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► **To cite this version:**

Fabien Caron, Mickael Rivallan, Severine Humbert, Antoine Daudin, Pascal Raybaud, et al.. Active Sites Speciation of Supported CoMoS Phase Probed by NO Molecule: A combined IR and DFT Study. Journal of Catalysis, 2018, 361, pp.62-72. 10.1016/j.jcat.2018.02.017 . hal-01980690

HAL Id: hal-01980690

<https://ifp.hal.science/hal-01980690>

Submitted on 14 Jan 2019

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1 **Active Sites Speciation of Supported CoMoS Phase Probed**
2 **by NO Molecule: A combined IR and DFT Study**

3

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13

14 ABSTRACT

15 By using infrared spectroscopy and second derivative analysis, we identify key vibrational components of
16 NO adsorbed the sulfided phases present in hydrodesulfurization (HDS) supported catalysts: MoS₂, cobalt
17 promoted MoS₂ (CoMoS) and Co₉S₈. With the help of density functional theory (DFT) calculations, five
18 components (A, A', B, B', C) identified by the second derivative analysis are assigned to mononitrosyls
19 and dinitrosyls species on the various Mo and Co sites of the MoS₂, CoMoS and on Co₉S₈ phases. In
20 particular, the component (A') at ~1846 cm⁻¹ is due to mononitrosyl species on Co sites of the partially
21 promoted M-edge or to dinitrosyl species on Co sites of the fully promoted S-edge of the CoMoS phase.
22 This component (A') appears as a descriptor of the promoted sites and is present on the δθ- and γ-Al₂O₃
23 supports. By contrast, on silica supported catalyst, (A') decreases significantly in favor of component (A)
24 at 1859-1863 cm⁻¹ assigned mainly to nitrosyls on Co₉S₈ sites. Simultaneously, on silica, the component
25 (B) at 1788-1790 cm⁻¹ is assigned to dinitrosyls on the non-promoted Mo-edge and/or Co promoted S-
26 edge and can be distinguished from the component (B') at 1799 cm⁻¹ assigned to nitrosyls on the Co₉S₈
27 phase. A complementary chemometric analysis highlights that different evolution of the sites population
28 as a function of NO contact time occurs as a function of the various sulfided phases and supports. In
29 particular, chemometry suggests the presence of the two edges on the non-promoted MoS₂ phase. We
30 finally discuss the implication of these findings for HDS catalysts.

31

32 KEYWORDS: MoS₂, CoMoS, alumina, silica, NO, infrared, density functional theory,

33 hydrodesulfurization

34

1. INTRODUCTION

Due to the evolution of the worldwide environmental concerns, hydrodesulfurization (HDS) is a key industrial catalytic process to reach the targeted specifications on cleaner diesel and gasoline by removing undesirable sulfur compounds in petroleum feeds.[1] The industrial catalysts are usually based on an active transition metal sulfides MoS₂ phase promoted by cobalt or nickel atoms.[1, 2]

The atomic scale understanding of HDS catalysts remains a major concern for current research in order to provide innovative pathways for improving their intrinsic performances by design leading to more efficient process. Regarding the active phase, several studies based on numerous characterization techniques such as XPS,[3] EXAFS[4, 5] and high resolution TEM[6, 7] were conducted to better understand the atomic scale features of the active phase. The MoS₂ phase is highly dispersed on the alumina support and reveals crystallites of 3-4 nm size, which are decorated at the edges by cobalt atoms in order to form a so-called mixed CoMoS phase.[8] Density functional theory (DFT) calculations have also brought relevant insights into the atomistic description of the active phase such as the morphology of the MoS₂ nano-crystallite,[9, 10] location of the promoters,[11] and its impact on electronic properties[12] and reactivity.[13] These studies have in particular highlighted the crucial role of the sites located at the edges or close to the edges of the MoS₂ nano-crystallites.[14]

Further investigations of the active sites of HDS catalysts have used probe molecule adsorption followed by Fourier transform infrared spectroscopy (FTIR).[15] For instance, pyridine has been used to probe the Lewis and Brønsted acid sites of the MoS₂ and Co(Ni)MoS phase, leading to its protonation in presence of sulfhydryl groups at the edges.[16, 17] CO molecule has also been widely used to differentiate the coordinatively unsaturated sites (CUS) Mo and Co sites located at the edge of the MoS₂ nano-crystallites according to their local structure and coordination, although some open questions remain on the precise nature of these sites.[18, 19]

58 Nitric oxide (NO) probe is widely used in the literature to depict the surface atoms speciation present on
59 DeNO_x catalysts.[20-23] Moreover, NO has also been used to shed light into the surface state of the
60 CoMoS active phase catalyst and into the nature of active edge sites.[24-28] Contrary to CO, it has been
61 shown that NO is able to probe all the active sites of the CoMoS without being affected by the sulfur
62 coverage. In particular, Tøpsøe et al. [27] have shown that NO molecules adsorption on the sulfided phase
63 could lead to a total removal of the S atoms at 298 K via a so-called “push-pull” mechanism. In the same
64 study, a first assignment has been proposed for main vibrational contributions of NO bond considering
65 the non-promoted edges and promoted S-edge, but excluding the promotion of the M-edge,[27] which
66 seems not fully consistent with previous DFT calculations[10, 11] and CO FTIR experiments.[29]

67 Moreover, this atomic scale understanding cannot be decoupled from considering the direct or indirect
68 role played by the support which is a key component of the catalyst. Industrially, γ -alumina is the most
69 widely used support in HDS of middle distillates into gasoil products[1, 30] but for specific applications
70 such as HDS of gasoline produced by fluid catalytic cracking gasoline, other alumina polymorphs such as
71 δ -alumina[7] may be preferentially chosen. At the laboratory scale, changing the nature of support (such
72 as silica, zirconia, titania) has also revealed significant effect on the catalytic activity[31-36] and
73 selectivity.[36-38] The support is thus suspected to impact the nature and intrinsic properties of the active
74 sites linked to the number of promoter atoms engaged in the MoS₂ phase [34] or even the nano-structure
75 (size, morphology) [35, 39] of the catalytically active phase.

76 In the present work, we propose to go beyond those previous studies related to the NO-FTIR, in order to
77 investigate in more details the edge sites of the MoS₂ and CoMoS nano-crystallites and to highlight the
78 speciation sensitivity on the type of support. For that purpose, we will first characterize CoMoS/ $\delta\theta$ -Al₂O₃
79 catalysts as well as MoS₂/ $\delta\theta$ -Al₂O₃ and Co₉S₈/ $\delta\theta$ -Al₂O₃ reference materials (Section 3.1). Then, with the
80 help of DFT calculations extended to two types of possible edges, we will provide a detailed assignment
81 of the IR-spectrum analysed through its second derivative (Section 3.2). In section 3.3, we will analyze

82 the effect of three relevant supports ($\delta\theta$ -Al₂O₃, γ -Al₂O₃, and SiO₂) on the spectral features of the CoMoS
83 edges. We underline that it is beyond the scope of the present work to identify the origin of this
84 support effect. By changing the support, we aim at changing the nature of the active phase and explore the
85 evolution of its spectral features. Section 3.4 will be devoted to chemometric treatments on IR spectra
86 series which provide additional insights on the evolution of site population as a function of NO contact
87 time. Finally, in section 3.5 we will discuss some implications for catalysis.

88

89 2. METHODS

90 2.1. Catalysts preparation

91 The different transition metal sulfides were prepared by incipient wetness impregnation on three different
92 supports: γ -Al₂O₃, $\delta\theta$ -Al₂O₃ and SiO₂. Silica support was provided by Norpro St Gobain as porous pellets
93 (crushed and sieved in a diameter range of 0.315-1 mm). The alumina supports were provided by IFPEN
94 as trilobal extrudates (length of around 2-4 mm with diameter of 1.6 mm). γ -Al₂O₃ was obtained by
95 kneading-extrusion of boehmite powder followed by calcination at 813 K. and $\delta\theta$ -Al₂O₃ by high
96 temperature calcination (1223 K) from γ -Al₂O₃ extrudates. XRD of both aluminas and textural properties
97 of the supports are reported in **supporting information 1**.

98 Impregnation solutions were prepared from MoO₃ and Co(OH)₂ precursors dissolved in aqueous solution
99 in presence of H₃PO₄. Impregnation was performed on the three supports followed by an ageing step for
100 12 h to allow metal diffusion throughout the extrudates or pellets. Then, solids were dried in an oven at
101 393 K for 24 h and calcined in air at 723K for 2h15. Finally, oxide catalysts are presulfided *ex situ* by
102 heating at 5 K.min⁻¹ from 298 to 623 K at atmospheric pressure in a flow of 15 vol.% H₂S in H₂ (1.5 L.h⁻¹
103 g⁻¹ of catalyst). Sulfidation was achieved at 623 K for 2h15min. *Ex situ* sulfided materials were then
104 isolated under vacuum at 473 K in a sealed glass flask.

105 On each support, molybdenum loadings were selected to obtain fixed molybdenum surface densities
106 (labeled dMo in what follows) of 2.2 atoms by nm² of support. In order to compare catalysts at iso-dMo
107 and iso-support, Co/Mo and P/Mo molar ratios are also kept constant at 0.4 and 0.27 respectively.
108 MoS₂/δθ-Al₂O₃ and Co₉S₈/δθ-Al₂O₃ reference materials are also prepared on δθ-Al₂O₃ (according to the
109 same preparation procedure mentioned above for CoMoS supported catalysts). The XRF elemental
110 analysis of Co, Mo and P on different supports (**supporting information 1**), ensures the consistency with
111 the targeted elemental contents.

