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1 Rethinking Electronic and Geometric Structure of Real
2 Hydrodesulfurization Catalysts by In Situ Photon-
3 In/Photon-Out Spectroscopy

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8
9 HDS catalysts, Co K edge HERFD XAS, Co RIXS 1s2p, XPS.

10
11 ABSTRACT: Core level spectroscopic is a powerful tool to achieve a fine understanding of both the
12 electronic and the geometric structure of heterogeneous catalysts . The present work shows use of Photon-
13 In/Photon-Out Spectroscopy to investigate the structures of hydrodesulfurization catalysts active sites.
14 Despite countless studies carried out to understand the working phase of this class of catalyst, the exact
15 localization of the promoter (Cobalt) remain an open question for “real HDS catalyst”. The difficulty
16 comes from the segregation of cobalt in different phases during the catalyst activation step. As a conse-
17 quence, most collected spectroscopic signal of cobalt involved in the catalyst, will corresponds to a
18 weighted average of the contributions arising from all cobalt centers (active phase, non-active sulfide
19 phase and the remaining cobalt oxide phase). To overcome this problem, a first time in situ Co K edge

1 HERFD-XAS is used to discriminate between oxide ($\text{Co}^{\text{II}}\text{-O}$) and sulfide ($\text{Co}^{\text{II}}\text{-S}$) phases arising during
2 HDS catalysts activation, allowing the localization of cobalt in the active phase of the catalysts. We find
3 that Co is localized at S-edges of the MoS_2 layers. Furthermore, in situ Co K edge 1s2p RIXS of the
4 sulfided catalyst shows excitations to band-like unoccupied states revealing the metallic nature of cobalt
5 in these structures. A new XPS fitting procedure, considering the exact electronic structure of the active
6 phase is proposed bringing us to reconsider earlier Co-promotion rate published in the literature for a
7 better correlation with the catalytic activity.

8 INTRODUCTION

9
10 The paradigm of energy production is shifting from a simple conversion of source material to an emphasis
11 on sustainable energy production based on the development of more efficient and environmental friendly
12 processes in a context of feedstock diversification (heavier feedstock, biomass, ...) as well the production
13 of alternative fuels like hydrogen.¹⁻¹⁰ Within this context of chemical industry renewal, heterogeneous
14 catalysts by transition metal sulfides (TMSs) holds great promises as they are used as hydrotreatment
15 catalysts to remove pollutants (S, O, N, and metals) from crude oil¹¹ and for the treatment of lignocellu-
16 losic biomass to reduce their oxygen content (hydrodeoxygenation).¹²⁻¹⁴ They also attract a fast-growing
17 interest in the field of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) to replace
18 the scarce and expensive platinum for electrochemical water splitting which is a fundamental process for
19 the development of fuel cell technology.^{4,15}

20 Due to their economic and environmental relevance TMSs catalysts have been the subject of countless
21 studies by both academic and industrial research centers. It is especially true for hydrodesulfurization
22 (HDS) catalysts¹⁶⁻²² whose design has been improved continuously to comply with more and more strin-
23 gent environmental specifications on maximum sulfur content allowed in transportation fuels.^{11,23} There
24 is a general consensus that HDS process is now mature for conventional oil, however, there is still a need

1 for improvement in the hydroprocessing of non-standard feedstock that are being more and more im-
2 portant in volume in a context of global decrease of available resources.^{11,23} To process these feedstocks,
3 there is a need of cracking large molecule as well desulfurizing them.^{22,24}

4 The HDS catalysts are consisting of Co(Ni) promoted nanometer scale Mo(W)S₂ particles dispersed on
5 high surface area alumina support (γ -alumina). Combination of Mo with Co (Ni) gives rise to a synergetic
6 effect in HDS activity due to the formation of the so-called active CoMoS phase. Numerous achievements
7 have been obtained during the last twenty years regarding the characterization of the structure of CoMoS
8 phase, thanks mainly to the progress in DFT simulations and to the application of Scanning Tunneling
9 Microscopy (STM) to characterize model HDS catalysts. DFT calculations and STM images of model
10 HDS catalysts (CoMo/Au (111)), revealed that the localization of the promotor occurs at the MoS₂ layers
11 edges.²⁵⁻²⁷ Non-promoted MoS₂ slabs show a triangular morphology²⁸ that becomes hexagonal in case of
12 promotion by cobalt.^{25,26} As for unpromoted MoS₂, there are two types of edges for the promoted MoS₂:
13 Sulfur-edge (S-edge), which correspond to the edges located along $(\bar{1}010)$ MoS₂ direction and metal-edge
14 (M-edge) located along the $(10\bar{1}0)$ MoS₂ direction. STM study show that cobalt atoms are located on the
15 S-edges, while the M-edges remain unpromoted.^{25,26} DFT-based Wulff equilibrium morphology calcula-
16 tions showed that under industrial sulfidation conditions (for 100% coverage of Co), the energy of the
17 Co-S-edge is about 0.20 eV (per cobalt atom) more stable than the Co-M-edges which in agreement with
18 STM results showing a 100 % Co-promotion at S-edges.¹⁶ Furthermore, it was reported that the substitu-
19 tion of Mo by Co atoms induces major change in the electronic structure of the S-edges giving rise to
20 "III_{co}" edges states which are metallic. Very recent studies shown that such new states play a key role for
21 the desulfurizing of large organosulfur molecules that require hydrogenation of one aromatic ring of the
22 molecule. Indeed, this hydrogenation pathway is initiated by the adsorption of the molecule that is driven
23 by interaction of this conducting state with the π -system of the aromatic ring. Such interaction was not
24 observed for the unpromoted Mo-edges.²⁹ However, this metallic character of the Co-S-edges as well as

1 the exact localization of the promotor were only observed for catalysts prepared by surface science tech-
2 niques where dispersed MoS₂ nanoclusters were obtained by the evaporation of the Mo under H₂S atmos-
3 phere on the (111) Au reconstructed surface. This contrasts with usual heterogenous catalysts synthesis
4 that occur in aqueous medium and involve oxide support with high surface area and high porosity. Very
5 recently, the use of α -Al₂O₃ single crystal as substitutes for γ -alumina support, to investigate the specific
6 role of individual support facets of the γ -Al₂O₃ have shown the crucial role of the oxide support on the
7 structure/size/orientation of the MoS₂ active phase.²⁰ However, such approach has been up to now re-
8 stricted to the non-promoted catalysts (MoS₂ phase) and fails to take into account the influence of the
9 porosity and surface defects presented by γ -Al₂O₃ oxide support.

10 The characterization of the CoMoS phase is still lacking for “real HDS catalysts” due to the segregation
11 of the Co element in different phases during the catalyst preparation and activation steps. As a conse-
12 quence, most collected spectroscopic signal of cobalt involved in the catalyst, will corresponds to a
13 weighted average of the contributions arising from all cobalt centers: the CoMoS active phase, the non-
14 active sulfide phase (Co_xS_y) and the remaining cobalt oxide phase. To overcome this problem and to study
15 the genesis of HDS catalysts, we propose during this work to use site selective K $\beta_{1,3}$ High Energy Reso-
16 lution Fluorescence Detected X-ray Absorption Spectroscopy (HERFD-XAS).³⁰⁻³² Indeed, thanks to the
17 advent of new crystal analyzers with high spatial angular acceptance and high-energy resolution it is now
18 possible to select a specific fluorescence channel, allowing a much better separation between the emission
19 lines before photon counting.^{33,34} This results in the development of two complementary photon-in pho-
20 ton-out spectroscopies: HERFD-XAS and Resonant Inelastic X-ray Scattering (RIXS).³⁵ For 3d transition
21 metal, the origin of the K $\beta_{1,3}$ fluorescence line selectivity is the overlap of the 3d valence orbitals with 3p
22 electronic states resulting in a 3p-3d exchange interaction.³⁶ This induces a shift in the energy of the K $\beta_{1,3}$
23 line as function of the electronic state of the absorber.^{36,37} By aligning the detector to the energy of the
24 K $\beta_{1,3}$ emission line, it is possible to obtain a pure or quasi-pure XAS spectrum of only one absorber atom
25 speciation. Furthermore, partial fluorescence detection mode gives rise to highly resolved XAS spectra as

1 the recorded spectrum is not broadened by the short 1s core hole lifetime but by the longer 2p final state
2 lifetime.³⁵ On the other hand, RIXS consists in recording emission lines through a resonance (K-edge for
3 1s2p RIXS) that results in a 2D spectrum: the RIXS plane is showing intensity vs excitation energy (x-
4 axis) and emission energy (y-axis).^{38,33} This allows solving the different contributions of the XAS pre-
5 edge structure by probing the different electronic intermediate states whereas in classical XAS K edge of
6 3d transition metal, the pre-edge corresponds to the sum of these states.³³
7 Hence, the present work address both electronic and geometric structure of cobalt in “real HDS catalysts”
8 by using two complementary photon-in photon-out spectroscopies. *In situ* Co K edge HERFD-XAS is
9 used for the first time to discriminate between oxide (Co^{II}-O) and sulfide (Co^{II}-S) phases arising during
10 HDS catalysts activation in order to determine the exact localization of the promotor. To investigate
11 whether Co metallic states arise for real catalyst, as suggested by STM images for model HDS catalysts,
12 *in situ* Co K edge 1s2p RIXS is applied to probe the electronic structure of the promotor. The results are
13 then compared to the ones obtained by X-ray Absorption (XAS) and X-ray Photoelectron Spectroscopy
14 (XPS) that are widely used in HDS scientific community for the characterization of HDS catalysts. As a
15 matter of fact, XPS spectra show usually a sulfidation rate of the cobalt between 40 and 60% while XAS
16 suggests an almost total sulfidation of the cobalt oxide phase.³⁹⁻⁴⁷ This disagreement although well known
17 by the HDS scientific community has not been deeply investigated. In the conclusion of this work we will
18 try to tackle this problem and to figure out the origin of this discrepancy.

