Sulphidation study of a dried Ni/Al₂O₃ catalyst by time-resolved XAS-MS combined with in situ Raman spectroscopy and multivariate Quick-XAS data analysis

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ABSTRACT
Insights into the nickel sulphide speciation of a dried oxidic Ni catalyst supported on deltalumina were obtained by temperature-programmed sulphidation monitored by Quick-X-ray absorption with online mass spectrometry. Combination with Raman spectroscopy enabled the phase identification of sulphide phases isolated by multivariate curve regression with alternating least square analysis of the time-resolved X-ray absorption spectroscopy data.

Introduction
Nickel sulphides can be found as active phases on supported catalysts for important industrial processes aiming to remove sulphur from oils [1] or as poisons for anodes involved in solid oxide fuel cell technology [2]. Even for hydrodesulphurisation (HDS) reaction, there is a competition between inactive bulk or supported nickel sulphides and the active phase, where Ni decorates corners or edges of MoS₂/WS₂ slabs [3] with a level of promotion rarely exceeding 60% [4]. Actually the binary Ni–S phase diagram system presents several bulk phases stable below 400 °C such as Ni₃S₂, Ni₉S₈, NiS, Ni₃S₄ and NiS₂ [5]. Despite the importance of controlling the nickel sulphide species on real catalysts, their chemical nature during sulphidation is not well documented. At the laboratory scale, HDS catalysts are obtained by heating under H₂S/H₂ gas stream, oxidic nickel and Mo(W) species dispersed at the surface of alumina support. Only a few studies based on temperature-programmed sulphidation (TPS) and X-ray photoemission spectroscopy methods report some insights about the sulphidation of supported calcined catalysts. Sulphidation starts at room temperature (RT), with the formation of stable sulphides with high S content (NiS₁±ₓ, Ni₇S₆….) at low temperatures (T < 400 °C) [6,7]. Recently, Keggin or Anderson heteropolyanions (HPA) associating in the same entity Co(Ni) with Mo(W) have shown better catalytic performances than those prepared from ammonium heptamolybdate precursors [8]. In order to preserve the vicinity of Mo/W with its promoter, no calcination is carried out before starting sulphidation of HPA-based precursors. In that case, the sulphidation patterns of 3d promoters become more complicated than those observed for calcined catalysts. To better understand the sulphidation process of only dried HPA precursors, it appears of prime importance to investigate nickel speciation upon sulphidation of only dried nickel oxidic precursors supported on alumina.
Herein, an in-depth time-resolved characterisation by X-ray absorption spectroscopy (XAS) has been carried out during in situ gas stream sulphidation of a dried Ni/Al₂O₃ catalyst with a careful monitoring of the gas composition at the cell outlet. XAS is a powerful technique for unraveling the chemical state and detailed local environment of nickel under harsh conditions and real time of TPS. The performances of Quick-EXAFS (extended X-ray absorption fine structure) beamlines installed on 3rd generation of synchrotron radiation facilities [9, 10] combined with the use of efficient chemometric tools, such as the multivariate curve regression with alternating least square (MCR-ALS) method [11–17], give access to the XAS spectra of intermediate species formed upon reaction and to quantify them. The complementary information obtained by in situ Raman spectroscopy has been used to propose sulphidic structures able to satisfactorily fit the isolated MCR-ALS XAS spectra. Finally, speciation obtained by XAS and Raman have been discussed in light of gas effluent composition and sulphidation mechanisms have been proposed.

**Experimental section**

**Sample preparation and characterisation**

The Ni/Al₂O₃ catalyst was prepared by incipient wetness impregnation of a δ-alumina support (specific area 143 m²/g) with an aqueous solution of nickel(II) nitrate (metallic loading (NiO) of 2.1 wt%). After impregnation, the solid was matured in a saturated water atmosphere during 12 h to ensure a good diffusion of nickel into the alumina porosity (pore volume 0.99 mL/g). Then a drying step overnight at 120 °C in a static air oven was carried out to obtain the dried Ni/Al₂O₃ catalyst.

It was carefully characterised at helium cryo-cooling temperature on the SAMBA beamline (SOLEIL) using the sagitally focusing Si(2 2 0) monochromator [11]. The crystalline phases present in the dried Ni/Al₂O₃ catalyst were analyzed by X-ray powder diffraction (XRD) using a Bruker D2 Phaser diffractometer and Cu–Kα radiation (1,5418 Å).

