

Table S1.1 Textural properties of the γ -Al₂O₃, $\delta\theta$ -Al₂O₃ and SiO₂.

Supports	γ -Al ₂ O ₃	$\delta\theta$ -Al ₂ O ₃	SiO ₂
S _{BET} (m ² .g ⁻¹)	285	81	232
V _{mesopores} (ml.g ⁻¹)	0.65	0.76	0.78
V _{macropores} (ml.g ⁻¹)	0.01	-	0.21
Pore diameter (nm)	7.0 – 11.0	36	15

As shown in Table S1.2, the XRF elemental analysis ensures that the targeted constant Mo surface coverage, Co/Mo and P/Mo ratios are obtained in order to investigate a coherent set of supported catalyst.

Table S1.2. XRF elemental analysis on the calcined oxide CoMo, Co and Mo precursors of the CoMoS, Co₉S₈ and MoS₂ phases respectively on the three supports.

Catalysts	dMo (at.nm ⁻² of support)	Co/Mo (molar)	P/Mo or P/Co (molar)	%wt Co	%wt Mo	%wt P
CoMoS/ γ -Al ₂ O ₃	2.1	0.38	0.29	1.95	8.40	0.79
CoMoS/ $\delta\theta$ -Al ₂ O ₃	2.2	0.39	0.27	0.71	2.94	0.26
MoS ₂ / $\delta\theta$ -Al ₂ O ₃	2.2	-	0.27	-	3.06	0.26
Co ₉ S ₈ / $\delta\theta$ -Al ₂ O ₃	-	-	2.56	0.74	-	0.97
CoMoS/SiO ₂	2.4	0.39	0.23	1.86	7.78	0.58

SUPPORTING INFORMATION 2. Complementary information on DFT calculations

Three examples of periodic supercells used for the DFT calculations are given in Figure S2.1. For the non-promoted system, each stripe contains 4 MoS₂ layers in z direction (Figure S2a). For the promoted cells, one supplementary CoMoS layer is added on top of the stripe (Figure S2b and c). In x direction, 4 non-equivalent metallic sites are considered to allow up to 8 NO molecules to be adsorbed (1 dinitrosyl per metallic site) at maximal NO coverage.

The periodic supercell parameters are : 12.80 Å x 12.29 Å x 27 Å. This ensures a sufficient vacuum interlayer in the z and y directions to avoid spurious interactions between the adsorbed molecule and the periodically repeated stripe.

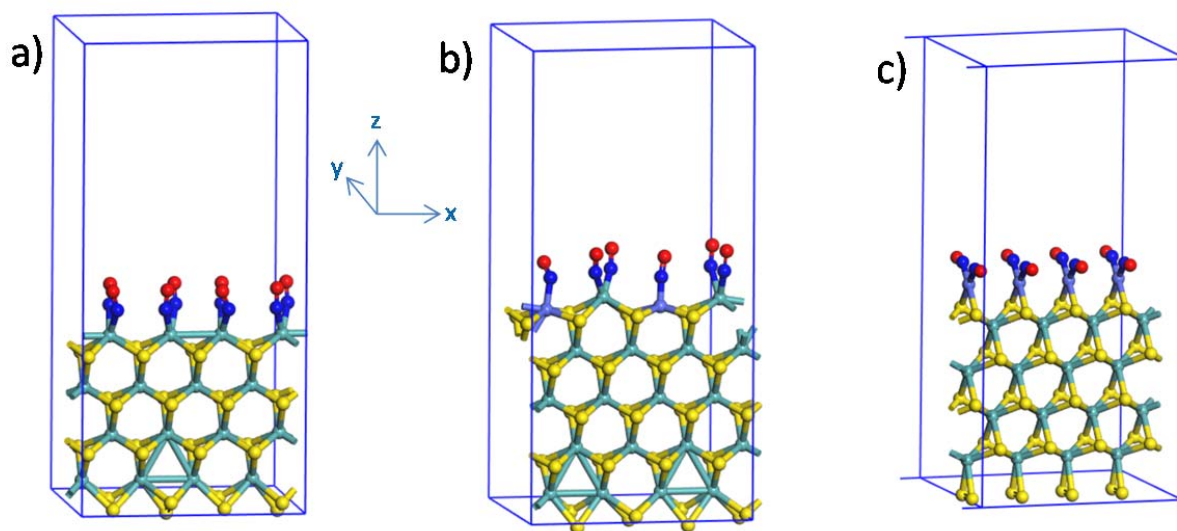


Figure S2.1 Ball and sticks representation of the supercells used for the DFT calculations: a) 8 NO molecules adsorbed on the non-promoted M-edge, b) 6 NO molecules adsorbed on the cobalt promoted M-edge, c) 8 NO molecules adsorbed on the cobalt promoted S-edge. Color legend: Green balls: molybdenum, yellow balls: sulfur, blue balls: cobalt, dark blue balls: nitrogen, red balls: oxygen.

