Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

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

*Vincent Girard,[1, 3] David Chiche,[1] Arnaud Baudot,[1] Delphine Bazer-Bachi,[1] Laurent Lemaitre,[1] Virginie Moizan-Baslé,[1] Amélie Rochet,[2] Valérie Briois,[2] Christophe Geantet[3]**

[1]IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP3, 69360 Solaize, France

[2]Synchrotron SOLEIL, L'Orme des Merisiers, BP 48, Saint Aubin, 91192 Gif sur Yvette, France

[3]Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), UMR5256 CNRS – Université de Lyon, 2 avenue Albert Einstein, 69626 Villeurbanne cedex, France

* To whom correspondence should be addressed. E-mail: christophe.geantet@ircelyon.univ-lyon1.fr

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 H_2S trapping and sequential regeneration of oxide mixtures (ZnO and MoO_3) and a mixed oxide ($ZnMoO_4$) 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: $\boldsymbol{D} = \boldsymbol{C}\ \boldsymbol{S}^{\boldsymbol{T}} + \boldsymbol{E}$ (where $\boldsymbol{S}^{\boldsymbol{T}}$ 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) method [13], 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 study [15], sulfidation and regeneration of the ZnO-MoO_3 mixture and $ZnMoO_4$ mixed oxide were shown to involve four distinct Zn-based crystalline phases (ZnO, ZnS, $ZnMoO_4$ and $ZnMoO_3$) and five Mo-based crystalline phases (MoO_3, MoO_2,

MoS_2, $ZnMoO_4$ and $ZnMoO_3$). 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-MoO_3 mixture, and those recorded for the treatment of $ZnMoO_4$ 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 H_2S up to 500°C under N_2) 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-MoO_3 mixture and 928 spectra belonging to the treatment of $ZnMoO_4$ 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.

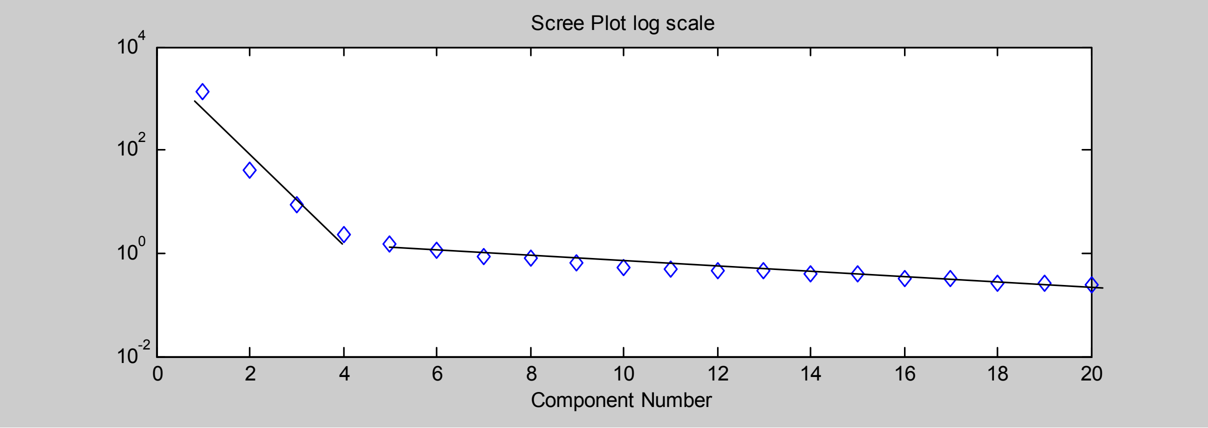
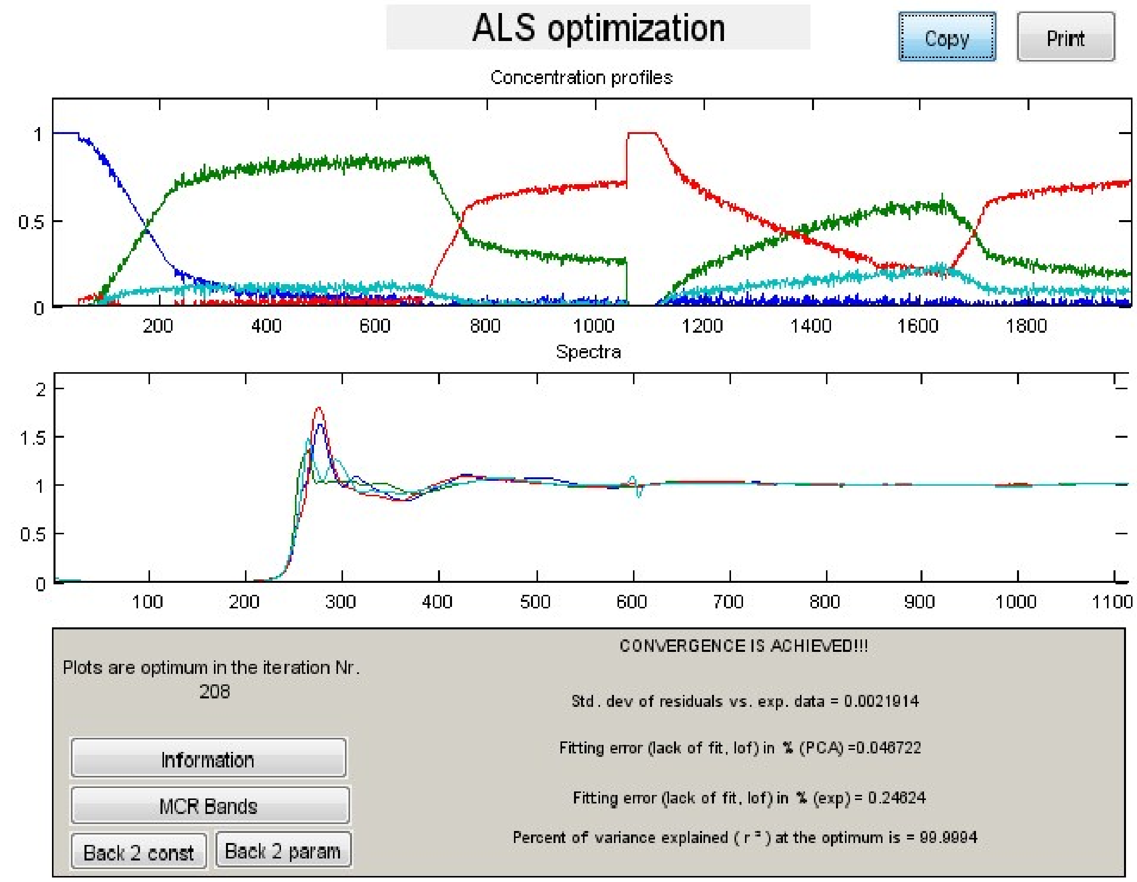