**Quick-EXAFS monitoring of in situ sulphidation**

Quick-EXAFS monitoring of the in situ sulphidation was carried out on the ROCK beamline (SOLEIL) [9] equipped with two-equivalent SOLEIL-made Quick-EXAFS monochromators [19]: the first one operates a Si(111) channel-cut crystal for working in the 4.5 to 20 keV energy range and the second one a Si(2 2 0) channel-cut crystal for working in the 5.5 to 40 keV energy range. Using a cam-driven tilt table supporting the Si(111) channel-cut monochromator used herein, the crystal oscillates with a frequency of 2 Hz and an amplitude of 2.4° around a Bragg angle of 12.97°. This allows the measure of 2 spectra per 500 ms, one with increasing Bragg angles followed by one with decreasing Bragg angles. Data were continuously recorded during sulphidation and 30 consecutive spectra with upward angles were merged in order to improve the signal to noise ratio. Then the elapsed time between two merged spectra is 15 s.

50 mg of powdery catalyst was loaded in the cell presented in a previous work (Section 3.1) [20]. Sulphidation treatment was carried out by raising the cell temperature from RT to 400 °C (3 °C/min) under a H₂S/H₂ flow (15%, 2ml/min), followed by 45min of isothermal treatment at 400 °C. The gases composition at the cell outlet was monitored by mass spectrometry (MS) using a MKS-Cirrus spectrometer.

**Raman monitoring of in situ sulphidation**

In a second experiment, Raman monitoring of the in situ sulphidation was performed with a Raman RXN1 spectrometer (Kaiser Optical Systems, Incorporation) using the 532 nm exciting line of a diode pumped solid state laser. The average resolution was 2 cm⁻¹. The laser beam was focused with a Mitutoyo 32 mm-long working distance objective (×20 magnification, power at the sample position: 11 mW). A spectrum was collected every 90 s and the data presented herein were the average of 10 spectra. 46 mg of powdery catalyst was loaded in a Harrick Raman high temperature reaction chamber equipped with a quartz window facing the incoming laser [21]. The sulphidation was carried out up to 400 °C (2 °C/min) under a H₂S/H₂ flow.

**MCR-ALS analysis**

As recently proven by the SOLEIL group, the MCR-ALS analysis [22] is effective in the qualitative and quantitative investigation of XAS data [11–15]. A series of normalised XAS experimental spectra D, recorded upon reaction whose relative concentrations vary with time/temperature … is defined as a matrix resulting from the combination of three matrices: C (concentration of the pure components), S (normalised XAS spectra of the pure components) and E (experimental uncertainties) following the equation: $D = CS^T + E$ (where $S^T$ is the transposed matrix of S). The principle of the MCR-ALS analysis is to mathematically determine a likely set of concentrations C (varying along the series) and spectra $S$ (constant along the series) which can explain the whole set of D$_p$ by iteration and least-squares minimisation of the $E$ matrix. For this scope, physically and chemically meaningful constraints on C and $S$ are used to help the convergence of the multivariate curve resolution. In the present work, the matrix of concentrations C contains only positive values and the matrix S contains normalised XAS spectra with nonnegative absorbance. The only information required by the MCR-ALS minimisation is the number of pure components describing D. Singular
value decomposition (SVD) method which describes $D$ into orthogonal vectors is at first used for the rank analysis of $C$ and $S$. SVD analysis suggests that the variance of $D$ is described considering 3 components (Figure S1, Supporting Information). Further details on the SVD and MCR-ALS methods applied to XAS data can be found in references [11,14]. SVD and MCR-ALS analysis were carried out on energy calibrated and normalised XAS data. The MCR-ALS minimisation was carried out using the MCR-ALS GUI 2.0 developed by Tauler et al. [23] on the Matlab® platform. The MCR-ALS result window available with the Tauler’s graphical user interface is shown in Supporting Information (Figure S2). The pre-analysis step was done using Python Gui developed in our group [24] allowing to handle hundreds of spectra in a couple of seconds (herein 739 spectra). The EXAFS analysis of the pure components spectra determined by MCR-ALS was carried out using the Athena program [25].

