First *in situ* Temperature Quantification of CoMoS species upon Gas Sulfidation enabled by New Insight on Cobalt Sulfide Formation

L. PLAIS^{1,2}, C. LANCELOT¹, C. LAMONIER¹, E. PAYEN¹, V. BRIOIS^{2,*}

¹- Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

²- Synchrotron SOLEIL, CNRS-UR1, BP 48, L'orme des Merisiers, Gif-sur-Yvette, France

*Corresponding Author

Abstract

Insights into the cobalt sulfide formation upon sulfidation (10% H₂S/H₂) of cobalt-based materials with 4 wt % CoO supported on alumina or silica were obtained by Quick-X-ray absorption spectroscopy monitoring analysed by multivariate curve regression analysis. A common pathway is evidenced involving the formation of supported defective CoS₂ species transformed around 200-250°C into supported Co₉S₈ species. Upon cooling down under sulfiding atmosphere, a reverse transition towards CoS₂ was observed by XAS multivariate analysis and supported by Raman analysis. This reverse transition is sensitive to the Co₉S₈ crystallite size: the smaller the Co₉S₈ nanoparticles the higher the amount of formed CoS₂ after cooling. The knowledge gained on the sulfidation of monometallic cobalt-based catalysts has been used in order to isolate the X-ray absorption spectrum of the CoMoS active species formed during the sulfidation of a calcined cobalt-promoted HDS catalyst. The evolution of the concentration of the CoMoS species upon temperature increase is determined for the first time, together with those of the pristine oxidic CoMo catalyst and CoS₂ and Co₉S₈ supported species. Although the conversion of Co₉S₈ into CoS₂ is still observed for the HDS catalyst when temperature is decreased under H₂S/H₂ atmosphere, no change of the CoMoS percentage is evidenced.

Keywords: Co₉S₈; CoS₂; cobalt promoted HDS Catalyst; Raman; Quick-XAS

1. Introduction

Supported cobalt sulfides have been studied for decades as heterogeneous catalysts in several reactions such as hydrogenolysis of dimethyl disulfide to methanethiol [1, 2], but mainly because they are present in the hydrotreating (HDT) processes [3]. In the latter case, during sulfidation treatment of oxidic CoMo precursors, Co₉S₈ is mainly reported as monometallic species formed in competition [4] with the CoMoS active phase described since the Topsoe works as MoS₂ slabs decorated at the corner and edge by cobalt atoms [5]. Recently, cobalt sulfides have attracted also overwhelming research interests as efficient electrocatalysts for oxygen evolution reaction (OER) [6, 7], oxygen reduction reaction (ORR) [8] or hydrogen evolution reaction (HER) [9-12]. The interest for the use of cobalt sulfides is the quest of earth-abundant electrocatalysts which can rival the efficiency of costly noble metal-based materials [13] and improve the long-term stability of the devices for large scale commercial applications.

The binary Co–S phase diagram presents several bulk phases stable below 600 °C such as Co_9S_8 , Co_3S_4 and CoS_2 [14]. CoS_2 and Co_9S_8 -based materials are the most studied electrocatalysts but with unequal consistency related to their structural identification. On the one hand, most of the characterizations done on CoS_2 -based electrocatalysts [8, 9, 12, 15] are consistent with the reported bulk CoS_2 characterizations, using either X-ray diffraction (XRD) or short range order technique like Raman spectroscopy [16]. On the other hand, when Co_9S_8 -based samples are reported as electrocatalyst active phases, their poor crystallinity related to their high dispersion on support and/or nanometric-sized structure hinders conventional identification by XRD. Short range order techniques such as X-ray Absorption (XAS) and Raman spectroscopies are then used for identification of those different phases [17-23]. However, the claimed fingerprints used in Raman spectroscopy for identifying Co_9S_8 in most of those papers show large discrepancies in the wavenumber of the related lines, making difficult to use them further as reference spectra for identification. Although appropriate synthesis conditions can easily yield to large crystals of Co_9S_8 species [24,25], the reason for the discrepancy in reported Raman fingerprints could be found in the lack of Raman spectrum reported in the literature for bulk Co_9S_8 for which the structure has been certified by XRD.

Additionally, the description of the sulfidation of monometallic cobalt or nickel oxidic species is of prime importance to better understand the sulfidation of bimetallic Co(Ni)Mo oxidic precursors used for hydrodesulfurization (HDS) processes due to the competitive formation of monometallic sulfide species with the Co(Ni)MoS active phase. We have previously reported that during sulfidation of nickel oxidic precursors supported on alumina, several nickel sulfides are involved [26]. The high sensitivity of XAS for monitoring *in situ* phase transitions associated to chemometric analysis [27] to disentangle the complexity of phase mixture during transition were unique for reporting the XAS spectra of two pure nickel sulfides supported on alumina with NiS_2 and Ni_3S_2 compositions. NiS_2 is first formed before being abruptly transformed in Ni_3S_2 around 250°C. This phase transition is accompanied by a strong release of H_2S and consumption of H_2 as commonly reported in Temperature Programmed Sulfidation (TPS) analysis of mono and bimetallic HDS catalysts [28]. We study herein by ***Quick-EXAFS spectroscopy combined to Multivariate Curve Regression with Alternating Least Square (MCR-ALS) fitting analysis*** the fate of cobalt oxidic precursors (4 wt % CoO) supported on alumina and silica upon sulfidation under $\text{H}_2\text{S}/\text{H}_2$ gaseous mixture. The goal is to ***reveal potential intermediate cobalt sulfide species*** before the formation of Co_9S_8 and accordingly similarity between sulfidation of monometallic nickel (already reported in [26]) and cobalt precursors. Two supports were investigated in order to confirm or refute the single phase dispersion of Co_9S_8 at the end of sulfidation. The speciation measured at RT under inert atmosphere will be in particular important for comparison purpose with previous results. For instance, using RT ^{59}Co NMR characterizations, Ledoux *et al.* [29] reported for silica Co supported catalyst with low loading a distorted octahedral site, which was assumed as a new sulfide species, coexisting with Co_9S_8 . Comparison will be also of prime importance with results obtained by the RT X-ray Photoelectron Spectroscopy (XPS) analysis most currently carried out today [30].

Finally, the knowledge gained on the sulfidation pathways of supported Co oxidic precursors will be used to solve the composition of sulfide cobalt-based species formed by sulfidation of a calcined cobalt promoted molybdenum-based HDS catalyst. To this purpose, the sulfidation of this catalyst will be alternately monitored by quick-EXAFS at the Mo and Co K edges using the unique capability of the ROCK beamline of SOLEIL synchrotron [31]. The MCR-ALS analysis of the evolution of Co K edge XAS data recorded upon sulfidation of the HDS catalyst precursor will be carried out through the simultaneous analysis of the data set recorded for the monometallic cobalt species previously

studied and the one recorded for the HDS catalyst, assuming that both samples share common monometallic sulfide species. By this approach, ***we will isolate the XAS spectrum characterizing the active CoMoS species and report for the first time the in situ temperature quantification of the CoMoS species during sulfidation.*** The cobalt speciation at 400°C and after decreasing the temperature at RT will be also discussed.

2. Experimental

2.1 Samples preparation

Preparation of bulk crystalline Co_9S_8 was carried out by heating bulk crystalline CoS_2 from Alfa Aesar (99.5%) from RT to 450°C under 0.5% H_2S - H_2 gaseous mixture.

Dried Co oxidic samples were prepared by incipient wetness impregnation of 5g of γ alumina trilobe extrudates (specific surface of 260 m^2/g and pore volume 1 mL/g) or 5g of silica (specific surface of 140 m^2/g and pore volume 1.6 mL/g) with 5 or 8 mL of an aqueous solution containing 0.854 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, respectively. This preparation allows us to get 4 wt % of CoO on the supports. After maturation in a saturated water atmosphere at RT for 4 h, the samples were dried at 100°C for 11h under static air leading to so-called dried $\text{Co}/\text{Al}_2\text{O}_3$ and dried Co/SiO_2 samples. Part of the dried samples was calcined at 500°C under air flow for 2h with a heating ramp of 1°C/min leading to the so-called calcined $\text{Co}/\text{Al}_2\text{O}_3$ and calcined Co/SiO_2 samples.

A $\text{CoNiMo}/\text{Al}_2\text{O}_3$ oxidic HDS catalyst precursor containing 14 wt % of MoO_3 was prepared by incipient wetness impregnation of the same γ alumina trilobe extrudates with an aqueous solution of ammonium heptamolybdate, cobalt nitrate and nickel nitrate in the ratios $\text{Co}/\text{Mo} = 0.27$ and $\text{Ni}/\text{Mo}=0.09$. After maturation in a saturated water atmosphere at RT for 5 h, the samples were dried at 100°C for 12h under static air before calcination at 480°C under air flow for 3h with a heating ramp of 1°C/min.

2.2 Samples sulfidation

Sulfidation of the monometallic samples was carried out either using the high temperature Harrick cell [32] suitable for Raman spectroscopy measurements or the SAXO cell described in [33] for XAS ones. About 45 mg of powdered samples were loaded in the respective cavities of the cells. Irrespective to the techniques, as the same quantity of samples is loaded in both cells, the flow of gases is identical and equal to 10 mL/min of 10% $\text{H}_2\text{S}/\text{H}_2$ mixture atmosphere mixture. Sulfidation of the different supported oxidic cobalt precursors was carried out heating the samples from RT to 400°C at 3 or 5°C/min followed by a plateau of 30 min at 400°C. The gases at the cell outlet were analysed by an online quadrupole mass spectrometer (Cirrus MKS). Sulfidation of the calcined CoNiMo oxidic precursor (22 mg) supported on alumina was carried out using the SAXO cell [33] with a heating ramp from RT to 400°C at 3°C/min under 10 mL/min of 10% H_2S - H_2 mixture followed by a plateau of 2h at 400°C.

2.3 Characterization

In situ Raman spectra were acquired using a 532 nm RXN1 Raman spectrometer (Kaiser Optical Systems, Incorporation) equipped with a long working distance objective (Mitutuyo, x20) facing perpendicularly the 1 mm-thick quartz window confining the reactive $\text{H}_2\text{S}/\text{H}_2$ atmosphere in the Harrick cell [30]. The nominal laser power was 11 mW. *Ex situ* Raman were measured under air using

a 785 nm RXN1 Raman spectrometer (Kaiser Optical Systems, Incorporation) coupled to an optical microscope (x10 magnification).