19

20 EXPERIMENTAL SECTION

21 **Preparation of the catalyst.** Alumina supported Mo promoted by Co catalyst (CoMo/Al₂O₃) was pre-
22 pared by simultaneous incipient wetness impregnation of a solution of Ammonium Heptamolybdate
23 ((NH₄)Mo₇O₂₄·4H₂O) and Co^{III} ethylene diamine (Co(en)₃·6H₂O) on γ -alumina support with specific sur-
24 face area of 200 m²/g. The catalyst composition is 11 %wt of Mo with Co/Mo molar ratio of 0.4. It was
25 then calcined 4h at 400 °C in air. Raman spectrum of CoMo/Al₂O₃ show a main line at 967 cm⁻¹ and a

1 broad shoulder at about 844 cm^{-1} which are spectral signature characteristic of a polymolybdate species.⁴⁸
2 No further peak line of CoMoO_4 oxide (line at 820 cm^{-1} , doublet at 945 and 952 cm^{-1}) or oxide MoO_3
3 (fine lines at 819 and 995 cm^{-1}) are observed on the spectrum (Supporting Information (figure S1)).

4 **In situ photon-in/photon-out spectroscopy.** Co K edge HERFD-XAS and 1s2p RIXS spectra were rec-
5 orded at SOLEIL synchrotron facility (Gif sur Yvette, France) on the GALAXIES beamline.⁴⁹ The energy
6 of the incident radiation was selected using fixed-exit Si(111) double-crystal monochromator. Co K edge
7 HERFD-XAS and Co 1s2p RIXS spectra were recorded with spherically bent crystals in a Rowland ge-
8 ometry: the K_α fluorescence line of cobalt was selected by a silicon crystal Si (531) whereas for the K_β
9 fluorescence line of cobalt, a germanium crystal Ge (444) was used. A bag filled with helium was posi-
10 tioned between the sample and the analyzer crystal to limit the absorption of the fluorescence signal into
11 the air. The fluorescence signal was then collected on the avalanche photodiode detector (APD). A pho-
12 tography of this experimental set up is given in Supporting Information (figure S2). The catalyst compo-
13 sition is 4.4 %wt of Co, which rule out any self-absorption effects. The sample placed on the *in situ*
14 catalytic cell⁵⁰ was heated up to $400\text{ }^\circ\text{C}$ with a ramp of $1\text{ }^\circ\text{C}/\text{min}$ under a flux of $\text{H}_2/\text{H}_2\text{S}$ (10% H_2S). Note
15 that the acquisition time of one RIXS plane needs 4h making only possible the recording of RIXS planes
16 of the start (room temperature, under air) and the end ($400\text{ }^\circ\text{C}$, under a flux of $\text{H}_2/\text{H}_2\text{S}$) points. Neverthe-
17 less, recording one Co K edge HERFD-XANES spectra needs 3 min making possible to record spectra
18 all along the temperature ramp.

19 **The X-ray photoelectron spectroscopy (XPS).** XPS experiments were carried out in a Kratos AXIS
20 Ultra DLD spectrometer equipped with a hemi-spherical analyser operating at a fixed pass energy of 20
21 eV. The pressure during analysis was lower than $5 \cdot 10^{-9}$ mbar. Before analyses, the samples were freshly
22 sulfided and transferred into the analysis chamber under nitrogen atmosphere to avoid their partial reoxi-
23 dation. The absence of a contribution around 168.9 eV in the S 2p spectrum (which would correspond to
24 sulfates species) is used to check that oxidation of the samples did not occur during the transfer. Powdered
25 samples were deposited on conductive tape and during all the acquisition the Kratos charge compensation

1 system was used. Prior to and after Co 2p energy region analysis, O 1s spectra were recorded and compared
2 to make sure that no charge shifting was affecting the spectra. The binding energies and shapes of all
3 spectra from the catalyst present no shifting nor broadening or asymmetrical features as compared to
4 CoAl₂O₄ and Co₉S₈ references. Thus, no differential charging effect was ongoing during the XPS analysis
5 that could affect the spectra. All the data was acquired using monochromatic Al K α radiation (1486.6 eV)
6 operating at 225 W. The binding energies (BE) were corrected taking C 1s (284.8 eV) as reference. The
7 Mo 3d, S 2p, Al 2p, O 1s, Co 2p and Valence Band (VB) spectra were analyzed using the CasaXPS
8 software (version 2.3.16, Casa Software Ltd.).⁵¹ For the Co 2p signal, in order to keep a good energy
9 resolution and to allow decomposition, a 20 eV pass energy was selected for analysis. Thus, to increase
10 the signal to noise ratio, 70 scans were acquired on the Co 2p energy range with a step of 50 meV and an
11 acquisition dwell time of 300 ms, leading to a total acquisition time for the Co 2p spectra only of 6.4 h.
12 Spectra decomposition and quantification was performed after a Shirley type background subtraction and
13 Gaussian–Lorentzian decomposition parameters with 30/70 Gaussian/Lorentzian proportion, except for
14 metallic Co 2p peak which was fitted with an asymmetric main peak and two plasmon loss peaks at 3.0
15 eV and 5.0 eV above the main peak.^{52,53} To remove possible surface oxidation, Co₉S₈ reference compound
16 was pressed as a pellet and analysed after a Cs⁺ sputtering (1 kV, 65 nA) carried out using a ToF-SIMS
17 V instrument (ION-TOF GmbH Germany) over an area of 500 μm \times 500 μm . The reference sample was
18 then transferred under ultra-high vacuum ($< 5.10^{-9}$ mbar) into the XPS analysis chamber. The surface area
19 analyzed on the sample was 110 μm \times 110 μm centered on sputter gun crater.

20

21 THEORITICAL SECTION

22 **XANES.** XANES spectra simulations have been performed using the FDMNES package.⁵⁴ The FDMNES
23 code is based on real space mono-electronic approach to calculate the XANES spectra of clusters built
24 around each non-equivalent absorbing atom of the structure. To calculate the final states, we used the full

1 potential Finite Difference Method (FDM). The core-hole lifetime (1.3 eV at Co K-edge) was taken into
2 account by applying a convolution procedure to the calculated spectra.⁵⁵

3 **DFT calculations.** Total energy calculations were performed within the Density Functional Theory (DFT)
4 framework using the generalized gradient approximation of Perdew, Burke and Ernzerhof (PBE).⁵⁶ The
5 Vienna Ab initio Simulation Package (VASP) was used to solve the Kohn-Sham equations.^{57–59} The plane
6 wave basis set to express the electron wave functions was controlled with an energy cut-off of 400 eV.
7 The electron–ion interactions were described within the Projector Augmented Waves (PAW) approach
8 with the pseudopotential files provided with the VASP software.^{60,61} The slab, representing the CoMoS
9 structures, is constituted of 4 stoichiometric layers in the z direction (out of which 2 are allowed to relax
10 and two are fixed to simulate the bulk) and the unit cell dimension perpendicular to the surface plane has
11 been chosen large enough to avoid interaction between slabs (*i.e.* a distance of 15 Å is always kept be-
12 tween successive slabs). Two MoS₂ layers are used in the y direction to have both S and M termination
13 for the surface and 4 MoS₂ units are used in the x direction. All calculations are performed with two k-
14 points in the x direction, which, owing to the size of the system under investigation, proved to be sufficient
15 to integrate the Brillouin zone. The geometry of the CoMoS structures were optimized until the modulus
16 of the forces acting on the every atoms was lower than 0.03 eV.Å⁻¹ and the total energy variation between
17 successive geometries was below 1 meV.

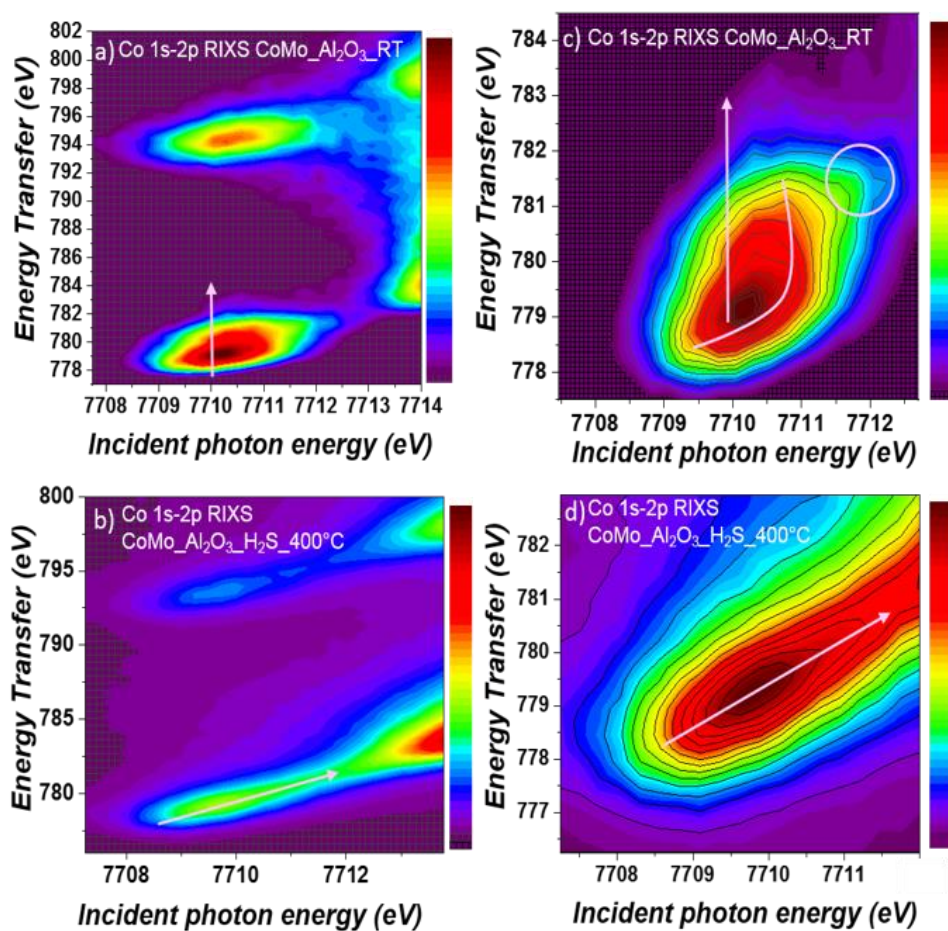
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19 RESULTS AND DISCUSSION