Table S2.1. Local structures of the non-promoted and Co promoted M-edge and S-edge with different sulfur coverages used for the NO vibrational frequencies calculations. For sake of clarity, only the 2 upmost Mo or CoMo layers are shown. Green balls: molybdenum, yellow balls: sulfur, blue balls: cobalt.

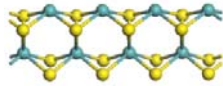
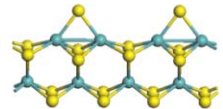
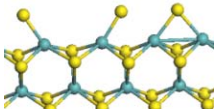
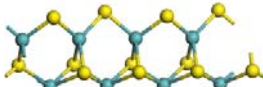
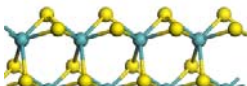
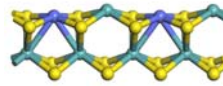
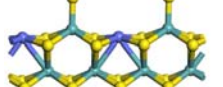
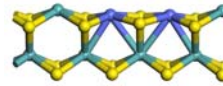
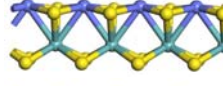
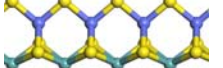
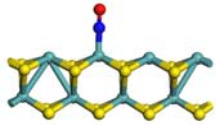
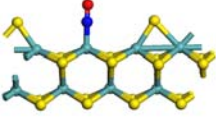
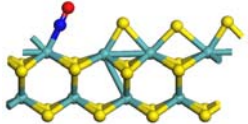
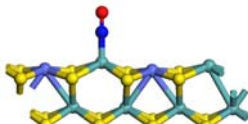
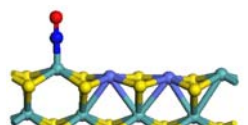
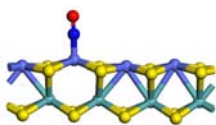
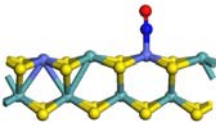
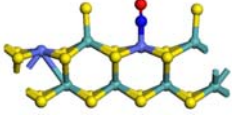
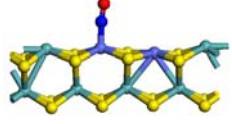
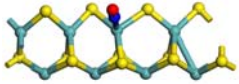
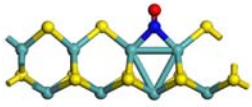
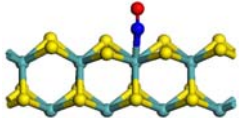
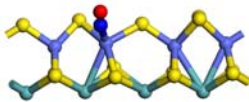
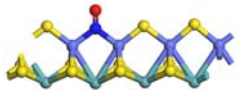
Type of edge	Sulfur and cobalt content	Edge structure
Non promoted M-edge	0% S	
	25 %S	
	37.5 %S	
Non promoted S-edge	50 %S	
	100 %S	
Promoted M-edge	50 %Co (alternate) and 0%S	
	50 %Co (alternate) and 25%S	
	50 %Co (pair) and 0%S	
	100 %Co and 0%S	
Promoted S-edge	100 %Co and 50%S	

Table S2.2 Calculated adsorption energies and corresponding vibrational frequencies of NO adsorbed on the various possible M-edge sites at low NO coverage. Green balls: molybdenum, yellow balls: sulfur, blue balls: cobalt, dark blue balls: nitrogen, red balls: oxygen.

Sites	Configurations	ΔE_{ads} (kJ/mol)	ν_{NO} (cm ⁻¹)*
Mo on non-promoted M-edge 0%S		-362	1671
Mo on non-promoted M-edge 25 %S		-355	1690
Mo on non-promoted M-edge 37.5 %S		-214	1714
Mo on the promoted M-edge 50% Co (alternated) and 0%S		-335	1682
Mo on the promoted M-edge 50% Co (paired) and 0%S		-344	1687
Co on the promoted M-edge 100% Co and 0%S		-242	1868
Co on the promoted M-edge 50% Co (alternated) and 0%S		-177	1834
Co on the promoted M-edge 50% Co (alternated) and 25%S		-191	1882
Co on the promoted M-edge 50% Co (paired) and 0%S		-199	1831

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

Table S2.3 Calculated adsorption energies and corresponding vibrational frequencies of NO adsorbed on the various possible S-edge sites at low NO coverage. Same color legend as Table S2.2.

Sites	Configurations	ΔE_{ads} (kJ/mol)	ν_{NO} (cm ⁻¹) ^a
Mo on non-promoted S-edge 50%S		-170	1726
Mo on non-promoted S-edge 50 %S (S-exchange)		-321	1456
Mo on non-promoted S-edge 100 %S		-107	1760
Co on the promoted S-edge 100% Co and 75%S		-60	1863
Co on the promoted S-edge 100% Co and 50%S (S-exchange)		-287	1574

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

SUPPORTING INFORMATION 3. Complementary analysis of the IR spectra as a function of NO contact time – Identification of minor contributions.

