

In-situ QXAS study of sulfidation/oxidative
regeneration reactions of zinc molybdate ZnMoO_4
and ZnO-MoO_3 materials

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MCR-ALS minimization principle

In recent works, multivariate analysis based on the so-called MCR-ALS method (Multivariate Curve Resolution with Alternating Least Squares) has been used in the qualitative and quantitative investigation of time-resolved evolving XAS data recorded during solid-state reactions.¹⁻¹⁰ The purpose of this chemometric approach is to extract the spectrum of each component whose sum constitutes the experimental spectrum and to determine the concentrations of each of these components in the mixture.¹¹

The set of normalized XAS experimental spectra, recorded upon H₂S trapping and sequential regeneration of oxide mixtures (ZnO and MoO₃) and a mixed oxide (ZnMoO₄) is defined as a matrix D resulting from the combination of three matrices: C (concentration of the pure components); S (normalized XAS spectra of the pure components); and E (experimental uncertainties), following the matricial equation: $D = C S^T + E$ (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 which can explain the whole set of D , by iteration and least-squares minimization of the E matrix. For this scope, physically and chemically meaningful constraints on the C and S matrices are used in order to help the convergence of the multivariate curve resolution. In the present work, for all the investigated samples, the matrix of concentrations C contains only positive values and the sum of the species concentrations is equal to 100% at any time of the reaction (closure relation). Additionally, the matrix S contains normalized XAS spectra with non-negative absorbance. The only information required by the MCR-ALS method to start the minimization is the number of components describing the matrix D to provide an initial guess either of the concentration matrix or of the component spectra matrix. To this purpose, Singular Value Decomposition (SVD) method is used for the determination of the number of components. *Scree plots*, displaying the eigenvalues determined by SVD for each component arranged in descending order as a function of number of spectra in D , were used for the estimation of the number of chemical components to include in the MCR-ALS minimization.

The MCR-ALS minimization on the Quick-XAS data presented herein was carried out using the MCR-ALS GUI 2.0 developed by Roma Tauler and his group on the Matlab® platform.¹² At the Mo K-edge, an initial guess of the concentration in the ALS minimization was performed using the Evolving Factor Analysis (EFA) method¹³, whereas at the Zn K-edge, an initial guess of the spectra in the ALS minimization was performed using the SIMPLISMA (SIMPLe to use Interactive Self-modeling Mixture Analysis) method.¹⁴

As reported in a previous XRD study¹⁵, sulfidation and regeneration of the ZnO-MoO₃ mixture and ZnMoO₄ mixed oxide were shown to involve four distinct Zn-based crystalline phases (ZnO, ZnS, ZnMoO₄ and ZnMoO₃) and five Mo-based crystalline phases (MoO₃, MoO₂,

MoS₂, ZnMoO₄ and ZnMoO₃). The number of components and systems complexity led us to consider for MCR-ALS minimization at a given edge the experimental data matrix D built from the concatenation of the data recorded for the treatment (sulfidation and regeneration) of the ZnO-MoO₃ mixture, and those recorded for the treatment of ZnMoO₄ mixed oxide. The data set includes the thermal treatment (heating under He up to 350°C) before sulfidation and thermal treatment (heating after exposure of H₂S up to 500°C under N₂) before regeneration. This strategy was used in order to give more variance to the system in order to overcome potential rank deficiency data issue. Indeed, this issue arises when two or more species are evolving at the same transformation rates, giving rise to a correlation between the concentrations of those species. In that case, MCR-ALS is not able to separate those species, except if the correlation is broken by the introduction of supplementary data.

MCR-ALS minimization for the Zn K-edge data set

The data set at the Zn K-edge was composed of 1057 spectra belonging to the treatment of the ZnO-MoO₃ mixture and 928 spectra belonging to the treatment of ZnMoO₄ mixed oxide. According to the Scree Plot presented in Figure S1 from which the number of components to be retained are those in the steep curve before the first point that starts the asymptotic line trend, and in agreement with the previous XRD study, 4 components are necessary to explain the variance of the data set related to both systems.