20 **Electronic structure of cobalt centers in HDS catalysts.** Figure 1 shows overview of the cobalt 1s2p
21 RIXS contour plot of the catalyst recorded under air at room temperature (denoted hereafter as
22 CoMo₂Al₂O₃_RT) and at 400 °C under a flux of H₂/H₂S (denoted hereafter as CoMo₂Al₂O₃_H₂S_400°C)
23 together with a zoom on the structures around 7709 eV incident energy and 779 eV energy transfer. The
24 incident photon energy range of the Co^{II} 1s2p RIXS planes correspond to the energy range of pre-edge
25 peak of the Co^{II} K edge XANES spectra. Co^{II} 1s2p RIXS occurs through a quadrupole transition from

1 $1s^2 2p^6 3d^7$ ground state to $1s^1 2p^6 3d^8$ intermediate states followed by the $1s^1 2p^6 3d^8$ to $1s^2 2p^5 3d^8$ dipole
 2 decay.^{33,35,38} The pre-edge structure in the RIXS planes (Figure.1 a) exhibits therefore two resonances
 3 due to the splitting of the final states into $2p_{3/2}$ and $2p_{1/2}$ by 2p spin-orbit coupling. Above the energy
 4 range of the pre-edge (7712 eV Figure 1.a, b), the observed structures correspond to X-Ray Emission
 5 lines $K_{\alpha 1}$ and $K_{\alpha 2}$.⁶² The electronic structure of the catalyst undergo a major change after sulfidation as
 6 shown by the evolution of RIXS structures form vertical contour for the oxide catalyst (Figure 1.a,c) to
 7 a diagonal contour for the sulfide catalyst (Figure 1.b,d).

8



9

10 **Figure 1.** Experimental Co 1s-2p RIXS planes of CoMo₂Al₂O₃_RT (a) and CoMo₂Al₂O₃_H₂S_400°C
 11 (b) catalysts. Zoom on the $2p_{3/2}$ resonance on RIXS plane of CoMo₂Al₂O₃_RT (c) and
 12 CoMo₂Al₂O₃_H₂S_400°C (d)

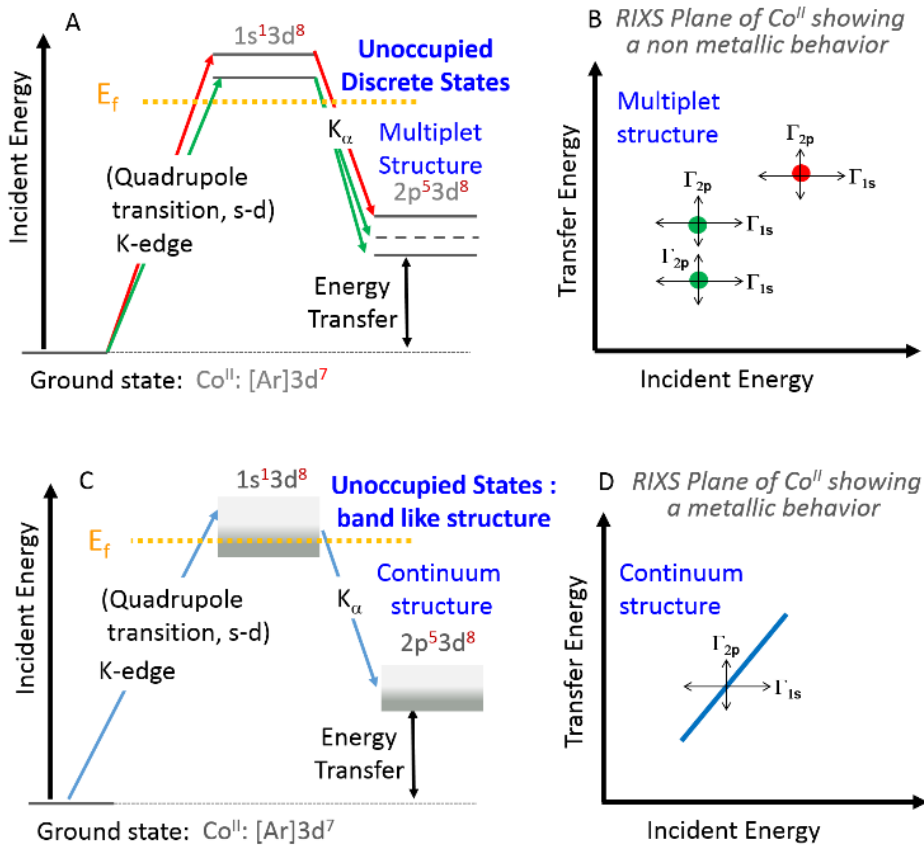
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2 Figure 2 is a schematic sketch of the RIXS transitions together with a schematic representation of the
3 expected RIXS planes as reported by Glatzel and collaborators in their tremendous effort to provide an
4 accessible way to understand the RIXS process to the scientific community.^{33,35} We focus first on the
5 upper part of Figure 2 (A, B) representing RIXS transitions to discrete excited states. Green lines in Figure
6 2.A show that lower energy intermediates states reached by RIXS transitions are detected in the RIXS
7 map at lower incident energy (green circles, Figure 2.B) while states at higher energies (red lines, Figure
8 2.A) are localized at higher incident energies in the RIXS plane (red circles, Figure 2.B). Note that cuts
9 in the RIXS map at Constant Incident Energy (CIE) provide resonant X-ray emission spectra. Such spectra
10 correspond to the excitation of discrete intermediates states (green lines, Figure 2.A) which deexcitation
11 may occur through different channels giving rise to various final states energies (green lines, Figure 2.A;
12 green circles, Figure 2.B). Hence if discrete excited states are concerned the RIXS map will exhibit vari-
13 ous resonances. Such discrete excited states will necessarily occur in the oxide catalyst because of the
14 strong Coulomb interaction between the electrons in the d-orbitals, as well as (2p,3d) and (3d,3d) ex-
15 change interactions. These on-site electronic interactions induce a splitting in different energy levels⁶³⁻
16 ⁶⁵ of the $2p^5 3d^8$ final electronic configuration reached through $Co^{II} 1s2p$ RIXS process. This results in a
17 multiplet structure of $Co 1s2p$ RIXS spectra of $CoMo_Al_2O_3_RT$ catalyst. However due to core-hole
18 lifetimes of the intermediate and the final excited states (Γ_{1s}, Γ_{2p} respectively), the multiplet structure is
19 broadened along the vertical and horizontal axis (see Figure.2 B).^{33,35,38} This added to experimental res-
20 olution broadening of excitation energy (0.8 eV), leads to resonances that are not very well resolved with
21 an asymmetrical shape as observed for $CoMo_Al_2O_3_RT$ (figure 1.C). Nevertheless, the multiplet struc-
22 tures could be evidenced through CIE lines as shown in Figure 3. To better understand the origin of the
23 resonances, Kramers-Heisenberg equation^{66,67} (eq.1, see experimental section) can be used to calculate
24 $Co^{II} 1s2p$ RIXS plane of $CoMo_Al_2O_3_RT$. Ω is the frequency of the incident x-ray and ω is the frequency
25 of the outgoing x-ray; D and Q correspond to dipole and quadrupole operators, $E_{1s^2 2p^6 3d^7}$, $E_{1s^1 2p^6 3d^8}$ are

1 the energies of ground and intermediate states, Γ_i is the core-Hole lifetime of the intermediate states and
 2 L_f indicates the final state Lorentzian broadening.^{33,35,38}

3
4

$$5 \quad F(\Omega, \omega) = \sum_f \left[\sum_i \frac{\langle 1s^2 2p^5 3d^8 | D | 1s^1 2p^6 3d^8 \rangle \langle 1s^1 2p^6 3d^8 | Q | 1s^2 2p^6 3d^7 \rangle}{E_{1s^2 2p^6 3d^7} + \Omega - E_{1s^1 2p^6 3d^8} + 1/2i\Gamma_i} \right]^2 \cdot L_f \text{ Eq. 1}$$