Co K-edge XAS data were recorded on the ROCK beamline at the SOLEIL synchrotron [31]. Time resolved *in situ* Quick-XAS measurements were performed in transmission mode with 3 ionization chambers filled with gaseous N₂. The Si(111) channel-cut crystal was tuned to a Bragg angle near to the Co K-edge energy (14°) whereas the cam-driven tilt table supporting the channel-cut was allowed to oscillate with an amplitude of 2.3° around this value and a frequency of 2 Hz allowing us to obtain each second 2 spectra with upward Bragg angles and 2 spectra with downward Bragg angles. The monochromator was energy-calibrated by setting the first inflection point of the K-edge spectrum of a standard metallic cobalt foil at 7709 eV and the reference foil was continuously measured to correct monochromator energy drift. Twenty spectra collected with upward Bragg angles and previously interpolated in a common energy grid were merged to improve the signal-to-noise ratio leading to a time resolution of 10 s per presented spectrum during sulfidation.

The monitoring of the sulfidation of the CoNiMo/Al₂O₃ catalyst was carried out using the edge-jumping capability available at the ROCK beamline [31, 34] with the alternate acquisition of Co and Mo K edge data as previously described in [34]. Frequency of the Si(220) channel cut oscillation used for Mo K edge recording was also 2Hz. Data at both edges were alternately recorded for 28 s with in between a blind period of 30 s used for changing monochromators, stripes of the harmonic rejection mirrors and ionization chambers. A common 2.75 mrad grazing incidence of the beam on the mirrors was used at both edges, but with exchange of the mirror stripes from B₄C to Pd coating when changing from Co to Mo K edges, respectively.

XRD patterns of bulk cobalt sulfides and supported cobalt sulfide on silica were recorded in ambient conditions using the Cu K α radiation ($\lambda=1.5418$ Å) on a Bruker D2 phaser diffractometer, with a 0.05° scan step and 2 s time step. To preserve the samples from reoxidation, they were loaded in a glove box in an airtight sample holder. The average crystallite size (D) of CoS₂ and Co₉S₈ was evaluated by the Scherrer's equation, $D = 0.9 \lambda / \beta \cos \theta$ where β is the full width at half-maximum of the most intense reflection.

The XPS sampling of the sulfided catalyst was performed in a glove box under argon atmosphere, with controlled oxygen and water level (less than 20 ppm) in order to avoid their partial reoxidation. The sample was crushed and pressed onto an indium foil that was attached to the sample holder *via* a double side carbon tape. The sample holder, thanks to the special connection of the glove box to the XPS spectrometer, was then moved in a transfer chamber for a first vacuum pumping before its introduction in the analysis chamber. The XPS spectra were recorded on a Kratos Axis Supra instrument with Al monochromator source (1486.6 eV) and a hemi-spherical analyser operating at fixed pass energy of 20 eV. The measurements were made at RT in steps of 0.05 eV for cobalt and 0.1 eV for sulfur, and at a pressure close 10⁻⁹ Torr in the sample analysis chamber. Binding energies (BE) of the elements are referenced to the C 1s level of the contamination carbon at 284.6 eV. The curves were integrated applying a Shirley type baseline. The collected spectra were analysed by using CasaXPS software, Version 2.0.71. The decomposition of the Co 2p and S 2p spectra were performed using the appropriate Gaussian-Lorentzian (GL30) contributions or asymmetric ones (LA(1.2,5,5)) for the main Co 2p_{3/2} and Co 2p_{1/2} levels according to their metallic character [35].

2.4 XAS data analysis

Normalization of the XAS data recorded during *in situ* sulfidation was performed by using the Python *normal_gui* graphical user interface developed at SOLEIL for the fast handling of the Quick-XAS data. This interface has been recently described in [36]. The normalized experimental XAS spectra are then concatenated in ascending time of sulfidation in a matrix, $\mathbf{D}$, and processed by MCR-ALS analysis [27, 37] which decomposes $\mathbf{D}$ into a matrix $\mathbf{C}$ containing the concentration of the n pure species involved in the reaction and a matrix $\mathbf{S}^T$ containing the normalized XAS spectra of the pure species according to the equation:

$$\mathbf{D} = \mathbf{C} \mathbf{S}^T + \mathbf{E} \quad (1)$$

where the matrix $\mathbf{E}$ contains the experimental noise. The rank of matrix $\mathbf{D}$, *i.e.* n , is first determined by Principal Component Analysis (PCA), which is a dimensionality-reduction method allowing to reduce the number of highly correlated spectra contained in $\mathbf{D}$ into a smallest number of components explaining most of the $\mathbf{D}$ variance. Then MCR-ALS minimization is carried out considering the number of species known and starting for the minimization with an initial guess of the matrix of concentration derived by Evolving Factor Analysis [38]. After successive loops, leading to the alternate minimization of $\mathbf{S}$ and $\mathbf{C}$ matrices, iterations are stopped when the convergence criterion is achieved. For suppressing rotational ambiguity leading to non-unique mathematical solutions determined by MCR-ALS [37], physically and chemically meaningful constraints are used such as non-negativity of the absorbances contained in $\mathbf{S}$ and of the concentrations in $\mathbf{C}$, closure constraint for the concentrations (mass balance). One of the parameter used to measure the fit quality of the MCR-ALS solution is the Lack Of Fit, LOF (%), defined as follows:

$$\text{LoF (\%)} = 100 \sqrt{\frac{\sum_{ij} e_{ij}^2}{\sum_{ij} d_{ij}^2}} \quad (2)$$

where d_{ij} is an element of $\mathbf{D}$ (i^{th} spectrum at the energy value j) and e_{ij} is the related residual value obtained from the difference between $\mathbf{D}$ and the rebuilt data over the n components from the $\mathbf{C} \cdot \mathbf{S}^T$ matrix product obtained by MCR-ALS. e_{ij} is calculated according to the relation:

$$e_{ij} = d_{ij} - \sum_{k=1}^n C_{ik} \cdot S_{kj}^T \quad (3)$$

where C_{ik} is an element of $\mathbf{C}$, S_{kj} an element of $\mathbf{S}$ and the sub-index k is related to the index of the component isolated by MCR-ALS.

For the XAS spectrum with index i in the matrix $\mathbf{D}$, a R_f factor can be calculated according to the relation:

$$R_f^{(i)} (\%) = 100 \sqrt{\frac{\sum_j e_{ij}^2}{\sum_j d_{ij}^2}} \quad (4)$$

Details about the use of PCA and MCR-ALS methods applied to XAS data can be found in references [26, 36, 39-40]. MCR-ALS minimizations on time-resolved XAS data presented herein were carried out using the MCR-ALS 2.0 gui developed on Matlab platform by the Roma Tauler's group [41].

The EXAFS oscillations were extracted from the normalized Co Kedge XAS data using the Athena graphical Interface software [42]. The EXAFS data were Fourier transformed using a k^3 -weighting Kaiser Bessel window ($dk = 2$) over the 2.8-10.6 $\text{\AA}^{-1}$ k -range. EXAFS fitting of distances, coordination numbers and Debye-Waller factors was performed with the Artemis interface to IFFFIT using least-squares refinements, firstly checked on a CoO standard [43] and bulk CoS₂ [44], for which coordination numbers and distances are known. The use of those references allows us to determine 0.71 as value for the passive electron reduction factor S_0^2 .

3. Results

3.1 Raman characterization of bulk Co_9S_8

Bulk crystalline Co_9S_8 was prepared by solid-gas reaction of commercial CoS_2 under sulfiding atmosphere.

The purity of CoS_2 was first analysed by XRD and XAS. Figures S1 to S3 in supporting information display the XRD pattern of CoS_2 and XAS analysis for this sample recorded under inert atmosphere. The diffraction peaks in Figure S1 can be indexed with the hkl reflections of cubic pyrite-like structure [44] reported for CoS_2 in the JCPDS card n° 41-1471. The mean size of the CoS_2 crystallites was determined at ≈ 48 nm using the Scherrer's formula. The XANES spectrum reported for CoS_2 in Figure S2 displays the characteristic broad spectral shape of cobalt sulfide species with no white line [45, 46]. The ill-defined pre-edge structure assigned to transition from cobalt 1s atomic level to 3d molecular orbitals hybridized with metal p states is characteristic of the octahedral symmetry in which cobalt atoms are embedded in the CoS_2 structure [45, 46]. A satisfactory simulation of the EXAFS signal in the 1-4 Å R-space (Figure S3, Table S1) has been obtained using the crystallographic distances reported for CoS_2 [44].

The phase obtained by solid-gas reaction of crystalline CoS_2 under 0.5% H_2S - H_2 was *ex situ* characterized by XRD and XAS at RT. The diffraction pattern recorded for this phase (Figure S4) is consistent with the formation of Co_9S_8 (JCPDS 86-2273) and a mean crystallite size around 67 nm. The XANES spectrum (Figure S5) is well in line with the spectra reported in the literature for Co_9S_8 [39, 46] with a more resolved and intense pre-edge feature compared to CoS_2 , which is ascribed to the increase of 3d-4p atomic orbital hybridization since cobalt sites characterizing Co_9S_8 are essentially non centrosymmetric (8 sites in tetrahedral symmetry for 1 site in octahedral ones) [45- 47]. The simulation of the EXAFS signal in the 1-6 Å R-space (Figure S6, Table S2) fully confirms the formation of bulk Co_9S_8 .