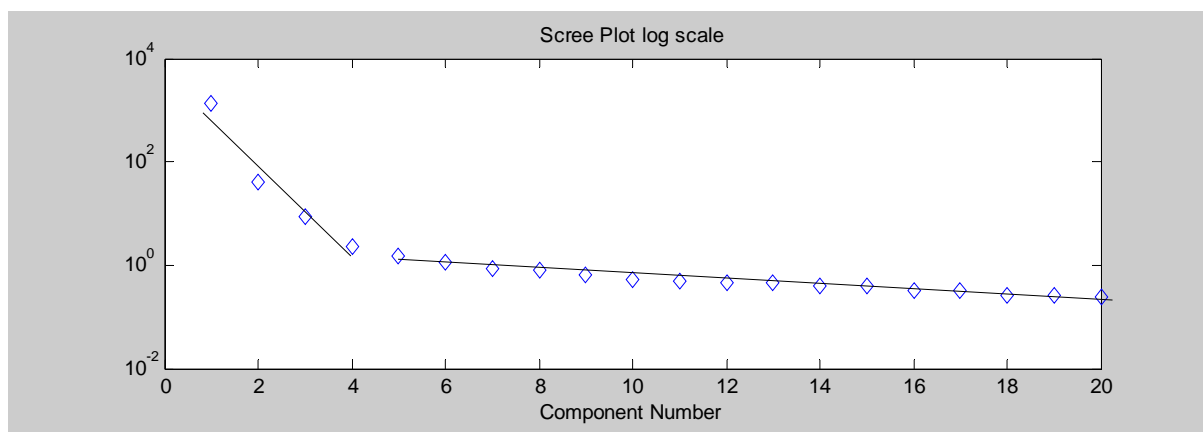


Figure S1: Scree plot representation used to determine the number of components to be retained for the description of the variance associated to the XAS data set matrix associated to the concatenation of spectra recorded at the Zn K-edge for sulfidation and regeneration of the ZnO-MoO₃ mixture and of the ZnMoO₄ mixed oxide.

In a first MCR-ALS minimization, a convergence was achieved as shown in Figure S2. For 3 of the 4 components, satisfactory spectra in relation to the chemical nature of the identified phases were obtained (see Figure S3), *i.e.* for ZnO, ZnS and ZnMoO₄. The last component (in cyan in Figure S2) was approaching to ZnMoO₃ but not perfectly.