6



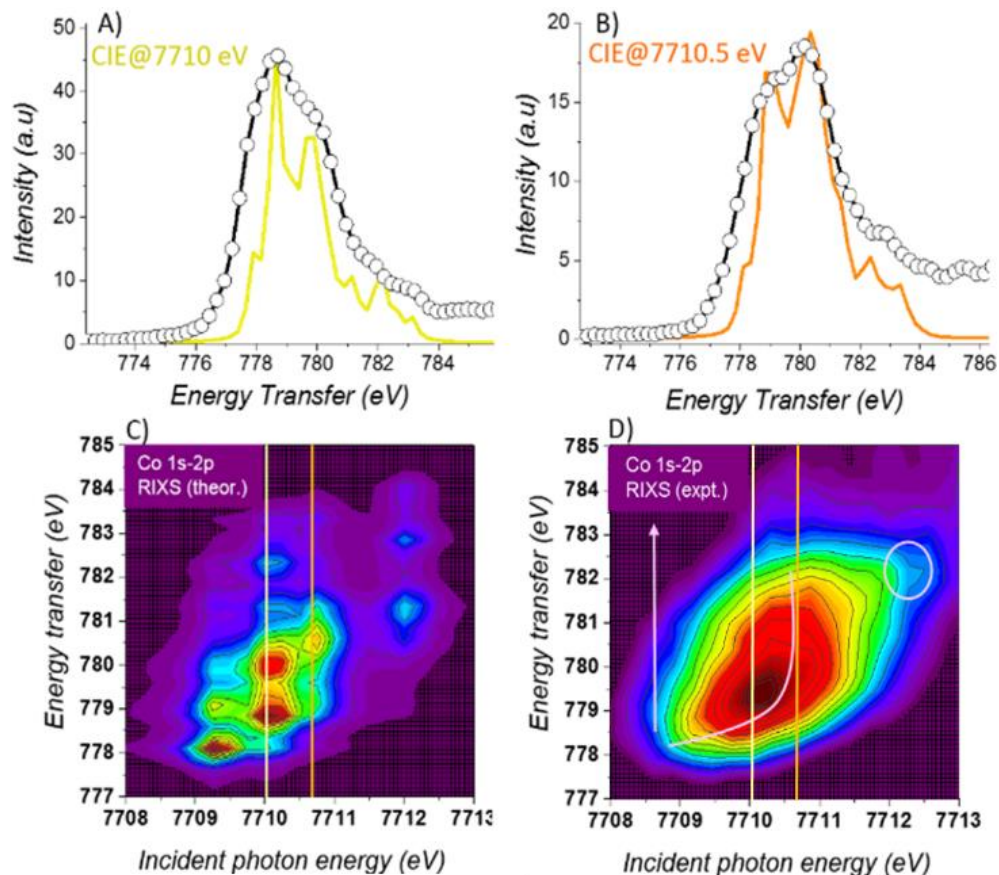
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8 **Figure 2.** Schematic sketch of the RIXS transitions to discrete (A) and continuum (C) excited states to-
 9 gether with schematic representation of the expected RIXS maps for discrete (B) and continuum (C) ex-
 10 cited states. E_f is the fermi energy level. Adapted from *Glatzel et al*^{33,35}

11

1 Based on Eq. 1, simulation of RIXS plane of CoMo₃Al₂O₃ RT catalyst is performed by using the crystal
2 field multiplet approach^{63,65}, as implemented in CTM4XAS and CTM4RIXS softwares.⁶⁸ The best agree-
3 ment between experiment and theory is obtained for Co^{II} in octahedral symmetry in high spin configura-
4 tion with a 10 Dq equal to 0.8 eV. A reduction of the Slater integrals and valence spin orbit coupling to
5 90% of their atomic values is required to match the experimental shape. To validate the accuracy of these
6 parameters, CoMo₃Al₂O₃ RT XANES Co L_{2,3} edges spectrum was recorded and the parameters used to
7 calculate the RIXS map have been used to simulate the spectrum. A good agreement between experiment
8 and theory have been obtained as shown in figure S3 of the Supporting Information. Note also that the
9 calculated RIXS map (figure 3.C) was obtained by using higher resolution for the excitation energy (0.3
10 eV) than the experimental one (0.8 eV) in order to better resolve the multiplet structure. This choice of
11 higher resolution simulation parameter is not to investigate deeply multiplet structure of the oxide catalyst
12 since experimental data do not allow it, but to make obvious to the reader the occurrence of multiplet
13 structure for Co^{II} in CoMo₃Al₂O₃ RT. Here, we merely restrict our discussion to show that the of origin
14 of RIXS resonances can be explained by Co^{II} in octahedral symmetry in high spin configuration. Our real
15 purpose at this point, is to shed on light the underlying cause of the change of the resonances RIXS shapes
16 during the transition from the oxide to sulfide phase.

17



1

2 **Figure 3.** Experimental (dot line) and theoretical (yellow, orange) CIE lines at 7710 eV (A) and 7710.5
 3 (B) eV together with simulated (C) and experimental (D) Co 1s2p RIXS plane of CoMo_Al2O3_RT
 4 catalyst.

5

6 Calculations for an octahedral Co^{II} in a high spin configuration shown in Figure.3C show that the pre-
 7 edge of CoMo_Al2O3_RT XAS will present three peaks at three incident energies: 7709.3 eV with trans-
 8 fer energy of 778 eV, 7710 eV with energy transfer of 779, 780 and 782.5 eV, 7712 eV with transfer
 9 energies at 781 and 783 eV (Figure.3C). As discussed above, such peaks are not well distinguished ex-
 10 perimentally due to the low resolution. However, it allows us to explain the asymmetrical shape of the
 11 $2p_{3/2}$ resonance RIXS (Figure.3D). In fact, the asymmetrical shape marked by a circle in Fig.3D is due to
 12 RIXS resonance at 7712 eV incident energy while the elongation along the vertical originates from three
 13 RIXS resonances with energy transfer of 779, 780 and 782.5 eV at 7710 eV incident energy (yellow line

1 fig.3C). The multiplet structure is better evidenced on CIE lines. Indeed, CIE line at 7710 eV extracted
 2 from the calculated RIXS map shows a doublet structure (Fig3.A, yellow curve) that is observed experi-
 3 mentally (Fig3.A, dotted curve). The CIE line at 7710 eV shows inversion of the doublet intensity com-
 4 pared to the CIE line at 7710.5 eV). This is due to the resonances at 781 eV (transfer energy) which
 5 exhibits a higher intensity at 7710.0 eV incident energy (Figure.3.C).

6 The RIXS plane of CoMo₃Al₂O₃H₂S (figure 1.d) shows a diagonal elongation with a broadening in the
 7 horizontal and vertical directions due to 1s and 2p core lifetimes respectively as it was observed for the
 8 oxide catalyst. However, no other asymmetry of the RIXS resonance is observed. Such result is surprising
 9 if one considers the Co^{II} final states as 2p⁵3d⁸ configuration as observed for oxide catalyst where a mul-
 10 tiplet structure is expected. Here the RIXS plane (Fig. 1d) describes rather excitations to band-like unoc-
 11 cupied states (Figure 2 (C, D)). Indeed, the continuous structure of a band in comparison to a discrete
 12 states will give rise to continuous resonance feature along the diagonal (figure 2.D) instead of separated
 13 resonances (figure 2.B). To confirm this band structure, the RIXS plane of CoMo₃Al₂O₃H₂S_400°C
 14 catalyst was simulated by the continuum model^{53,69-71} based on equation 2, (see experimental section).
 15 where Ω is the frequency of the incident x-ray and ω is the frequency of the outgoing x-ray, E_{Co} is the
 16 deep core-level energy and Γ_b the inverse core-Hole lifetime. μ_{XES} and μ_{XAS} are the absorption cross sec-
 17 tion and the emission cross section respectively which can be expressed as the X-ray Absorption spectrum
 18 and the X-ray Emission spectrum (XES). As shown in Fig.4 a very good agreement between experiment
 19 and theory is obtained. The CIE line plots are also well reproduced by calculation.

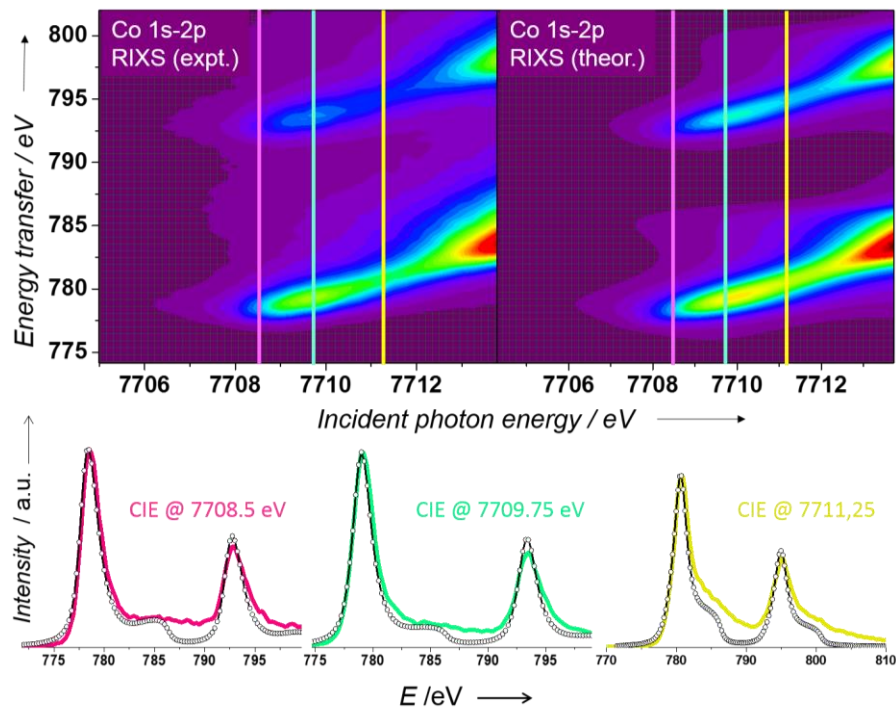
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$$\sigma(\Omega, \omega) \propto \int \frac{\mu_{XES}(\omega_1) \cdot \mu_{XAS}(\Omega - \omega - \omega_1 + E_{Co})}{\left| \omega - \omega_1 + \frac{\Gamma_b}{2} \right|^2} d\omega_1 \text{ Eq. 2}$$

23



1

2 **Figure 4.** Experimental and simulated Co 1s2p RIXS plane of CoMo₃Al₂O₃-H₂S_400°C catalyst to-
 3 gether with theoretical (grey) and experimental (pink, green, yellow) CIE lines at 7708.5, 7709.75 and
 4 7711.25 eV.

