, which dissolved during the very first potential cycles. This hypothesis is supported by the much lower quantities of Mo, Co and Pt dissolved in the last three cycles of the electrochemical protocol (**Figure S1**) showing less than 0.08% of Mo cumulatively dissolved. This result is in line with former findings of Ledendecker *et al.* who reported more pronounced dissolution for Mo compared to MoS₂ during potential steps from open circuit voltage to -0.5 mA cm⁻².³²

Another interesting point relates to the interplay between activity and stability. Indeed, similar to what was found for Ir-based catalysts for the OER, the most active electrocatalysts are the least stable. Quantitatively speaking, more Mo leached out from the bi and trimetallic doped catalysts, which are more active for HER compared to the bare MoS₂/C. The same holds true for Co as 0.04 % of Co was dissolved from Co-MoS₂/C, this quantity being more than twice lower than for the more active Pt-CoMoS₂. This relationship confirms the link between HER activity (and the formation of [MoS₂]¹⁻ for adsorption of the first proton) and dissolution having in mind that in the present experiments, the lower potential limit was similar for each catalyst. Further work will be performed to evaluate metal dissolution in potentiostatic conditions.

4. CONCLUSIONS

In conclusion, MoS₂/C, promoted Co-MoS₂/C and Pt_{1%}-CoMoS₂/C nanoclusters were synthesized by an original incipient wetness impregnation method. Addition of a chelating agent in the synthesis protocol allowed to control the crystallite size, and thus the density of active sites. Similar morphology and structure (2H phase) were obtained for the mono-, bi, and trimetallic sulfide catalysts. Doping with Co resulted in a 40 mV decrease of the overpotential at 10 mA cm⁻²geo (η_{10}) confirming that substituting the edge Mo atoms of the 2H MoS₂ slabs with only 2-3 wt. % of Co is a promising route to enhance the HER activity of MoS₂. Pt_{1%}-CoMoS₂/C combines the beneficial effects of Co and Pt doping to further reduce the η_{10} value. **However, at similar Pt loading on the electrode, the HER performance of Pt/C nanoparticles still remains far more active.** Since the crystallite size, the structure and the density of active sites of the doped and undoped MoS₂/C catalysts are similar, the improved HER activity is attributed to the weakening of H binding energy via an electronic effect. Moreover, the on-line dissolution experiments revealed that doping/promoting with metal is a sustainable route according to the very low amount of Co and Pt dissolved in HER conditions.

AUTHOR INFORMATION

Corresponding authors:

* E-mail address for L.D.: laetitia.dubau@grenoble-inp.fr

* E-mail address for L.O.: laetitia.oliviero@ensicaen.fr

ORCID

Luz Zavala-Sanchez: <https://orcid.org/0000-0002-9643-3825>

Kavita Kumar: <https://orcid.org/0000-0003-3844-1082>

Vincent Martin: <https://orcid.org/0000-0002-9521-4137>

Frédéric Maillard: <https://orcid.org/0000-0002-6470-8900>

Xavier Portier: <https://orcid.org/0000-0002-5361-719X>

Laetitia Oliviero: <https://orcid.org/0000-0002-7931-439X>

Laetitia Dubau: <http://orcid.org/0000-0001-9520-1435>

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

LZ: Investigation, Visualization, Writing-Original draft preparation, VM: Investigation, Methodology, Writing-Review, FM: Investigation, Methodology, Writing-Review, XP: Investigation, Methodology, Writing-Review, FM: Writing-Review, supervision, KK: Investigation, Methodology, Writing-Review, LO: Methodology, Writing-Review and Editing, Funding acquisition, Supervision, LD: Methodology, Writing-Review and Editing, Funding acquisition, Supervision.

CONFLICT OF INTEREST

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>. It comprises:

- Stability of MoS₂-based electrocatalysts monitored by online FC-ICP-MS

ACKNOWLEDGEMENTS

The authors acknowledge the financial support of ANR CARNOT Energie et Systèmes de Propulsion (ESP) and ANR CARNOT Energies du Futur (EF) through the HERMOS project.