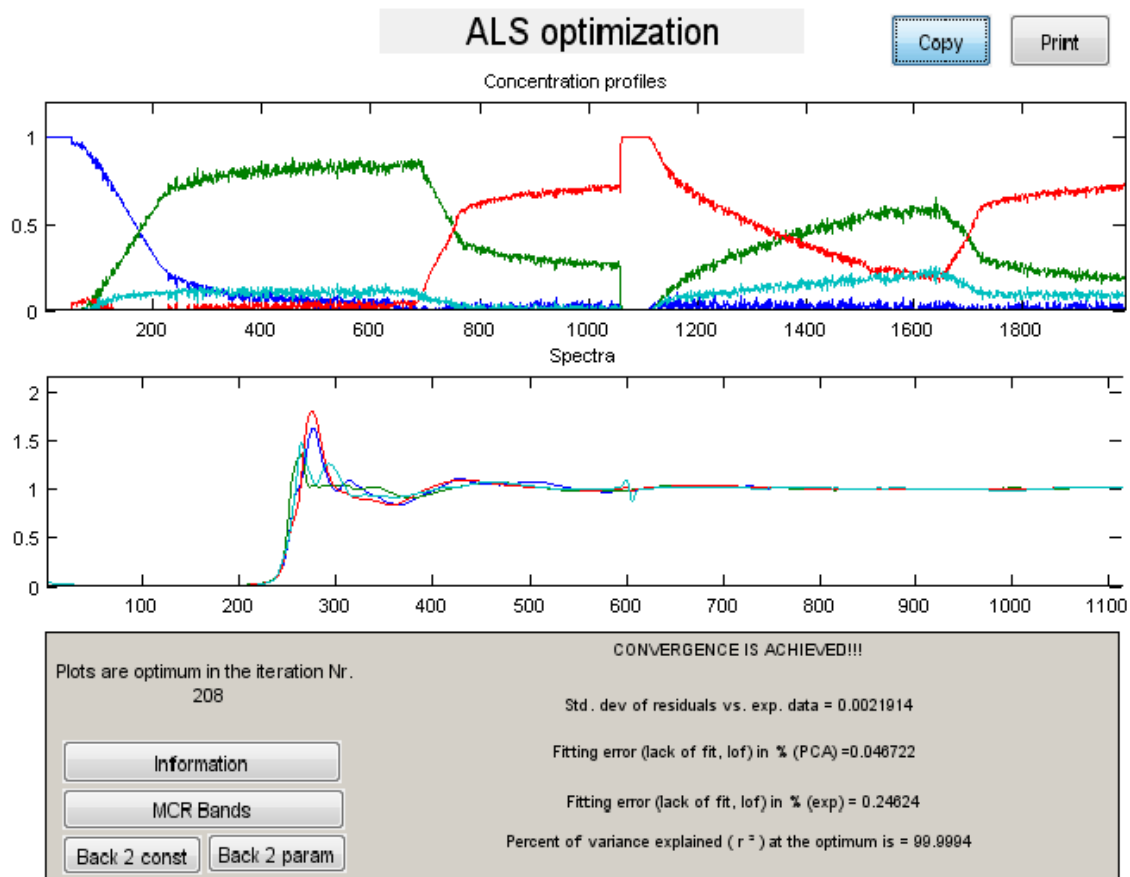


Figure S2: Results of the minimization by MCR-ALS of the XAS data set matrix associated to the concatenation of spectra recorded at the Zn K-edge for sulfidation and regeneration of the ZnO-MoO₃ mixture (data from 1 to 1057) and of the ZnMoO₄ mixed oxide (data from 1058 to 1985).

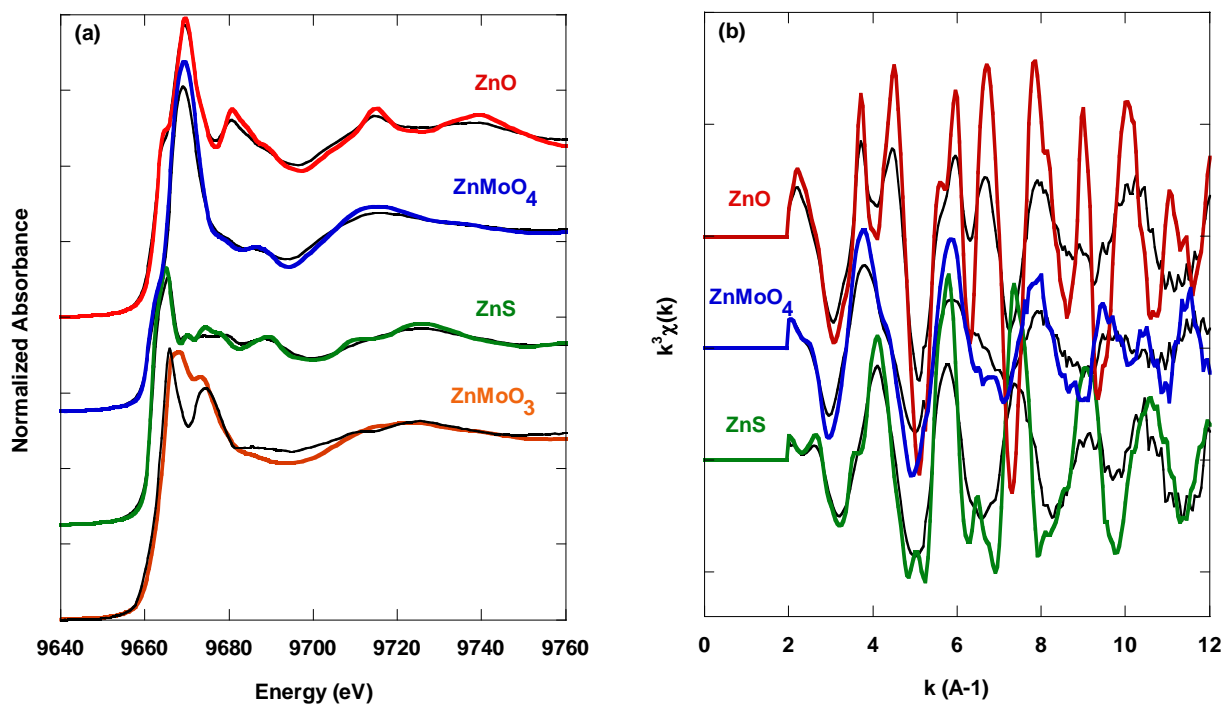


Figure S3: Comparison of the MCR-ALS spectra (black curves) with the Zn K-edge spectra (colored curves) of crystalline references ZnO, ZnMoO₄, ZnS and ZnMoO₃; (a) XANES spectra and (b) EXAFS spectra.