Figure S1: Scree plot representation used to determine the number of components to be retained for the description of the variance associated to the XAS data set matrix associated to the concatenation of spectra recorded at the Zn K-edge for sulfidation and regeneration of the ZnO-MoO_3 mixture and of the $ZnMoO_4$ 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 $ZnMoO_4$. The last component (in cyan in Figure S2) was approaching to $ZnMoO_3$ but not perfectly.



```
Plots are optimum in the iteration Nr.
208

CONVERGENCE IS ACHIEVED!!!

Std. dev of residuals vs. exp. data = 0.0021914

Fitting error (lack of fit, lof) in % (PCA) =0.046722

Fitting error (lack of fit, lof) in % (exp) = 0.24624

Percent of variance explained ( r² ) at the optimum is = 99.9994
```

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-MoO_3 mixture (data from 1 to 1057) and of the $ZnMoO_4$ mixed oxide (data from 1058 to 1985).

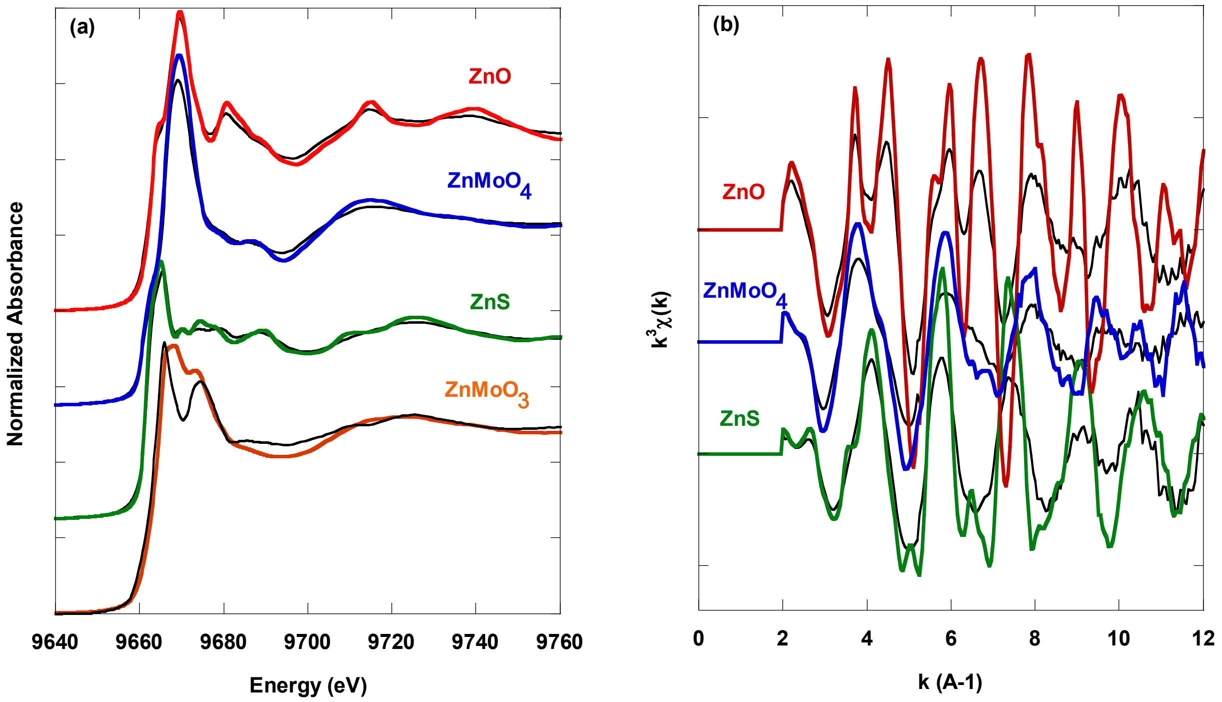
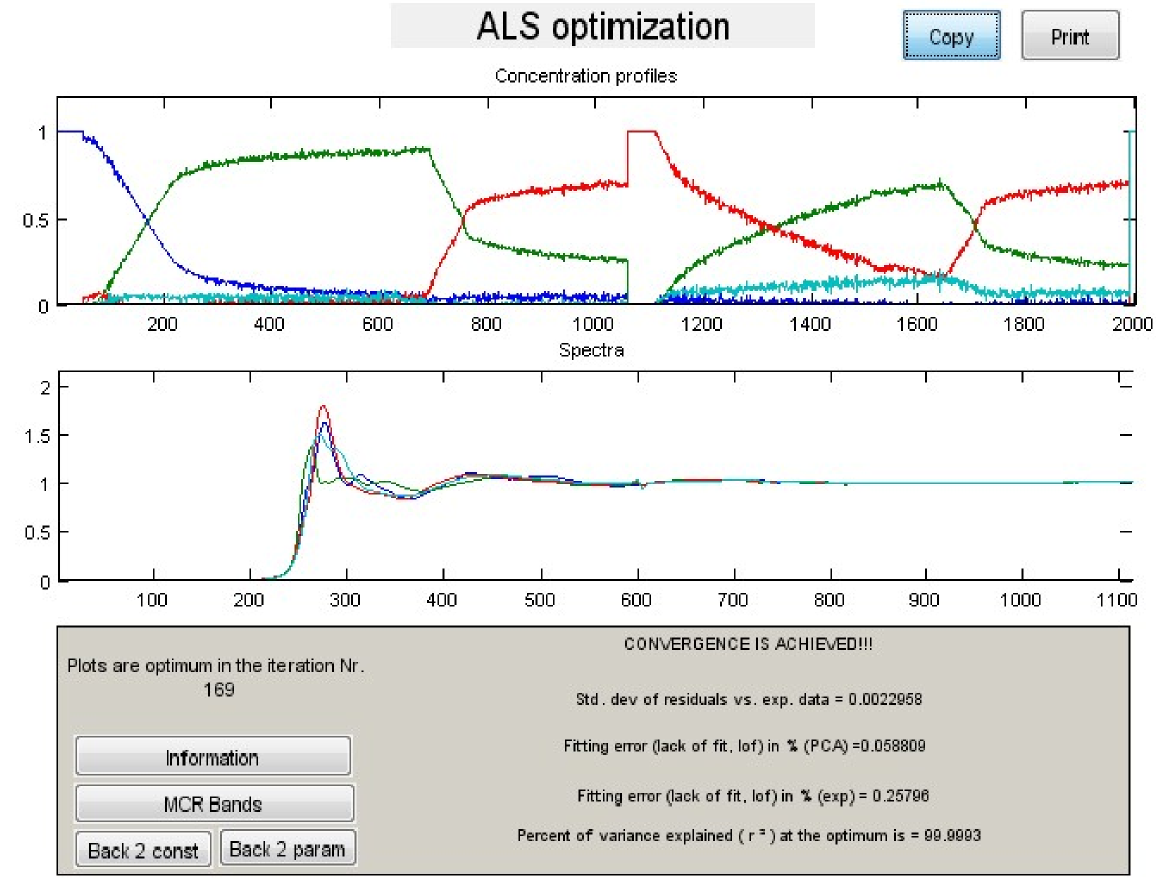