5. REFERENCES

- (1) Wang, J.; Hu, C.; Shi, L.; Tian, N.; Huang, H.; Zhang, Y. Energy and Environmental Catalysis Driven by Stress and Temperature-Variation. *J. Mater. Chem. A* **2021**, No. 21, 12400–12432. <https://doi.org/10.1039/D1TA02531G>.
- (2) Dubau, L.; Asset, T.; Vanpeene, V.; Nelayah, J. Tuning the Performance and the Stability of Porous Hollow PtNi/C Nanostructures for the Oxygen Reduction Reaction. *ACS Catal.* **2015**, *5*, 5333–5341. <https://doi.org/10.1021/acscatal.5b01248>.
- (3) Asset, T.; Job, N.; Busby, Y.; Crisci, A.; Martin, V.; Stergiopoulos, V.; Bonnaud, C.; Serov, A.;

- Atanassov, P.; Chattot, R.; Dubau, L.; Maillard, F. Porous Hollow PtNi/C Electrocatalysts: Carbon Support Considerations to Meet Performance and Stability Requirements. *ACS Catal.* **2018**, *8* (2), 893–903. <https://doi.org/10.1021/acscatal.7b03539>.
- (4) Benck, J. D.; Hellstern, T. R.; Kibsgaard, J.; Chakthranont, P.; Jaramillo, T. F. Catalyzing the Hydrogen Evolution Reaction (HER) with Molybdenum Sulfide Nanomaterials. *ACS Catal.* **2014**, *4*, 3957–3971.
- (5) Hua, W.; Sun, H.; Xu, F.; Wang, J. A Review and Perspective on Molybdenum-Based Electrocatalysts for Hydrogen Evolution Reaction. *Rare Met.* **2020**, *39* (4), 335–351. <https://doi.org/10.1007/s12598-020-01384-7>.
- (6) Raybaud, P.; Hafner, J.; Kresse, G.; Kasztelan, S.; Toulhoat, H. Ab Initio Study of the H₂–H₂S/MoS₂ Gas – Solid Interface: The Nature of the Catalytically Active Sites. **2000**, *146*, 129–146. <https://doi.org/10.1006/jcat.1999.2698>.
- (7) Chen, J.; Maugé, F.; Fallah, J. El; Oliviero, L. IR Spectroscopy Evidence of MoS₂ Morphology Change by Citric Acid Addition on MoS₂/Al₂O₃ Catalysts – A Step Forward to Differentiate the Reactivity of M-Edge and S-Edge. *J. Catal.* **2014**, *320* (320), 170–179. <https://doi.org/10.1016/j.jcat.2014.10.005>.
- (8) Hellstern, T. R.; Kibsgaard, J.; Tsai, C.; Palm, D. W.; King, L. A.; Abild-Pedersen, F.; Jaramillo, T. F. Investigating Catalyst-Support Interactions to Improve the Hydrogen Evolution Reaction Activity of Thiomolybdate [Mo₃S₁₃]²⁻ Nanoclusters. *ACS Catal.* **2017**, *7* (10), 7126–7130. <https://doi.org/10.1021/acscatal.7b02133>.
- (9) Dai, X.; Du, K.; Li, Z.; Liu, M.; Ma, Y.; Sun, H.; Zhang, X.; Yang, Y. Co-Doped MoS₂ Nanosheets with the Dominant CoMoS Phase Coated on Carbon as an Excellent Electrocatalyst for Hydrogen Evolution. *ACS Appl. Mater. Interfaces* **2015**, *7* (49), 27242–27253. <https://doi.org/10.1021/acsami.5b08420>.