It was then decided to repeat the MCR-ALS minimization imposing the spectrum of the ZnMoO_3 component, the three others spectra being still minimized. Additionally, a constraint on concentrations was considered for both systems imposing that before sulfidation, 100 % of ZnO composed the ZnO-MoO_3 mixture, and 100% of ZnMoO_4 was the starting composition of the ZnMoO_4 mixed oxide. The results of minimization so-achieved are presented in Figure S4.

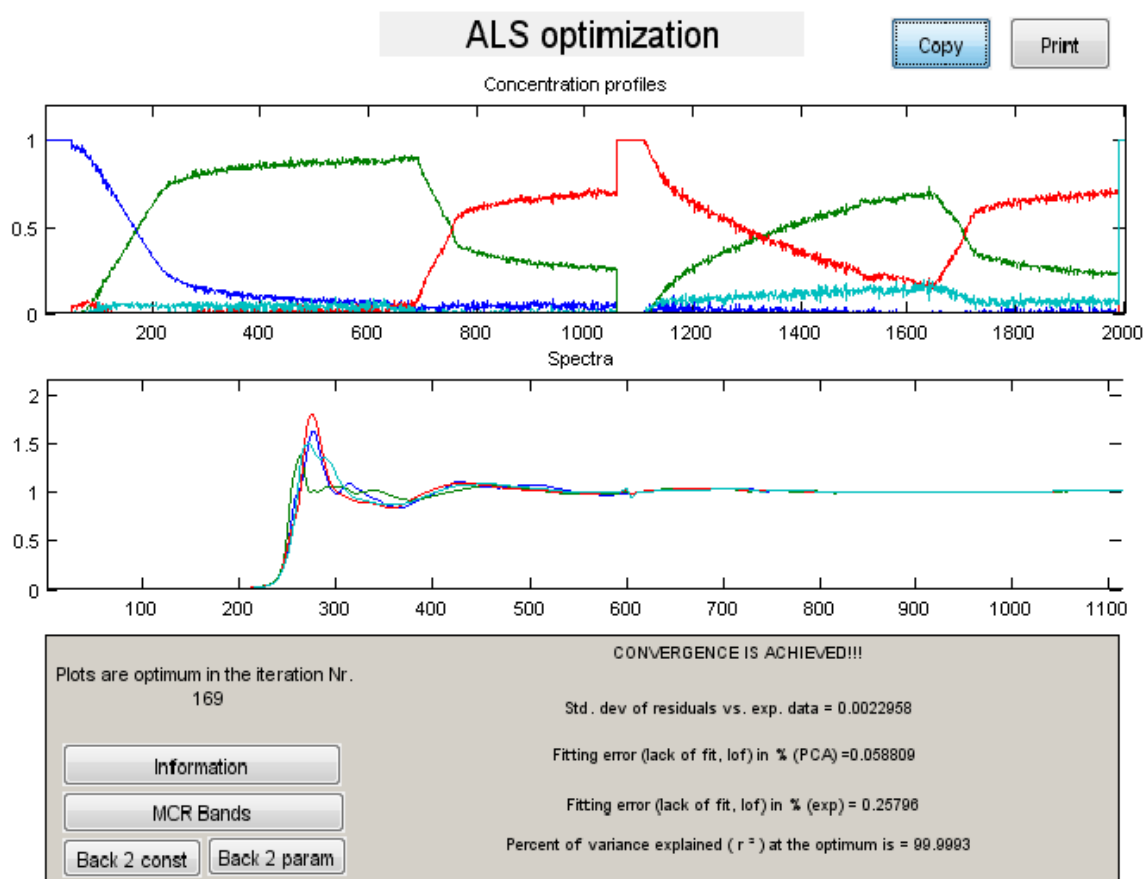


Figure S4: Results of the minimization by MCR-ALS of the XAS data set matrix associated to the concatenation of spectra recorded at the Zn K-edge for sulfidation and regeneration of the ZnO-MoO_3 mixture (data from 1 to 1057) and of the ZnMoO_4 mixed oxide (data from 1058 to 1985), imposing the presence of the spectrum of ZnMoO_3 .