The evolution of the IR spectra during the NO adsorption on CoMoS/ $\delta\theta$ -Al₂O₃ as well as derivative spectra is presented as a function of NO contact time at RT in **Figure S3.1**.

It can be noted that the second derivative analysis of the IR spectra allows more specific identification of small and overlapping contributions which are not resolved in the initial spectrum. In particular, numerous separated vibrational contributions appear clearly in the spectra of **Figure S3.1 b**, whereas only 3 main contributions are revealed on the original IR spectra.

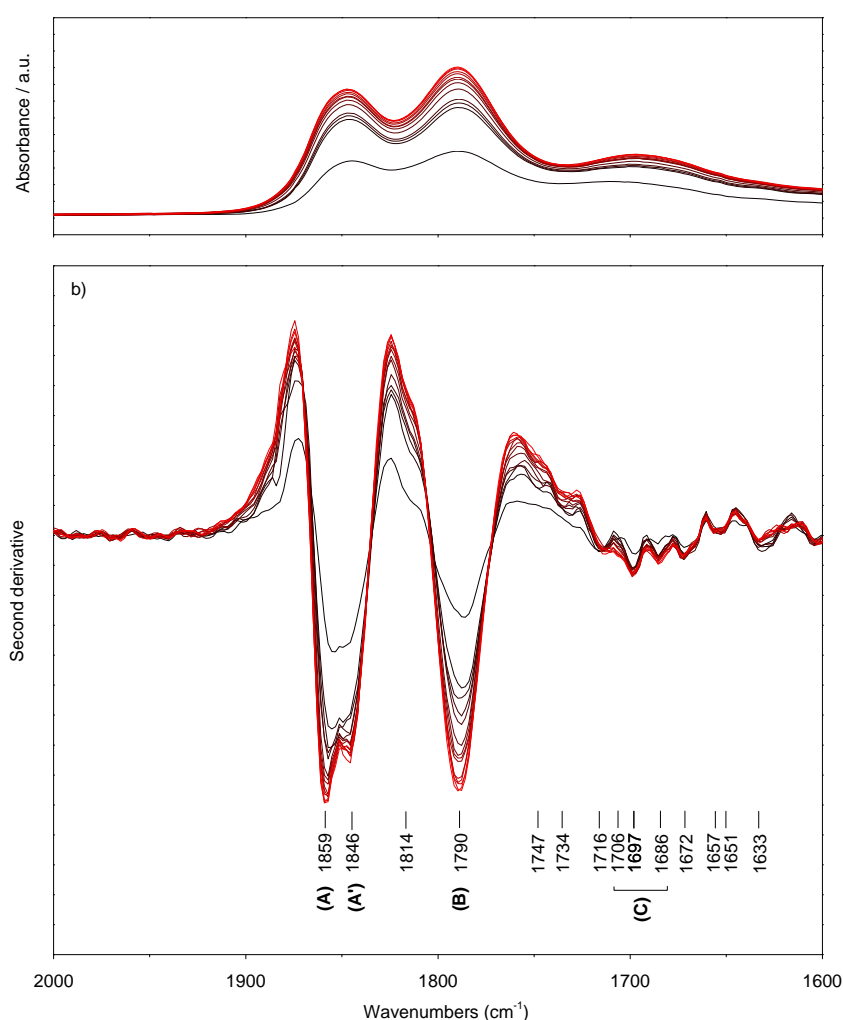


Figure S3.1. a) Evolution in the IR spectra (background subtracted) of CoMoS/ $\delta\theta$ -Al₂O₃ as a function of NO contact time at RT (from black to red); b) corresponding Second derivative spectra (similar code color).

The evolution of the IR spectra during the NO adsorption on CoMoS on γ -Al₂O₃ and SiO₂ as well as derivative spectra is presented as a function of NO contact time at RT in **Figure S3.2** and **S3.3**.

Again, the second derivative analysis of the IR spectra (**Figure S3.2 b** and **Figure S3.3 b**) allows more specific identification of small and overlapping contributions which are not resolved in the initial spectra of CoMoS/ γ -Al₂O₃ and CoMoS/SiO₂ whereas only 3 main vibrational contributions were revealed on the original IR spectra.