112 2.2 FTIR experiment

113 Characterization NO-FTIR experiments were performed with a static experimental set-up under vacuum.
114 An IR cell made in quartz equipped with KBr windows was used. The *ex situ* sulfided catalyst powders
115 were pressed and used as wafer of 16 mm diameter and ca. 20 mg which represent 10 mg.cm⁻² under
116 controlled atmosphere (argon). Catalyst wafer was introduced in the IR cell under argon. Prior to NO
117 contact, the cell was evacuated under primary vacuum and closed. The vacuum line is then filled with NO
118 at pressure equilibrium of 150 mbar. NO was afterwards expanded in the FTIR cell to reach 70 mbar
119 equilibrium pressure. Interactions of NO on the surface of the sulfided catalyst wafer are followed by
120 FTIR as function of time. After 5 min NO contact, the gas phase spectra were recorded and the in situ
121 FTIR cell and Schlenck line were evacuated under primary vacuum. A spectrum of the catalyst after NO
122 evacuation was also recorded. Subtractions of IR spectra of the catalyst wafer under vacuum before
123 adding NO (reference spectrum) and of the NO gas phase spectra to catalyst wafer under NO atmosphere
124 were performed in order to evidence the IR contributions of the stable nitrosyl species sorbed on the
125 surface of sulfided phases: CoMoS, MoS₂ and Co₉S₈. Second derivatives of the IR spectra absorbance of
126 the NO sorbed on δθ-Al₂O₃ supported catalysts were calculated with a Savitzky-Golay function (9 points,
127 3 order polynomial).

128 2.3 Chemometric method

129 Chemometric calculations were performed by using the multivariate curve resolution-alternating least
130 squares (MCR-ALS) method directly on the subtracted FTIR spectra. MCR-ALS is based on a linear
131 model assuming the generalized law of Lambert–Beer where the individual response of each component
132 is addable. The aim of this mathematical method[40] is the decomposition of the original data matrix D ,
133 which contains all the spectra recorded during NO contact (from $t = 0$ to 5 min), into the product of two
134 matrices, C and S^T , $D = C.S^T + E$ where C and S^T contain the calculated concentration profiles and
135 corresponding reference IR signals respectively. The error of the fit is contained in matrix E . We apply a
136 single constraint of non-negativity for the concentration profiles and reference spectra. This method has
137 already been successfully applied for size discrimination of supported Pt particles,[41] however to the
138 best of our knowledge, it has not been yet applied to FTIR spectra of supported sulfides catalysts.

139

140 2.4 DFT calculations

141 2.4.1 Total energy

142 Periodic density functional calculations have been performed using the VASP code.[42-44] Spin polarized
143 general gradient approximation (GGA) with the PW91[45, 46] exchange correlation functional and
144 projected augmented-wave (PAW) formalism have been used for total energy calculations. The cut-off
145 energy for the plane-wave basis was fixed to 500 eV and the Brillouin zone integration is performed on a
146 $(3 \times 3 \times 1)$ k-point mesh for the supercell described in the next section with a Methfessel and Paxton
147 smearing method ($\sigma=0.1$).

148 2.4.2 Models

149 Relevant examples of the periodic supercells and technical aspects related to them are described in details
150 in the **supporting information 2**. Previous DFT studies [9-11] have shown the impact of the chemical

151 potential of sulfur on the sulfur coverages and 2D morphology of non-promoted and Co promoted MoS₂
 152 crystallites. In sulfo-reductive conditions such as the one used in the experimental section for activating
 153 the sulfided phase (623 K and p_{H₂S}/p_{H₂} = 0.18), the predicted shape for non-promoted MoS₂ crystallites
 154 is a deformed hexagon where 70-75% of the edges are made of the so-called M-edge and 30-25% of S-
 155 edge. For the Co-promoted MoS₂, the shape is close to an hexagon. DFT calculations were performed in
 156 order to determine the most stable adsorption mode of NO on these M- and S-edges of the MoS₂ and
 157 CoMoS phases for various S and NO coverages. Nevertheless, it was shown by Topsøe et al. that the
 158 adsorption energy of NO is so high that the NO molecule could displace/remove the S-atoms via a “push-
 159 pull” mechanism (trend confirmed by the present study, see further). Thus, the equilibrium S-coverage
 160 found in H₂S/H₂ environment becomes unstable in presence of NO and we consider in what follows,
 161 configurations where S-atoms have been fully removed at the edge and replaced by NO molecules. **Table**
 162 **S2.1** reports the various S-coverages at S- and M-edges and their local configurations considered for
 163 probing NO adsorption.

164 2.4.3 Geometry optimization and adsorption energy

165 The geometry optimization has been completed when the convergence criteria on forces becomes smaller
 166 than 0.02 eV/Å. The configurations reported here, result from geometry optimization performed in two
 167 steps: (i) First the bare surface composed of four (or five in the case of CoMoS) atomic layers have been
 168 fully optimized, (ii) Then the geometry of the adsorption of the *n*NO molecules adsorbed on the
 169 adsorption sites has been optimized, relaxing the atoms of the molecules and the ones of the two atomic
 170 layers of the surface, and fixing the position of the atoms of the two (or three) deepest atomic layers.
 171 Once the most stable configuration is found, the adsorption energy of the NO molecules (ΔE_{ads}) is
 172 calculated at 0 K using the following expression:

$$173 \quad n\Delta E_{ads} = E(nNO - \text{stripe}) - E(\text{stripe}) - nE(NO) \quad (1)$$

174 $E(\text{stripe})$ is the energy of the stripe representing the reference bare MoS_2 or CoMoS edge, $E(n\text{NO} -$
175 $\text{stripe})$ is the energy of the $n\text{NO}$ molecules adsorbed on the corresponding edge and $E(\text{NO})$ is the energy
176 of the isolated NO molecule.

177 For some specific configurations where the stability of the reference bare MoS_2 or CoMoS edge is not
178 stable, we calculate the exchange energy corresponding to the removal of n sulfur atoms upon the
179 adsorption of $n\text{NO}$ molecules:

$$\Delta E_{\text{exch}} = E(n\text{NO} - (\text{stripe} - n\text{S})) - E(\text{stripe}) - n(E(\text{NO}) - E(\text{H}_2\text{S}) + E(\text{H}_2))$$

180 $E(n\text{NO} - (\text{stripe} - n\text{S}))$ is the energy of the $n\text{NO}$ molecules adsorbed on the edge where $n\text{S}$ atoms have
181 been removed, $E(\text{H}_2\text{S})$ and $E(\text{H}_2)$ are the energies of the isolated H_2S and H_2 molecules.

182 2.4.4 Frequency calculations

183 Harmonic frequency calculations for the NO molecules were performed with VASP through numerical
184 differentiation of the force matrix, including all vibrational degrees of the atoms of the molecules and of
185 the metallic atoms of the adsorption site. Including the relaxation of the neighboring sulfur atoms of the
186 adsorption sites does not impact the frequency values reported here. The calculations were performed on
187 the configuration that was previously subjected to a geometry optimization. The displacement step was
188 fixed to 0.02 \AA . In order to compare the theoretical frequencies to the experimental frequencies, a scaling
189 factor of 0.985 is used, which corresponds to the ratio between the experimental frequency of the NO
190 molecule in gas phase (1876 cm^{-1}) and the calculated frequency of the isolated NO (1905 cm^{-1}).

191

192

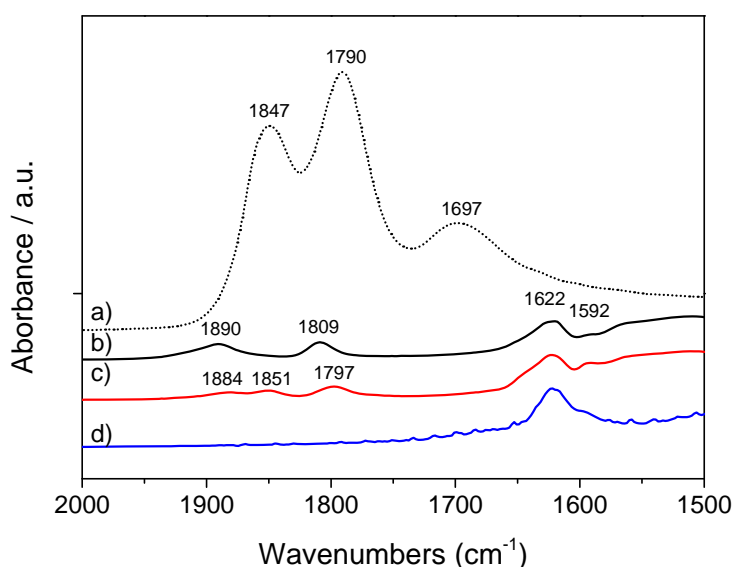
193

194 3. RESULTS AND DISCUSSION

195 3.1 Case of $\delta\theta$ -Al₂O₃ supported samples

196 3.1.1 IR analysis

197 IR spectra of NO adsorbed on the calcined Mo, Co and CoMo oxides and the CoMoS sulfide (obtained by
198 sulfo-reduction of the CoMo oxide) supported on $\delta\theta$ -Al₂O₃ are shown in **Figure 1**.