Figure S3: Comparison of the MCR-ALS spectra (black curves) with the Zn K-edge spectra (colored curves) of crystalline references ZnO, $ZnMoO_4$, ZnS and $ZnMoO_3$; (a) XANES spectra and (b) EXAFS spectra.

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.



```
CONVERGENCE IS ACHIEVED!!!
Plots are optimum in the iteration Nr.
169
Std. dev of residuals vs. exp. data = 0.0022958
Fitting error (lack of fit, lof) in % (PCA) =0.058809
Fitting error (lack of fit, lof) in % (exp) = 0.25796
Percent of variance explained ( r ² ) at the optimum is = 99.9993
```

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 systems[14]. Nevertheless it is noteworthy that $ZnMoO_3$ was not evidenced by *in situ* XRD upon treatment of the $ZnO-MoO_3$ mixture[15].

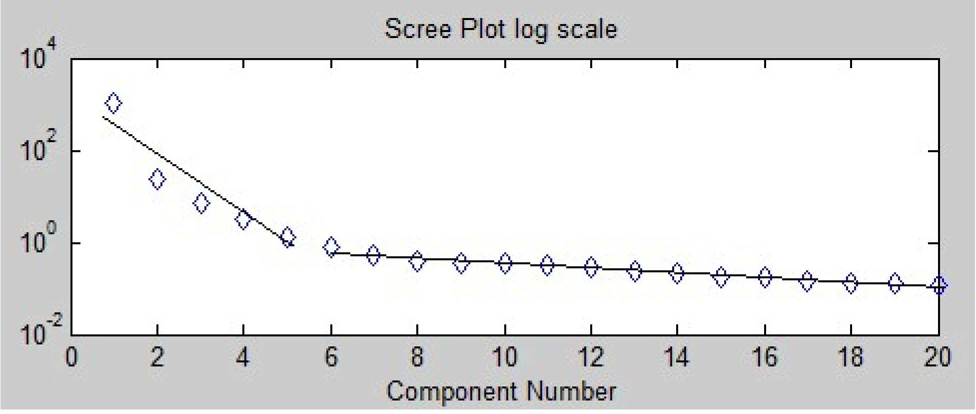
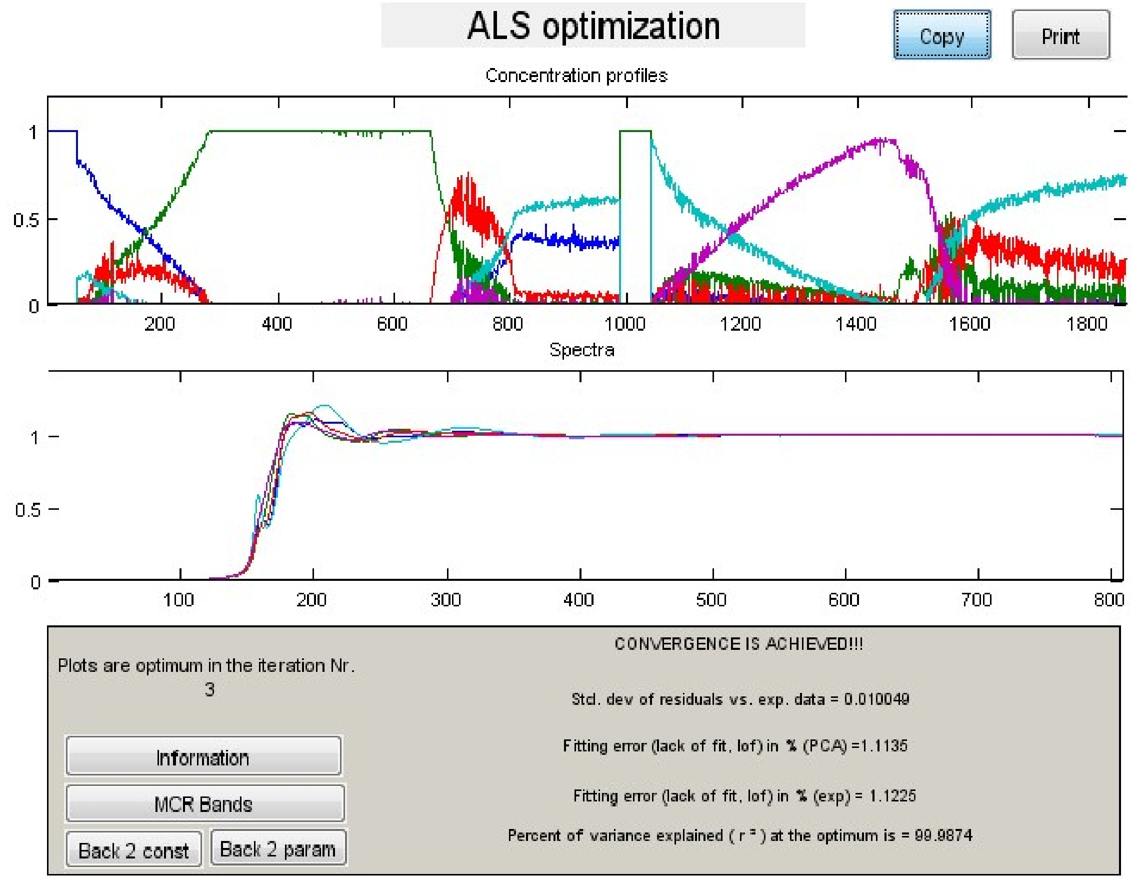