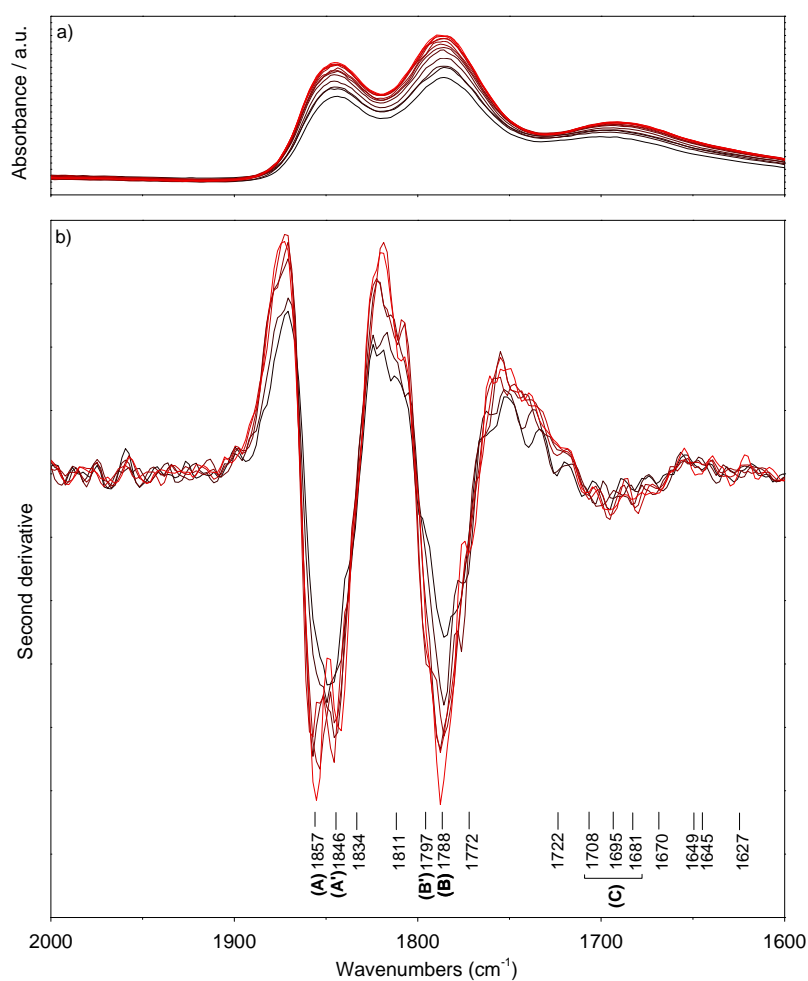


Figure S3.2. a) Evolution in the IR spectra (background subtracted) of CoMoS/ γ -Al₂O₃ as a function of NO contact time at RT (from black to red); b) corresponding Second derivative spectra (similar code color).