The solid-gas reaction of CoS_2 under sulfiding atmosphere was *in situ* monitored by Raman spectroscopy. Figure 1 displays the Raman spectra recorded at RT before solid-gas reaction, at 450°C and at RT after cooling down the as-prepared Co_9S_8 . The measurements being carried out under reactive atmosphere ($\text{H}_2\text{S}/\text{H}_2$), the lines at 355 and 588 cm^{-1} marked by a star are characteristic of gaseous H_2 [40]. The RT Raman spectrum of CoS_2 displays a main intense line located at 390 cm^{-1} characteristic of the A_g mode associated to the in-phase stretching vibrations of sulfur atoms in the disulfide ligands of CoS_2 [16]. The line at 286 cm^{-1} and shoulder at 417 cm^{-1} emerging slightly from the noise on Figure 1 are associated in the literature to E_g and $T_g(2)$ modes of CoS_2 corresponding respectively to the pure librational mode of the disulfide ligands and out-of-phase stretching vibrations of sulfur atoms in disulfide [16]. Actually those modes are more intense using a 785 nm laser excitation wavelength (Figure S7). It is noteworthy that irrespective of the excitation wavelength, a shift of the CoS_2 lines to lower wavenumber is observed when $\text{H}_2\text{S}/\text{H}_2$ atmosphere is replaced by N_2 (Figure S8 (a)). The RT Raman spectrum of bulk Co_9S_8 under sulfiding atmosphere (Figure 1) displays two lines, a main line at 400 cm^{-1} and another one with lower intensity at 336 cm^{-1} . As for CoS_2 , the change of atmosphere from H_2S to N_2 leads on the spectrum of Co_9S_8 to a shift of these lines to 392 and 332 cm^{-1} (Figure S8 (b)). To the best of our knowledge, among dozens of papers [19-23] where lines mostly located above 500 cm^{-1} were attributed to Co_9S_8 , only one [17] reported recently similar line positions to the ones published herein for bulk Co_9S_8 , with a small shift

which could be ascribed to the atmosphere at which measurements were carried out (unfortunately not specify in [17]).

Finally, under a given atmosphere, herein $\text{H}_2\text{S}/\text{H}_2$, a shift of the Co_9S_8 lines towards low wavenumbers is evidenced when the temperature is increased. At 400°C , for instance, the main line is located at 386 cm^{-1} with a broad shoulder at 323 cm^{-1} instead of 400 and 336 cm^{-1} at RT (Figure 1). This shift monitored during the temperature decrease (Figure S9) from 450°C to RT varies linearly with the temperature. Taking into account the aforementioned variation of line positions of Co_9S_8 and the Raman spectrum of CoS_2 , for which we verified that the position of the lines does not change with heating in this temperature range, we determined that only the broad line around 330 cm^{-1} can be used as a fingerprint of the formation of Co_9S_8 . Figure 2 reports a 2D evolution of its Raman spectra intensity as a function of the temperature. The onset of Co_9S_8 formation from heating of CoS_2 under sulfiding atmosphere is determined around 200°C with the emergence of the broad band in the $326\text{--}330\text{ cm}^{-1}$ range.

3.2 Sulfidation of dried and calcined Co oxidic precursors supported on alumina

Dried oxidic cobalt supported on alumina has been first characterized by XRD, XAS and Raman spectroscopies (Figures S10-S12). The XRD pattern is similar to the one of the alumina support. Only a linear combination fitting of XAS allows us to determine the composition of cobalt oxidic phases dispersed at the surface of the support as a mixture of CoAl_2O_4 , CoAl-based Layered Double Hydroxide (LDH) and $\text{Co}(\text{H}_2\text{O})_6^{2+}$ oxidic species [48]. The lack of lines characteristic of CoAl_2O_4 and CoAl-based LDH both in Raman and XRD suggests a nanometric character of those phases dispersed on the support.

The monitoring of the sulfidation of the dried $\text{Co}/\text{Al}_2\text{O}_3$ sample by Quick-XAS is presented in Figure 3. The transformation of the oxidic species towards sulfided ones is characterized by the progressive decrease of the intense white line at 7726.5 eV and continuous shift of the position of the rising edge from 7718 to 7715 eV (inset of Figure 3). We can estimate that the complete vanishing of the white line occurs around 200°C . Above this temperature, the shape of spectra is characteristic of sulfide cobalt species with the emergence of two characteristic spectra in Figure 3: the cyan and the red ones. The shape of those spectra is very similar to the shape of bulk CoS_2 and Co_9S_8 reported in Figures S2 and S5, respectively. The PCA analysis (Figure S13) carried out on this data set reveals that 3 components are necessary to explain most of the variance of the data evolution. The spectra of those components isolated by MCR-ALS are presented in Figure 4. Figure S14 reports the R_f factors calculated for each spectrum of the data set and compares it to the Lack Of Fit (LOF) of the MCR-ALS solution which is equal to 0.37% whereas Figure S15 displays some characteristic experimental spectra recorded during the sulfidation together with their rebuilt spectra and corresponding residual spectra. Reasonable LOF value and R_f factors characterize the solution provided by MCR-ALS for the data set. The first species is identified as the pristine oxidic mixture of phases supported on alumina (Figure 4 (a)). Due to probable correlated variation of the concentrations of the different oxidic species dispersed at the surface of alumina upon sulfidation, CoAl_2O_4 , CoAl-based LDH and $\text{Co}(\text{H}_2\text{O})_6^{2+}$ species cannot be isolated by the multivariate analysis and are labelled hereafter CoO_x . This failure for isolating the different oxidic components is responsible to the increase of R_f factors (Figure S14 (b)) at the onset of sulfidation (*i.e.* spectra in **D** with index < 100 as shown in Figure S14 (a)) where the proportion of the oxidic species is greater than 50% in the mixture. Noteworthy, despite this increase, the R_f factors still keep satisfactory values, which do not exceed 1.2% . Two different sulfide species are also isolated, Sulfide 1 and Sulfide 2 (Figure 4). Those species are

identified as being CoS_2 and Co_9S_8 , respectively, first by comparison of their XANES spectra with those of bulk cobalt sulfide phases previously discussed and second through the results of EXAFS fitting (Figure S16 and Table 1). For Sulfide 1, although a slight shortening of distances in the first coordination Co-S shell ($-0.06 \text{ \AA}$) and Co-Co shell ($-0.10 \text{ \AA}$) is noted compared to crystalline CoS_2 [44], the shape of the first FT contribution for this species is symmetric with no shoulder on the right side which could be ascribed to the formation of Co_9S_8 [45, 47] or CoS [45, 49] associated with the Co-Co or Co-S contributions around $2.5 - 2.6 \text{ \AA}$ due to edge sharing tetrahedrons or square pyramids in these structures. Although the accuracy in the coordination number for the second coordination shell of Sulfide 1 is very poor ($N(\text{Co-Co}) = 12.1 \pm 4.4$) due to a high correlation between Debye Waller factors and N , and, a probably highly disordered structure associated to the nanometric size of crystallites, the error bar reported for the first coordination shell (5.9 ± 0.2 sulfur atoms) is small and allows us to conclude to the formation of cobalt with octahedral symmetry. Then the similarity of the XANES spectrum with the one of bulk CoS_2 together with this octahedral site for cobalt gives reliable hints to identify Sulfide1 as CoS_2 . The EXAFS spectrum of Sulfide 2 is satisfactorily fitted with parameters fully in agreement with the structure of Co_9S_8 [47]. Additionally, the Raman spectrum recorded at 400°C for Sulfide 2 supported on alumina displays lines at similar positions than those reported for bulk Co_9S_8 (Figure S17), confirming its formation.

The evolution of concentration profiles of those three species as a function of the temperature is displayed in Figure 5, together with the Mass Spectrometry (MS) signals associated to H_2S ($m/Z = 32$) and H_2 ($m/Z = 2$) measured at the cell outlet. The oxidic species are first transformed into CoS_2 species, the transformation being complete at 200°C . The supported CoS_2 species are stable in the $200\text{--}228^\circ\text{C}$ temperature range before being transformed abruptly into Co_9S_8 . The conversion of CoS_2 into Co_9S_8 reaches about 80% at 270°C and is complete after 30 min of isothermal treatment at 400°C . The abrupt conversion of CoS_2 into Co_9S_8 is accompanied by a MS signal corresponding to H_2 consumption and a one corresponding to H_2S release. It is noteworthy that the abrupt transition revealed by the MCR-ALS analysis around 235°C can be also directly seen from the experimental data with the plot of the position of the rising edge, $E_{1/2}$ corresponding to 50% level of the normalized absorbance as a function of temperature (inset Figure 3). $E_{1/2}$ moves abruptly from 7715.3 to 7714.7 eV around 235°C in agreement with the change of the formal cobalt oxidation state from +2 for CoS_2 to +1.77 for Co_9S_8 .

The calcination at 450°C of the dried oxidic precursor under synthetic air leads to the dispersion at the surface of alumina of a mixture of Co_3O_4 , CoAl_2O_4 , CoAl-based LDH phases and $\text{Co}(\text{H}_2\text{O})_6^{2+}$ species [48] (Figures S10-S12). Besides the linear combinations using those references for rebuilding the RT XANES spectrum of the calcined $\text{Co}/\text{Al}_2\text{O}_3$ sample, Raman spectroscopy confirms the formation of Co_3O_4 (Figure S12) whereas XRD evidences that those phases keep a nanometric size since no peaks other than those related to the support are observed.

The monitoring of the sulfidation by quick-EXAFS of the calcined $\text{Co}/\text{Al}_2\text{O}_3$ sample is presented in Figure S18. Still 3 components are necessary for explaining the variance of the data set with LOF = 0.48 %. Contrarily to the dried precursor, the calcined one is not fully sulfided at the end of the treatment: $\approx 6\%$ of irreducible oxide is observed even after 30 min of isothermal treatment at 400°C . As for the dried $\text{Co}/\text{Al}_2\text{O}_3$ sample, the sulfidation of calcined $\text{Co}/\text{Al}_2\text{O}_3$ is still described by the formation of CoS_2 and Co_9S_8 but with incomplete conversion of oxidic species into CoS_2 ($\approx 55\%$ at 140°C) as previously observed (Figure 5) and concomitant formation of Co_9S_8 ($\approx 25\%$) between $25\text{--}140^\circ\text{C}$. The acceleration of the conversion of CoS_2 into Co_9S_8 occurs above 140°C with a transformation rate of $0.4\%/^\circ\text{C}$ up to 240°C and a much slower conversion above 240°C ($\approx 0.09\%/^\circ\text{C}$).

At the end of 30 min of isothermal treatment at 400°C, the composition is 80.5 ± 0.3 % of Co_9S_8 , 13.9 ± 0.3 % of CoS_2 and 5.6 ± 0.1 % of oxidic species ($R_f = 0.35$ %).