MCR-ALS minimization for the Mo K-edge data set

The data set at the Mo K-edge was composed of 988 spectra belonging to the treatment of the ZnO-MoO_3 mixture and 874 spectra belonging to the treatment of ZnMoO_4 mixed oxide. Scree plot representation of the SVD analysis (Figure S5) suggested to consider in the minimization 5 components, in agreement with the number of crystalline species revealed by XRD considering both systems¹⁴. Nevertheless it is noteworthy that ZnMoO_3 was not evidenced by *in situ* XRD upon treatment of the ZnO-MoO_3 mixture¹⁵.

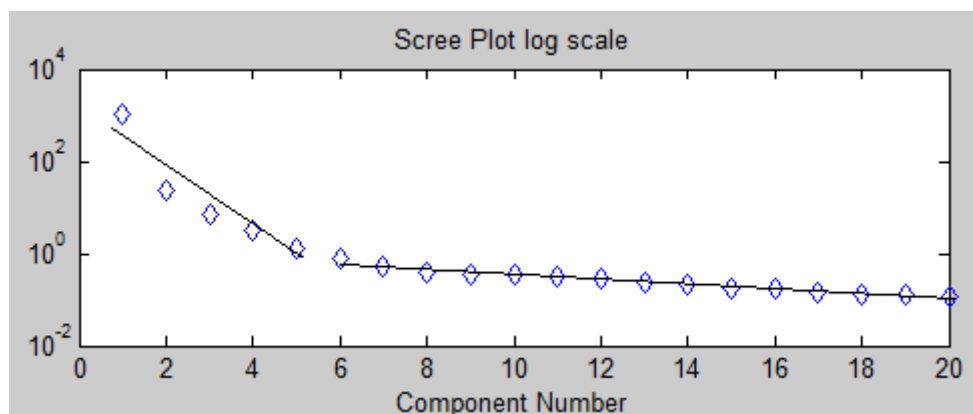


Figure S5: Scree plot representation used to determine the number of components to be retained for the description of the variance associated to the XAS data set matrix associated to the concatenation of spectra recorded at the Mo K-edge for sulfidation and regeneration of the ZnO-MoO₃ mixture and of the ZnMoO₄ mixed oxide.

As presented in Figure S6, convergence was verified, using as only constraint that pure species are encountered before sulfidation.