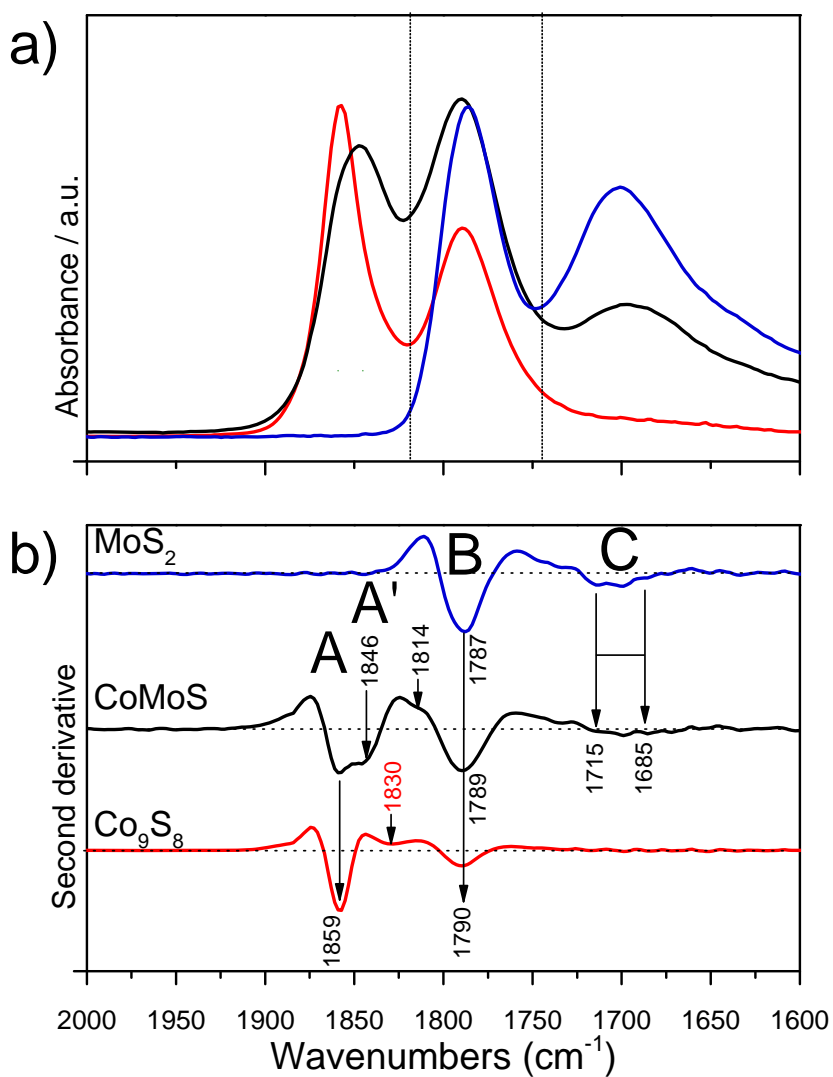
199 **Figure 1.** IR spectra (background subtracted and normalized by the mass of the wafer) of NO adsorbed
200 on $\delta\theta$ -Al₂O₃ supported Mo (d) in blue, Co (c) in red, CoMo oxides (b) in black. For comparison, sulfided
201 CoMoS (a) in dotted line) after 5 min contact in NO (P = 70 mbar) and subsequent evacuation at 298K is
202 reported.
203
204

205 In the spectra obtained for metal oxides supported on $\delta\theta$ -Al₂O₃, two regions can be distinguished: at 1650
206 – 1500 and at 2000 – 1650 cm⁻¹ which are attributed to nitrite/nitrate species formed upon NO contact and
207 to nitrosyl adsorbed on the surface of the oxide or sulfided phases respectively. The contributions of NO
208 adsorbed on the oxides Mo, Co and CoMo supported on $\delta\theta$ -Al₂O₃ are weak. Indeed, for calcined Mo/ and
209 Co/ $\delta\theta$ -Al₂O₃ samples, Mo and Co are present as Mo⁶⁺ and Co²⁺ (d⁰ and d⁵ states respectively) which are

210 not expected to adsorb strongly NO molecule.[28] For cobalt oxide supported on $\delta\theta$ -Al₂O₃ (spectrum c,
211 Figure 1) three distinct NO contributions appear at 1884, 1851 and 1797 cm⁻¹ in the nitrosyl region. The
212 two bands at 1884 and 1797 cm⁻¹ are due to the formation of Co²⁺(NO)₂ complexes (v_s(NO) and v_{as}(NO)
213 modes respectively), while the band at 1851 cm⁻¹ is assigned to mononitrosyl Co²⁺ species.[20] The oxide
214 Mo/ $\delta\theta$ -Al₂O₃ material (spectrum d, Figure 1) does not display any contribution due to nitrosyl species in
215 the spectrum. In that case, only nitrite/nitrate species formation is observed (1620 and 1592 cm⁻¹).[47]
216 Considering the CoMo oxide material (spectrum b), two contributions are found at 1890 cm⁻¹ and 1809
217 cm⁻¹. These components are close to those observed for the oxide Co/ $\delta\theta$ -Al₂O₃ sample and could be
218 assigned to similar Co²⁺(NO)₂ species.[20] It is interesting to note first that the dinitrosyl contributions
219 are more intense than on Co/ $\delta\theta$ -Al₂O₃ and secondly that mononitrosyl species is not observed on CoMo
220 sample. It may indicate that cobalt oxide is better dispersed when introduced in presence of molybdenum.
221 The nature of the species in the aqueous solution of impregnation should be different and may lead to
222 different state of metal dispersion.

223 For comparison, NO titration have been undertaken on sulfided CoMoS materials and the corresponding
224 IR spectrum after NO saturation reports three distinct contributions in the 1850 – 1700 cm⁻¹ range
225 (**Figure 1**). The contributions are much more intense compared to the oxide materials due to i) the great
226 affinity of NO for edge sites of the promoted or non-promoted sulfided phases and the surface sites of
227 Co₉S₈, ii) the possible higher molar absorption coefficient of nitrosyls adsorbed on the sulfided phase and
228 iii) the higher concentration of surface sites prompt to adsorb NO. Thus, NO is a relevant probe molecule
229 of the sulfided phase in agreement to previous works.[20] Under specific conditions, NO molecule was
230 claimed to be a reactive probe towards the sulfided phase which might be oxidized.[48] In the present
231 case, one can nevertheless remark that unlike supported metal oxide, oxidation mechanisms with further
232 formation of nitrite or nitrate species remain very limited on CoMoS catalyst in interaction with NO at
233 298 K in agreement with data reported in former works.[20, 24-28]

234 The IR spectra of NO adsorbed on sulfided CoMoS and references MoS₂, Co₉S₈ supported on $\delta\theta$ -Al₂O₃
235 with constant Mo loading and Co/Mo ratio are shown in **Figure 2a**.



236

237 **Figure 2.** a) IR spectra of the sulfided catalysts: MoS₂ (blue), Co₉S₈ (red) and CoMoS (black) supported
238 on $\delta\theta$ -Al₂O₃ (normalized by gram of catalyst) after 5 min contact in NO (P = 70 mbar) and subsequent
239 evacuation at 298K; b) Second derivative of the IR spectra (similar code color) with minima identified
240 according to the method described in **supporting information 3**.

241

242 As previously discussed, three components are observed in the IR spectra recorded at NO saturation for
243 the series of samples supported on $\delta\theta\text{-Al}_2\text{O}_3$: 1880 – 1840 cm^{-1} ; 1810 - 1790 cm^{-1} and 1715 - 1685 cm^{-1}
244 (broad) which will be hereafter referenced as (A), (B) and (C) components respectively. The IR spectrum
245 of NO on the Co sulfided material gives rise to (A) and (B) components while, IR spectrum of Mo
246 sulfided sample in interaction with NO exhibits two contributions (B) and (C). From the comparison with
247 NO adsorption complexes and metal cluster complexes, these two absorption bands have been tentatively
248 assigned to the symmetric and asymmetric stretching vibrations of dinitrosyl species adsorbed on the edge
249 sites of the CoMoS and MoS₂ phases.[24] It can be noticed that (B) and (C) components are also close to
250 those generally observed for reduced Mo supported catalyst in interaction with NO.[47, 49, 50] However,
251 IR NO spectra obtained on CoMoS / $\delta\theta\text{-Al}_2\text{O}_3$ reveals (A), (B) and (C) components which seem to result
252 from the superposition of the two doublet bands observed for MoS₂/ $\delta\theta\text{-Al}_2\text{O}_3$ and Co₉S₈/ $\delta\theta\text{-Al}_2\text{O}_3$. [24,
253 51-53] Hence, vibrational contributions of NO adsorbed on MoS₂ and Co₉S₈/ $\delta\theta\text{-Al}_2\text{O}_3$ overlap and are
254 very close with the contributions of NO adsorbed on CoMoS on $\delta\theta\text{-Al}_2\text{O}_3$. This makes thus difficult to
255 identify the contributions due to the nitrosyl species adsorbed on the edges of the promoted CoMoS slabs
256 without further treatments of the IR spectra as proposed in what follows.

257

258 3.1.2 Analysis of the second derivative of the IR spectra

259 To obtain a more detailed description of the vibrational contributions observed after NO contact on
260 CoMoS, MoS₂ Co₉S₈, the second derivative of the IR spectra was plotted in **Figure 2 b** and the minima
261 have been identified according to the analysis reported in **supplementary information 3** considering the
262 evolution as a function of the contact time. **Table 1** reports the corresponding vibrational frequencies
263 obtained from this analysis. As revealed in **Figure 2b**, second derivative analysis obviously allows the
264 identification of minor contributions (**supplementary information 3**) and also overlapping ones which
265 are not resolved in the initial spectrum. This analysis was proposed recently on non-promoted MoS₂

266 phase.[25] The second derivative spectra obtained for NO adsorbed on $\delta\theta$ -Al₂O₃ supported Co₉S₈ and
 267 MoS₂ confirm the existence of two doublets already visible in the initial spectra: (A) 1859 / (B) 1789 cm⁻¹
 268 and (B) 1787 cm⁻¹ / (C) 1715 – 1685 cm⁻¹ respectively. It should be noted that the region corresponding to
 269 the (C) component contains actually several contributions with lower intensities than in (A) and (B)
 270 component (**supplementary information 3**). The CoMoS/ $\delta\theta$ -Al₂O₃ catalyst reveals three intense
 271 contributions : (A) 1859 cm⁻¹, (A') 1846 cm⁻¹, (B) 1790 cm⁻¹ and more broaden contributions within the
 272 (C) component region. The three contributions (A), (B) and (C) reveal that either CoMoS phase exhibits
 273 edge sites with similar electronic properties as the non-promoted Mo edge and Co₉S₈ sites or that non
 274 promoted MoS₂ crystallites and/or Co₉S₈ phases are present. However, the component located at 1846
 275 cm⁻¹ (A') appears as a specific feature of the promoted CoMoS phase. Hence, the two contributions (A)
 276 and (A') overlapping in the IR spectrum of CoMoS/ $\delta\theta$ -Al₂O₃ are now distinguished: (A) being assigned
 277 to Co₉S₈ sites and (A') to CoMoS. Moreover, it appears that the intensity of the bands at 1715 – 1685 cm⁻¹
 278 ¹ corresponding to the (C) region is less pronounced for the CoMoS catalyst than for the non-promoted
 279 one.