5

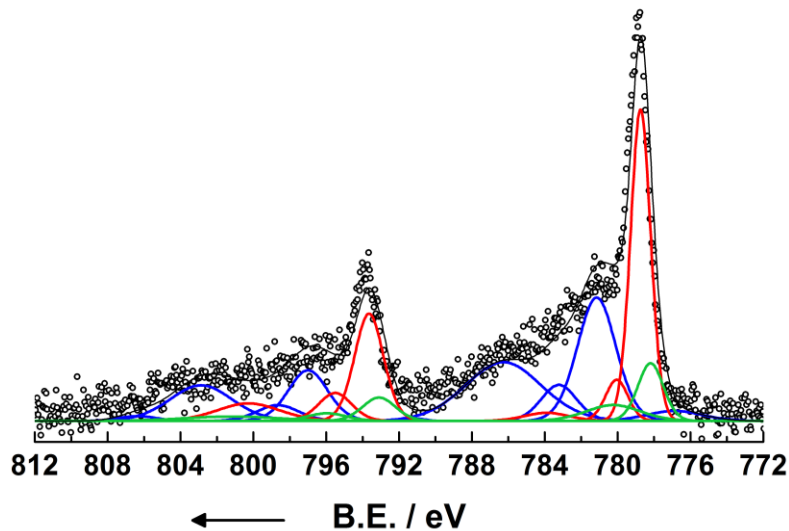
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7 Different hypotheses can be suggested to explain excitations to band-like unoccupied states observed for
 8 Co1s2p RIXS plane of CoMo₃Al₂O₃-H₂S catalyst. First, multiplet effects should be larger than the ex-
 9 perimental resolution in order to be observed. It is possible that the change of cobalt coordination shell,
 10 under H₂S flux, from oxygen ligands to sulfur ones, gives rise to less separated multiplet peaks that could
 11 not be resolved within our experiment. However, the absence of any asymmetry on RIXS features make
 12 this hypothesis unlikely. Second, edge calculation within the frame of Kramers-Heisenberg equation
 13 (Eq.1) describes a local quadrupole transition. The pre-edge of CoMo₃Al₂O₃-H₂S catalyst could present
 14 a dipolar contribution (1s → p-band) dominating the quadrupolar one.⁵⁸ Last hypothesis to explain the
 15 peculiar structure of the sulfide RIXS map is to take into account excitations to band-like unoccupied d-
 16 states revealing a metallic character of Co (figure 2.c-d). Such a metallic character is consistent with the

1 results obtained for model HDS catalysts and DFT calculations^{25,26}. However, to the best of our
2 knowledge, it has never been reported for “real” catalysts. X-ray Photoelectron Spectroscopy (XPS) and
3 $K\beta_{1,3}$ X-ray emission spectroscopy (XES) will be used to provide additional evidences of this metallic
4 character.

5 Earlier XPS data processing published in the literature for HDS catalysts use nonmetallic fitting parame-
6 ters.^{39,41,42,72} Fig.5 shows CoMo₃Al₂O₃-H₂S XPS Co2p spectrum adjusted according to the method usu-
7 ally used in the literature.^{39,41,42,72} This method consists on fitting the Co2p spectral envelope of a oxidic
8 precursor of the catalyst. These oxide contributions are then introduced in the spectrum of a monometallic
9 (Co) sulfided catalyst, while maintaining the extracted constraints for Co oxide fixed (Binding Energies:
10 BE, Full Width at Half Maximum : FWHM, and area ratios; as well as the FWHM ratio of the Co2p main
11 peak to the Al2p peak). The Co₉S₈ spectral envelope is deduced from the difference between the cobalt
12 sulfide sample global envelope and the Co oxide contributions. The CoMoS phase Co2p spectral envelope
13 is finally deduced from the difference between a bimetallic catalyst Co2p spectral envelope and the two
14 aforementioned Co oxide and Co₉S₈ spectral contributions. Following this methodology, three conven-
15 tional spectral shape were used to fit the CoMo₃Al₂O₃-H₂S catalyst Co2p envelope: Co₉S₈, CoMoS and
16 Co^{II} oxide phases. The main Co2p_{3/2} peak of cobalt atoms within in these three phases lie respectively at
17 778.2 eV, 778.7 eV and 781.2 eV. Based on the above described decomposition of the XPS spectra, we
18 determined the relative concentrations of each Co species. A proportion of only 39 % of Co in CoMoS
19 phase is obtained, while the percentage of remaining Co oxide is equal to 49%.

20



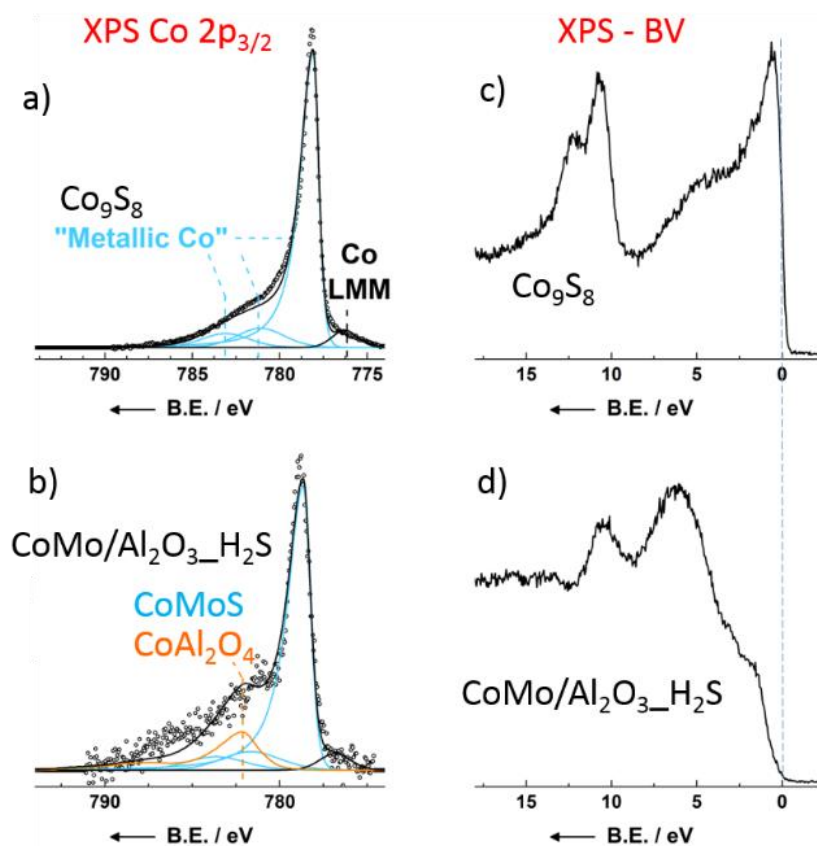
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2 **Figure 5.** XPS Co 2p spectrum of the CoMo/Al₂O₃/H₂S catalyst. The decomposition previously re-
 3 ported in the literature is applied here (blue: Co²⁺ oxide contributions; green: Co₉S₈ contributions; red:
 4 CoMoS contributions).

5

6 Figure 6 now presents the same Co 2p_{3/2} XPS spectrum for CoMo/Al₂O₃/H₂S sample compared to the
 7 Co 2p_{3/2} XPS spectrum of a clean cobalt sulfide Co₉S₈ reference sample, which is known to be metallic.⁷³
 8 The high-resolution spectrum for Co₉S₈ presents a distinct asymmetric line shape that has already been
 9 observed previously.⁷⁴ This asymmetrical shape can be explained by the metallic behavior of this com-
 10 pound.^{75,76} Indeed, due to unfilled electron levels above the Fermi energy, shake-up-type events following
 11 core electron photoionization exist and are responsible for a tail at the high binding energy side of the
 12 core photoelectron peak.⁷⁷ Co₉S₈ spectrum was thus fitted following the decomposition proposed for Co
 13 metal and Co phosphide,⁵² with an asymmetric main peak with binding energy of 778.1 eV, FWHM value
 14 of 0.8 eV and two plasmon loss peaks at 3.0 eV and 5.0 eV above the main peak, which constitute the
 15 surface and bulk plasmons, respectively, with FWHM values of 3.3 eV in both cases.^{52,53} The metallic
 16 character of this compound is also highlighted in this work with XPS valence Band (VB) showing a sharp
 17 edge localized at the Fermi level (Figure 6.C).

18



2

3 **Figure 6.** XPS Co 2p_{3/2} spectrum of a) Co₉S₈ reference and b) CoMo_Al₂O₃_H₂S catalyst, XPS-VB of
 4 c) Co₉S₈ reference and d) CoMo_Al₂O₃_H₂S catalyst

5

6 The CoMo_Al₂O₃_H₂S catalyst VB (figure 6.D) shows an edge localized at the Fermi level, confirming
 7 its metallic behavior. However, the VB is largely dominated by MoS₂ and alumina bands (Supporting
 8 Information (Figure S4)), making the determination of the electronic state of cobalt difficult. Neverthe-
 9 less, Co 2p_{3/2} orbital shape of CoMo_Al₂O₃_H₂S is very similar to the one of Co₉S₈. This shape together
 10 with excitations to band-like unoccupied states shown by RIXS measurements, support the use of Co
 11 metal parameters to fit Co2p_{3/2} peak (Fig.6b). The main peak corresponding to Co atoms involved in
 12 CoMoS phase lies at 778.6 eV with a FWHM value of 0.9 eV. This small value of FWHM is close to the
 13 bulk Co₉S₈ reference one, suggesting the presence of only one sulfide Co phase in CoMo_Al₂O₃_H₂S

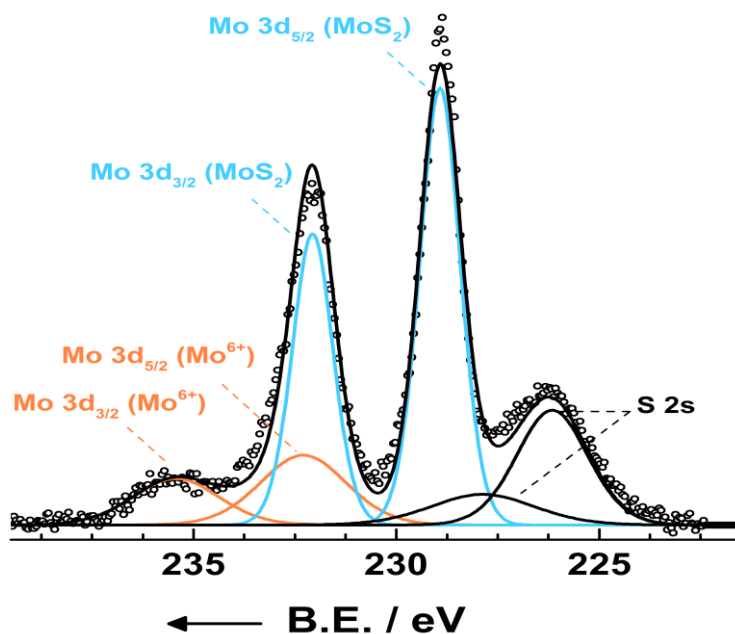
1 sample. It is however possible to add a small proportion of Co_9S_8 phase (maximum 10 %) in the decom-
2 position even if the CoMoS and the Co_9S_8 $\text{Co}2\text{p}$ main peak are separated by 0.5 eV. Finally, the fitting
3 requires addition of Co^{II} oxide contribution. This contribution is responsible for 20 % of the total $\text{Co}2\text{p}_{3/2}$
4 orbital.