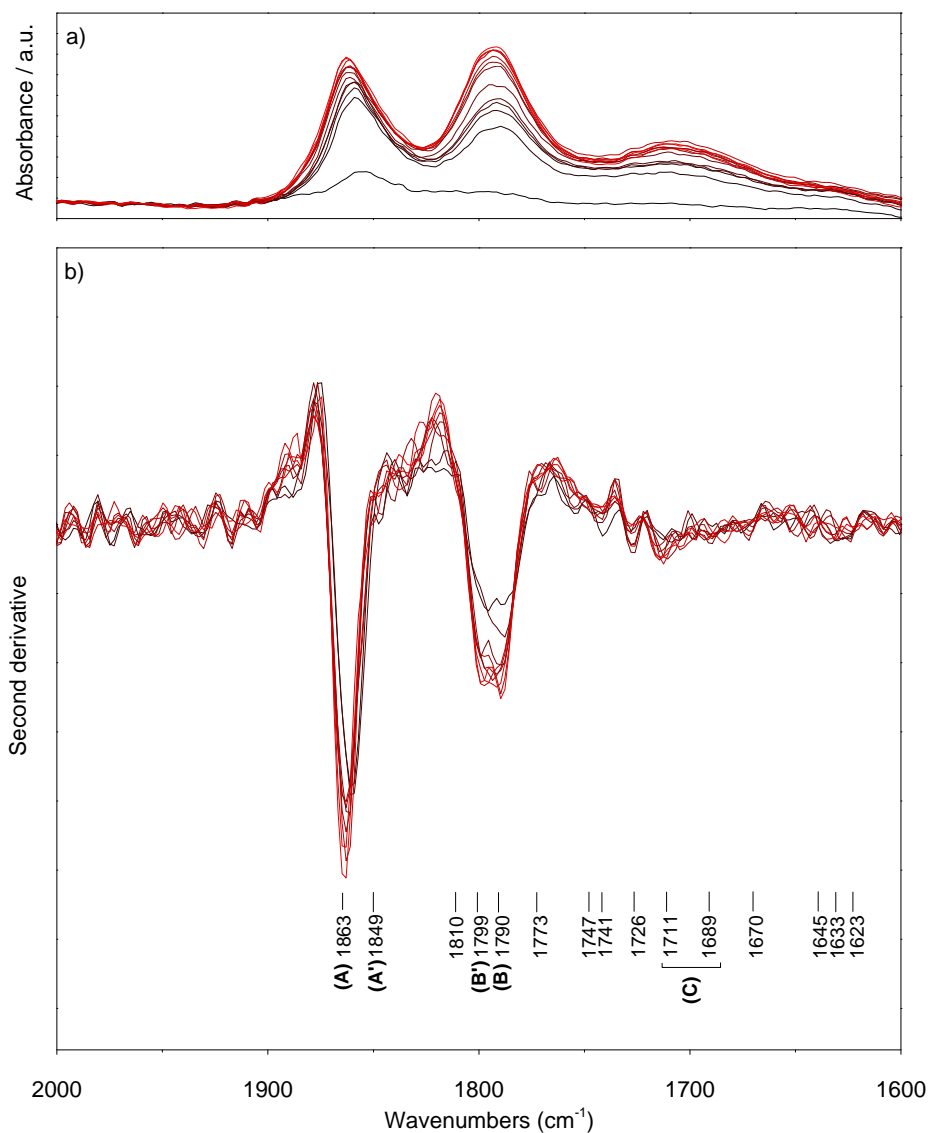


Figure S3.3. a) Evolution in the IR spectra (background subtracted) of CoMoS/SiO₂ as a function of NO contact time at RT (from black to red); b) corresponding Second derivative spectra (similar code color).

Finally, the evolution of the IR spectra during the NO adsorption on MoS₂/δθ-Al₂O₃ and on Co₉S₈/δθ-Al₂O₃ as well as the derivative spectra are presented as a function of NO contact time at RT in **Figure S3.4 and S3.5**.

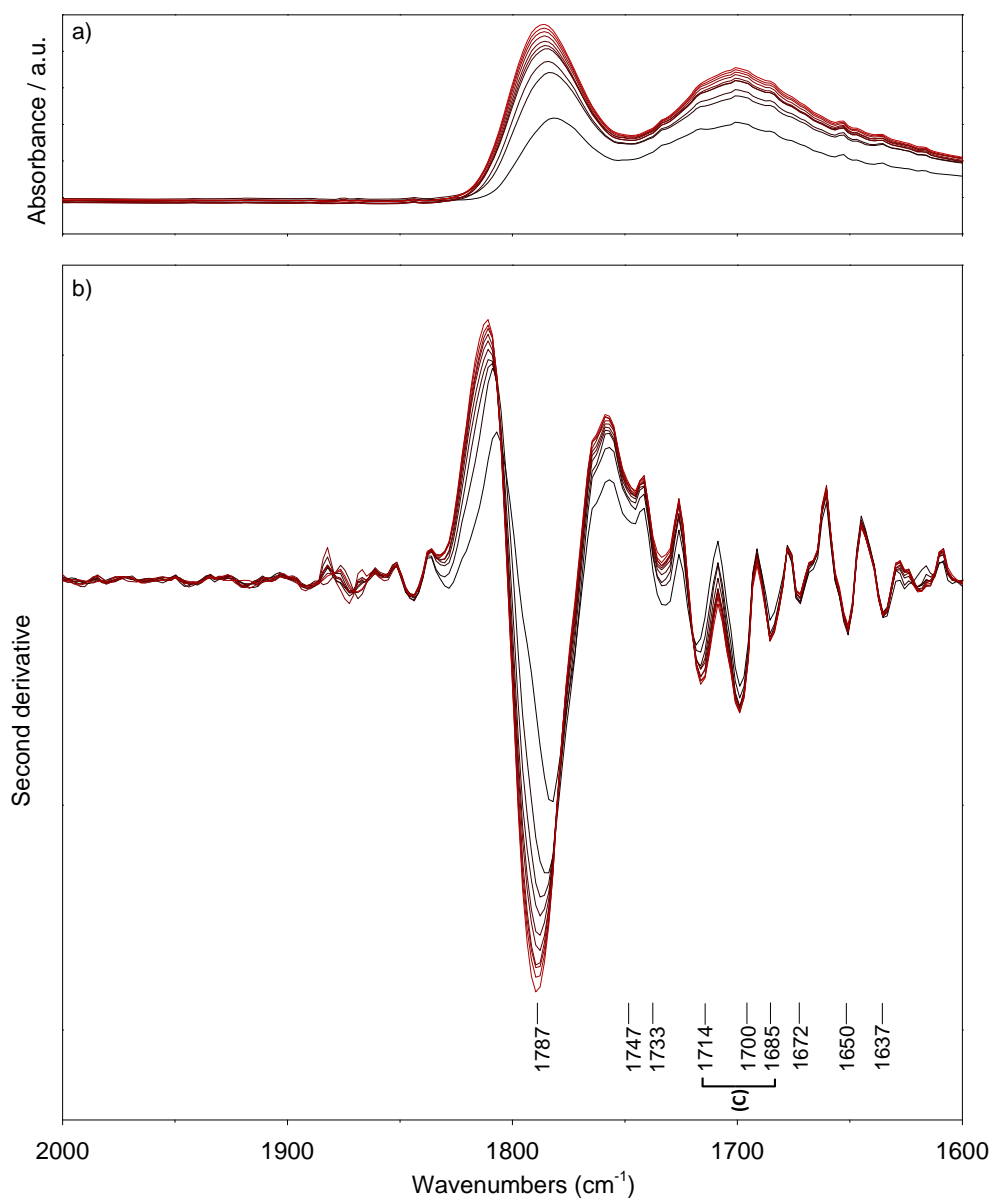


Figure S3.4 a) Evolution in the IR spectra (background subtracted) of $\text{MoS}_2/\delta\theta\text{-Al}_2\text{O}_3$ as a function of NO contact time at RT (from black to red); b) corresponding Second derivative spectra (similar code color).