280 **Table 1. Observed components of the NO adsorbed on the sulfided MoS₂, Co₉S₈ and CoMoS phases**
 281 **supported on $\delta\theta$ -Al₂O₃.**

Region	ν (cm ⁻¹)	CoMoS	MoS ₂	Co ₉ S ₈
A	1859	✓		✓
A'	1846	✓		
B	1790 – 1787	✓	✓	✓
C	1715 – 1685	✓	✓	

282

283 It must be added that minor components are also identified at different wavenumbers for the different
 284 samples (**supporting information 3**). Some of these vibrational contributions are present exclusively on
 285 the CoMoS sample such as 1814 cm⁻¹, while the minor contribution at 1830 cm⁻¹ seems to be specific of

286 the Co₉S₈ phase. These major or minor components will be considered for the forthcoming comparison
287 with DFT calculations. These features are probably key to identify the CoMoS phase and will be further
288 discussed with DFT calculations and its evolution will also be considered with respect to other supports.

289

290 3.2 DFT calculations of NO adsorption on MoS₂ and CoMoS edges

291 Before providing a direct comparison with experimental results, it is worth presenting a preliminary
292 theoretical analysis of NO adsorption on the different type of sites at low NO coverage in order to provide
293 some general chemical trends.

294 3.2.1 M-edge at low NO coverage

295 As expected the adsorption energies are significantly higher (ΔE_{ads} from -177 to -362 kJ/mol, **Table S2.2**)
296 than those calculated for the CO molecule on similar systems (smaller than -140 kJ/mol).[18, 19] Due to
297 the presence of the unpaired electron in the π^* orbital of NO, this molecule is highly reactive and interacts
298 more strongly with any Lewis Mo or Co sites than CO. The adsorption energy on Mo site is about -362
299 kJ/mol for the non-promoted site, which is significantly higher than for the adsorption energy of one
300 sulfur atom on the same site (\sim -250 to -295 kJ/mol).[54] On the Co site, this trend is even more
301 pronounced: $\Delta E_{\text{ads}} = -242$ kJ/mol whereas the adsorption energy of one sulfur atom is about
302 \sim 20kJ/mol.[55] Thus, this analysis confirms that NO molecule certainly replaces or displaces S atoms at
303 the edge as proposed in a previous work.[27]

304 Moreover, **Table S2.2** shows that the adsorption energy of NO molecule is more favorable on any Mo
305 Lewis acid sites (when no sulfur atom is present), while the downward frequency shift is significantly
306 larger on Mo than on Co sites: the difference between the two sites is close to 200 cm⁻¹ for the ideal case
307 of isolated mononitrosyl species. This trend results from two intricate effects: on the one hand, the
308 acceptor character (involved in the donation) of the Co site is weaker than the one of the Mo site, on the

309 other hand, the δ - π overlap (resulting from back donation) is also weaker for the Co-3*d* electrons than for
310 the Mo-4*d* electrons. Although these preliminary configurations on edge sites at low coverages are not
311 obligatory relevant for our IR experiments, they readily help to understand the intrinsic site-driven
312 parameters of the vibrational frequencies of NO adsorbed on the CoMoS systems. The experimental main
313 bands are covering a wide frequency range of about 170 cm^{-1} where Mo sites should generate vibrational
314 frequencies located at the lower region of the IR spectrum (C band), whereas Co sites on the M-edge may
315 impact the upper region (close to the A band).

316 In addition, the vibrational frequency depends on the nature of the neighboring sites and local
317 environment on the edge. In particular, on the partially promoted M-edge, the presence of Co atoms in the
318 close vicinity of the Mo site where NO is adsorbed, induces a slight increase of the vibrational frequency
319 (+20 to 25 cm^{-1}). Conversely, the presence of Mo atoms in the close vicinity of the Co site where NO is
320 adsorbed induces a slight decrease of the vibrational frequency (-34 to -37 cm^{-1}).

321 Another environment effect may be studied here by considering the presence of sulfur atoms on the
322 neighboring sites. For the non-promoted and promoted M-edge, adding 2 or 3 sulfur atoms on the
323 neighboring sites where NO is adsorbed leads to an increase of the vibrational frequency by up to + 40 –
324 50 cm^{-1} . This may be considered as a surface coverage effect with dipole-dipole interaction between the
325 neighboring Mo-S and Mo-NO species due to the overlap between the Mo 4*d* electrons and π^* orbital of
326 NO.

327 3.2.2 S-edge at low NO coverage

328 If we now consider the adsorption of NO on the S-edge, **Table S2.3** shows that on the non-promoted S-
329 edge with a S-coverage of 50% as encountered in usual sulfidation conditions, the NO adsorption energy
330 is significantly lower than on the M-edge with 0% S (Mo sites are 4 fold coordinated in both cases). At
331 the same time, the corresponding vibrational frequency is also higher at 1726 cm^{-1} for the isolated

332 mononitrosyl. If we consider the higher S-coverage (100%), the calculated NO vibrational frequency is
333 even higher 1760 cm^{-1} . As a consequence, in these two S-edge cases as well as for the M-edge, it appears
334 difficult to find Mo sites where the NO vibrational frequency is greater than 1800 cm^{-1} , which seems to be
335 consistent with the experimental observations where the two main observed bands (B and C) are below
336 1800 cm^{-1} .

337 By contrast, considering the Co-promoted S-edge with S-coverage of 75%, when NO is adsorbed on top
338 of a Co site, it is observed that the calculated adsorption energy is significantly lower than on the M-edge
339 while the vibrational frequency is equal to 1864 cm^{-1} as high as for the Co site on the M-edge with
340 neighboring S-sites. This may indicate again that NO adsorbed on Co sites are generating bands in the
341 high frequency region (A), however due to the rather low adsorption energy on this Co S-edge site, this
342 low coverage configuration may not be considered as relevant.

343 It should also be noticed that when one S atom is exchanged by one NO molecule in a bridging position,
344 the NO vibrational frequency decreases tremendously at 1456 cm^{-1} . A similar trend is observed for the
345 Co-promoted S-edge (1574 cm^{-1} , **Table S2.3**) and for the non-promoted M-edge (for specific NO
346 bridging position not reported here). These low frequency values do not match any of the main observed
347 IR bands. Considering the analysis of the second derivatives of the absorbance, one may not exclude that
348 some minor contributions at low frequencies could be eventually assigned to isolated defect sites, if not
349 beyond the experimental accuracy.

350 3.2.3 Effect of NO coverage

351 Due to the rather strong adsorption energy of NO adsorbed on the Mo or Co sites (often more than -200
352 kJ/mol), it is expected that even small doses of NO as used experimentally may lead to high NO coverage
353 at the edges, even if the S-coverage after sulfo-reducing conditions would be high. Hence, the S-exchange
354 process will be thermodynamically favored, and may lead to the complete removal of S-atoms on the

edges and allowing several NO molecules to be adsorbed.[27] Thus, the sulfur coverage should drastically diminish with respect to the sulfiding conditions, while the NO coverage increases as a function of the experimental pressure of NO applied.

- *Case of the non-promoted edges*

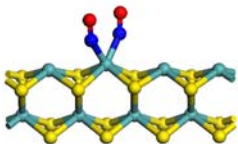
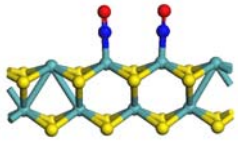
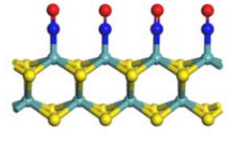
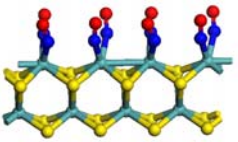
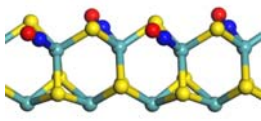
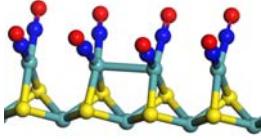
Considering first the non-promoted M-edge, increasing the NO coverage may lead either to dinitrosyl species or neighboring mononitrosyls which exhibit coupled vibrational modes: generally one symmetric and one asymmetric mode. If these species are assumed to be isolated, **Table 2** shows that the adsorption energies remain highly exothermic in both cases, while the symmetric modes exhibit higher frequencies (1705 and 1718 cm^{-1} respectively) than the isolated mononitrosyl (1671 cm^{-1}). This trend is also consistent with previous DFT calculations on $\text{Mo}_{16}\text{S}_{32\pm x}$ clusters.[56] This well-known coverage effect results from the through space interaction of the Mo-NO dipole leading to dynamic shifts of about +34 to +47 cm^{-1} which are in line with those reported for NO on NiO surface.[57] At the same time, the asymmetric modes appear at significantly lower frequencies (1604 and 1670 cm^{-1} respectively.)