**Results**

**Characterisation of the dried Ni/Al$_2$O$_3$ catalyst before sulphidation**

At first, the dried Ni/Al$_2$O$_3$ catalyst was characterised at 20 K. The XANES spectrum (not shown) is very similar to the one recorded at RT and presented below as the first spectrum of the in-situ TPS monitoring. It presents a high white line characteristic of nickel oxide in an octahedral geometry. Figure 1 compares the corresponding EXAFS and Fourier transform (FT) with the ones measured at RT for a layered double hydroxide sample based on Ni$^{2+}$ and Al$^{3+}$ cations (NiAICL-LDH) from Ref. [26]. LDH materials have a brucite-like Ni(OH)$_2$ structure in which trivalent cations (Al$^{3+}$) have replaced a fraction of the divalent cations (Ni$^{2+}$) in octahedral coordination [26,27] leading to positively charged structure, which is balanced, herein, by the presence of Cl$^-$ anions in the interlamellar space. It is worth to note the similarity of the EXAFS oscillations shape and of the P1 to P4 contributions on the FT of both samples. Those contributions for EXAFS are related to single and multiple scattering paths (in particular, a focusing effect for P4) within the positively charged layers as discussed in Ref. [27]. Thus the comparison suggests that the local order around Ni in the catalyst is similar to the one in LDH structure. A satisfactorily fit, presented in Figure 2(a), has been achieved for the P1 and P2 FT contributions considering $6.1 \pm 0.4$ oxygen atoms at 2.04 Å and a total of 6 second nearest neighbours (equivalent numbers of Ni and Al) at $\sim 3.06$ Å (Table 1). Those parameters are in full agreement with a local order around Ni described by a LDH-like structure [28]. Furthermore, the RT XRD characterisation of the dried Ni/Al$_2$O$_3$ catalyst, displayed Figure 2(b), reveals a peak at low 2$\theta$ value (marked by a star), together with the diffraction peaks characteristic to the $\delta$-Al$_2$O$_3$ support [29]. This low-angle peak is characteristic to a basal distance ($d_{003}$) of 8.88 Å between consecutive layers compatible with the intercalation of nitrate and water in the interlayer space [30]. This feature achieves to fully confirm the dispersion after impregnation of NiAl LDH-like phase at the surface of the alumina support. As reported in Ref. [31], the formation of such kind of NiAl-based LDH-like structure is well known during the impregnation of alumina with a solution of nickel nitrate followed by a subsequent drying step. This is related to the dissolution and reprecipitation of the support involving metallic cations present in the impregnation solution.

**Figure 1.** (a) EXAFS spectra and (b) FTs of the dried Ni/Al$_2$O$_3$ catalyst (20 K) and NiAICL-LDH sample (RT). Fourier transformation was done using a Kaiser–Bessel apodisation window (dk = 2) between 4.3 and 13.5 Å$^{-1}$. 
Figure 2. (a) Fitting of the Ni K edge EXAFS spectrum of the dried oxidic Ni/Al$_2$O$_3$ catalyst. (b) XRD signal of the dried oxidic Ni/Al$_2$O$_3$. The mark indicates the characteristic peak of the basal distance in LDH-like structure.

Table 1. Best fitted EXAFS parameters of the oxidic dried Ni/Al$_2$O$_3$ catalyst measured at 20 K and of the sulphided species identified by MCR-ALS during the sulphidation of the dried Ni/Al$_2$O$_3$ catalyst. N: coordination number, R: atomic distance from the absorbing atom, $\sigma^2$: square of the Debye–Waller factor, $\Delta E_0$: energy shift. $R_f$ measures the relative misfit of the theory with respect to the experimental spectrum. Italic parameters are fixed values. $E_0 = 8340$ eV and the passive electron reduction factor $S_0^2 = 0.94$. The coordination number for Al neighbours in the second coordination shell for the oxidic dried Ni/Al$_2$O$_3$ catalyst has been constrained by the relation $N_{\text{Al}} + N_{\text{Ni}} = 6$, according to the LDH structure.