3.3 Sulfidation of dried and calcined Co oxidic precursors supported on silica

The speciation of oxidic species on silica is different to the one described on alumina. On the one hand, silica being not prone to be lixiviated by the solution used during the impregnation and maturation stages contrarily to alumina [50], no oxidic precursor involving Si is formed. The dried oxidic precursor supported on silica is described as hydrated Co^{2+} species dispersed at the surface of silica as determined by XAS (Figures S19-S20). On the other hand, due to the lower dispersing ability of silica compared to that of alumina, crystalline phases on the calcined catalyst, mainly composed of Co_3O_4 , have been evidenced by XRD, Raman and XAS (Figures S20-S22). The average crystallite size deduced from the Scherrer's analysis of the well-defined reflections peaks of Co_3O_4 is 16 nm.

Figures S23 and S24 report the monitoring of sulfidation for both samples and the related MCR-ALS solutions characterized by good LOF values similar to those obtained for the alumina support. Again CoS_2 and Co_9S_8 are the two sulfidic species formed upon sulfidation. Irrespective of the sample supported on silica, the transformation of CoS_2 in Co_9S_8 occurs around 200°C with an abrupt transformation rate between 200 and 210°C (3%/°C and 5%/°C for the dried and calcined Co/SiO_2 , respectively) and then more slowly at higher temperature. For both samples, sulfidation is complete but a few percentage of CoS_2 is still present (10-15 %) after the 30 min of isothermal treatment at 400°C. Contrarily to the calcined $\text{Co/Al}_2\text{O}_3$ sample, no refractive oxide against sulfidation is observed for the calcined Co/SiO_2 sample. Starting from large Co_3O_4 crystallites (16 nm) supported on silica, the sulfidation of calcined Co/SiO_2 sample resulted in the formation of large Co_9S_8 crystallites detectable by XRD (Figure S25). The average crystallite size determined by the Scherrer's formula is 14 nm.

3.4 Phase speciation after cooling down supported sulfidic cobalt supported species

The measurements of the cooling down of the different supported samples **under $\text{H}_2\text{S}/\text{H}_2$** surprisingly reported a partial re-sulfidation of Co_9S_8 towards CoS_2 when the temperature decreased. Namely, as shown in Figure 6 (a), a modification of the shape of the XANES spectra is observed for the sulfided dried $\text{Co/Al}_2\text{O}_3$ sample when the temperature is decreased from 400°C to 30°C. Actually the composition at 30°C determined by MCR-ALS is: 46.0 ± 1.1 % of Co_9S_8 and 54.0 ± 1.1 % of CoS_2 (Figure 6 (b)). This transition of Co_9S_8 towards CoS_2 is confirmed by the Raman analysis of the sample measured at RT (Figure S26). Indeed, the main Raman line for this sample is located at 395 cm^{-1} which is at an intermediate position between the ones of CoS_2 (390 cm^{-1}) and Co_9S_8 (400 cm^{-1}) when both are measured at RT under $\text{H}_2\text{S}/\text{H}_2$ atmosphere (Figure 1). Figure 7 reports the evolution of Co_9S_8 and CoS_2 percentages determined by MCR-ALS analysis of the XAS data recorded under $\text{H}_2\text{S}/\text{H}_2$ atmosphere when the cell temperature is decreased after sulfidation from 400 to 30°C (LOF = 0.64 %). A slow transformation occurs between 400 and 200°C with a conversion rate of 0.05%/°C which clearly accelerates below 200°C for reaching a mixture of 50 % of both sulfides at 92°C. Below 100°C, a nearly steady state in the reverse conversion of Co_9S_8 into CoS_2 seems to be reached. The sulfiding atmosphere used for decreasing the temperature from 400°C to RT is responsible for the reversible transition of Co_9S_8 to CoS_2 , as it corresponds to a transition from a sulfide-poor species ($\text{S/Co}=0.89$) toward a richer one ($\text{S/Co}=2$). For example, for the dried $\text{Co/Al}_2\text{O}_3$, the conversion of Co_9S_8 into 54% of CoS_2 corresponds to an uptake of 0.5 sulfur per cobalt atoms. We verified that no formation of

CoS₂ was observed under cooling down of the cell under argon atmosphere from 400 to 40°C (Figure S27).

Similar behaviours after cooling under sulfiding atmosphere were evidenced for the supported cobalt sulfides prepared herein, regardless the support, as soon as the phases do not display a long range order which could be characterized by XRD. Figure 8 compares the composition of the different samples measured at high temperatures, labelled herein HT (450 or 400°C), and the ones determined after sample cooling at RT, labelled RT back. When 68 nm-large bulk Co₉S₈ or 16 nm-large supported crystallites of Co₉S₈ on silica (calc-Co/SiO₂) were prepared, no change of the composition was observed, whereas for the other supported samples, prepared from nanometric sized oxidic species and characterized by nanometric sized sulfidic species, a reverse transition towards CoS₂ formation is observed. This finding emphasizes the highest reactivity of small particles towards the H₂S gas phase compared to the large ones inducing the reversible transformation of Co₉S₈ towards the formation of CoS₂ when the cell is cooled down to RT.

3.5 Quantification of the CoMoS active species formed upon sulfidation of the calcined trimetallic CoNiMo/Al₂O₃ catalyst

The in-depth characterization carried out in this paper on the sulfidation of supported monometallic cobalt oxidic species has been motivated also by our interest to use those results to better characterize cobalt sulfidic species formed on a HDS catalyst. Our motivation is methodological in order to evaluate the use of quick-EXAFS sulfidation monitoring combined with MCR-ALS analysis to determine the relative percentage of the CoMoS HDS active species among the cobalt phases dispersed on alumina during and after activation. It is noteworthy that the rate of cobalt promotion is among many other descriptors a well-known parameter in the literature to be correlated with model molecules HDS catalyst activity [51, 52]. This information can be derived from XPS measurements [30, 53] or from IR measurements of probe-molecule adsorption [54]. Irrespective of the techniques used for the evaluation of the amount of Co-promoted sites, they are always carried out after cooling down of activated catalysts, often under sulfiding atmospheres [53, 54]. Taking into account the afore presented results on the behaviour of supported monometallic Co₉S₈ species during cooling for which a reverse solid-gas reaction under sulfiding atmosphere converts Co₉S₈ into CoS₂, the question of the stability of the CoMoS active phase is relevant to be addressed.

We choose for this proof-of-concept analysis a relatively conventional calcined catalyst prepared from ammonium heptamolybdate and cobalt nitrate. In order to have a composition of oxidic cobalt species closely related to the ones studied herein for the monometallic species, we selected a composition for which no CoMoO₄ species was detected in the pristine oxidic precursor [55, 56]. In the preparation conditions and loading used herein bimetallic CoMo calcined catalysts leading to the formation of CoMoO₄ [56], the catalyst retained is a trimetallic calcined CoNiMo/Al₂O₃ oxidic precursor for which the Raman spectrum (Figure S28) exhibited characteristic lines of bulk MoO₃, in particular the most intense one at 819 cm⁻¹, together with a broad and intense line centered at 950 cm⁻¹, characteristic of polymolybdate species [57] but no lines related to the formation of CoMoO₄ [55, 56]. The linear combination fitting of the RT Co-K edge XANES spectrum of the pristine oxidic HDS catalyst precursor (Figure S29) reveals the dispersion of nanometer-sized CoAl₂O₄ (47.4 ± 0.7 %), Co(H₂O)₆²⁺ (47.5 ± 0.6 %) and CoAl-based LDH (5.1 ± 1.0 %) species [48]. The monitoring of the sulfidation of Co and Mo elements using the alternate recording of quick-XAS spectra at each edge is presented in Figure 9. The sulfidation of cobalt when added as promotor of molybdenum is faster than the ones observed for the monometallic cobalt catalyst (Figure S18) since it has been observed

a more drastic reduction of the white line intensity as soon as the catalyst is in contact with $\text{H}_2\text{S}/\text{H}_2$ gaseous atmosphere at 30°C (Figure 9). Contrariwise, the evolution observed at the molybdenum K edge is in line with those already reported for $\text{CoMo}/\text{Al}_2\text{O}_3$ and $\text{Mo}/\text{Al}_2\text{O}_3$ catalysts [36, 39] with a progressive shift of the rising edge towards lower energy and vanishing of the pre-edge intensity characteristic of the exchange of oxygen ligands by sulfur ones. Due to the close vicinity of nickel K edge with the one of cobalt, the evolutions of nickel species have been also recorded (Figure S30) simultaneously to the ones of cobalt species. However, as the purpose of the paper is to illustrate the methodology for quantifying the CoMoS species during the sulfidation of HDS catalyst precursor, no further investigation has been done herein for the nickel promotor. Obviously for a complete structure-activity relationship understanding, the formation of NiMoS and monometallic NiS_x species should be also considered.

The multivariate analysis of the evolution recorded at the Mo K edge under $\text{H}_2\text{S}/\text{H}_2$ for the CoNiMo oxidic precursor was performed considering 3 components, as determined by Principal Components Analysis (Figure S31). As detailed in Supplementary Information (Figure S32), the first component is related to the initial oxidic molybdenum-based species, the second one to an oxysulfide MoO_xS_y species whereas the third is identified as the MoS_2 species. The MoS_3 species, which is an intermediate usually described before the formation of MoS_2 in the literature [58, 36, 39, 40], is surprisingly not isolated herein by MCR-ALS. We assume that this finding is related both to its low abundance (in proportion but also in number of spectra in the data set in which the species contributes) in the Mo K edge data set reported herein, and to the RT nucleation and growth of MoS_2 . When MoS_3 was isolated by MCR-ALS [36, 39, 40], its presence was detected over a large temperature range with onset of formation around 80°C and characterized by a maximum of abundance around $200 - 220^\circ\text{C}$ corresponding to the onset of formation of MoS_2 . It is noteworthy that RT nucleation of MoS_2 has been also observed in the literature by XPS [59], meaning that sulfidation kinetics are dependent of many parameters, in particular the hydration level of the oxidic precursors [40, 60]. Strategies to isolate MoS_3 during the sulfidation of this trimetallic oxidic precursor could then be proposed such as other sulfidation conditions (heating ramp, dehydration...) and/or other data recording in order to increase the number of spectra in which MoS_3 is present in the mixture of species. For instance, by changing the edge jumping acquisition mode by a one with data only recorded at the Mo K edge over the full life span of activation multiplies by 4 the total number of spectra in the data set. But in that case, we lose the simultaneous recording of evolution of Co and Mo and the unambiguous comparison of fate of both elements upon sulfidation, as we will discuss later (*vide infra*).