5 The new XPS fitting, proposed in this work, explains the discrepancy of the results concerning the quan-
6 tification of cobalt sulfidation rate by XAS and XPS (sulfidation rate between 40 and 60% by XPS process
7 while XAS show an almost total sulfidation). As shown above, processing XPS data implies fitting the
8 catalyst spectral shape of the various contributions of Co species through the decomposition of the exper-
9 imental spectra by mathematical functions showing adjustable fitting parameters (FWHM, peak posi-
10 tion... etc). The accuracy of fitting parameters depends on the precise knowledge of the electronic struc-
11 ture of the probed element (multiplet structure, metallic structure, plasmons...). In the present work we
12 used $\text{Co}1\text{s}2\text{p}$ RIXS to probe the electronic structure cobalt that suggest the use of metallic parameters
13 fitting to adjust the experimental XPS spectra. This new fit moves the ratio Co^{II} oxide/ Co^{II} sulfide from
14 50%/50% to 20%/80% (see table 1). This ratio eventually allows to reach an agreement between XPS and
15 XAS spectroscopies quantification.

16 Taking into account the correct electronic structure for Co, raises a Co-promotion rate (Co/Mo atomic
17 ratio) issue. Indeed, in HDS community, the cobalt promotion rate is determined based on $\text{Co}2\text{p}$ and Mo
18 3d XPS spectra. Figure 7 show XPS Mo 3d spectrum of $\text{CoMo_Al}_2\text{O}_3\text{-H}_2\text{S}$ catalyst. The Mo 3d envelope
19 can be adjusted by the spectral contributions of $\text{Mo}^{\text{IV}}\text{S}_2$ (75%) and $\text{Mo}^{\text{V}}\text{oxide}$ (25%). Contributions of
20 $\text{S}_{2\text{s}}$ should be added as this latter is overlapping with the Mo $3\text{d} (5/2)$ of the $\text{Mo}^{\text{IV}}\text{S}_2$. Using previous fit
21 from the literature and the new fit proposed in this work, the Cobalt involved in the CoMoS phase is equal
22 to 39% and 80% respectively (table 1). This gives a Co/Mo atomic ratio in the CoMoS phase equal to
23 0.46 (actual fit) and 0.31 (previous fit). Consequently, Co-promotion rates available in literature seems
24 underestimated and should be reevaluated for a proper correlation to HDS activity. This questions the

1 strategy of trying to increase a Co-promotion rate (already very high), and suggests that synthesis route
 2 increasing the amount/size/dispersion of the CoMoS active phase may be more useful.

3
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 7
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Figure 7. XPS Mo 3d spectrum of CoMo₂-Al₂O₃-H₂S catalyst

	Co(II) oxide	CoMoS phase	Co ₉ S ₈ phase
Literature	49	39	12
This work	20	80	0

9 **Table 1.** XPS at. % of the different Co phases contributions obtained for CoMo₂-Al₂O₃-H₂S catalyst
 10 using decomposition from literature and from this work.

1 Geometric structure of cobalt centers in HDS catalysts. HERFD-XAS and XES have been used to monitor
2 the genesis of the CoMoS active phase and to resolve the local environment of cobalt. The catalyst was
3 heated up to 400 °C in a ramp of 1 °C/min under a flux of H₂/H₂S (10% H₂S). Fig.8b show Co K β _{1,3}
4 emission lines of CoMo₂Al₂O₃ catalyst recorded at room temperature (CoMo₂Al₂O₃_RT) under air flux
5 and at 400°C under H₂/H₂S flux (CoMo₂Al₂O₃_H₂S). The K β fluorescence line is observed after pho-
6 toionization of a 1s electron. After photon absorption, 1s core hole is filled by relaxation of a 3p electron.
7 This relaxation process is at the origin of the K β emission. The shape of the Co K β line consists of one
8 main peak at high fluorescence energy (K β _{1,3}) and a “satellite structure” denoted as K β ' at low fluorescence
9 energy. This latter is due to the (3p, 3d) exchange interaction and is therefore highly sensitive to the
10 valence spin density.³⁸ Fig.9 show a schematic sketch of the process involved in the K β emission line. The
11 photoionization involves a spin down and spin up transitions (red arrows Figure 9). The relaxation process
12 will therefore present two decay channels corresponding to spin down and spin up desexcitation (green
13 arrows, Figure 9).⁷⁸ The electronic state of Co^{II} reached through a spin down desexcitation is ⁵G, while it
14 is ³G for the spin up transition (Figure.9). After the sulfudation, the K β _{1,3} peak of
15 CoMo₂Al₂O₃_H₂S_400°C is shifted about 1 eV to higher energies with respect to CoMo₂Al₂O₃_RT to-
16 gether with a vanishing of Co K β ' structure at 7638 eV as denoted in Figure.8B. The vanishing of Co K β '
17 structure account for a major change of the spin state of the HDS catalyst during the sulfidation step. This
18 change is again related to the Cobalt metallic character giving rise to non-distinguishable collective va-
19 lence electrons: only one 3p-1s channel decay is observed as K β ' merges into K β _{1,3} main line as shown in
20 Figure.8B.⁷⁹ This metallic character will allow us to make site selective measurements that one may think
21 unlikely. Indeed, the promoter in both the sulfide and oxide phases show the same oxidation state (+II).
22 Therefore, and if the metallic nature of the promotor is not considered, no significant energy shift of
23 emission lines is expected during the catalyst activation. Thanks to the global change of the electronic
24 structure a shift of the order of 1 eV is observed making possible site selective XAS study to discriminate
25 between oxide (Co^{II}-O) and sulfide (Co^{II}-S) phases arising during the catalyst activation. However, since

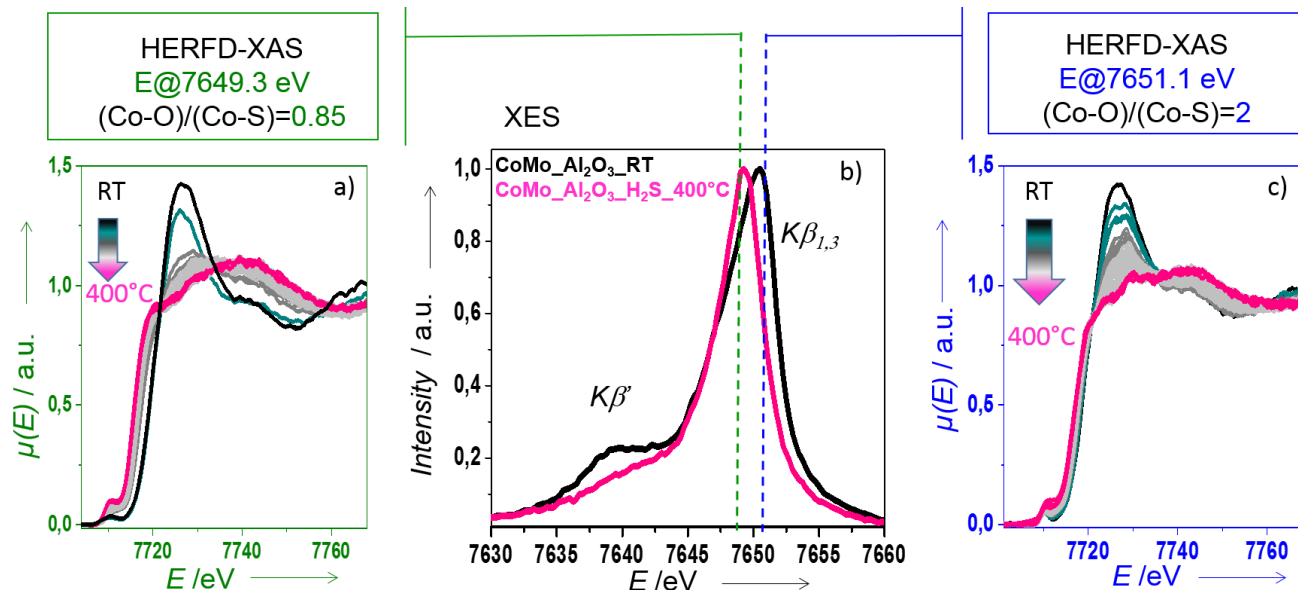
1 the $K\beta_{1,3}$ peaks of (Co-O) and (Co-S) species are overlapping (figure 8.b), only partial selective HERFD-
2 XAS spectra are obtained by measuring directly the XAS spectra at a given spectrometer energy. To
3 achieve total selectivity, a deconvolution of experimental spectra recorded for two emission energies of
4 the spectrometer is required. For this purpose, the spectrometer was aligned at two energies, *i.e.*, 7651.1
5 eV, with $K\beta_{1,3}$ (Co-O) / (Co-S) intensity ratio equal to 2 (Figure 8.c), and 7649.3 eV with $K\beta_{1,3}$ (Co-O) /
6 (Co-S) ratio equal to 0.85 (Figure 8.a). The recorded HERFD-XAS for each of these two energies ($S_{@7649.3}$
7 and $S_{@7651.1}$) can be written as a linear combination of the pure spectrum of the oxide phase (S_{ox}) and the
8 sulfide phase (S_{sul}). This gives rise to a system of two equations (equations 3 and 4) with two variables
9 (S_{ox} and S_{sul}). γ_{ox} and γ_{sul} are the fraction of the oxide and the sulfide respectively, corrected by (Co-O) /
10 (Co-S) ratio rising from the energy of the spectrometer. γ_{ox} and γ_{sul} fractions were obtained based on
11 XPS fitting of the Co 2p envelope as discussed above.