|                | N      | R (Å)     | $\sigma^2$ (Å$^2$) | $\Delta E_0$ | $R_f$ |
|----------------|--------|-----------|--------------------|--------------|-------|
| Oxidic dried Ni/Al$_2$O$_3$ | 6.1 ± 0.4 O | 2.043 ± 0.008 | 0.0060 ± 0.0006 | 1.43 | 0.00358 |
| 3.0 ± 0.2 Ni    | 3.062 ± 0.010 | 0.0081 ± 0.0010 |                |        |      |
| 3.0 Al          | 3.050 ± 0.020 | 0.0107 ± 0.0050 |                |        |      |
| Comp.2          |        | 2.320 ± 0.003 | 0.0142 ± 0.0005 | 0.31 | 0.00106 |
| 6 S             | 6 S    | 3.550 ± 0.012 | 0.0167 ± 0.0022 |                |      |
| 2 S             | 2 S    | 3.837 ± 0.034 | 0.0063 ± 0.0034 |                |      |
| 12 Ni           | 12 Ni  | 3.960 ± 0.064 | 0.0210 ± 0.0053 |                |      |
| 2 S             | 2 S    | 4.773 ± 0.034 | 0.0241 ± 0.0079 |                |      |
| Comp.3          |        | 2.289 ± 0.009 | 0.0158 ± 0.0015 | 0.31 | 0.00645 |
| 4 S             | 4 S    | 2.557 ± 0.072 | 0.0436 ± 0.0151 |                |      |

**Time resolved Quick-XAS and in situ Raman monitoring of the sulphidation**

Figure 3 displays the XANES data recorded during the Quick-EXAFS monitoring of the sulphidation of the dried Ni/Al$_2$O$_3$ catalyst. Upon heating under $H_2S/H_2$, one can observe a progressive decrease of the white line intensity (at 8351.8 eV). It results from the transformation of oxidic species into sulphided ones. Above ~260 °C, the white line is totally vanishes as evidenced by the plot displaying the white line intensity vs. temperature (insert of Figure 3). This suggests that the Ni sulphidation is complete at this temperature. Nevertheless, the position of rising edge, shifting from ~8343 to ~8340 eV between RT and ~260 °C, abruptly moves in position above this temperature as evidenced by the plot showing the evolution of the rising edge, $E_{1/2}$, corresponding to 50% level of the normalised absorbance as a function of temperature (insert of Figure 3). It suggests that around 260 °C the nickel oxidation state suffers an important evolution.

Figure 4 displays the XANES spectra of the pure MCR-ALS components extracted from the minimisation, the EXAFS oscillations and their corresponding FTs. The spectrum of the first component (Comp.1) is superimposible to the initial oxidic Ni species. The second (Comp.2) and third (Comp.3) components display XANES spectra with a shape characteristic of nickel sulphide species. It is noteworthy that the rising edge of both XANES spectra is not superimposable, since the one related to Comp.2 (8340.0 eV) is shifted at higher energy than the one related to Comp.3 (8338.8 eV). It suggests that the formal nickel oxidation state is higher for Comp.2 than Comp.3. At this stage, even with the comparison with bulk nickel sulphide references spectra, the phases identification based on the XANES spectra is not straightforward. Actually, different shapes of XANES spectra are reported in the literature for the same bulk composition, as for example for Ni$_3$S$_2$ [32–34]. Such differences probably arise from the difficulty to prepare or
and 2.34 ± 0.07 Å Ni(O\textsubscript{h})\[38], 2.31 ± 0.06 Å for NiS\[39] and 2.39 ± 0.01 Å for NiS\textsubscript{2}\[40]. Phases containing edge sharing tetrahedrons or square pyramids, such as Ni\textsubscript{3}S\textsubscript{2}, Ni\textsubscript{9}S\textsubscript{8} and NiS have short Ni-Ni distances around 2.50–2.60 Å but also a strong distribution of Ni-Ni and Ni-S distances in the vicinity of the absorbing atom. Due to the out-of-phase of both contributions in the EXAFS signals when they are located at nearly the same distances, such species are characterised by a nearly flat FT beyond the first coordination shell. At the opposite, cubic-like structures such as Ni\textsubscript{3}S\textsubscript{4} and NiS\textsubscript{2} present a more regular distribution of sulphur and nickel neighbours susceptible to present defined contributions on