- (10) Deng, J.; Li, H.; Xiao, J.; Tu, Y.; Deng, D.; Yang, H.; Tian, H.; Li, J.; Ren, P.; Bao, X. Triggering the Electrocatalytic Hydrogen Evolution Activity of the Inert Two-Dimensional MoS₂ Surface via Single-Atom Metal Doping. *Energy Environ. Sci.* **2015**, *8* (5), 1594–1601. <https://doi.org/10.1039/c5ee00751h>.
- (11) Topsøe, H.; Clausen, B. S. .; Massoth, F. E. . *Catalysis Science and Technology*; Anderson, John R., M. B., Ed.; Springer: Berlin, 1996. https://doi.org/10.1007/978-3-642-61040-0_1.
- (12) Raybaud, P.; Hafner, J.; Kresse, G.; Kasztelan, S.; Toulhoat, H. Structure, Energetics, and Electronic Properties of the Surface of a Promoted MoS₂ Catalyst: An Ab Initio Local Density Functional Study. *J. Catal.* **2000**, *190* (1), 128–143. <https://doi.org/10.1006/jcat.1999.2743>.
- (13) Zhang, J.; Xu, X.; Yang, L.; Cheng, D.; Cao, D. Single-Atom Ru Doping Induced Phase Transition of MoS₂ and S Vacancy for Hydrogen Evolution Reaction. *Small Methods* **2019**, *3* (12), 1–9. <https://doi.org/10.1002/smtd.201900653>.
- (14) Ji, L.; Yan, P.; Zhu, C.; Ma, C.; Wu, W.; Wei, C.; Shen, Y.; Chu, S.; Wang, J.; Du, Y.; Chen, J.; Yang, X.; Xu, Q. One-Pot Synthesis of Porous 1T-Phase MoS₂ Integrated with Single-Atom Cu Doping for Enhancing Electrocatalytic Hydrogen Evolution Reaction. *Appl. Catal. B Environ.* **2019**, *251* (March), 87–93. <https://doi.org/10.1016/j.apcatb.2019.03.053>.
- (15) Luo, Z.; Ouyang, Y.; Zhang, H.; Xiao, M.; Ge, J.; Jiang, Z.; Wang, J.; Tang, D.; Cao, X.; Liu, C.; Xing, W. Chemically Activating MoS₂ via Spontaneous Atomic Palladium Interfacial Doping towards Efficient Hydrogen Evolution. *Nat. Commun.* **2018**, *9* (1), 1–8. <https://doi.org/10.1038/s41467-018-04501-4>.
- (16) Weise, C. F.; Falsig, H.; Moses, P. G.; Helveg, S.; Brorson, M.; Hansen, L. P. Single-Atom Pt Promotion of Industrial Co-Mo-S Catalysts for Ultra-Deep Hydrodesulfurization. *J. Catal.* **2021**, *403*, 74–86. <https://doi.org/10.1016/j.jcat.2021.03.008>.

- (17) Geantet, C.; Bacaud, R.; Vrinat, M.; Guyen, T. S. N.; Soldo, Y.; Hazemann, J. L. Platinum Doped Hydrotreating Catalysts for Deep Hydrodesulfurization of Diesel Fuels. **2007**, 3877–3883.
- (18) Chen, J.; Mi, J.; Li, K.; Wang, X.; Dominguez Garcia, E.; Cao, Y.; Jiang, L.; Oliviero, L.; Oise, F. Role of Citric Acid in Preparing Highly Active CoMo/Al₂O₃ Catalyst: From Aqueous Impregnation Solution to Active Site Formation. *Ind. Eng. Chem. Res.* **2017**, *56*, 14172–14181. <https://doi.org/10.1021/acs.iecr.7b02877>.
- (19) Zavala-Sanchez, L. A.; Portier, X.; Maugé, F.; Oliviero, L. Promoter Location on NiW/Al₂O₃Sulfide Catalysts: Parallel Study by IR/CO Spectroscopy and High-Resolution STEM-HAADF Microscopy. *ACS Catal.* **2020**, *10* (11), 6568–6578. <https://doi.org/10.1021/acscatal.0c01092>.
- (20) Zavala-sanchez, L.; Portier, X.; Maugé, F.; Oliviero, L. Formation and Stability of CoMoS Nanoclusters by the Addition of Citric Acid: A Study by High Resolution STEM-HAADF Microscopy. *Catal. Today* **2020**, No. October. <https://doi.org/10.1016/j.cattod.2020.10.039>.
- (21) Xu, D.; Zhu, Y.; Liu, J.; Li, Y.; Peng, W.; Zhang, G.; Zhang, F.; Fan, X. Microwave-Assisted 1T to 2H Phase Reversion of MoS₂ in Solution: A Fast Route to Processable Dispersions of 2H-MoS₂ Nanosheets and Nanocomposites. *Nanotechnology* **2016**, *27* (38). <https://doi.org/10.1088/0957-4484/27/38/385604>.
- (22) Holzapfel, P. K. R.; Bühler, M.; Escalera-López, D.; Bierling, M.; Speck, F. D.; Mayrhofer, K. J. J.; Cherevko, S.; Pham, C. V.; Thiele, S. Fabrication of a Robust PEM Water Electrolyzer Based on Non-Noble Metal Cathode Catalyst: [Mo₃S₁₃]²⁻ Clusters Anchored to N-Doped Carbon Nanotubes. *Small* **2020**, *16* (37), 1–10. <https://doi.org/10.1002/sml.202003161>.
- (23) Ye, J.; Chen, W.; Xu, S.; Yu, Z.; Hou, S. Synthesis of Co-Doped MoS₂/Graphene Hybrids as an Enhanced Electrocatalyst for Hydrogen Evolution Reaction. *RSC Adv.* **2016**, *6* (106), 104925–104932. <https://doi.org/10.1039/C6RA23412G>.