Figure S5: Scree plot representation used to determine the number of components to be retained for the description of the variance associated to the XAS data set matrix associated to the concatenation of spectra recorded at the Mo K-edge for sulfidation and regeneration of the ZnO-MoO_3 mixture and of the $ZnMoO_4$ mixed oxide.

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



```
CONVERGENCE IS ACHIEVED!!!

Plots are optimum in the iteration Nr.
3

Std. dev of residuals vs. exp. data = 0.010049

Fitting error (lack of fit, lof) in % (PCA) =1.1135

Fitting error (lack of fit, lof) in % (exp) = 1.1225

Percent of variance explained ( r ² ) at the optimum is = 99.9874
```

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-MoO_3 mixture (data from 1 to 988) and of the $ZnMoO_4$ 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.

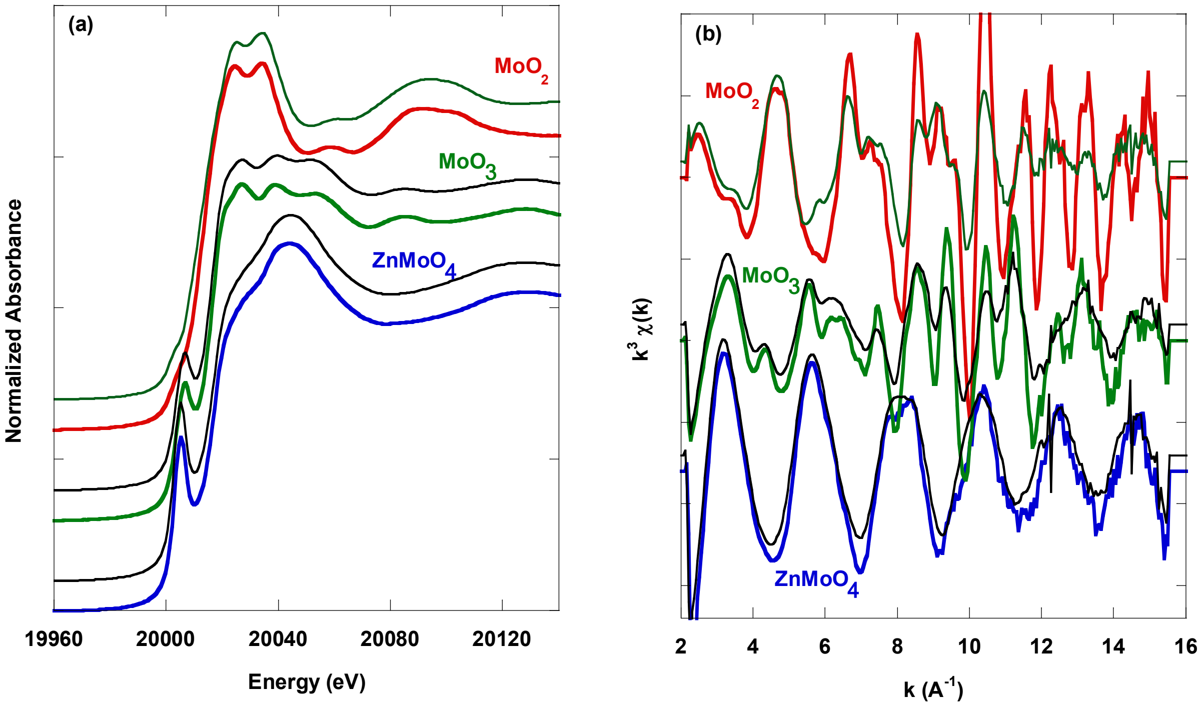
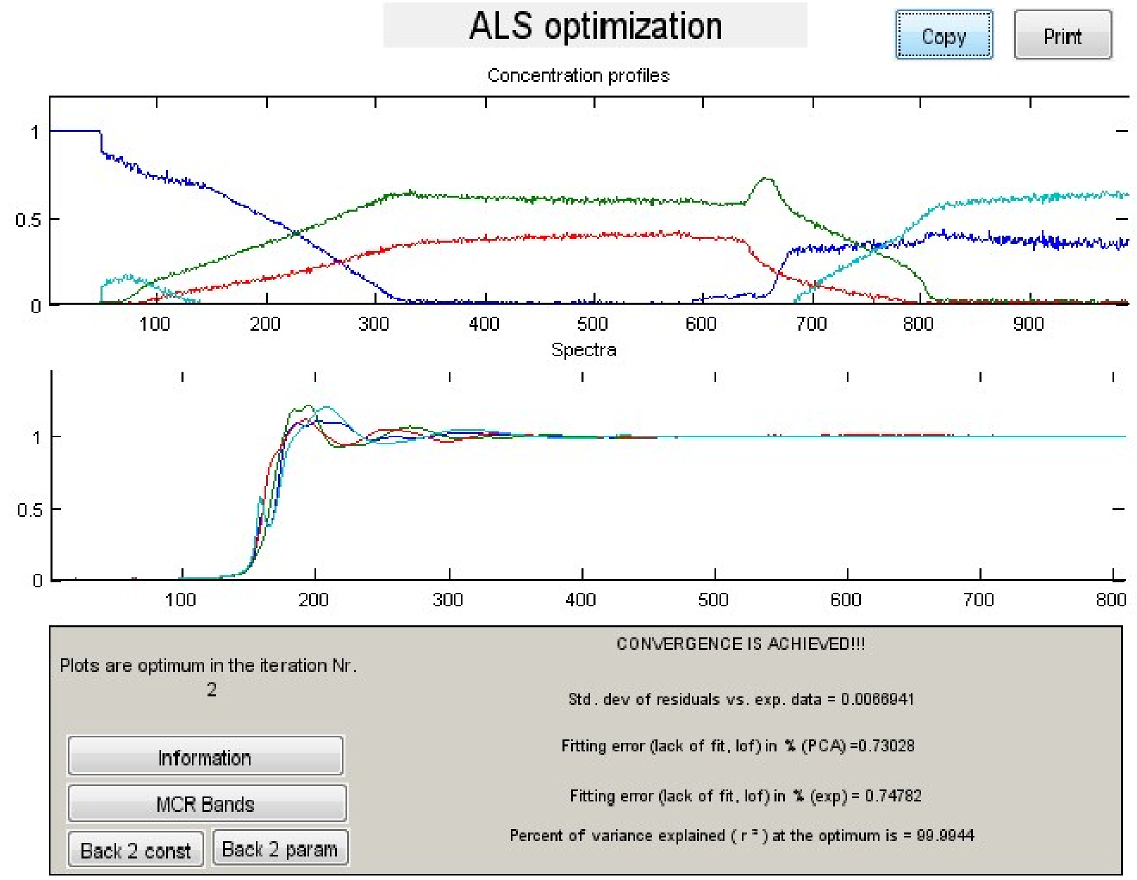
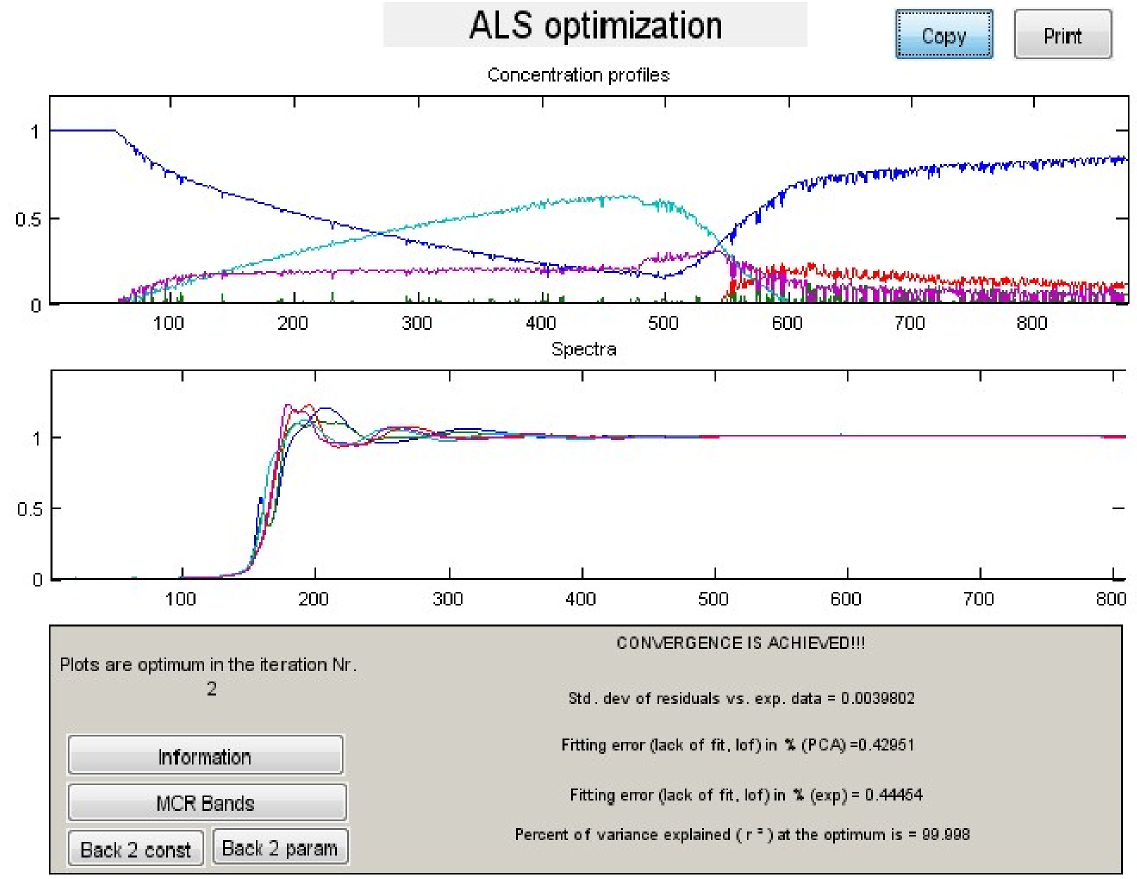