purchase pure nickel sulphide phases as emphasised in Ref. [32,35]. The FTs of the MCR-ALS nickel sulphide components presented Figure 4(c) display for both species a first contribution located at slightly different R positions shifting of about −0.08 Å from Comp.2 to Comp.3. Additionally, second neighbour’s contributions up to 4.5 Å are clearly observed for Comp.2. These findings will be helpful for the phases identification guided by complementary techniques, such as Raman. The mean Ni-S distances reported for the different phases stable at atmospheric pressure and RT [5] are 2.27 ± 0.02 Å for Ni\textsubscript{3}S\textsubscript{2} [36], 2.29 ± 0.10 Å for Ni\textsubscript{9}S\textsubscript{8} [37], 2.29 Å for the spinel-like Ni\textsubscript{3}S\textsubscript{4} (2.15 ± 0.06 Å Ni(T\textsubscript{d}) and 2.34 ± 0.07 Å Ni(O\textsubscript{h})) [38], 2.31 ± 0.06 Å for NiS [39] and 2.39 ± 0.01 Å for NiS\textsubscript{2} [40]. Phases containing edge sharing tetrahedrons or square pyramids, such as Ni\textsubscript{3}S\textsubscript{2}, Ni\textsubscript{9}S\textsubscript{8} and NiS have short Ni-Ni distances around 2.50–2.60 Å but also a strong distribution of Ni-Ni and Ni-S distances in the vicinity of the absorbing atom. Due to the out-of-phase of both contributions in the EXAFS signals when they are located at nearly the same distances, such species are characterised by a nearly flat FT beyond the first coordination shell. At the opposite, cubic-like structures such as Ni\textsubscript{3}S\textsubscript{4} and NiS\textsubscript{2} present a more regular distribution of sulphur and nickel neighbours susceptible to present defined contributions on

Figure 3. In situ quick-XAS monitoring of the sulphidation of the dried Ni/Al\textsubscript{2}O\textsubscript{3} catalyst. The insert displays the evolution of the white intensity at 8351.8 eV and of the position of rising edge at half absorption E\textsubscript{1/2} as a function of the sulphidation temperature.

Figure 4. (a) XANES spectra, (b) EXAFS spectra and (c) corresponding FT of the MCR-ALS components describing the sulphidation of the dried Ni/Al\textsubscript{2}O\textsubscript{3} catalyst. Fourier transformation was done using a Kaiser–Bessel apodisation window (dk = 2) between 3.8 and 11.7 Å\textsuperscript{−1}. 
the FT beyond the first coordination shell (e.g. for NiS$_2$: 6 sulphur at 3.58 Å, 2 ones at 3.84 Å associated to 12 nickel atoms at 4.02 Å).

In order to help in the identification of the sulphide species isolated by MCR-ALS, we have also monitored the sulphidation by Raman spectroscopy. Figure 5 reports some typical Raman spectra so-recorded. The signal to noise ratio decreases a lot with the time under gas stream due to the sample colour change and the proportion increase of nickel sulphides, known to be very poor Raman scatterers. Nevertheless, we can clearly observe in the first 5 spectra measured at the early stage of sulphidation ($T < 195 \, ^\circ\text{C}$), a broad intense Raman signal located ~457 cm$^{-1}$ together with three resolved lines at 294, 333 and 356 cm$^{-1}$ (Figure 5(a)). The first Raman line is unambiguously assigned to the NiS$_2$ formation [41], since it is the only nickel sulphide phase presenting Ni–S vibration modes above 400 cm$^{-1}$ [42]. The lines observed below 400 cm$^{-1}$ closely match those of Ni$_3$S$_2$ [35]. It is noteworthy that the presence of two phases is well in agreement with the speciation reported by XAS-MCR-ALS revealing two sulphide species formed upon sulphidation. Around 202 °C, two well defined lines, located at 219 and 474 cm$^{-1}$, appear. These lines, which quickly increase in (Figure 5(b)), are characteristic of the formation of elemental sulphur [43]. Due to the geometry of the Harrick cell, with a RT thermalised quartz window facing the cup containing the heated sample, the elemental sulphur is quickly condensed at the inner surface of the window, hindering to focus the laser at the surface of the sample between 210 and 400 °C. At high treatment temperature, the glass window is free of sulphur that allows us to measure the last spectrum presented Figure 5(c). This spectrum, corresponding to the merge of spectra collected at the beginning of the isothermal treatment at 400 °C, displays a line with a maximum at 331 cm$^{-1}$ and shoulders at 295 and 318 cm$^{-1}$. We assume that these lines are still related to the presence of Ni$_3$S$_2$. The shift in position and the line broadening compared to those observed at lower temperatures is comparable to those observed for the spectrum of Ni$_3$S$_2$ measured at 440 °C [35] and ascribed to the thermal expansion of the lattice increasing with the temperature [42].