If the NO coverage is increased up to one dinitrosyl species per Mo site (saturation level in the experiments), an even broader distribution of frequencies is found from 1625 cm^{-1} to 1809 cm^{-1} . Moreover, it appears that the adsorption energy for the multiple mononitrosyls remains high ~ -343 kJ/mol which means that the energy required to exchange the 4 S bridging atoms obtained at equilibrium in $\text{H}_2\text{S}/\text{H}_2$ environment is estimated at about $\Delta E_{\text{exch}} = -160$ kJ/mol.[54] A similar exothermic exchange energy is found for the multiple dinitrosyl configuration. Thus, this confirms that thermodynamically these S-atoms can be removed from the edge by NO at high coverage.

A fruitful assignment is furnished in **Table 2**: it can be noticed that the increase of NO coverage induces the appearance of higher frequencies closer to the IR region (B) located around 1787 cm^{-1} on the experimental spectrum of the non-promoted MoS_2 . This component (B) can be due to the symmetric coupling of mononitrosyls or dinitrosyls as shown by DFT calculations (**Table 2**). Several lower

379 frequencies at 1714, 1700 and 1685 cm^{-1} (**supporting information 3**) of component (C) correspond to
 380 asymmetric coupling of mononitrosyls (calculated at 1708 cm^{-1}) or of dinitrosyls (1712 and 1688 cm^{-1}).

381 **Table 2. Calculated adsorption energies and corresponding vibrational frequencies of NO adsorbed**
 382 **on the various possible M- and S-edge sites of non-promoted MoS₂ at various NO coverages. Green**
 383 **balls: molybdenum, yellow balls: sulfur, blue balls: cobalt, dark blue balls: nitrogen, red balls:**
 384 **oxygen.**

Site	Configuration	ΔE_{ads} (kJ/mol NO)	Calculated ν_{NO} (cm^{-1}) ^a	Experimental ν_{NO} (cm^{-1}) ^b
Mo on the non-promoted M-edge 0%S	Dinitrosyl 	-224	1705 _s ^c 1604 _a	
	Coupled mononitrosyl 	-349	1718 _s 1670 _a	
	Multiple mononitrosyl 	-343	1769_s (B) 1708_a (C) 1708_a (C) 1660 _a	1787 (B) 1747, 1733 1714 (C) 1700/1685 (C)
	Multiple dinitrosyl 	-189	1809_{ss} (B) 1762 _{sa} , 1740 _{sa} 1712_{sa} (C) 1688_{as} (C) 1659 _{aa} , 1650 _{as} 1625 _{as}	1672 1650 1637
Mo on the non-promoted S-edge 50%S and 0%S	Multiple Mononitrosyl 	-167	1763 1745 1738 1736	
	Multiple dinitrosyl 	-136 ^d	1831_{ss} (B) 1772 _{sa} , 1770 _{sa} , 1768 _{as} 1739 _{sa} , 1731 _{aa} , 1727 _{aa} 1693_{aa} (C)	

385 ^a vibrational frequency is corrected by a factor of 0.985 (see methods for explanation).

386 ^a and ^b bold values correspond to the experimentally observed main regions (A), (B) or (C). Non bold values
 387 correspond the minor contributions also identified in the second derivative analysis (**supporting information 3**).

388 ^c abbreviation for modes: s=symmetric mode, a=antisymmetric, ss=symmetric within each dinitrosyl complex and
 389 between all neighboring sites, sa= symmetric within each dinitrosyl complex and antisymmetric between
 390 neighboring sites, as=antisymmetric within each dinitrosyl complex and symmetric between neighboring site, aa=
 391 antisymmetric within each dinitrosyl complex and antisymmetric between neighboring site.

392 ^d exchange energy ΔE_{exch}

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Finally, as reported in **Table 2**, other minor contributions at lower frequencies such as 1672 and 1650 and 1637 cm^{-1} (**supporting information 3**) are also recovered by the DFT calculations and they should correspond to both mononitrosyls and dinitrosyl species. These experimental values as well as their DFT assignment are generally coherent with the previous experimental work[25] with the exception that the minor lower frequencies (1637 cm^{-1}) cannot be assigned to isolated mononitrosyls as proposed by van Haandel et al. but rather to asymmetric-symmetric coupling between dinitrosyls. Due to their very low intensities in the second derivative analysis, it may probably be difficult to assign them without ambiguity on the pure basis of experiments.

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As recalled in the methods, previous DFT calculations[10, 11] have predicted that the shape of the MoS_2 crystallite is a deformed hexagon where 70-75% of the edges are constituted of the M-edge in sulfidative conditions as used for the synthesis of the sulfided catalyst. Hence, we have checked the vibrational frequencies in the cases of the multiple mononitrosyls and dinitrosyls adsorbed on the S-edge with 50% S and 0% S respectively. Apparently the multiple dinitrosyls configuration leads to vibrational frequency calculated at 1831 cm^{-1} which seems a little bit too high to fully agree with experimental component (B). The calculated frequency at 1693 cm^{-1} falls within the range of component (C) but does not fully recover all contributions of component (C). Even if one cannot fully rule out the contribution of the S-edge, the predominance of the M-edge should be sufficient to interpret the experimental observations. This point will be further discussed with the chemometry analysis.

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- *Case of the promoted edges*

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On the cobalt promoted M-edge with 50% cobalt and 50% Mo sites, the dinitrosyl species cannot be stabilized on Co sites where only mononitrosyl species are stable. On the Mo site, **Table 3** shows that the two NO vibrational frequencies corresponding to the symmetric and asymmetric modes are shifted to

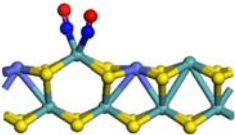
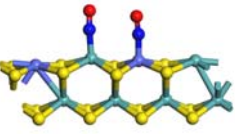
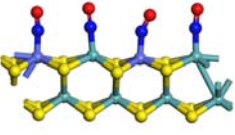
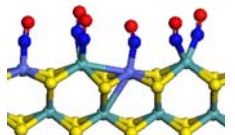
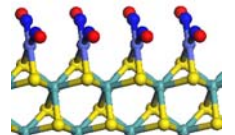
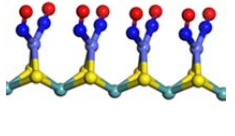
417 higher values (1772 and 1708 cm^{-1} respectively) than the ones of the non-promoted edge. This trend
418 confirms the non-negligible effect of the chemical nature of neighboring sites on the NO vibrational
419 frequencies. For the highest NO coverage which corresponds to the saturation level, Mo sites are thus
420 covered by dinitrosyls and Co sites by mononitrosyls which generate vibrational frequencies from 1639 to
421 1867 cm^{-1} . It should be stressed that the higher calculated frequencies reported in **Table 3** are induced by
422 the predominant contribution of NO adsorbed on the Co sites. This trend is in line with our previous
423 analysis on the low NO coverage regime, and highlights that the M-edge partially decorated by cobalt
424 may contribute to component (A') observed around 1846 cm^{-1} in the IR experiments to be specific of the
425 CoMoS/ $\delta\theta$ - Al_2O_3 catalyst (**Figure 2b**). In addition, the frequency calculated at 1774 cm^{-1} may
426 correspond to component (B) observed on promoted MoS_2 . By contrast, NO adsorbed on this edge (either
427 as multiple mononitrosyls or dinitrosyls) does not contribute strongly to the bands of component (C) at
428 1715 – 1685 cm^{-1} . By contrast, the minor contributions observed at 1734, 1672, 1657 and 1633 cm^{-1}
429 (**supporting information 3**) are recovered by the DFT calculations on this edge, which may indicate that
430 these bands are features of the CoMoS phase (even if some of them are also found on the MoS_2 phase.)

431 For NO saturating the cobalt sites located on the S-edge, two configurations are found very close in
432 energy. The first one (called parallel) exhibits dinitrosyl species present on each cobalt site lead to
433 vibrational frequencies in the range of 1650 to 1787 cm^{-1} with contributions in the range of components
434 (B) and (C) but not in component (A'). **Table 3** reveals a reasonable agreement between all calculated
435 frequencies and the experimental ones (major and minor components) analyzed by the second derivative
436 of the IR spectra. In this case, all NO molecules are lying in the same plane parallel to the edge surface
437 and each dinitrosyl species are aligned according to an ON---NO scheme.

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Table 3. Calculated adsorption energies and corresponding vibrational frequencies of NO adsorbed on the various possible Co promoted M- and S-edge sites at various NO coverages. Same color legend as Table 2.

Site	Type	Adsorption configuration	ΔE_{ads} (kJ/mol NO)	Calculated ν_{NO} (cm^{-1}) ^a	Experimental ν_{NO} (cm^{-1}) ^b
Co on the promoted M-edge with 50% Co	Dinitrosyl		-206	1772 _s ^c 1708 _{as}	
	Coupled mononitrosyl		-251	1858 _{Co-s} 1655 _{Mo-as}	
	Multiple mononitrosyls		-251	1887 _{Co-s} 1808 _{Co-s} 1662 _{Mo-as} 1649 _{Mo-as}	1846 (A') 1814 1790 (B) 1734
	Multiple dinitrosyls		-184	1867 _{Co (A')} 1774 _{Mo-ss (B)} 1740 _{Mo-sa} , 1670 _{Mo-aa} 1656 _{Mo-as} 1639 _{Mo-aa}	1716 (C) 1697/1685 (C) 1672 1657 1634
Co on the promoted S-edge with 100% Co	Multiple dinitrosyls parallel		-108 ^d	1787 _{ss (B)} 1729 _{sa} , 1720 _{sa} / 1719 _{sa} / 1689 _{aa} / 1686 _{aa (C)} 1678 _{sa} , 1650 _{aa}	
	Multiple dinitrosyls upright-tilted		-106 ^d	1861 _{ss (A')} 1813 _{sa} / 1810 _{sa} / 1782 _{sa (B)} 1698 _{as (C)} 1657 _{aa} , 1651 _{aa} , 1614 _{aa}	

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^a vibrational frequency is corrected by a factor of 0.985 (see methods for explanation).