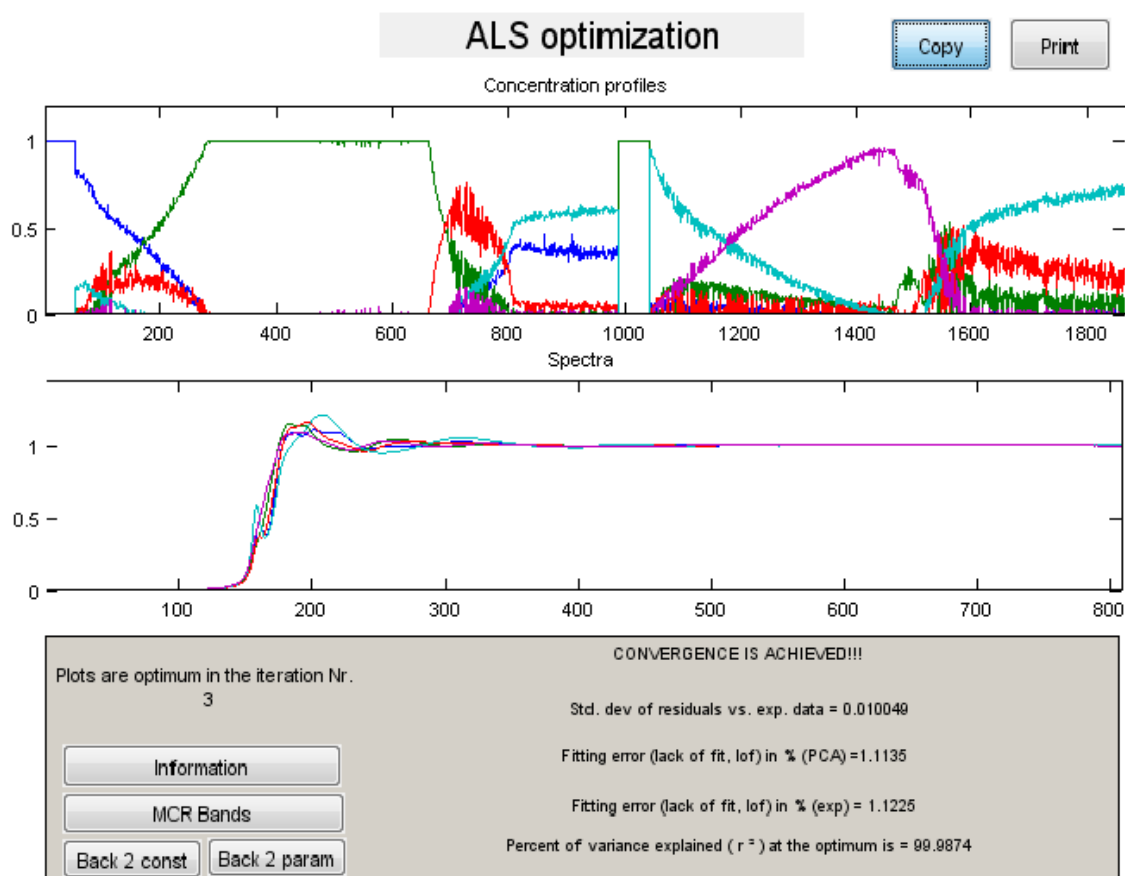


Figure S6: Results of the minimization by MCR-ALS of the XAS data set matrix associated to the concatenation of spectra recorded at the Mo K-edge for sulfidation and regeneration of the ZnO-MoO₃ mixture (data from 1 to 988) and of the ZnMoO₄ mixed oxide (data from 989 to 1862).

Among the five species determined by this first minimization, only 3 can be considered as pure species: MoO_3 , MoO_2 and ZnMoO_4 as evidenced with the comparison of EXAFS spectra of crystalline references (Figure S7). The 2 other spectra appear as linear combinations including those pure species and MoS_2 and ZnMoO_3 . The minimization was repeated separately for each data set introducing as constraint the matrix of pure spectra composed of the MCR-ALS spectra determined for MoO_3 , MoO_2 and ZnMoO_4 and of the spectrum of the MoS_2 reference (for the ZnO-MoO_3 related data set) and if any the spectrum of the ZnMoO_3 reference (for the ZnMoO_4 related data set). Figure S8 and Figure S9 display the results of the ALS minimization for the ZnO-MoO_3 system and the ZnMoO_4 system, respectively.