The complementary information gained on the nickel sulphide speciation by Raman spectroscopy allows us to evaluate models for fitting the EXAFS spectra of Comp.2 and Comp.3 determined by MCR-ALS. Table 1 gathers the structural parameters determined by least square fitting procedure of their EXAFS oscillations. The coordination numbers were kept fixed to the theoretical values for each crystallographic structure. As shown Table 1 and Figure 6, comparing the simulated EXAFS spectra with the ones corresponding to each MCR-ALS component, a very good agreement is found for fitting Comp.2 and Comp.3 with the structures reported for NiS$_2$ and Ni$_3$S$_2$, respectively. The crystallographic distances for both nickel sulphides are reported in Table S1 in Supporting Information. Despite a slightly shorter distance in the first coordination shell of Comp.3 (2.32 Å) compared to the crystallographic one (2.39 Å), the fit agreement reported up to 5 Å with the NiS$_2$ crystallographic structure [40] strongly supports the identification of the signal extracted by MCR-ALS for this component with NiS$_2$. Additionally, the identification of Comp.2 to NiS$_2$ and Comp.3 to Ni$_3$S$_2$ is also in good
agreement with the position of the respective rising edge position of both XANES spectra and the formal oxidation state of nickel (+2 and +1.3, respectively).

Discussion

The sulphided nickel species formed during sulphidation under gas stream of a dried oxidic Ni catalyst supported on δ-alumina are unambiguously identified by Raman spectroscopy and Quick-XAS combined to MCR-ALS analysis. The strength of the MCR-ALS method is not only to provide the XANES spectra but also to determine the concentration profiles of the involved species: NiS₂ and Ni₃S₂ phases. Those concentration profiles are presented Figure 7 and compared to the evolution of H₂S and H₂ concentrations determined by MS. The monitoring of the raw XAS absorption level at a given energy, herein just before the rising edge at 8300 eV, is also reported in Figure 7 for comparison purpose. This absorption level is informative about the catalyst capacity to trap H₂S. The absorption level increases as soon as the catalyst is in contact with the gas flow and displays evolutions which match those of gas profiles and nickel species. In the following, we will discuss the profiles evolution considering the 4 successive steps highlighted Figure 7. Moreover, we will propose a sulphidation mechanism explaining the formation of Ni₃S₂ and NiS₂. It is noteworthy that the profiles of gases measured at the cell outlet exhibit sulphiding characteristics comparable to those reported by conventional TPS of Ni/Al₂O₃ catalysts [6] with positive peaks corresponding to gas production and negative peaks to gas consumption.

![Figure 6. Fittings of the Ni K edge EXAFS spectra of (a) Component 2 and (b) Component 3 determined by MCR-ALS.](image6)

![Figure 7. Comparison of the concentration profiles of NiOₓ, NiS₂ and Ni₃S₂ determined by MCR-ALS with the raw X-ray absorption level and the evolution of gas effluent concentrations determined by mass spectrometry.](image7)
The sulphidation of the oxidic species starts at RT indicating no mass transfer limitations as expected for dispersed Ni oxidic species. At step 1 ($T < 90 \, ^\circ C$), the formation of Ni$_x$S$_y$ is first verified whereas H$_2$S is trapped into the support porosity. The global reaction for step 1 leading to the conversion of $\sim 28\%$ of oxidic precursor is:

(a) $3 \text{NiO}_x + 2\text{H}_2\text{S} + (3x - 2)\text{H}_2 \rightarrow \text{Ni}_x\text{S}_y + 3x\text{H}_2\text{O}$

It is noteworthy that at step 1, the peaks observed on the H$_2$S and H$_2$ profiles correspond to the switch of the electrovalve towards the cell hindering to extract information from MS for this step.

In step 2, ranging from $\sim 90$ to $\sim 215 \, ^\circ C$, NiS$_x$ is formed with a rate matching pretty well the consumption of H$_2$S, i.e. slow up to $\sim 165 \, ^\circ C$ and faster above 165 $^\circ C$. The quantity of Ni$_x$S$_y$ reaches a maximum ($\sim 35\%$) at the onset of acceleration of NiS$_3$ formation and then decreases to $\sim 14\%$. The global reactions for the formation of NiS$_3$ involving the observed H$_2$S consumption are consequently:

(b) $\text{NiO}_x + 2\text{H}_2\text{S} \rightarrow \text{Ni}_x\text{S}_3 + x\text{H}_2\text{O} + (2 - x)\text{H}_2$