At the Co K edge, the variance evaluation by PCA of the only data set composed of spectra recorded upon sulfidation of the CoNiMo precursor reveals 3 components (Figure S33). However, the minimization carried out on the basis of 3 components does not allow to properly isolate the pure chemical species involved during sulfidation, as discussed in Supplementary Information (Figure S34). In particular, the intermediate component extracted considering a solution with 3 components still presents a reminiscence of the white line characteristic of the oxide species. This is strong evidence that this component is not a pure species but a mixture of the oxidic species and of a sulfide one. Furthermore, the concentration of the third component is equal to 100% at 400°C which is not consistent with the formation of a mixture of Co_9S_8 and CoMoS species reported in the literature [3, 30, 39, 45, 51, 53]. As aforementioned, the species composing the pristine oxidic cobalt precursor in the trimetallic HDS catalyst are similar to those dispersed on the dried $\text{Co}/\text{Al}_2\text{O}_3$ sample. Consequently, their evolution upon sulfidation should be related to the formation of CoS_2 and Co_9S_8

supported species, together with the expected formation of the active CoMoS species. The number of components which should be highlighted by the PCA analysis of the data recorded for the CoNiMo oxidic precursor should be therefore 4 with the 3 different sulfide species, CoS₂, Co₉S₈ and CoMoS, and the initial cobalt oxidic species. The failure of detection of 4 components by PCA of the evolving data of CoNiMo oxidic precursor upon H₂S/H₂ exposure reveals a rank deficiency of the data, an issue which can occur when large similarity among species spectra or co-evolving concentration profiles exist [61]. The so-called column-wise augmented (CWA) data strategy consisting in adding to the data presenting rank deficiency an additional data set sharing some components with the former ones is powerful to break rank-deficiency and separate the three sulfide cobalt-based species. For this purpose, the CoNiMo oxidic precursor data recorded upon sulfidation were added to the one recorded for the dried Co/Al₂O₃ sample for T > 200°C (Figure 3), *i.e.* a data set containing only the mixture of CoS₂ and Co₉S₈ supported species. In that case, the PCA analysis of the CWA data set, which is presented on Figure S35, is consistent with the use of 4 components for explaining its variance. The CWA data set is further treated with the additional constraints that the oxidic species and the CoMoS species do not contribute to the concentration matrix for the data related to the dried Co/Al₂O₃ sample. The results using this approach are presented in Figures S36 and S37. At the Co K edge, the 1st component is related to the pristine cobalt oxidic species whereas the shape of the XANES spectra of the three other components is characteristic of three sulfide-based species (Figure S37). The EXAFS spectra extracted from the XAS data isolated by CWA-MCR analysis are presented in Figure 10. The spectra of the 3rd (Figure 10 (b)) and 4th (Figure 10 (c)) components are compared to the experimental spectra of CoS₂ and Co₉S₈ species obtained during the sulfidation of the dried Co/Al₂O₃ sample recorded in temperature or at RT after cooling under the appropriate atmosphere for which no change of phase is observed as afore discussed. Therefore, the 2nd component, for which its EXAFS spectrum is presented in Figure 10 (a), is assumed to be related to the active CoMoS phase. Noteworthy are the differences of EXAFS oscillation shape between the spectra characteristic of the monometallic species in Figure 10 (b) and (c), with a monotonous decrease in intensity of oscillations beyond 6 Å⁻¹, which corresponds to the maximum of the scattering amplitude of S backscatters, and the spectrum of the 2nd component (Figure 10 (a)) with a two-maxima behaviour, one around 6 Å⁻¹ for sulfur backscatters and a second one around 10 Å⁻¹. The second maximum is related to the contribution of molybdenum backscatters in agreement with the reported position of the maximum of backscattering amplitude for this element [62] and gives strong support to relate this species as the CoMoS active phase as discussed also in [51]. To validate this assignment, the EXAFS spectrum for this 2nd component was simulated by a least square fitting procedure considering two contributions of neighbours: a first coordination shell of sulfur and a second coordination shell of molybdenum atoms. A satisfactory simulation reported in Figure S38 and Table 2 is obtained with distances for the Co-S (at 2.22 Å) and Co-Mo (at 2.84 Å) contributions in agreement with the description of the CoMoS active phase reported from density functional theory (DFT) calculations [63] or from EXAFS fitting [45, 64].

Figure 11 displays the MCR-ALS evolution profiles of the CoO_x, CoS₂, Co₉S₈ and CoMoS species characterizing the sulfidation of the CoNiMo oxidic precursors. We observe for the concentration profiles of CoMoS and Co₉S₈ a very close evolution upon temperature increase, which is consistent with the observed rank deficiency characterizing the data set of CoNiMo catalyst when minimized without considering the CWA approach. Finally, as Co and Mo K edge data for this catalyst were recorded alternately during the same experiment, both data sets share the same temperature dependence. Then for comparison purpose and further detailed discussion, the evolution profile of

the species isolated at the Mo K edge is also plotted with the concentration profile of cobalt-based species in Figure 11.

4. Discussion

In this paper, ***the Raman spectrum of bulk Co₉S₈ with characteristic lines at 400 cm⁻¹ and satellite at 336 cm⁻¹ when measured at RT under H₂S/H₂ with 532 nm laser excitation was reported*** in agreement with the spectrum recently published by Wang *et al.* [17]. The slight shift of the lines to low wavenumber (- 4 cm⁻¹) between our results and the spectrum in [17] could be related to the atmosphere under which both spectra were collected, as evidenced herein when the atmosphere was changed from H₂S/H₂ to inert atmosphere (Figure S8 (b)). But the atmosphere dependence of the line position is not responsible for the inconsistency of published results in the abundant literature related to electrocatalysts because the lines used in those papers are shifted by several hundreds of cm⁻¹ compared to our positions. The formation of Co₉S₈ is concluded from the presence of a main line at 573 [23], 586 [20], 650 [19], 667 [21] or 685 cm⁻¹ [22] to cite only a few of these papers. We ascribe that those lines arise from laser radiation damage, since we have experienced by ourselves the high sensitivity of bulk Co₉S₈ under air when the laser power was increased. (Figure S39). Two lines are present at low laser nominal power (less than 6 mW) at 400 and 278 cm⁻¹ and stable for more than 12 h under air for recording of 14 spectra corresponding to the merge of 12 spectra each acquired for 10s. The line at 400 cm⁻¹ is well in line with the one reported for Co₉S₈ under H₂S/H₂ (Figure 1) whereas the line at 278 cm⁻¹ could be related to surface oxidation of Co₉S₈ crystallites. As soon as the laser power is increased above 6 mW, a broad line at 335 cm⁻¹, with additional lines at 473-475 and 678-680 cm⁻¹ with quite similar intensities at 16 mW, replaced the former lines. Finally, above 25 mW, the line at 335 cm⁻¹ strongly decreases and the characteristic intense lines of Co₃O₄ appear at 475, 515, 612 and 681 cm⁻¹. By comparison with the reported values in the previous papers with the ones observed upon increasing the laser power, we suggest that these lines are due to irradiation damages with the formation of oxysulfide and/or oxidic phases.

The ***sulfidation of cobalt oxidic species supported on alumina and silica displays common intermediate sulfidic species identified as CoS₂ and Co₉S₈***. The monitoring of gaseous products by Mass Spectrometry allows us to propose as reaction for the formation of Co₉S₈:

This transition is more abrupt when starting from the dried oxidic precursors than from the calcined ones. Irrespective of the samples, this transition occurs around 180-240°C, which is a temperature close to the temperature at which bulk CoS₂ starts to be transformed into bulk Co₉S₈ (Figure 2). The abruptness of transition from a sulfur-rich phase, CoS₂, towards a sulfur-poor phase, Co₉S₈, is very similar to the one reported for dried Ni oxidic species supported on alumina [26], highlighting the similarity of behaviours for supported oxidic species with a low metal loading (2.1 wt % for Ni and 4.0 wt % for Co). The structural parameters reported from the MCR-ALS analysis of the XAS data sets recorded during sulfidation for the supported pyrite MS₂ phase, M = Ni or Co, have a common feature which is a shortening of distances between the metal and sulfur in the first coordination shell and metal nearest neighbours compared to those reported for bulk pyrites. The shortening of both distances could be ascribed to a contraction of cubic cell parameters of about 2-3 %. Recent DFT calculations have shown that single sulfur and cobalt vacancies and double Co-S vacancies are easily formed in bulk cobalt pyrite [65]. In particular, the DFT calculation of the lattice parameter dependence on S vacancy concentration shows that a contraction of 3 % can be associated with 2S

vacancies [66]. In order to confirm the presence of sulfur vacancies in the phase formed at 200°C upon sulfidation of dried Co/Al₂O₃, this phase was analysed by XPS. The 200°C-Co/Al₂O₃ sample was prepared by stopping the sulfidation at 200°C and immediately decreasing the temperature up to RT under H₂S/H₂ atmosphere. The purge of the cell under argon was carried out at RT. Figure S40 reports the Co 2p and S 2p XPS spectra for this as-prepared 200°C-Co/Al₂O₃ sample. The decomposition of the Co 2p spectrum has been performed considering the metallic character of the pyrite which leads to introduce plasmonic and Auger peaks in the decomposition as reported in [67] and gives a main 2p_{3/2} contribution located at 778.1 eV, in agreement with the value reported for bulk CoS₂ [68]. The S 2p spectrum consists of two doublets with S 2p_{3/2} energies of 161.7 eV and 164 eV together with a small contribution of sulfate ions at higher energies ($\approx$ 169 eV). The doublet located at 164 (2p_{3/2}) and 165.2 eV (2p_{1/2}) could be ascribed to elemental sulfur whereas the position of the 2p_{3/2} at 161.7 eV is different to the one reported for S₂²⁻ for bulk CoS₂ by $\approx$ -0.9 eV, which could be related to a slight band structure modification associated to vacancy formation as discussed in [65]. The chemical composition of the 200°C-Co/Al₂O₃ sample determined by XPS is CoS_{1.9} which is consistent with the formation of a defective CoS₂ structure deduced from XAS analysis in agreement with DFT calculations.