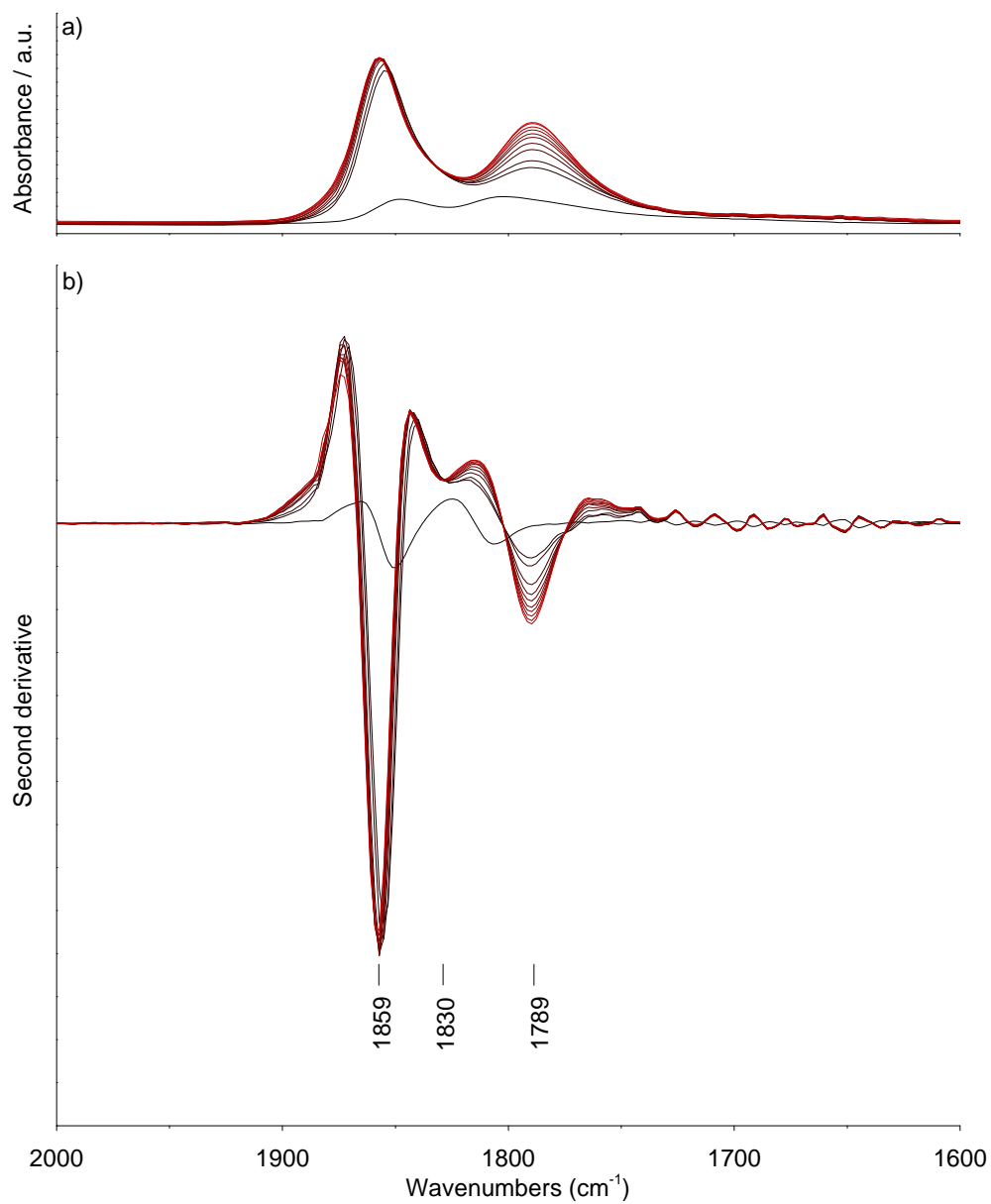


Figure S3.5 a) Evolution in the IR spectra (background subtracted) of $\text{Co}_9\text{S}_8/\delta\theta\text{-Al}_2\text{O}_3$ as a function of NO contact time at RT (from black to red); b) corresponding Second derivative spectra (similar code color).

SUPPORTING INFORMATION 4. Complementary chemometric data and analysis

Table S4.1 Main components identified on the reference spectra (RS) of the chemometric analysis on MoS₂/ $\delta\theta$ -Al₂O₃.

Reference spectrum	Percentage of the variance explained (%)	B (cm ⁻¹)	C (cm ⁻¹)
1	92	1780	1699
2	8	1796	1705

Table S4.2. Main components identified on the reference spectra (RS) of the chemometric analysis on CoMoS/ $\delta\theta$ -Al₂O₃.

