

Surface-dependent activity of model CoMoS hydrotreating catalysts

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SUPPORTING INFORMATION

I. Mo and Co loadings for model catalysts in the sulfide phase

Table S.1 Average Mo and Co loadings and Co/Mo ratio for model catalysts after sulfidation at 400 °C supported on the A(11 $\bar{2}$ 0), C(0001), M(10 $\bar{1}$ 0) and R(1 $\bar{1}$ 02) crystal planes of α -Al₂O₃ calculated from Eq. 1 of the main text.

Crystal Plane	Loading / atoms · nm ⁻²		Co/ Mo ratio
	Mo	Co	
C(0001)	3.9 ± 1.0	1.7 ± 0.6	0.44
A(11 $\bar{2}$ 0)	4.3 ± 1.9	1.8 ± 0.7	0.42
M(10 $\bar{1}$ 0)	3.8 ± 1.7	1.6 ± 0.7	0.42
R(1 $\bar{1}$ 02)	4.7 ± 1.2	1.9 ± 0.9	0.40

II. Mo3d, Co2p, S2p and S2s parameters for XPS peak deconvolution.

Table S.2 Summary of the constraining parameters for the different contributions in a Mo3d XPS spectrum for a sulfided model Co-Mo-based catalyst.

MoO₃				
Peak	Type	Binding Energy /eV	Area	FWHM
Main Peaks	Mo3d _{5/2}	[232.9, 233.1] (A)	(B)	(C)
	Mo3d _{3/2}	A + 3.2	B * 2/3	C * 1
MoO_xS_y				
Peak	Type	Binding Energy /eV	Area	FWHM
Main Peaks	Mo3d _{5/2}	[229.7, 229.9] (D)	(E)	(F)
	Mo3d _{3/2}	D + 3.2	E * 2/3	F * 1
MoS₂				
Peak	Type	Binding Energy /eV	Area	FWHM
Main Peaks	Mo3d _{5/2}	[228.8, 229.0] (G)	(H)	(I)
	Mo3d _{3/2}	G + 3.2	H * 2/3	I * 1

Table S.3 Summary of the constraining parameters for the different contributions in a S2p XPS spectrum for a sulfided model Co-Mo-based catalyst.

S₂²⁻				
Peak	Type	Binding Energy /eV	Area	FWHM
Main Peaks	S2p _{3/2}	[163.2, 163.4] (A)	(B)	(C)
	S2p _{1/2}	A + 1.2	B * 0.5	C * 1
S²⁻				
Peak	Type	Binding Energy /eV	Area	FWHM
Main Peaks	S2p _{3/2}	[161.7, 161.9] (D)	(E)	(F)
	S2p _{1/2}	D + 1.2	E * 0.5	F * 1

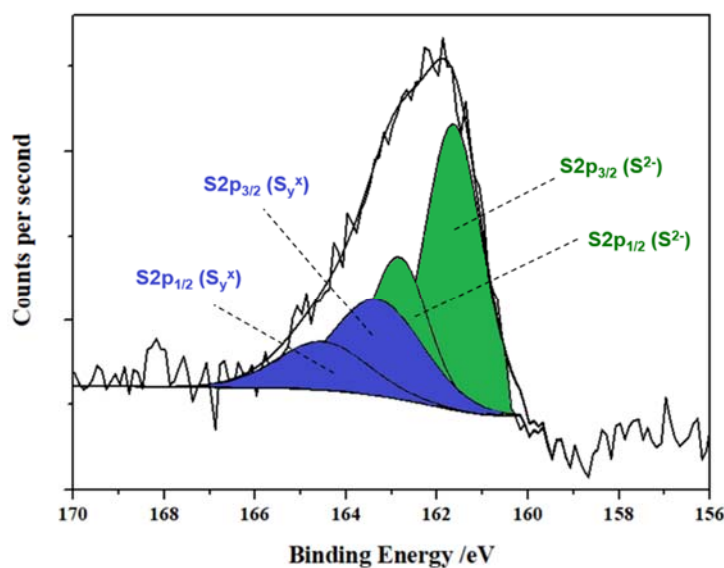


Figure S.1 Spectral decomposition of the S2p region of a model catalyst supported on the M(10 $\bar{1}$ 0) plane of α -Al₂O₃ after its sulfidation at 300 °C. The S²⁻ contribution is associated to MoS₂ while the S_{x^y} contribution is associated to the mixed oxysulfide phase MoS_xO_y

Table S.4 Relative proportion (%) of the different sulfur species detected on the S2p XPS region on the surface of a model catalyst supported on the M(10 $\bar{1}$ 0) plane of α -Al₂O₃ with the corresponding binding energies of the S2p_{3/2} peaks for both contributions.

Sulfur (S2p, 3/2 peaks)		
Species	%	Binding Energy /eV
S ²⁻	65.5	161.6
S _{y^x}	34.5	163.3

Table S.5 Summary of the constraining parameters for the different contributions in the S2s XPS region for a sulfided model Co-Mo-based catalyst.