- (24) Chia, X.; Adriano, A.; Lazar, P.; Sofer, Z.; Luxa, J.; Pumera, M. Layered Platinum Dichalcogenides (PtS₂, PtSe₂, and PtTe₂) Electrocatalysis: Monotonic Dependence on the Chalcogen Size. *Adv. Funct. Mater.* **2016**, *26* (24), 4306–4318.
<https://doi.org/https://doi.org/10.1002/adfm.201505402>.
- (25) Mijoin, J.; Pérot, G.; Bataille, F.; Lemberon, J. L.; Breyse, M.; Kasztelan, S. Mechanistic Considerations on the Involvement of Dihydrointermediates in the Hydrodesulfurization of Dibenzothiophene-Type Compounds over Molybdenum Sulfide Catalysts. *Catal. Letters* **2001**, *71* (3–4), 139–145. <https://doi.org/10.1023/A:1009055205076>.
- (26) Bonde, J.; Moses, P. G.; Jaramillo, T. F.; Nørskov, J. K.; Chorkendorff, I. Hydrogen Evolution on Nano-Particulate Transition Metal Sulfide. *Faraday Discuss.* **2008**, *140*, 9–10.
<https://doi.org/10.1039/b814058h>.
- (27) Conway, B. E.; Tilak, B. V. Interfacial Processes Involving Electrocatalytic Evolution and Oxidation of H₂, and the Role of Chemisorbed H. *Electrochim. Acta* **2002**, *47* (22–23), 3571–3594. [https://doi.org/10.1016/S0013-4686\(02\)00329-8](https://doi.org/10.1016/S0013-4686(02)00329-8).
- (28) Liu, Q.; Fang, Q.; Chu, W.; Wan, Y.; Li, X.; Xu, W.; Habib, M.; Tao, S.; Zhou, Y.; Liu, D.; Xiang, T.; Khalil, A.; Wu, X.; Chhowalla, M.; Ajayan, P. M.; Song, L. Electron-Doped 1T-MoS₂ via Interface Engineering for Enhanced Electrocatalytic Hydrogen Evolution. *Chem. Mater.* **2017**, *29* (11), 4738–4744. <https://doi.org/10.1021/acs.chemmater.7b00446>.
- (29) Abbou, S.; Chattot, R.; Martin, V.; Claudel, F.; Solà-Hernandez, L.; Beauger, C.; Dubau, L.; Maillard, F. Manipulating the Corrosion Resistance of SnO₂ Aerogels through Doping for Efficient and Durable Oxygen Evolution Reaction Electrocatalysis in Acidic Media. *ACS Catal.* **2020**, *10* (13), 7283–7294. <https://doi.org/10.1021/acscatal.0c01084>.
- (30) Oliviero, L.; Travert, A.; Dominguez Garcia, E.; Chen, J.; Maugé, F. Catalysis by Sulfides: Advanced IR/CO Spectroscopy for the Identification of the Most Active Sites in

Hydrodesulfurization Reactions. *J. Catal.* **2021**, *403*, 87–97.

<https://doi.org/10.1016/j.jcat.2021.02.018>.

- (31) Huang, Y.; Nielsen, R. J.; Goddard, W. A.; Soriaga, M. P. The Reaction Mechanism with Free Energy Barriers for Electrochemical Dihydrogen Evolution on MoS₂. *J. Am. Chem. Soc.* **2015**, *137* (20), 6692–6698. <https://doi.org/10.1021/jacs.5b03329>.
- (32) Ledendecker, M.; Mondschein, J. S.; Kasian, O.; Geiger, S.; Göhl, D.; Schalenbach, M.; Zeradjanin, A.; Cherevko, S.; Schaak, R. E.; Mayrhofer, K. Stability and Activity of Non-Noble-Metal-Based Catalysts Toward the Hydrogen Evolution Reaction. *Angew. Chemie - Int. Ed.* **2017**, *56* (33), 9767–9771. <https://doi.org/10.1002/anie.201704021>.