Reference Spectrum (RS)	Percentage of variance explained (%)	A or A' (cm ⁻¹)	B (cm ⁻¹)	C (cm ⁻¹)
(1)	51.85	1857	1792	1695
(2)	22.57	-	1805	1718
(3)	25.56	1847	1785	1670

Chemometric treatment performed on IR spectra after NO additions on Co_9S_8 on $\delta\theta\text{-Al}_2\text{O}_3$ are reported in **Figure S4.1**. In that case, two reference spectra were sufficient to explain more than 99% of the variance of the IR spectra evolution recorded as function of NO contact time on the Co_9S_8 phase.

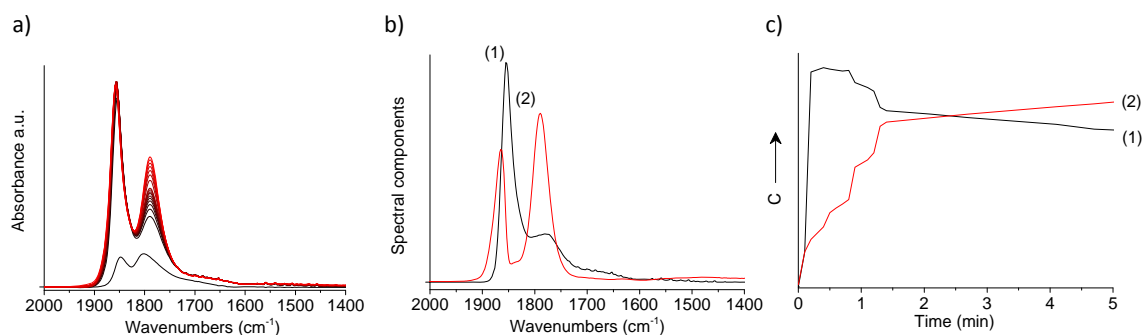


Figure S4.1 (a) Evolution in the IR spectra (background subtracted) of $\text{Co}_9\text{S}_8/\delta\theta\text{-Al}_2\text{O}_3$ as a function of NO contact time at RT (from black to red); (b) Corresponding MCR decomposition into 3 reference spectra and (1 – 3); (c) concentration profiles of each reference spectrum. C is dimensionless and expressed as the relative contribution of the three reference spectra in (b) to the spectra displayed in (a).

Table S4.3. Main components identified on the reference spectra (RS) of the chemometric analysis on $\text{Co}_9\text{S}_8/\delta\theta\text{-Al}_2\text{O}_3$.

Reference spectrum	Percentage of the variance explained (%)	A (cm^{-1})	B (cm^{-1})
1	66	1854	1778
2	34	1865	1790

The concentration of RS(1) rapidly increases as soon as NO is introduced in the IR cell ($t = 0$) and then progressively diminishes as a function of NO contact time. In parallel, this diminution is accompanied by the growth of RS(2) concentration. It may indicate that populations of RS(1) and RS(2) are correlated which may correspond predominantly to mononitrosyls to dinitrosyls transition. In that case the evolution of RS(1) into RS(2) could be due to the increasing NO coverage at the surface (similarly to what is observed for MoS_2 phase in contact with NO).

For CoMoS/SiO₂, two main reference spectra (RS) were required to recover 99.59% of the IR spectra evolution recorded as function of NO contact time (**Figure S4.2** and **Table S4.3**).

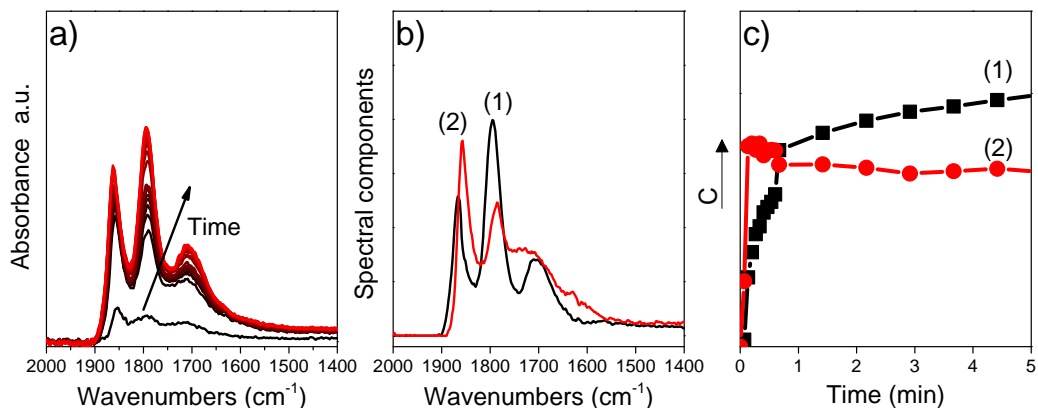


Figure S4.2. (a) Evolution in the IR spectra (background subtracted) of CoMoS/SiO₂ as a function of NO contact time at RT (from black to red); (b) Corresponding MCR decomposition into 3 reference spectra and (1 – 3); (c) concentration profiles of each reference spectrum. C is dimensionless and expressed as the relative contribution of the three reference spectra in (b) to the spectra displayed in (a).