S ²⁻			
Type	Binding Energy /eV	Area	FWHM
S2s	[225.9 , 226.1] (A)	(B)	(C)
S ₂ ²⁻			
S2s	A + BE [S2p _{3/2} (S ₂ ²⁻ - S ²⁻)]	B * Area [S2p _{3/2} (S ₂ ²⁻ /S ²⁻)]	C*FWHM [S2p _{3/2} (S ₂ ²⁻ /S ²⁻)]

Table S.6 Summary of the constraining parameters for the different contributions in a Co2p XPS spectrum for a sulfided model Co-Mo-based catalyst.

Co²⁺				
Peak	Type	Binding Energy /eV	Area	FWHM
Main Peaks	Co2p_{3/2}	[780.9, 781.9] (A)	(B)	1.85* A1 (C)
	Co 2p_{1/2}	A + 15.8	B * 0.5	C *1
Co₉S₈				
Peak	Type	Binding Energy /eV	Area	FWHM
Main Peaks	Co2p_{3/2}	[778 , 779] (D)	(E)	0.85* A1 (F)
	Co2p_{1/2}	D + 14.7	E * 0.5	F *1
CoMoS				
Peak	Type	Binding Energy /eV	Area	FWHM
Main Peaks	Co2p_{3/2}	D + 0.5 (G)	(H)	1.5* A1 (I)
	Co2p_{1/2}	G + 15.3	H * 0.5	I * 1
SATELLITE PEAKS				
	Type	Binding Energy /eV	Area	FWHM
1	Peak 1	A + 2.5	-	[2 , 5]
2	Peak 2	A + 18.4	-	[2 , 5]

III. Evaluation of the amount of Co_9S_8 .

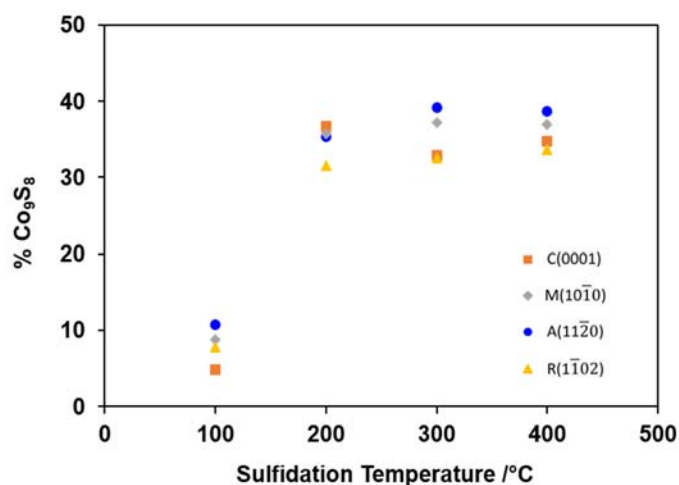


Figure S.2. Relative amount of Co_9S_8 (in percentage) for model Co-only catalysts supported on the A(11 $\bar{2}$ 0), C(0001), M(10 $\bar{1}$ 0) and R(1 $\bar{1}$ 02) crystal planes of $\alpha\text{-Al}_2\text{O}_3$ as a function of the sulfidation temperature.

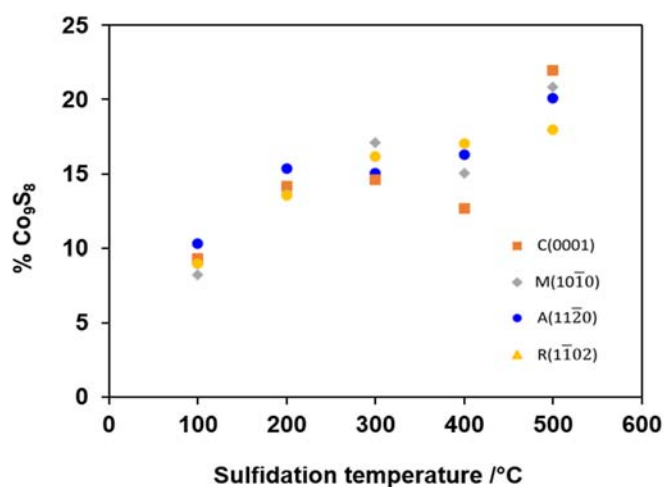


Figure S.3. Relative amount of Co_9S_8 (in percentage) for model Co-Mo based HDT catalysts supported on the A(11 $\bar{2}$ 0), C(0001), M(10 $\bar{1}$ 0) and R(1 $\bar{1}$ 02) crystal planes of $\alpha\text{-Al}_2\text{O}_3$ as a function of the sulfidation temperature.

IV. Root mean square roughness calculation

The root mean square roughness (R_{rms}) is defined as the average of profile height deviations from the mean line or surface, for 1D and 2D surface analysis, respectively. Quantitatively, this definition can be expressed as the square root of the average height deviation from the mean line (or surface) squared, as displayed in Eq. SI.1

$$R_{rms} = \sqrt{\frac{1}{n} \cdot \sum_{i=1}^n (Z_i - Z_{mean})^2} \quad (SI.1)$$

Where Z_i are the individual height deviations (peaks or valleys) from the average (Z_{mean}), and n is the total number of considered deviations from the mean line.