(c) $\text{Ni}_x\text{S}_3 + 4\text{H}_2\text{S} \rightarrow 3 \text{NiS}_2 + 4\text{H}_2$

Accordingly with (b) and (c), a slight H$_2$ production peak is observed by MS. During this stage, considering the raw absorption level, the quantity of H$_2$S trapped by the catalyst is still increasing. Nevertheless, considering the Raman results, the end of this stage is characterised by the adsorption of elemental sulphur at the surface of the catalyst. Consequently, we ascribe the formation of elemental sulphur as resulting from the conversion of H$_2$S adsorbed at the surface of catalyst into adsorbed elemental sulphur according to reaction:

(d) $\text{H}_2\text{S}_{\text{ads}} \rightarrow \text{S}_{\text{ads}} + \text{H}_2$

Since elemental sulphur is adsorbed at the surface of the catalyst, like H$_2$S was, no decrease of raw absorption level is expected.

Step 3, ranging from $\sim 215$ to 262 $^\circ C$, is characterised by a sharp H$_2$S production peak coupled with H$_2$ consumption and a concomitant decrease of the raw absorption level, indicating the desorption of elemental sulphur through the reaction:

(e) $\text{S}_{\text{ads}} + \text{H}_2 \rightarrow \text{H}_2\text{S}$

At this point the nickel speciation, characterised by a quasi-complete conversion of NiO$_x$ into sulphidic nickel species, reveals two different stages. At stage 3.1, the Ni$_x$S$_3$ and NiS$_2$ quantities reach a quasi-steady state with $\sim 6$ and 93%. At stage 3.2, an abrupt change in phase composition occurs in a few minutes with a Ni$_x$S$_y$ enrichment (78%) at the detriment of NiS$_3$ (22%).

Since H$_2$S is no more consumed by conversion of NiO$_x$, one can observe an increase of the gas-phase H$_2$S concentration, which is possibly responsible for the desorption of elemental sulphur, as reported in Ref. [44]. The observed elemental sulphur desorption strongly indicates that the chemisorbed sulphur becomes energetically unstable causing the fall of the formation enthalpy of Ni$_x$S$_2$ below that of the adsorption enthalpy of sulphur. Consequently, at stage 3.2, the reduction of Ni$_x$S$_3$ into NiS$_2$ takes place through the reaction:

(f) $3 \text{NiS}_2 + 4\text{H}_2 \rightarrow \text{Ni}_x\text{S}_2 + 4\text{H}_2\text{S}$

Finally, in step 4, a continuous increase of the Ni$_x$S$_2$ proportion occurs at the detriment of NiS$_2$ and 100% of conversion is achieved at the beginning of the isothermal treatment (400 $^\circ C$). The evolution of gas composition at the outlet of the cell suggests a thermal decomposition of H$_2$S into H$_2$ and gaseous sulphur S$_2$ since NiS$_2$ is known to catalyse S hydrogenation in this temperature range [45]. When the isothermal treatment at 400 $^\circ C$ is reached and 100% of NiS$_2$ has been converted into NiS$_3$, the H$_2$S evolution (not shown) starts to increase showing that the hydrogenation of sulphur is no more catalytically activated.

**Conclusion**

Unlike the use of reference spectra that may not be appropriate, the MCR-ALS method allowed to extract the components whose sum constitutes the experimental spectra without introducing biases [22]. Its use for the analysis of Quick-XAS appears very robust enabling to isolate pure spectra of nickel sulphides involved during the TPS of an only dried Ni/Al$_2$O$_3$ catalyst. Helped by the Raman fingerprints measured in situ on the same system, the EXAFS spectra of those sulphides were successfully fitted with a sulphur rich phase, NiS$_2$, for the intermediate phase, and Ni$_3$S$_4$ as final sulphide species. The comparison of the MCR-ALS concentration profiles with the monitoring of gas effluent by mass spectrometry points out desorption of elemental sulphur leading the system in thermodynamically favourable conditions for the abrupt reduction of NiS$_3$ into Ni$_x$S$_2$. Beyond the understanding of sulphidation process for preparing HDS catalysts, and the use of isolated supported nickel sulphides spectra for the further determination by XAS of promotion level, the results gained herein are potentially useful to shed light on phase compositions of other active nickel sulphide catalysts and/or poisoning nickel sulphides.

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