A complete sulfidation of oxidic precursor is observed for most of the supported monometallic samples, except for the calcined oxidic precursors supported on alumina where about 6% of oxidic species is still remaining after 30 min of sulfidation at 400°C. Co₃O₄ and CoAl₂O₄ species were both detected as composing the calcined Co/Al₂O₃ sample but the full sulfidation of the calcined Co/SiO₂ sample mainly composed of Co₃O₄ crystallites is a strong indication that the remaining oxidic species on the sample supported on alumina must be ascribed to the well-known difficulty to sulfide spinel-like cobalt aluminate [3]. Everything else being equal, in particular the heating ramp of 3°C/min (Figure 8), dried samples give rise after 30 min of isothermal treatment at 400°C to the higher proportion of Co₉S₈ (90%) still mixed with CoS₂. It is noteworthy that increasing the ramp to 5 (Figures 3 and 5) or 10°C/min (not shown) for the dried Co/Al₂O₃ sample gives rise to complete sulfidation into Co₉S₈. As discussed in the next section of this paper related to the sulfidation of the CoNiMo sample, the fine description of the monometallic cobalt species involved upon sulfidation will be important for unravelling the complexity of sulfidation of cobalt in presence of molybdenum.

Another striking result coming from the monitoring of species formed upon sulfidation of supported cobalt catalysts and subsequent cooling is the **reactivity of the supported Co₉S₈ phase**. When the temperature is decreased under H₂S/H₂ (Figure 7), the rich-sulfiding atmosphere is responsible for the new uptake of sulfur with respect to cobalt when the sample is back at RT. This uptake is higher for the samples presenting a high dispersion of Co₉S₈, *ie* those supported on alumina or the one resulting from the sulfidation of dried Co/SiO₂. At the opposite, the composition of the bulk Co₉S₈ and calcined Co/SiO₂ samples does not change upon cooling. As already mentioned, this is a strong indication that the dispersion of Co₉S₈ plays a key role in the reverse Co₉S₈ $\rightarrow$ CoS₂ transition. It is noteworthy that the presence of the defective CoS₂ in highly dispersed samples is well in line with the results obtained by Ledoux *et al.* [29] using solid state ⁵⁹Co NMR to determine cobalt speciation on silica. Their characterization evidenced four different cobalt sites after sulfidation with two of them corresponding to the regular octahedral and tetrahedral Co₉S₈ sites found regardless the studied cobalt loading that ranged from 38.3 to 2.5 wt % and two additional sites corresponding to a distorted tetrahedral site and a distorted octahedral site, only observed for the lowest loadings. The distorted octahedral site which was surmised by Ledoux *et al.* to be related to the CoS phase [29] is ascribed, considering our results, to be the defective CoS₂ which is reformed during cooling for

dispersed species on silica and alumina. As Ledoux could not study alumina-supported catalysts under the NMR conditions they used, our study enlarges their conclusions to alumina support. Finally, similar $\text{Co}_9\text{S}_8/\text{CoS}_2$ reversibility has been also evidenced for silica and alumina supported Co-based catalysts by Dujardin [69] using low temperature CO adsorption followed by FTIR spectroscopy. Sulfidation of supported cobalt-based catalysts leads to a characteristic line at 2094 cm^{-1} for the alumina support [69, 70] and 2110 cm^{-1} for the silica one [69], which is characteristic of the interaction of CO with sulfide cobalt species. Upon further H_2 treatment of the sulfided catalysts at 300°C , the creation of sulfur vacancies in the sulfided species occurs by removing sulfur in the form of H_2S , with a new line appearing at 2056 cm^{-1} on the alumina support and 2063 cm^{-1} on the silica one. This behaviour was ascribed by Dujardin to the transformation of a rich-sulfide cobalt-based phase into a species with lower sulfur content which was associated to Co_9S_8 . Irrespective of the assignation done by Dujardin *et al.* on the different lines, this study still highlights the high solid-gas reactivity of the sulfided species formed by sulfidation towards defective ones in sulfur as the CoS_2 species was described at the light of our results.

Thanks to the extensive study of Co-supported materials sulfidation, we report in this paper ***for the first time the in situ quantification of the CoMoS species on a CoNiMo supported HDS catalyst*** from the MCR-ALS analysis of its gas sulfidation XAS monitoring. It is noteworthy that due to the use of an element-selective technique such as XAS, the methodology used for this purpose is general and can be applied to any HDT catalysts containing cobalt as promotor, irrespective of its chemical composition. By introducing the CoS_2 and Co_9S_8 spectra systematically observed for Co-based monometallic catalysts, regardless of the support, through the data set augmentation method, the spectrum of a third cobalt based sulfide species has been isolated and its concentration evolution profile described. The assignment of this sulfide species to the CoMoS active phase has been obtained from its EXAFS analysis and reproduction of the beat pattern at $10\text{ \AA}^{-1}$ characteristic of the backscattering of the photoelectron by heavy Mo backscatters (Figure 10 and Figure S38). It is important to keep in mind that the Co K edge EXAFS fingerprint which is used for the CoMoS phase described in the literature is a purely local point of view analysis highlighting only the characteristic Co-S-Mo interaction. From the Co K edge EXAFS data fitting, no information related about the extent of the MoS_2 slab promoted by Co can be obtained. This information is obtained indirectly by the Mo K edge XAS monitoring which provides the evidence of MoS_2 formation or directly by HAADF-STEM analysis [71, 72]. The “Co-S-Mo” species, when Co is in interaction with Mo at the early stage of nucleation of MoS_2 slabs involving a very few number of Mo atoms, displays an EXAFS signal similar to the CoMoS active species observed at 400°C when MoS_2 is mainly formed, except with a higher Debye-Waller factor due to the increase of temperature.

Our results highlight for the calcined CoNiMo catalyst the competitive formation of CoS_2 and CoMoS at the early stages of the sulfidation (Figure 11). At temperature higher than 150°C a clear conversion of CoS_2 into Co_9S_8 occurs leading at the end of heating (400°C) to 45 % of Co_9S_8 . The formation of “Co-S-Mo” species starting at RT, in agreement with the onset of nucleation of MoS_2 , is fast between 30 and 100°C with $\approx 27\%$ of CoMoS formed at 100°C and slows down with a quasi linear behaviour of $0.07\%/^\circ\text{C}$ until to reach 400°C . At this temperature, $\approx 49\%$ of CoMoS is formed with a percentage which does not change during the 2 hours of isothermal treatment (Figure S41). As expected for a calcined catalyst, about 6 % of Co species remains at the oxidic state probably associated to the formation of CoAl_2O_4 species. It is noteworthy that for a calcined CoMoP supported catalyst on alumina, the room temperature formation of CoMoS and MoS_2 nuclei, described by TEM as nonorganized particles as soon as the sulfidation temperature is below 200°C , has been also reported

by *ex situ* Co 2p and Mo 3d XPS characterization done for samples sulfided at different temperatures (25, 100, 200, 300, 350, 400, 500 and 600°C) [3, 59]. The *ex situ* XPS characterization required to repeat the sulfidation process at the different temperatures in order to access to the Co and Mo speciation. Herein a single experiment, where sulfidation is alternately monitored at Co and Mo K edges, allows for accessing to the same information but with a temperature step of 6°C between each measure. It is interesting to note also that the concomitant presence of CoS₂ and Co₉S₈ species observed by XAS are not resolved by the *ex situ* XPS characterisation [53, 59]. Due to the fact that we have demonstrated herein that a conversion of nano-sized Co₉S₈ particles towards nano-sized CoS₂ ones occurs when the temperature is decreased under sulfiding atmosphere and that both sulfides are characterized by a 2p peak emission located at the same position (778.1 eV) [68, 59], their distinction by XPS is impossible and makes incomplete the cobalt speciation of monometallic species reported by the photoemission technique. For the CoNiMo catalyst studied herein, we verified that the linear combination of the XAS spectrum recorded after sulfidation and temperature decrease to RT under H₂S/H₂ atmosphere evidences that the percentage of CoMoS is not affected and remains at the level of 45 ± 1%, but the conversion of Co₉S₈ into CoS₂ still occurs with 32 ± 1% of CoS₂ and 20 ± 1% of Co₉S₈ at RT (Figure 12). The invariance of amount of CoMoS species upon temperature decrease validates therefore the correlation observed between the catalyst activity for HDT reactions carried out in a temperature range close to the activation temperature (300-400°C) and the amount determined by *ex situ* techniques such as XPS [30, 53] or by IR probe molecule adsorption, which requires to measure under liquid nitrogen temperature [54, 71].

5. Conclusions

In this paper, the formation of bulk Co₉S₈ certified by its XRD pattern and Co K edge characterizations has been reported through the heating of bulk CoS₂ phase under sulfiding atmosphere. This allows us to unambiguously report the Raman spectrum of the Co₉S₈ phase in temperature and after cooling down at RT, which could be used further to identify Co₉S₈ nanometric-sized phases studied as supported (electro)-catalysts.

The sulfidation pathways under 10% H₂S/H₂ atmosphere of dried and calcined cobalt supported oxidic species on alumina and silica have been studied by Co K edge quick-XAS spectroscopy combined with multivariate analysis. These pathways share a common characteristic: first the cobalt oxidic species is transformed into nanometer-sized CoS₂ particles before to be converted into nanometer-sized Co₉S₈ particles. The nanometer character of the Co₉S₈ particles is responsible of their high reactivity against H₂S when they are cooled down to RT with the partial (re)conversion into CoS₂. The smaller the Co₉S₈ nanoparticles the higher the amount of formed CoS₂ after cooling.

Finally, for the first time, the *in situ* quantification of the CoMoS active species formed upon sulfidation of a calcined cobalt promoted molybdenum-based HDS catalyst has been achieved using the so-called column-wise augmented strategy consisting in minimizing the data set composed of the monitoring of the sulfidation of the supported HDS catalyst and those collected during quick-XAS data monitoring of monometallic dried cobalt oxidic species supported on alumina where only a mixture of the supported CoS₂ and Co₉S₈ species is present. The conversion of Co₉S₈ into CoS₂ is still observed for the HDS catalyst when temperature is decreased under H₂S/H₂ atmosphere but this conversion does not change the CoMoS percentage between the end of the sulfidation at 400°C and RT. The method described herein is unique for reporting the cobalt speciation and could significantly contribute to establishing a relationship between active phase formation, catalysis genesis on one hand and catalytic activity on the other hand for cobalt promoted HDS catalysts.