^a and ^b values written in bold correspond to the experimentally observed main regions (A), (B) or (C). Other values correspond to minor contributions also identified in the second derivative analysis (**supporting information 3**).

^c abbreviation for modes: s=symmetric mode, a=antisymmetric, ss=symmetric within each dinitrosyl complex and between all neighboring sites, sa= symmetric within each dinitrosyl complex and antisymmetric between neighboring sites, as=antisymmetric within each dinitrosyl complex and symmetric between neighboring site, aa=antisymmetric within each dinitrosyl complex and antisymmetric between neighboring site.

^d exchange energy ΔE_{exch}

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Each Co atom sits in a perfect square planar environment formed by the dinitrosyl ligands and the two S-atoms. This interesting configuration would thus imply that the partially promoted M-edge and fully

454 promoted S-edge do not contribute exactly to the same IR bands: in particular, the S-edge would not
455 contribute to the (A') component. This may provide an appealing way of distinguishing the two types of
456 sites at high level of NO saturation.

457 For NO saturating the cobalt sites located on the S-edge, two configurations are found very close in
458 energy. The first one (called parallel) exhibits dinitrosyl species present on each cobalt site lead to
459 vibrational frequencies in the range of 1650 to 1787 cm^{-1} with contributions in the range of components
460 (B) and (C) but not in component (A'). **Table 3** reveals a reasonable agreement between all calculated
461 frequencies and the experimental ones (major and minor components) analyzed by the second derivative
462 of the IR spectra. In this case, all NO molecules are lying in the same plane parallel to the edge surface
463 and each dinitrosyl species are aligned according to an ON---NO scheme. Each Co atom sits in a perfect
464 square planar environment formed by the dinitrosyl ligands and the two S-atoms. This interesting
465 configuration would thus imply that the partially promoted M-edge and fully promoted S-edge do not
466 contribute exactly to the same IR bands: in particular, the S-edge would not contribute to the (A')
467 component. This may provide an appealing way of distinguishing the two types of sites at high level of
468 NO saturation.

469 Nevertheless, a second configuration (called upright-tilted) must also be considered: it is only slightly less
470 stable (2 kJ/NO) and one half of the NO molecules (belonging to distinct dinitrosyls) is oriented in a
471 nearly upright position, and the second half is in a tilted position. This configuration was previously
472 reported in a combined experimental and DFT work[27] and our calculated frequencies (**Table 3**) match
473 well with these previous published ones. In this configuration, the symmetric coupling mode of the close
474 to tilted NO molecules leads to a calculated frequency (1861 cm^{-1}) value that remain compatible with the
475 (A') component. The antisymmetric coupling mode of the tilted NO molecules lead to a set of calculated
476 frequencies (1813/1810/1782 cm^{-1}) matching the component (B). Finally, the close to upright NO

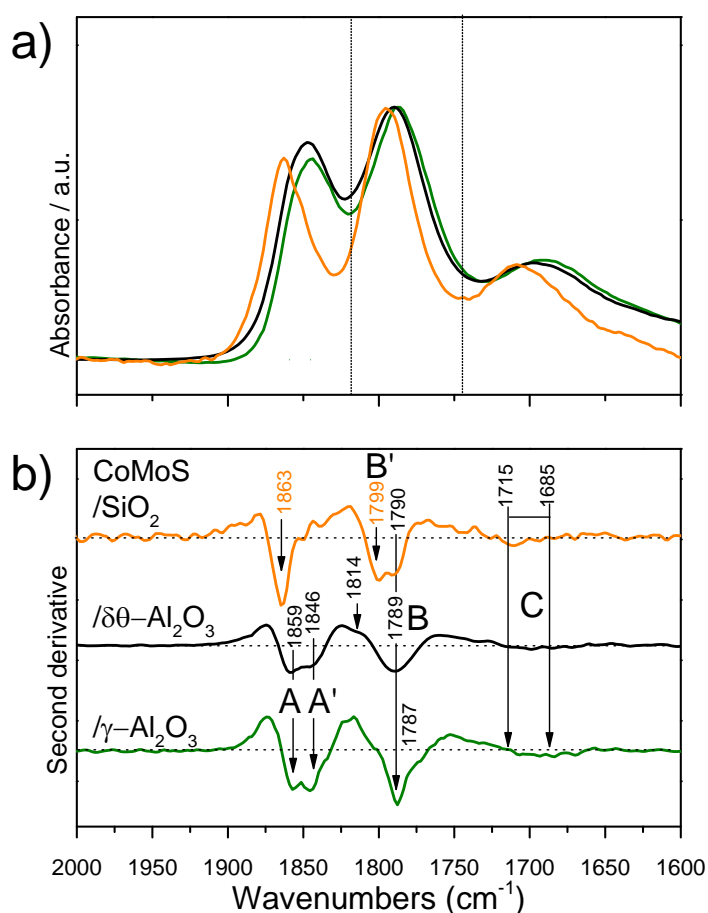
477 molecules give rise to the lowest four frequencies including the symmetric coupling mode at 1698 cm^{-1}
478 corresponding to the (C) component. Regarding the other contribution calculated at 1614 cm^{-1} (**Table 3**),
479 it seems however that the agreement with experimental data is less satisfactory for this configuration
480 which could be an indication that the parallel configuration is more relevant for the experimental data.
481 Coming back to the second derivative analysis (**Figure 2 b**), we have proposed that the overlap between
482 NO-CoMoS and NO-Co₉S₈ in region (A) is limited to the highest frequency at ca. 1859 cm^{-1} (A). For
483 CoMoS/ $\delta\theta$ -Al₂O₃, the intense shoulder at 1846 cm^{-1} may thus correspond to the NO adsorption on the
484 specific Co sites present in the CoMoS phase (and not in Co₉S₈) as identified by DFT calculations. Since
485 component (A') is not experimentally observed neither on the non-promoted MoS₂ (even at high NO
486 coverage) and nor on the Co₉S₈ phase but is present on the promoted MoS₂/ $\delta\theta$ -Al₂O₃ samples, it must be
487 considered as the signature of the presence of the promoter either at the M-edge or eventually at the S-
488 edge with NO in upright-tilted configuration, in CoMoS/ $\delta\theta$ -Al₂O₃ (considering the aforementioned
489 restrictions). The incidence of this key feature will be further analyzed in the next section devoted to
490 support effects.

491 3.3 Comparison with γ -Al₂O₃ and SiO₂ supported samples

492 To evaluate the sensitivity of the NO probe IR spectroscopy and identify potential support effect on the
493 sulfided phase, the second derivatives method was applied to spectra of NO adsorbed on CoMoS
494 supported on γ -Al₂O₃, $\delta\theta$ -Al₂O₃ and SiO₂ (**Figure 3**).

495 Analyzing firstly the three IR spectra (**Figure 3 a**), it appears that the two alumina supported catalysts
496 exhibit rather similar features, whereas the spectrum of NO-CoMoS/SiO₂ reveals obviously several
497 features which differ from the alumina supported catalysts. The three main components at (A), (B) (C) are
498 slightly shifted at higher frequencies and have narrower full width at half maximum (FWHM) than the
499 alumina supported catalysts. This observation might result from several effects. First, we cannot exclude

500 an indirect effect of the silica support on the NO vibration. Due to the different Brønsted acidity of the
 501 hydroxyl groups and different electrostatic fields exerted by alumina and silica,[58] the NO interaction
 502 with the sulfided phase is indirectly perturbed by the support which slightly shifts the NO frequency on
 503 aluminas with respect to silica. Moreover, the narrower FWHM of components (A) and (B) may indicate
 504 that the speciation of sites involved in NO adsorption are less numerous.



505
 506 **Figure 3.** (a) IR spectra of sulfided CoMoS supported on γ -Al₂O₃ (green), $\delta\theta$ -Al₂O₃ (black) and SiO₂
 507 (orange) (normalized per gram of catalyst) after 5 min contact in NO (P = 70 mbar) and subsequent
 508 evacuation at 298K; and (b) corresponding second derivative spectra (similar code color). Note: on silica,
 509 spectrum reports low signal to noise ratio.

510

511 Considering now the second derivative analysis, the four previously discussed components (A), (A'), (B)
512 and (C) are actually observed for both alumina supported CoMoS catalysts. In this case, the components
513 at high wavenumbers correspond to two minima (A) at 1859 cm^{-1} and (A') at 1846 cm^{-1} , whereas the
514 silica supported catalyst exhibits only one minimum (A) at 1863 cm^{-1} (with a very small shoulder at 1849
515 cm^{-1}). As previously analyzed, since IR spectrum of NO-Co₉S₈/ $\delta\theta$ -Al₂O₃ reveals a highest band (A) very
516 close to 1859 cm^{-1} , the second peak at 1846 cm^{-1} (A') is unambiguously assigned to NO on the CoMoS
517 sites on the alumina supported catalysts. At high NO coverage, (A') contribution should correspond to
518 multi-nitrosyl complexes stabilized on specific cobalt sites located either on the M-edge or on the S-edge
519 (with NO in upright-tilted configuration) of the CoMoS phase according to DFT calculations (**Table 3**).
520 Hence, the relative intensities of (A) and (A') components in the second derivatives differ from one
521 support to another and may consequently be the signature of the promotion degree reached in the CoMoS
522 phase: in particular, the intensity of (A') component decreases significantly on silica which indicates that
523 the Co-promoted sites are strongly diminished on silica. The comparison of the relative intensity of the
524 (A') and (A) components on the two alumina supports indicate (as expected) that the cobalt sites present
525 in the mixed CoMoS phase are similar than the ones present on silica. Nevertheless, we can notice that
526 the relative intensities of (A) and (A') differ slightly, which may also be a signature of the impact of the
527 alumina polymorphs on the CoMoS active phase.