Table S4.3. Main components identified on the reference spectra (RS) of the chemometric analysis on CoMoS/SiO₂.

Reference Spectrum (RS)	Percentage of variance explained (%)	A or A' (cm ⁻¹)	B or B' (cm ⁻¹)	C (cm ⁻¹)
1	49.39	1867	1795	1705
2	50.20	1857	1786	1726

RS(1) reports three maxima and amongst them, one centered at high wavenumber 1867 cm⁻¹ (A) which may indicate the presence of Co sites from Co₉S₈ phase. RS(2) also contains a contribution of high wavenumber (1857 cm⁻¹), which may be assigned to the (A') component corresponding to cobalt promoted MoS₂ sites. Nevertheless, (B) and (C) components are also present in both reference spectra, where the (C) components are at 1726 cm⁻¹ for RS(2) and 1705 cm⁻¹ for RS(1). These values are closer to the ones previously assigned to non-promoted MoS₂ sites. Thus, RS(1) seems to be related to a mix between Co₉S₈ and MoS₂ sites (predominantly non-promoted). Note that the concentration profile of RS(1) progressively increases as function of NO contact time as

observed for RS(1) of CoMoS/ $\delta\theta$ -Al₂O₃ sample which also contains a significant proportion of Co₉S₈ phase. As explained with the second derivative analysis, the two bands (A) and (B) are slightly shifted at higher wavelengths: 1867 and 1795 cm⁻¹ and may correspond to Co₉S₈ sites and the non-promoted M-edge. The (C) component is also close to the values (1714 and 1700 cm⁻¹) previously identified to the non-promoted MoS₂ site. The second reference spectrum RS(2) would be related to a mixture between promoted sites linked to the (A') component at 1857 cm⁻¹, and non-promoted sites of the MoS₂ phases. The non-promoted sites would be located on the M-edge, and the promoted ones on the S-edge. From a more general point of view, it appears more difficult to totally decouple the evolution of the three families of sites in the case of silica supported catalyst.

Finally, the chemometric treatment has also been performed for CoMoS/ γ -Al₂O₃ sample (**Figure S4.3**). In that case, one single reference spectrum was appropriate to explain 99.91% of the variance set of IR data recorded while the catalyst was adsorbing NO.

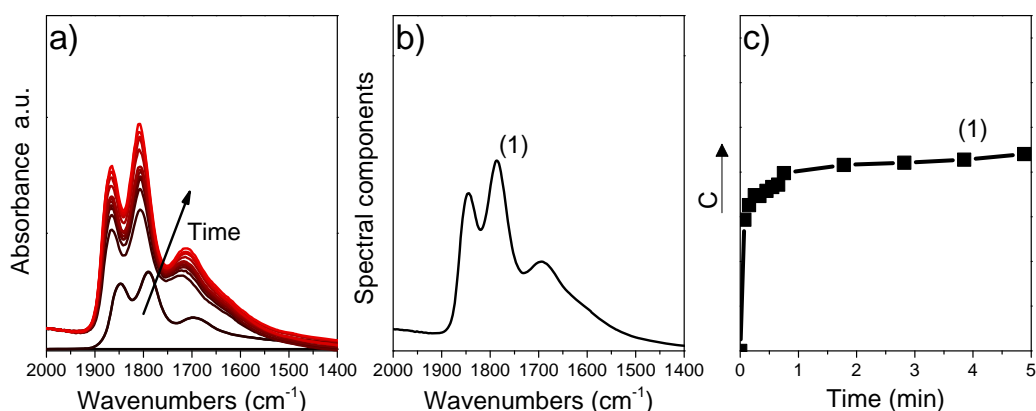


Figure S4.3 (a) Evolution in the IR spectra (background subtracted) of CoMoS/ γ -Al₂O₃ as a function of NO contact time at RT (from black to red); (b) Corresponding MCR decomposition into 3 reference spectra and (1 – 3); (c) concentration profiles of each reference spectrum. C is dimensionless and expressed as the relative contribution of the three reference spectra in (b) to the spectra displayed in (a).

Three components (A') 1845 cm⁻¹, (B) 1786 cm⁻¹, and (C) 1695 cm⁻¹ constitute the calculated reference spectrum (1), which indicate that CoMoS/ γ -Al₂O₃ sample is mainly composed of

promoted and non-promoted MoS₂ sites. The presence of Co₉S₈ phase is not discarded on γ -Al₂O₃ supported sample but its concentration is surely not high enough to be recovered by the chemometric analysis as it was the case on $\delta\theta$ -Al₂O₃ and SiO₂ supports.