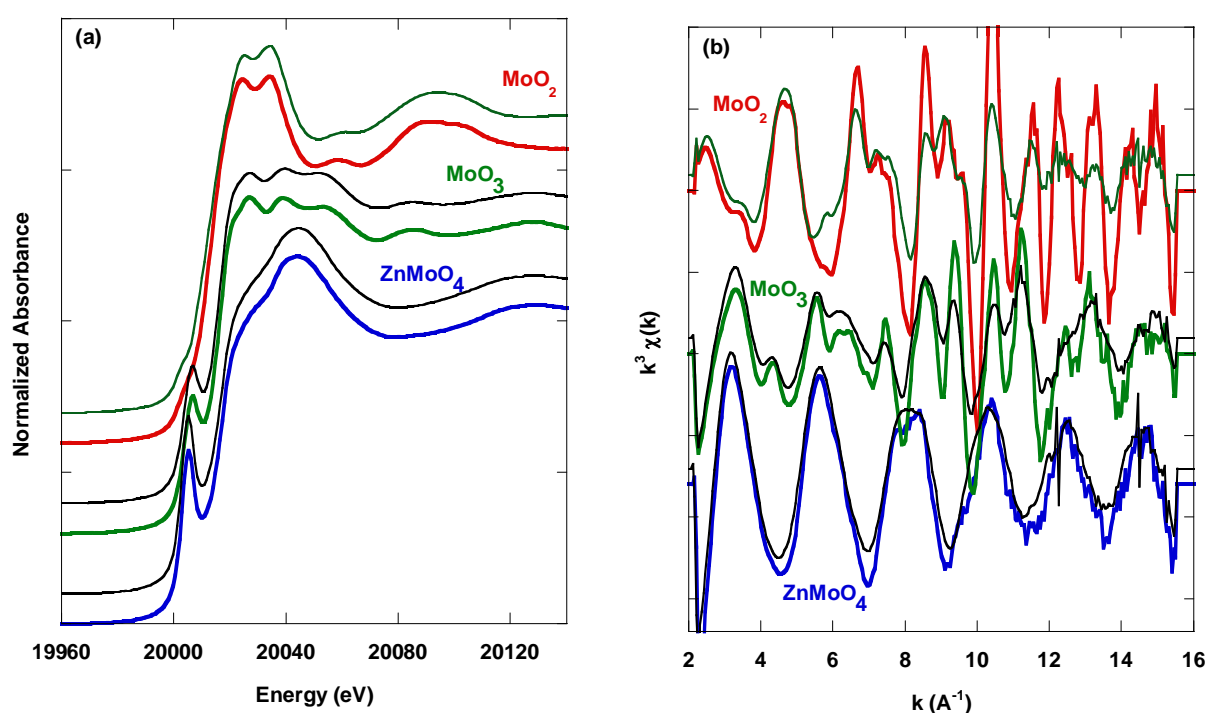


Figure S7: Comparison of the MCR-ALS spectra (black curves) with the Mo K-edge spectra (colored curves) of crystalline references MoO_2 , MoO_3 and ZnMoO_4 ; (a) XANES spectra and (b) EXAFS spectra.