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References

- [1] E. Cadot, M. Lacroix, M. Breysse, E. Arretz, J. Catal. 164 (1996) 490-492.
- [2] V Mashkina, A V Mashkina, O P Krivoruchko, L N Khairulina Kinetics and Catalysis, 49 (2008) 103-109.
- [3] "Catalysis by Transition Metal Sulphides.From molecular theory to industrial applications. H. Toulhoat and P. Raybaud, Editors, Technip Edition, Paris, 2013.
- [4] I. Alstrup, I. Chorkendorf, R. Candia, B. S. Clausen, H. Topsøe, J. Catal. 77 (1982) 397-409.
- [5] H Topsøe, R Candia, N Y Topsøe, B S Clausen, Bull. Soc. Chim. Belges 93 (1984) 783-806.
- [6] A S Bambal, V S Guggilla, E L Kugler, T H Gardner, D B Dadyburjor, Ind. Eng. Chem. Res 53 (2014) 5846-5857.
- [7] Y. Liu, C. Xiao, M. Lyu, Y. Lin, W. Cai, P. Huang, W. Tong, Y. Zhou, Y. Xie, Angew. Chem. Ind. Ed. 54 (2015) 11231-11235.
- [8] J. Zhang, X. Bai, T. Wang, W. Xiao, P. Xi, J. Wang, D. Gao, J. Wang, Nano-Micro Lett. 11 (2019) 1-13.
- [9] H. Zhang, Y. Li, T. Xu, J. Wang, Z. Huo, P. Wan, X. Sun, J. Mater. Chem. A 3 (2015) 15020-15022.
- [10] N. Kornienko, J. Resasco, N. Becknell, C. M. Jiang, Y. S. Liu et al. J. Am. Chem. Soc. 137 (2015) 7448-7455.
- [11] C. Su, J. Xiang, F. Wen, L. Song, C. Mu, D. Xu, C. Hao, Z. Liu, Electrochimica Acta 212 (2016) 941-949.
- [12] J. Zhang, W. Xiao, P. Xi, S. Xi, Y. Du, D. Gao, J. Ding, ACS Energy Lett. 2 (2017) 1022-1028.
- [13] Q. Shi, C. Zhu, D. Du, Y. Lin, Chem. Soc. Rev. 48 (2019) 3181-3192.
- [14] P. J Masset, R. A. Guidotti J. Power Sources 178 (2008) 456-466.
- [15] C. J. Chen, P. T. Chen, M. Basu, K. C. Yang, Y. R. Lu, C. L. Dong, C. G. Ma, C. C. Shen, S. F. Hu, R. S. Liu J. Mater. Chem. A 3 (2015) 23466-23476.
- [16] S. G. Lyapin, A. N . Utyuzh, A. E. Petrova, A. P. Novikov, T. A. Lograsso, Z. M. Stichov, J. Physics Condensed Matter 26 (2014) 396001.
- [17] J. Wang, H. Liu, W. Wang, Q. Sun, X. Wang, X. Zhao, H. Hu, M. Wu, Carbon 144 (2019) 259-268.
- [18] L. Chen, W. Yang, X. Li, L. Han and M. Wei, J. Mater. Chem. A 7 (2019) 10331-10337.
- [19] L. Yang, H. Li, S. Zhang, F. Yao, J. Lv, S. Xu, J. Alloys and Compounds 768 (2018) 485-494.
- [20] T. M. Mashikhwa, M. J. Madito, A. Bello, J. Lekitima, N. Marryala, RSC Advances 7 (2017) 20231-20240.
- [21] Q. Gao, Z. Shi, K. Xue, Z. Ye, Z. Hong, X. Yu, M. Zhi, Nanotechnology 29 (2018) 215601.
- [22] L. L. Feng, G. D. Li, Y. Liu, Y. Wu, H. Chen, Y. Wanf, Y. C. Zou, D. Wang, X. Zou, ACS applied Materials & Interfaces, 7 (2015) 980-988.
- [23] P. F. Yin, L. L. Sun, Y. L. Gao, S. Y. Wang, Bull. Mater. Sci. 31 (2008) 593-596.
- [24] N. Kumar, N. Raman, A. Sundaresan, Z. Anorg. Allg. Chem. 640 (2014) 1069-1074.
- [25] D. M. Pasquariello, R. Kershaw, J. D. Passaretti, K. Dwight, A. Wold, Inorg. Chem. 23 (1984) 872-874.
- [26] A. Rochet, A. Ribeiro Passos, C. Legens, V. Briois, Catal. Struct. React. 3 (2017) 33-42.
- [27] A. de Juan, J. Jaumot, and R. Tauler, Anal. Methods 6 (2014) 4964-4976.
- [28] B. Scheffer, J. C. M. de Jonge, P. Arnoldy, J. A. Moulijn Bull. Soc. Chim. Belg. 93 (1984) 751-762.
- [29] M. J. Ledoux, O. Michaux, G. Agostini, P. Panissod, J. Catal. 96 (1985) 189-201.
- [30] A. D. Gandubert, C. Legens, D. Guillaume, S. Rebours, E. Payen, Oil & Gas Science and Technology 62 (2007) 79-89.
- [31] V. Briois, C. La Fontaine, S. Belin, L. Barthe, T. Moreno, V. Pinty, A. Carcy, R. Girardot, E. Fonda, J. Phys. Conf. Ser. 712 (2016) 12149.

- [32] C. La Fontaine, F. Villain, V. Briois, X. Sécordel, A. Yoboué, A. Berrier, S. Cristol, Coupled XAS-Raman Operando analysis of TiO₂ supported oxomolybdate catalysts in methanol conversion. I. Harrick Scientific Products (Ed.), Applications Note n°91201. (2010).
- [33] C. La Fontaine, L. Barthe, A. Rochet, V. Briois, *Catal. Today* 205 (2013) 148–158.
- [34] E. Fonda, A. Rochet, M. Ribbens, L. Barthe, S. Belin, V. Briois, *J. Synchrotron Radiat.* 19 (2012) 417–424.
- [35] M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson, R. St. C. Smart, *Applied Surface Science* 257 (2011) 2717–2730.
- [36] C. Lesage, E. Devers, C. Legens, G. Fernandes, O. Roudenko, V. Briois, *Catal. Today* 336 (2019) 63–73.
- [37] C. Ruckebusch, L. Blanchet, *Anal. Chim. Acta* 765 (2013) 28–36.
- [38] H. R. Keller, D. L. Massart, *Chemom. Intel. Lab. Syst.* 12 (1992) 209–224.
- [39] A. Rochet, B. Baubet, V. Moizan, C. Pichon, V. Briois, *Comptes Rendus Chim.* 19 (2016) 1337–1351.
- [40] A. Rochet, B. Baubet, V. Moizan, E. Devers, A. Hugon, C. Pichon, E. Payen, V. Briois, *J. Phys. Chem. C* 121 (2017) 18544–18556.
- [41] J. Jaumot, R. Gargallo, A. de Juan, R. Tauler, *Chemometr. Intell. Lab. Syst.* 76 (2005) 101–110.
- [42] B. Ravel, M. Newville, *J. Synchrotron Radiat.* 12 (2005) 537–541.
- [43] W. Jauch, M. Reehuis, H. J. Bleif, F. Kubanek, P. Pattison, *Phys. Rev. B* 64 (2001) 052102-1–052102-3.
- [44] E. Nowack, D. Schwarzenbach, T. Hahn, *Acta Crystallogr. B Struct. Sci.* 47 (1991) 650–659.
- [45] S. M. A. M. Bouwens, J. A.R. van Veen, D. C. Koningsberger, V. H. J. de Beer, R. Prins, *J. Phys. Chem.* 95 (1991) 123–134.
- [46] S. M. A. M. Bouwens, D. C. Koningsberger, V. H. J. de Beer, R. Prins, *Catal. Letters* 1 (1988) 55–60.
- [47] S. Geller, *Acta Cryst.* 15 (1962) 1195–1198.
- [48] A. R. Passos, L. Martins, S. H. Pulcinelli, C. V. Santilli, V. Briois, *ChemCatChem* 9 (2017) 3918–3929.
- [49] N. Alsén, *Geol. Foereningen i Stock. Foerhandlingar* 47 (1925) 19–72.
- [50] J. B. d’Espinose de la Caillerie, M. Kermarec, O. Clause, *J. Am. Chem. Soc.* 117 (1995) 11471–11481.
- [51] L. van Haandel, G. M. Bremmer, E. J. M. Hensen, Th. Weber, *J. Catal.* 342 (2016) 27–39.
- [52] B. Guichard, M. Roy-Auberger, E. Devers, C. Legens, P. Raybaud, *Catal. Today* 130 (2008) 97–108.
- [53] A. D. Gandubert E. Krebs, C. Legens, D. Costa, *Catal. Today* 130 (2008) 149–159.
- [54] M. A. Lélías, J. van Gestel, F. Maugé, J. A. R. van Veen, *Catal. Today* 130 (2008) 109–116.
- [55] E. Payen, M. C. Dhamelinourt, P. Dhamelinourt, J. Grimblot, J. P. Bonelle, *App. Spectros.* 36 (1982) 30–37.
- [56] C. P. Cheng, G. L. Schrader, *J. Catal.* 60 (1979) 276–294.
- [57] S. Kasztelan, J. Grimblot, J. P. Bonnelle, E. Payen, H. Toulhoat, Y. Jacquin, *Appl. Catal.* 7 (1983) 91–112.
- [58] Th. Weber, J. C. Muijsers, J. H. M. C. van Wolput, C. P. J. Verhagen, J. W. Niemantsverdriet, *J. Phys. Chem.* 100 (1996) 14144–14150.
- [59] A. D. Gandubert, C. Legens, D. Guillaume, E. Payen, *Surf. Interface Anal.* 38 (2006) 206–209.
- [60] E. Le Guludec, L. Oliviero, J. P. Gilson, F. Maugé, M. Rebeilleau, V. De Grandi, S. A. van Donk, *Catal. Sci. Technol.* 5 (2015) 835–842.
- [61] C. Ruckebush, A. De Juan, L. Duponchel, J. P. Huvenne, *Chemometr. Intell. Lab. Syst.* 80 (2006) 209–214.