$$S_{@7649,3eV} =$$

$$\gamma_{ox@7649,3eV} \cdot S_{ox} + \gamma_{sul@7649,3eV} \cdot S_{Sulf} \text{ Eq. 3}$$

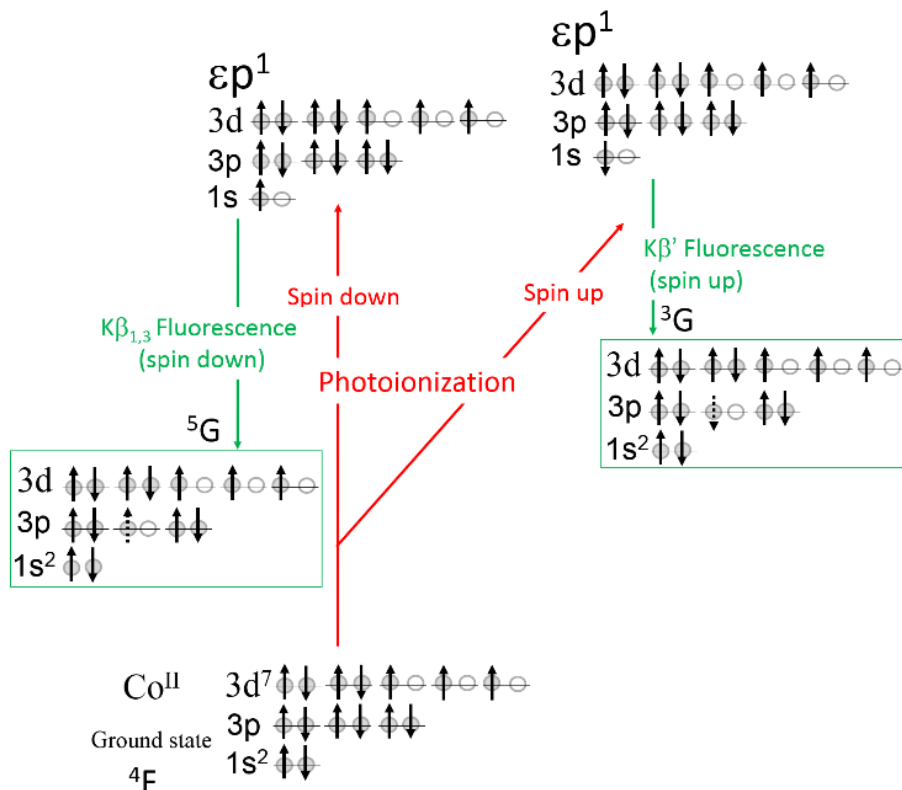
$$S_{@7651,1eV} =$$

$$\gamma_{ox@7651,1eV} \cdot S_{ox} + \gamma_{sul@7651,1eV} \cdot S_{Sulf} \text{ Eq. 4}$$



1
 2 Figure 8. S@7649.3 (a) and S@7651.1 (c) HERFD-XAS spectra recorded during CoMo₂Al₂O₃ catalyst
 3 activation, Co $K\beta_{1,3}$ emission lines (b) of the alumina supported CoMo catalyst recorded at room tem-
 4 perature (black curve) under air flux and at 400°C under H₂/H₂S flux (pink curve).
 5
 6 Fig 8.a and Fig 8.c show that before introducing the gas, an intense white line (wl) is observed (black
 7 curve) which is the signature of Co^{II} oxide in octahedral symmetry. At 400°C the wl is missing (pink
 8 curve, Fig 8. a and Fig8.c), illustrating that almost all of the initial oxide is converted to sulfide species in
 9 agreement with RIXS and XPS spectroscopies. Recording the spectra at a detection energy of 7651.1 eV
 10 where the (Co-O) / (Co-S) intensity ratio is equal to 2, will select the XAS signal of the oxide species. At
 11 a detection energy of 7649.3 eV ((Co-O) / (Co-S) intensity ratio equal to 0.85) the sulfide species XAS
 12 signal will be selected. This evidenced on S@7649.3 spectra (Fig 8a.) where the wl is vanishing right after
 13 introduction of the gas. A shift to lower energy is also observed. S@7651.1 spectra (Figure.8c) follows the
 14 same trend but is much smoother. This clearly shows that, from the experimental point of view, it is
 15 possible to be more sensitive to oxide or sulfide species by choosing the appropriate spectrometer energy.
 16 Regarding the access to pure spectra of oxide and sulfide, Eq.3 and Eq.4 should be applied. However, the

1 results obtained with such an approach are limited, insofar only part of the XANES signal might be used
2 for structural investigation of the catalyst active site. Indeed, HERFD-XAS spectra are recorded by fixing
3 one detection energy (emission energy) while scanning the excitation energy through the Co K absorption
4 edge, leading to the detection of only a fraction of electronic excited states, while, in “classical” XAS,
5 pre-edge structure corresponds to the sum of these states. It follows that any interpretation of the pre-edge
6 structure of HERFD-XAS spectra is improper.^{32,33} Therefore, neither intensity nor the structure of the pre-
7 edge is considered and only the global shape of the HERFD-XAS spectra will be discussed. Note that
8 even XANES features are modified as function of the selected emission energy due to lifetime broadening
9 distortions and spin configurations.⁷⁸ Indeed, as discussed above, $K\beta_{1,3}$ and $K\beta'$ peaks result from two
10 different spin configurations. It is therefore possible to record spin-dependent XAS spectra by fixing emis-
11 sion energy at the main peak ($K\beta_{1,3}$) and at the satellite ($K\beta'$) while scanning the incident energy.⁸⁰ The
12 two emission energies fixed in this work are very close and fall into the region of the main emission peak
13 ($K\beta_{1,3}$). These two emission energies were used to record Co K edge XAS references Co^{II} oxides com-
14 pounds and no change of the XAS shape was observed in agreement with previous results.^{32,79}
15



1

2

3 **Figure 9.** A schematic sketch of the process involved in the K β emission line for the Co^{II} configuration.

4

5 Based on Eq.3 and Eq.4, pure ligand-specific Co K edge HERFD-XAS spectra are extracted (figure 10).

6 Note that from RT to 50°C, the shape of the spectra evolves very quickly and the spectra were too noisy

7 to be used. From 50°C, the spectra evolution is smooth and it becomes possible to lower signal-to-noise

8 ratio by merging analogous spectra before deconvolution. From T= 50 to 216°C, the extracted S_{ox} spectra

9 (figure 10, blue curve) show a split up and a decrease of wl intensity. This is due to a mixture of Co^{II} in

10 octahedral symmetry with tetrahedral cobalt aluminate species. Indeed, it is well known that Co^{II} shows

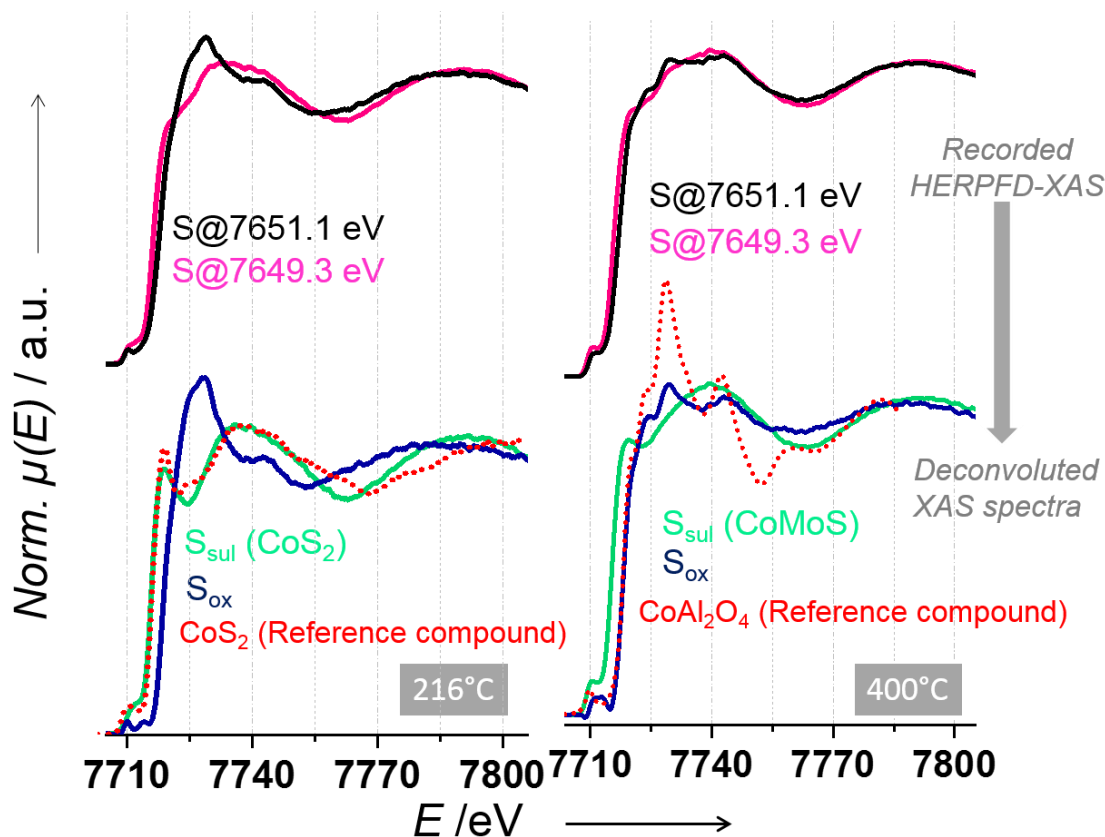
11 a high affinity to empty tetrahedral sites of the spinel γ -alumina oxide support leading to the formation of