528 Coming back to silica, the main contribution (B) is actually composed of two distinct contributions at
529 1799 cm^{-1} (B') and 1790 cm^{-1} (B) which is not the case for the Al₂O₃ supported samples. Two
530 complementary interpretations can be furnished. First of all, coming back to our previous DFT
531 calculations at maximal NO coverage (**Table 3**), the calculated frequencies of NO adsorbed on the cobalt
532 promoted M-edge and S-edge (1774 and $1782/1787\text{ cm}^{-1}$ respectively), and on the non-promoted M-edge
533 (1809 cm^{-1}). Thus, the promoted M-edge and S-edge may correspond to the contribution (B), while the
534 band (B') may originate from the non-promoted M-edge. Since on the silica supported sample, the level

535 of cobalt promotion is expected to be low compared to alumina supported catalysts (due to the low
536 intensity of (A')), the two components (B) and (B') should preferentially correspond respectively to the
537 non-promoted M-edge and to the promoted S-edge. If so, the respective behaviors of (A') and (B') are
538 decoupled on silica : the (A') component diminishes while (B') remains. Hence, (A') should be assigned
539 predominantly to the Co-promoted M-edge site, whereas (B') to the Co-promoted S-edge site. The second
540 possible interpretation is that the slightly shifted (B) component can also be assigned to the NO adsorbed
541 on Co₉S₈ phase (as the (A) component is also shifted), while the (B') still corresponds mainly to non-
542 promoted sites and/or some promoted S-edge sites.

543 Regarding the third main contribution (C), different maxima (with some shifts) are identified which may
544 also be assigned to the presence of non-promoted MoS₂ and promoted sites as calculated by DFT. If we
545 consider the reference sample NO-Co₉S₈/δθ-Al₂O₃, it appears that the positions of bands (A) and (B) are
546 rather close to the ones of NO-CoMoS/SiO₂.

547 3.4 Chemometric analysis

548 A chemometric approach was applied to the spectra series of NO sorbed (in excess) on CoMoS phase
549 supported on alumina and silica. The objective is to attempt to further identify the spectral features of
550 each population of surface sites on the sulfided phase probed by NO as a function of contact time in order
551 to distinguish the contribution of various site populations according to their intrinsic affinity for NO.

552 Chemometric approach undertaken on the non-promoted MoS₂/δθ-Al₂O₃ (**Figure 4**) shows that two main
553 reference spectra (RS) are needed to explain more than 99% of the variance IR spectra evolution recorded
554 as function of NO contact time (**Table S4.1**).

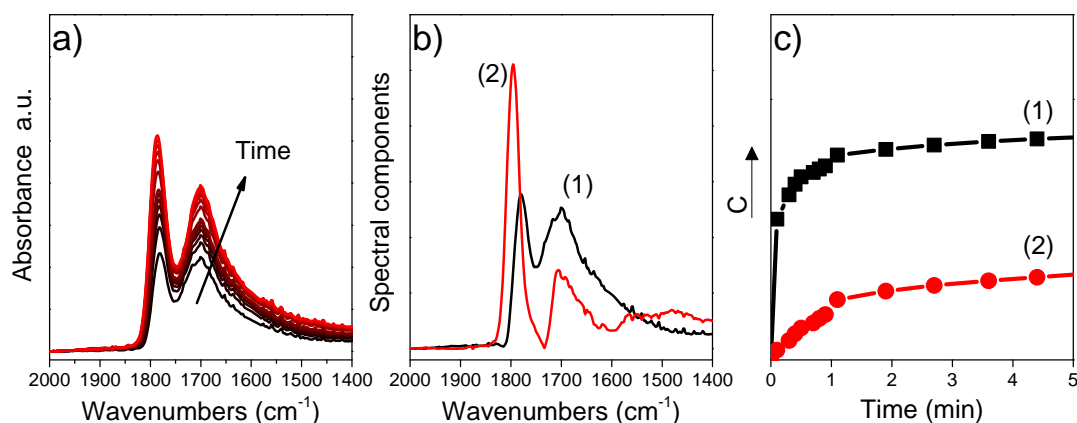
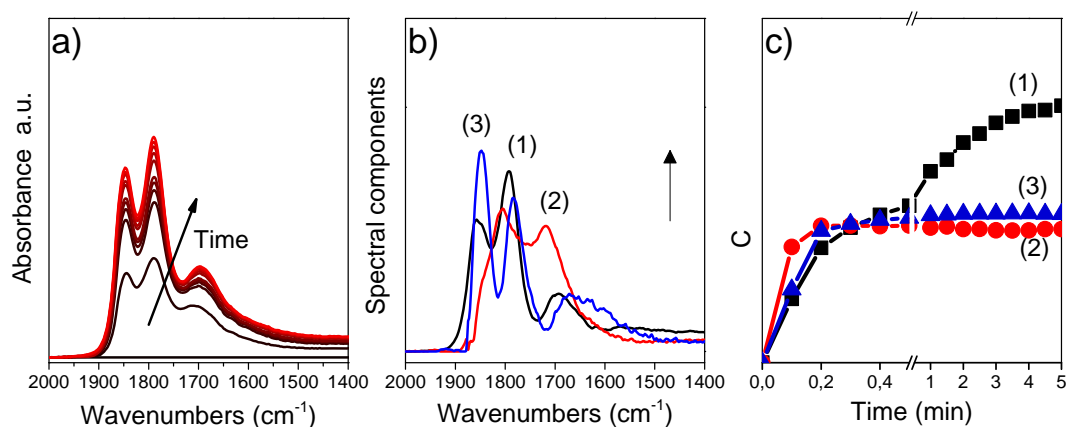


Figure 4. (a) Evolution in the IR spectra (background subtracted) of $\text{MoS}_2/\delta\theta\text{-Al}_2\text{O}_3$ as a function of NO contact time at RT (from black to red); (b) Corresponding MCR decomposition into 2 reference spectra RS(1) and RS(2); (c) profiles of proportion of each reference spectrum: C is dimensionless and expressed as the relative contribution of the three reference spectra in (b) to the spectra displayed in (a). The reference spectra are normalized as function of the total IR absorbance area in the $2000 - 1400 \text{ cm}^{-1}$.

First, the concentration profile of RS(1) increases as soon as NO is introduced in the IR cell ($t = 0$). Once the concentration of RS(1) reaches a plateau, then concentration of RS(2) starts to increase, which may indicate that populations of RS(1) and RS(2) are linked. Contributions of RS(2) are found at higher wavenumbers than those of RS(1). This trend can be interpreted in two ways. RS(2) could be related to the same population of surface sites as RS(1) but since it appears at higher NO coverage it would correspond to a mononitrosyl to dinitrosyl transition. However, the mononitrosyl to dinitrosyl transition would imply that RS(1) should completely progressively disappear at the expense of RS(2). Since it is obviously not the case in **Figure 4 c)**, this suggests that two distinct types of sites populations are revealed by the chemometric analysis. These two families of sites could be located on the M-edge and S-edge respectively. DFT calculations have shown that the (B) and (C) components of NO adsorbed on the S-edge are also shifted to higher frequency values than on the M-edge (**Table S4.1**). If so, this implies that the chemometry analysis is able to reveal the presence of the two edges exposed on the MoS_2 nanocrystallites as proposed in previous experimental[7] and theoretical[9] analysis.

575 Considering now CoMoS/ $\delta\theta$ -Al₂O₃, three main reference spectra RS (1-3) are necessary to explain the IR
 576 spectra evolution (**Table S4.2**). The profiles of the proportion of the different RS increase as soon as NO
 577 is introduced in the IR cell, which may indicate that the RS are not dealing with the same populations of
 578 surface sites interacting with NO. **Figures 5 b) and c)** illustrates how the chemometric analysis enables to
 579 distinguish the CoMoS phase from the MoS₂ (**Figure 4**) and Co₉S₈ phases (**Figure S4.1**).



580

581 **Figure 5.** (a) Evolution in the IR spectra (background subtracted) of CoMoS/ $\delta\theta$ -Al₂O₃ as a function of
 582 NO contact time at RT (from black to red); (b) Corresponding MCR decomposition into 3 reference
 583 spectra and (1–3); (c) Profiles of the proportion of each reference spectrum: C is dimensionless and
 584 expressed as the relative contribution (area) of the three reference spectra in (b) to the spectra displayed in
 585 (a). Time axis of c) panel is broken in order to visualize the evolution in the very first minute of NO
 586 contact.