- [62] S. P. Cramer, K. O. Hodgson, E. I. Stiefel, W. E. Newton, J. Am. Chem. Soc. 100 (1978) 2748-2461.
- [63] E. Krebs, A. Daudin, P. Raybaud, Oil& Gas Science and Techn. 64 (2009) 707-718.
- [64] D. Genuit, P. Afanasiev, M. Vrinat, J. Catal. 235 (2005) 302-317.
- [65] S. Li, Y. N. Zhang, X. Niu, Phys. Chem. Chem. Phys. 20 (2018) 11649-11655.
- [66] J. Zhang, W. Xiao, P. Xi, S. Xi, Y. Du, D. Gao, J. Ding ACS Energy Lett. 2 (2017) 1022-1028.
- [67] C. Desjacques « Apports des méthodes photon-in/photon –out à la compréhension des systèmes catalytiques complexes » PhD thesis University of Lille 1 (2018).
- [68] H. van der Heide, R. Hemmel, C. F. van Bruggen, C. Haas, J. Solid State Chem. 33 (1980) 17-25.
- [69] C. Dujardin « Caractérisation de catalyseurs d'hydrotraitement par réactions modèles et spectroscopie infrarouge : apport à la compréhension du fonctionnement sur charge réelle. » PhD thesis, University of Caen (2002).
- [70] A. Travert, C. Dujardin, F. Maugé, E. Veilly, S. Cristol, J.-F. Paul, E. Payen, J. Phys. Chem. B 110 (2006) 1291-1270.
- [71] L. A. Zavala Sanchez « Supported transition metal disulfide catalysts for ultra-deep HDS : Coupling of IR spectroscopy and high resolution microscopy for a deeper insight into active sites. » PhD thesis, University of Caen Normandie (2019).
- [72] M. Kulikova, A. Mozhaev, C. Lancelot, M. Marinova, P. Blanchard, E. Payen C. Lamonier, P. Nikulshin. Applied Catalysis B: Env. 224 (2018) 951-959.

	N	R(Å)	R(Å) from XRD	σ ² (10 ⁻³ Å ²)	enot (eV)	R _f (%)	χ ² _{red}
Sulfide 1							
Co-S	5.9 ± 0.2	2.25 ± 0.02	2.31	8.1 ± 0.6	0.73	0.3	29522
Co-S	7.2 ± 1.6	3.56 ± 0.02	3.545	23.4 ± 7.6			
Co-Co	12.1 ± 4.4	3.79 ± 0.03	3.89	40.6 ± 6.7			
Sulfide 2							
Co-S	4.0 ± 0.1	2.21 ± 0.01	2.22	9.6 ± 0.3	0.03	0.09	10089
Co-Co	2.1 ± 0.2	2.56 ± 0.03	2.50	15.3 ± 0.9			

Table 1: Structural parameters determined for Sulfide 1 and Sulfide 2 components isolated by MCR-ALS analysis of the data set recorded upon sulfidation of the dried Co/Al₂O₃ oxidic sample. Those parameters were obtained by least square fitting of the filtered EXAFS spectra resulting from a back Fourier transform over 1-3.8 Å (Sulfide 1) and 1-2.8 Å (Sulfide 2) of the Fourier transforms of the experimental EXAFS spectra ($k_{\text{min}}=2.8 \text{Å}^{-1}$ and $k_{\text{max}}= 10.6 \text{Å}^{-1}$, Kaiser Bessel window with $dk=2$). $S_0^2 = 0.71$, N, coordination numbers, R, distances between Co and neighbouring atoms, σ , Debye Waller factor, enot, scaling energy parameter. The reliability of the fit was assessed by the minimization of the reduced χ^2_{red} and R_f metrics defined by the IXS standards and criteria committee (http://ixs.iit.edu/subcommittee_reports/sc/err-rep.pdf). The mean distances determined from the crystallographic structure for CoS₂ and Co₉S₈ are reported for comparison purpose.

	N	R(Å)	σ^2 (10^{-3}Å^2)	enot (eV)	R _f (%)	χ^2_{red}
Co-S	4.7 ± 0.6	2.22 ± 0.01	7.8 ± 1.6	-5.2	0.3	630.6
Co-Mo	0.9 ± 0.4	2.84 ± 0.03	7.6 ± 10			

Table 2: Structural parameters determined by least square fitting of the filtered EXAFS spectrum (back Fourier transform over 1-3 Å) isolated for the second component by MCR-ALS analysis of the data recorded upon sulfidation of the CoNiMo oxidic catalyst precursor supported on alumina using the CWA strategy. $S_0^2 = 0.71$, N, coordination numbers, R, distances between Co and neighbouring atoms, σ , Debye Waller factor, enot, scaling energy parameter. The reliability of the fit was assessed by the minimization of the reduced χ^2_{red} and R_f metrics defined by the IXS standards and criteria committee (http://ixs.iit.edu/subcommittee_reports/sc/err-rep.pdf).

Figure 1: Raman spectra of bulk CoS_2 and bulk Co_9S_8 prepared by solid-gas reaction of bulk CoS_2 under 0.5% $\text{H}_2\text{S}/\text{H}_2$. The stars indicate the lines of gaseous H_2 . Laser excitation: 532 nm. Average over 6 spectra with integration time: 30 sec/spectrum.

Figure 2: Raman intensity map over the cell temperature upon solid-gas reaction of bulk CoS_2 under 0.5% $\text{H}_2\text{S}/\text{H}_2$. Laser excitation: 532 nm. Average over 3 spectra with integration time: 30 sec/spectrum. The increase of yellow signal around 326 cm^{-1} used as fingerprint of the formation of Co_9S_8 starts around 200°C. The color bar is related to the measured counts.

Figure 3: Evolution of the quick-XAS spectra recorded at the Co K edge during the heating at 5°C/min from RT to 400°C under 10% H₂S/H₂ gaseous mixture of the dried Co/Al₂O₃ sample. The temperature increases from the deep blue color (30°C) to the deep red one (400°C). The inset displays as a function of the sulfidation temperature the energy position at a normalized absorbance in the rising edge equal to 0.5.

Figure 4: (a) XANES spectra associated to the MCR-ALS components determined from the analysis of the data set presented in Figure 3 and (b) comparison of the MCR-ALS XANES spectra reported for both sulfide species with the ones recorded for bulk CoS_2 and bulk Co_9S_8 .

Figure 5: Evolution as a function of temperature (a) of the concentration of the Co species isolated by MCR-ALS (LOF = 0.37 %) from the analysis of the data set presented in Figure 3 and identified as supported CoO_x (black), CoS_2 (red) and Co_9S_8 (blue) and (b) of the m/Z signals recorded for H_2 and H_2S by mass spectrometry.

Figure 6: (a) Comparison of the XANES spectra recorded at 400°C after sulfidation of the dried Co/Al₂O₃ sample and at 30°C after cooling down the cell under H₂S/H₂ gaseous mixture. (b) Linear combination fitting for rebuilding the XANES spectrum of the sample after the cooling to room temperature leading to a proportion of 46.0 ± 1.1 % of Co₉S₈ and 54.0 ± 1.1 % CoS₂ ($R_f = 0.91$ %).

Figure 7: Evolution of concentration profiles determined by MCR-ALS for the XAS data recorded for the sulfided dried Co/Al₂O₃ sample when the temperature is decreased from 400 to 30°C under 10% H₂S- H₂ gaseous mixture. LOF = 0.64 % and percent of variance explained = 99.9996 %.

Decreasing Crystallite Size

Figure 8: Percentage of cobalt species obtained by linear combination fitting for rebuilding the XANES spectra of the different samples recorded at the end of the thermal treatment, at 400°C or 450°C labelled HT, and after cooling down under H₂S/H₂ gaseous mixture up to RT, labelled RT back. The sulfidation of supported samples was carried out with a heating ramp of 3°C/min. The average error bar for the percentage is 1.5 %.

Figure 9: Evolution of the quick-XAS spectra recorded at the Co K (a) and Mo K (b) edges during the heating at 3°C/min from RT to 400°C under 10% H₂S/90% H₂ gaseous mixture of the calcined CoNiMo/Al₂O₃ oxidic catalyst precursor. The temperature increases from the deep blue color (30°C) to the deep red one (400°C).

Figure 10: EXAFS spectra of the sulfide-based cobalt species isolated by CWA-MCR-ALS analysis of the Co K edge quick-XAS spectra recorded during the sulfidation of the CoNiMo HDS catalyst: (a) 2nd component identified as a CoMoS species, (b) 3rd component (red line) identified as CoS_2 by comparison with the experimental spectra recorded at 200°C (red dashed line) during the sulfidation of the dried $\text{Co}/\text{Al}_2\text{O}_3$ sample and at RT (blue dashed line, cooling under $\text{H}_2\text{S}/\text{H}_2$), (c) 4th component

(blue line) identified as Co_9S_8 by comparison with the experimental spectra recorded at 400°C (red dashed line) during the sulfidation of the dried $\text{Co}/\text{Al}_2\text{O}_3$ sample and at RT (blue dashed line, cooling under argon).

Figure 11: Comparison of the evolution of the percentage of the Co and Mo species isolated by MCR-ALS from the analysis of the $\text{CoNiMo}/\text{Al}_2\text{O}_3$ data set presented in Figure 9 and identified as supported CoO_x (black), CoS_2 (red), Co_9S_8 (blue) and CoMoS (green) for the Co-based species and MoO_x (grey), MoO_xS_y (purple) and MoS_2 (orange) for the Mo-based species.

Figure 12: Linear combination fitting (red line) for rebuilding the RT XANES spectrum of the calcined CoNiMo/Al₂O₃ (black line) after sulfidation under 10% H₂S-H₂ gaseous mixture leading to the proportion of 45.2 ± 1.1 % of CoMoS species, 32.2 ± 0.8 % of supported CoS₂, 19.6 ± 0.8 % of supported Co₉S₈ and 2.9 ± 1.6 % of CoO_x ($R_f=0.52\%$).