12 cobalt aluminate during synthesis steps.⁸¹ The activation of the catalyst converts only octahedral oxide

13 Co^{II} to sulfide species while the cobalt aluminate remains in its oxide state. This is consistent with the

1 observation of cobalt aluminate features only for S_{ox} at $T= 400^{\circ}C$ (Fig.10, blue curve). This is also con-
 2 sistent with XPS results discussed above in the article and showing that the fitting of the total Co $2p_{3/2}$
 3 orbital requires besides the cobalt sulfur phase, the addition of a tetrahedral Co^{II} oxide ($CoAl_2O_4$) contri-
 4 bution. Note that the wl of S_{ox} at $T= 400^{\circ}C$ (Fig.10, blue curve) is less intense for S_{ox} than for the $CoAl_2O_4$
 5 reference compound (Fig.10, purple curve). Indeed, the pure XAS spectrum of cobalt inserted in empty
 6 tetrahedral sites of the spinel γ -alumina is unknown, nevertheless such XAS spectrum is expected to show
 7 similar features to the one of $CoAl_2O_4$ reference compound due to the same symmetry and chemical en-
 8 vironment of Co in both case. For the catalyst, the cobalt shows high dispersion in contrast to the $CoAl_2O_4$
 9 bulk reference compound.

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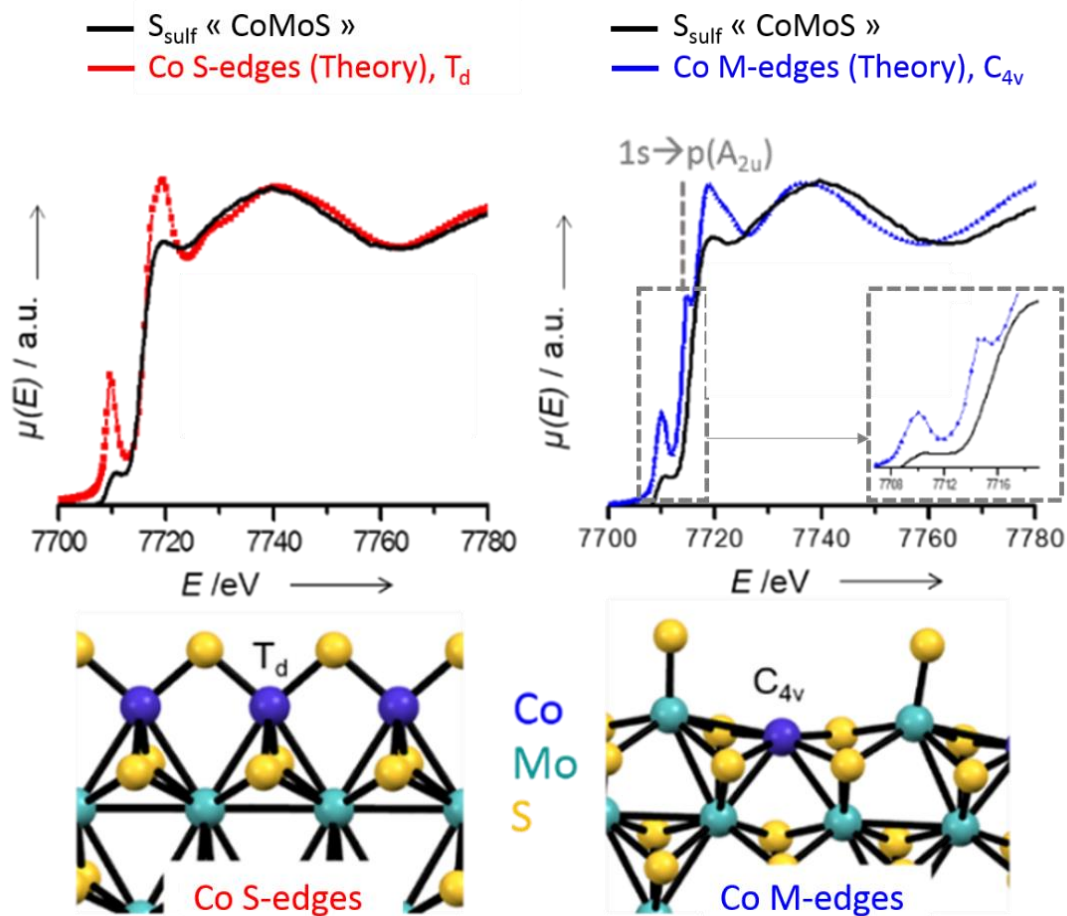
12 **Figure 10.** HERFD-XAS S@7649,3eV and S@7651,1eV spectra and their corresponding deconvoluted
 13 S_{ox} and S_{sul} spectra for two temperatures ranges together with CoS_2 and $CoAl_2O_4$ references compounds

1

2 From $T = 50$ to 216°C , the extracted S_{sulf} (green curve, Fig. 10) show spectrum fingerprints similar to CoS_2
3 compound (purple curve, Fig. 10). To the best of our knowledge, the formation of CoS_2 as HDS catalyst's
4 activation intermediate has never been reported in the literature. A Co monometallic catalyst (without
5 Mo) also shows CoS_2 formation upon exposure to $\text{H}_2/\text{H}_2\text{S}$ mixture (Supporting Information (figure S5-
6 1)). At higher temperature, CoS_2 is converted to thermodynamically stable Cobalt sulfide phase Co_9S_8
7 (Supporting Information (figure S5-2)).) while XANES spectra of the bimetallic catalyst show new fea-
8 tures that may be related to the genesis of CoMoS phase (Fig. 2, $T = 400^\circ\text{C}$, green curve).

9 Thanks to the partial fluorescence detection and to the removal of cobalt aluminate from the global signal,
10 XANES spectrum of CoMoS shows sharper features compared to those published in the literature making
11 comparison to theoretical XANES spectra possible. CoMoS structures showing S/M-edges were gener-
12 ated by DFT calculation and their corresponding Co K edge XANES spectra were calculated (Fig 11). Co
13 located at S-edges show tetrahedral symmetry while Co located M-edges are square planar (D_{4h}) in agree-
14 ment with previous DFT results.¹⁶ In the D_{4h} configuration, Co 4p-orbitals are split into A_{2u} and E_u sym-
15 metries. The latter overlap with E_u sulfur p-orbitals, whereas A_{2u} Co 4p-orbitals remain non-binding. This
16 gives rise to a shoulder at 7715 eV due to electron transition to the non-bonding A_{2u} for D_{4h} symmetry
17 (Fig 11). This shoulder is missing for tetrahedral Cobalt as its p-orbitals are degenerate. No shoulder is
18 observed for S_{sulf} HERFD XAS spectrum of the CoMoS phase. This absence and the dissimilarity of
19 global spectrum shape between theoretical Co M-edges spectrum and the experimental one, rules out a
20 Co square plane symmetry. S_{sulf} spectrum exhibits characteristics similar to the theoretical XANES Co S-
21 edges (tetrahedral symmetry) indicating that the Co substitution at the CoMoS edges seems to occur
22 mainly at the S-edges. Nevertheless, location of the promotor on defect sites as well the presence of S
23 vacancies will generate multiple Co's in similar local coordination (tetrahedral symmetry). Based on
24 HERFD XANES spectra, only information regarding the local coordination of the cobalt can be drawn

1 from our data. Therefore, it cannot be ruled out that some of the cobalt with tetrahedral symmetry is
 2 located close to S-vacancies and/or on defects sites.
 3



4
 5 **Figure 11.** S_{sulf} CoMoS HERFD XAS compared to theoretical Co K edge XANES spectra for Co S-
 6 edges and M-edges together with Co S and M edges after geometry optimization of the CoMoS struc-
 7 ture.

8 **Conclusion**

9 We have shown that $K\beta_{1,3}$ -HERFD-XAS and $1s2p$ RIXS are very powerful to characterize both electronic
 10 and geometric structure of TMSs heterogeneous catalysts active sites. These spectroscopies will play a
 11 key role throughout the design and the improvements of the TMS's catalysts formulation. For HDS cata-
 12 lysts, these techniques made possible the localization of Co in HDS catalysts (S-edge substitution) which

1 is in line with previous STM and DFT results obtained for model HDS catalysts. These findings pave the
2 way to future investigations on the impact of Co S/M-edges substitution on the final properties of the
3 catalyst allowing a deeper understanding of the catalytic activity and a more efficient HDS catalysts de-
4 sign. The application of Co 1s2p RIXS, XPS and Co K $\beta_{1,3}$ XES spectroscopies shed light on the metallic
5 character of Co in the CoMoS phase for “real” HDS catalysts explaining the reason of the disagreement
6 between sulfidation degree obtained by XPS and XAS reported in the literature. This is questioning the
7 Co promotion rate which seems to be often underestimated and should be reconsidered for a better corre-
8 lation with the catalytic activity.

9

10 ASSOCIATED CONTENT

11 Supporting Information

12 A photography of the experimental set up used for *in situ* Co K edge HERFD XAS and Co 1s2p RIXS
13 measurements; theoretical and experimental CoMo₃Al₂O₃-RT XANES Co L_{2,3} edges spectra; Valence
14 Band of MoS₂ and γ -alumina; details of synthesis and Co K edge HERFD XAS Characterization of mon-
15 ometallic Co catalyst (Co₃Al₂O₃).

16 The Supporting Information is available free of charge (PDF).

17

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21 Author Contributions

1 The manuscript was written through contributions of all authors. All authors have given approval to the
2 final version of the manuscript. ‡These authors contributed equally. (match statement to author names
3 with a symbol)

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14

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