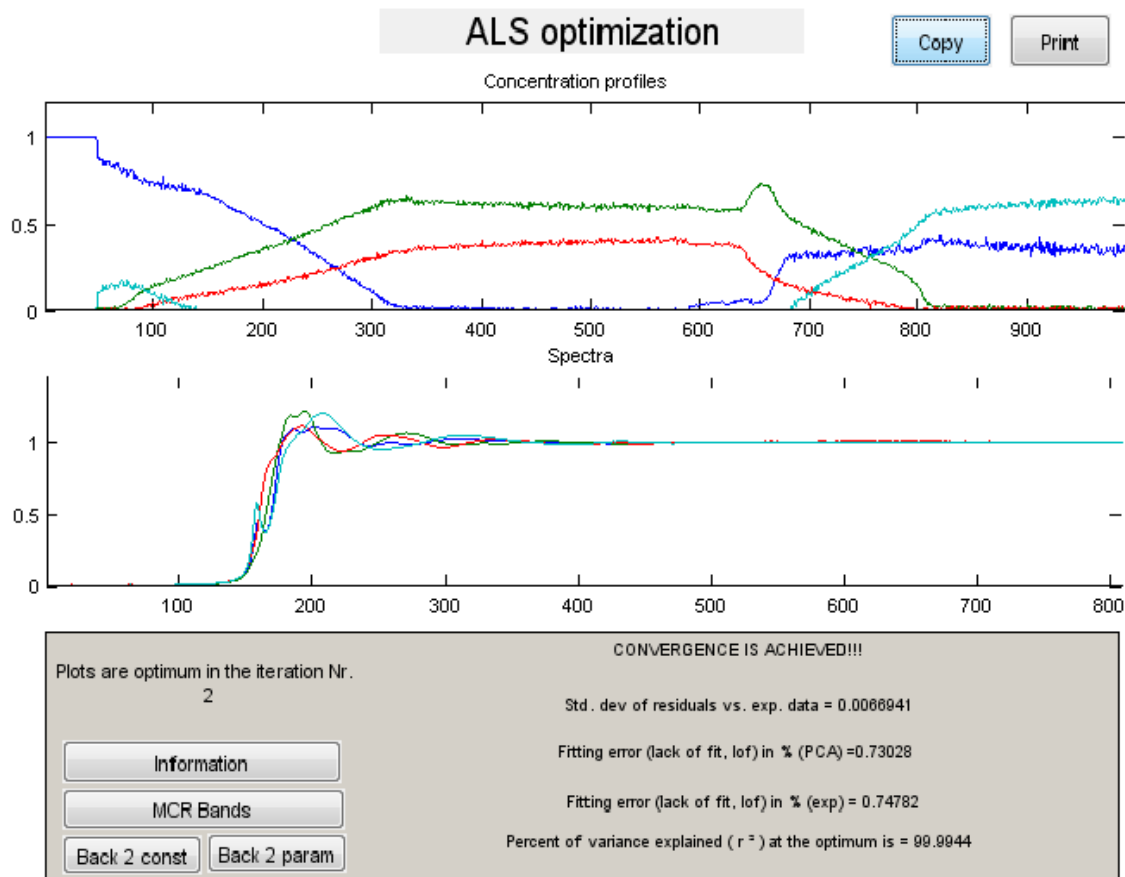


Figure S8: Results of the minimization by MCR-ALS of the XAS data recorded at the Mo K-edge for sulfidation and regeneration of the ZnO-MoO₃ oxide mixture.

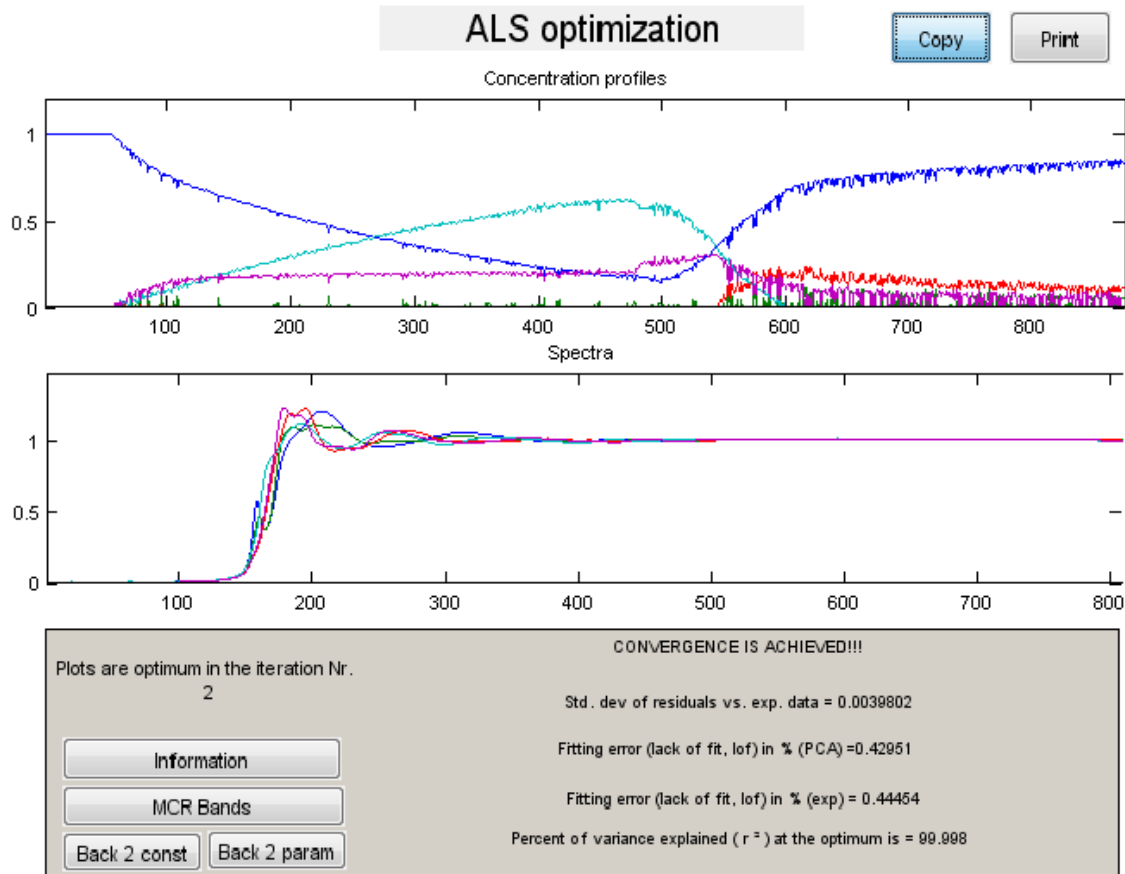


Figure S9: Results of the minimization by MCR-ALS of the XAS data recorded at the Mo K-edge for sulfidation and regeneration of the ZnMoO₄ mixed oxide.

Supplementary References

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