587

588 The reference spectra (1) and (3) report 3 main contributions located at 1857-1847 and 1792-1785 and
 589 1695-1670 cm⁻¹ referred as A-A', B, C in **Table S4.2**. The shape of the profiles indicates that different
 590 surface sites are contributing in these three reference spectra. DFT calculations have demonstrated that
 591 the partially promoted M-edge and fully promoted S-edge sites interacting with NO at high coverage may
 592 explain the (A')-(B) and (B)-(C) components respectively. Since the concentration profiles of the
 593 different RS increase as soon as NO is introduced in the IR cell, this also confirms that the (A')-(B) and
 594 (B)-(C) components are not linked together and do correspond to two populations of sites which could be

595 the promoted M-edge and/or S-edge as shown by DFT calculations. Consequently, RS(3) could
596 correspond to the spectral feature of NO on the promoted CoMoS phase. Considering RS(1), the
597 contribution centered at high wavenumbers 1857 cm^{-1} (A) is close to what is observed for the supported
598 Co_9S_8 reference material (**Figure 2**). It seems that RS(1) corresponds to a mix between Co_9S_8 and MoS_2
599 based phases since component (C) is also present in the spectrum (**Figure 5 b**). The reference spectrum
600 RS(2) reports two maxima at 1805 and 1718 cm^{-1} for components (B) and (C) respectively. In that case,
601 the nature of the corresponding sulfided phase population is expected to be non-promoted. Interestingly,
602 **Figure 5 c** shows that this population of sites is the first one to be revealed at small NO contact time. This
603 could correspond to the stronger adsorption energy of Mo sites with respect to Co sites as determined by
604 DFT calculations. Moreover, it is also interesting to stress that the component (C) at 1714 cm^{-1} seems to
605 be specific of the non-promoted phase whereas the cobalt sulfided phases reveal contributions to
606 component (C) at lower wavenumbers (1695 and 1670 cm^{-1}) which is consistent with the previous DFT
607 and IR analysis. The intensity of component (C) is also enhanced on RS(2).
608 Hence, from the chemometric analysis, it becomes possible to distinguish different populations of phases
609 present on $\delta\theta\text{-Al}_2\text{O}_3$ support which report different behavior in presence of NO: RS(1) assigned to a
610 combination of Co_8S_9 and MoS_2 (promoted/non-promoted); RS(2) due to MoS_2 phase and RS(3) due to a
611 mixture of promoted and non-promoted MoS_2 phases.
612 In order to explore also with this chemometric technique, the effect of the support, similar decompositions
613 have been undertaken for silica and $\gamma\text{-Al}_2\text{O}_3$ supported CoMoS catalysts. For sake of clarity, the detailed
614 analysis of these spectra are reported in **Supplementary information 4**. To summarize them, it appears
615 that the chemometric analysis is able to reveal different spectroscopic features for these two supported
616 catalysts from the $\delta\theta\text{-Al}_2\text{O}_3$ supported ones. In particular, two (respectively one) reference spectra were
617 required to explain the evolution of the IR spectrum on silica (respectively on $\gamma\text{-Al}_2\text{O}_3$). It appears thus
618 more difficult to totally decouple the evolution of the three families of sites observed on $\delta\theta\text{-Al}_2\text{O}_3$ in the

619 case of silica and γ -Al₂O₃ supported catalyst. This smaller number of reference spectra can also be
620 interpreted as the signature of the presence of less numerous surface site species. In particular, even if the
621 presence of Co₉S₈ phase cannot be discarded on γ -Al₂O₃ supported sample, its concentration is probably
622 not high enough to be recovered by the chemometric analysis as it is the case on $\delta\theta$ -Al₂O₃ and SiO₂
623 supports. On silica, a weaker concentration of promoted CoMoS sites at the profit of the Co₉S₈ phase and
624 non-promoted MoS₂ phase can be at the origin of the two reference spectra identified by chemometry.

625

626 3.5 Impact for hydrodesulfurization (HDS) catalysis

627 According to previous experimental studies,[1, 59, 60] it is now well-established that the formation of the
628 mixed CoMoS phase is a key parameter for reaching high HDS catalytic activity. Thus, featuring by IR
629 spectroscopy the degree of the promotion and the nature of cobalt sites present at the edges of the CoMoS
630 nano-crystallites is critical. According to previous DFT calculations,[10, 11] cobalt atoms located at the
631 M-edge are less stable than the ones located at the S-edge. Thus, the decrease of the (A') component
632 could be principally driven by a lower concentration of cobalt atoms located on the M-edge in particular.
633 It seems also to be simultaneously accompanied by an increase of the (C) component in the region of
634 1700-1714 cm⁻¹ assigned to mononitrosyl or dinitrosyl on the non-promoted M-edge (**Figure 2**). As a
635 consequence, the IR spectroscopic analysis (**Figure 3**) suggests that part of this silica supported sample
636 may contain a larger proportion of the Co₉S₈ phase at the expense of the cobalt promoted MoS₂ phases.
637 This lower concentration of the mixed CoMoS sites on silica is thus at the origin of the lower HDS
638 activities (normalized per Mo atom) generally reported for silica supported catalysts compared to the
639 alumina supported ones (for the same Co/Mo ratio and Mo loading).[31-34, 38] Moreover, if the decrease
640 of the promotion degree of silica supported CoMoS catalysts corresponds to the loss of cobalt atoms on
641 the M-edge, this would explain the higher selectivity observed in hydrodesulfurization of thiophenic
642 molecules over hydrogenation (HYD) of olefinic compound on silica supported catalysts.[34, 38, 61]

643 Indeed previous experimental and theoretical works[7, 62] show that the HDS/HYD selectivity is
644 correlated to the proportion of cobalt promoted S-edge in the CoMoS active phases. Thus the intrinsic
645 HDS/HYD selectivity of Co promoted S-edge is higher, which would be perfectly coherent with our NO-
646 FTIR analyses revealing that the M-edge would be not promoted on silica support. Regarding the
647 γ - and $\delta\theta$ -alumina polymorphs, the second derivative and chemometric analyses revealed different
648 behaviors which may also help to understand different HDS catalytic activities as a function of the
649 alumina polymorph used as a support.[36] We may in particular suspect that the promotion level of
650 γ -alumina supported CoMoS phase is higher than the one of $\delta\theta$ -alumina supported one. Thus, the
651 different CoMoS sites speciation supported either on silica or on aluminas is well revealed by NO-FTIR
652 spectroscopy, which appears as a useful technique to discriminate between optimal and non-optimal
653 CoMoS active phases featured by the (A') and (C) components.

654 4. CONCLUSIONS

655 By combining FTIR spectroscopy and DFT calculations, we have shown that NO is a relevant molecule
656 to probe and identify the sites of the MoS_2 , CoMoS and Co_9S_8 phases on three relevant catalytic supports:
657 $\delta\theta\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$ and SiO_2 . To help for the interpretation, we have undertaken periodic boundary DFT
658 calculations of NO adsorbed on the various possible non-promoted MoS_2 and promoted CoMoS sites at
659 various NO and sulfur coverages.

660 Second derivative spectroscopy has been applied to distinguish the overlapping contributions which are
661 not resolved in the initial IR spectrum of alumina and silica supported systems. **Table 4** summarizes the
662 main learning of the present study by combining second derivative analysis, chemometry and DFT
663 calculations regarding NO probe molecule adsorption and site speciation.

664 **Table 4. Summary of site speciation as a function of the different components identified by NO**
 665 **probe molecule according to second derivative analysis, chemometric analysis and DFT calculations**
 666 **undertaken on the various systems of the present study.**
 667

Component	ν^a (cm^{-1})	CoMoS		MoS ₂		Co ₉ S ₈
		M-edge	S-edge	M-edge	S-edge	
A	1857-1863					✓
A'	1846-1849	✓	✓			
B'	1789-1799				✓	✓
B	1787-1790		✓	✓		
	1714-1716		✓		✓	
C	1697		✓		✓	
	1685-1686		✓	✓	✓	

668 ^a the wavelength intervals are identified on the various supports: γ -Al₂O₃, $\delta\theta$ -Al₂O₃, and SiO₂

669 The specific contributions (A') at 1846 cm^{-1} and (B) at 1790 cm^{-1} have been identified for alumina
 670 supported samples and are assigned to cobalt-promoted sites, while the component (A) at ca. 1859 cm^{-1} is
 671 assigned to Co₉S₈. From DFT calculations, it is shown that mononitrosyls on Co site and dinitrosyls on
 672 Mo site of the promoted M-edge sites give rise to these (A')-(B) components. Depending on the local
 673 configuration (either parallel or upright-tilted) dinitrosyls on the cobalt S-edge give rise to either
 674 components (B)-(C) or (A')-(B)-(C) at high NO coverage. In addition, the region (C) is due to dinitrosyls
 675 on the promoted S-edge but also to the non-promoted M-edge sites.

676 The silica supported catalyst revealed a different spectroscopic feature which helped us to refine further
 677 the spectroscopic assignment. Indeed, silica supported sample displays a strongly diminished (A')
 678 component assigned to the loss of CoMoS sites on the promoted M-edge due to their lower intrinsic
 679 stability, previously shown by DFT calculations. However, it exhibits two intense contributions (B') at
 680 1799 cm^{-1} and (B) at 1790 cm^{-1} assigned to the presence of non-promoted M-edge or Co₉S₈, and to
 681 promoted S-edge sites, respectively. If the (B) component on silica is assigned to the promoted S-edge,
 682 this implies that the (A') is predominantly due to the promoted M-edge.

683 This spectroscopic approach may thus enable to explain the origin of the lower HDS activities generally
684 reported for silica supported catalysts compared to the alumina ones. More generally, the relative
685 intensity of contributions (A') and (A) should be considered as a good descriptor of the promotion degree
686 of CoMoS on the three supports: $\gamma\text{-Al}_2\text{O}_3 > \delta\theta\text{-Al}_2\text{O}_3 > \text{SiO}_2$. As a consequence, NO spectroscopy is a
687 relevant technique to characterize the “intrinsic quality” of the CoMoS phase as a function of the
688 supports: $\delta\theta\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$ and SiO_2 .

689 From chemometric analysis of IR spectra series, M-edge and S-edge sites have been identified for MoS_2
690 supported $\delta\theta\text{-Al}_2\text{O}_3$ catalyst. Among the different supports investigated, the concentration of promoted
691 sites on the M-edges of the CoMoS phase is the lowest on SiO_2 , which is in agreement with the lowest
692 activity and highest selectivity of this support.

693 The detailed combined spectroscopic and DFT study offers a rational and quantitative description of the
694 nature of edge sites of the MoS_2 and CoMoS phase as a function of the support. This will provide a robust
695 methodology allowing a better control and design of the optimal CoMoS active phase used in
696 hydrotreatment catalysts.

697 ACKNOWLEDGMENTS

698 This work was performed using HPC resources from GENCI-IDRIS-CINES (Grant 2017-A0020806134)
699 and the IFPEN supercomputer (ENER110).

700

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