Figure S7: Comparison of the MCR-ALS spectra (black curves) with the Mo K-edge spectra (colored curves) of crystalline references MoO_2, MoO_3 and $ZnMoO_4$; (a) XANES spectra and (b) EXAFS spectra.



```
Plots are optimum in the iteration Nr.
2
CONVERGENCE IS ACHIEVED!!!
Std. dev of residuals vs. exp. data = 0.0066941
Fitting error (lack of fit, lof) in % (PCA) =0.73028
Fitting error (lack of fit, lof) in % (exp) = 0.74782
Percent of variance explained ( r ² ) at the optimum is = 99.9944
```

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-MoO_3 oxide mixture.



```
Plots are optimum in the iteration Nr.
2
CONVERGENCE IS ACHIEVED!!!
Std. dev of residuals vs. exp. data = 0.0039802
Fitting error (lack of fit, lof) in % (PCA) =0.42951
Fitting error (lack of fit, lof) in % (exp) = 0.44454
Percent of variance explained ( r ² ) at the optimum is = 99.998
```

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 $ZnMoO_4$ mixed oxide.

Supplementary References

1. Carvalho, H. W. P., Pulcinelli, S. H.; Santilli, C. V.; Leroux, F.; Meneau, F.; Briois, V. XAS/WAXS Time-Resolved Phase Speciation of Chlorine LDH Thermal Transformation: Emerging Roles of Isovalent Metal Substitution. *Chem. Mater.* ***2013**, 25, 2855–2867.*
2. Cassinelli, W. H.; Martins, L.; Passos, A. R.; Pulcinelli, S. H.; Santilli, C. V.; Rochet, A.; Briois, V. Multivariate curve resolution analysis applied to time-resolved synchrotron X-ray Absorption Spectroscopy monitoring of the activation of copper alumina catalyst. *Catal. Today* **2014**, *229*, 114–122..
3. Voronov, A.; Urakawa, A.; Van Beek, W.; Tsakoumis, N. E.; Emerich, H.; Rønning, M. Multivariate curve resolution applied to in situ X-ray absorption spectroscopy data: An efficient tool for data processing and analysis. *Anal. Chim. Acta* **2014**, 840, 20–27.
4. Hong, J.; Marceau, E.; Khodakov, A. Y.; Gaberová, L.; Griboval-Constant, A.; Girardon, J.-S.; Fontaine, C. L.; Briois, V. Speciation of Ruthenium as a Reduction Promoter of Silica-Supported Co Catalysts: A Time-Resolved in Situ XAS Investigation. *ACS Catal.* **2015**, 5, 1273-1282.
5. Rochet, A.; Baubet, B.; Moizan, V.; Pichon, C.; Briois, V. Co-K and Mo-K edges Quick-XAS study of the sulphidation properties of Mo/Al_2O_3 and CoMo/Al_2O_3 catalysts. *Comptes Rendus Chim.* **2016**, 19, 1337–1351.
6. Rochet, A.; Ribeiro-Passos, A.; Legens, C.; Briois, V. Sulphidation study of a dried Ni/Al_2O_3 catalyst by time-resolved XAS-MS combined with *in situ* Raman spectroscopy and multivariate Quick-XAS data analysis. *Catal. Struct. Reactivity*, **2017**, 3, 33-42.
7. Rochet, A.; Baubet, B.; Moizan, V.; Devers, E.; Hugon, A.; Pichon, C.; Payen, E.; Briois, V. Influence of the Preparation Conditions of Oxidic NiMo/Al_2O_3 Catalysts on the Sulfidation Ability: A Quick-XAS and Raman Spectroscopic Study. *J. Phys. Chem. C* **2017**, *121, 18544-18556.*
8. Santos, R. M. M.; Tronto, J.; Briois, V.; Santilli, C. V. Thermal decomposition and recovery properties of ZnAl–CO_3 layered double hydroxide for anionic dye adsorption: insight into the aggregative nucleation and growth mechanism of the LDH memory effect. *J. Mater. Chem. A* **2017***, 5,* 9998-10009.
9. Passos, A. R.; Martins, L.; Pulcinelli, S. H., Santilli, C. V.; Briois, V., Correlation of sol-gel alumina supported Co catalyst processing to cobalt speciation, ethanol steam reforming activity and stability*, ChemCatChem*, **2017**, *9*, 3918–3929.
10. Martini, A.; Borfecchia, E.; Lomachenko, K. A., Pankin, I. A.; Negri, C.; Berlier, G.; Beato, P. Falsig, H.;Bordiga, S.; Lamberti, C., Composition-driven Cu speciation and reducibility in Cu-CHA zolite catalysts: a multivariate XAS/FTIR approach to complexity, *Chem Sci.*, **2017**, *8*, 6836-6851.
11. de Juan, A.Jaumot, J.; Tauler, R. Multivariate Curve Resolution (MCR). Solving the mixture analysis problem. *Anal. Methods* **2014**, *6*, 4964-4976.
12. Jaumot, J.; de Juan, A.; Tauler, R. MCR-ALS GUI 2.0: New features and applications *Chemom. Intel. Lab. Syst.* **2015**, 140, 1-12.
13. Keller, H. R.; Massart, D. L. Evolving factor analysis, *Chemom. Intel. Lab. Syst.* **1992**, 12, 209-224.
14. Windig, W.;. Guilment, J. Interactive self-modeling mixture analysis. *Anal. Chem.* **1991**, 63, 1425-1432.
15. Girard, V.; Chiche, D.; Baudot, A.; Bazer-Bachi, D.; Clémençon, I.; Moreau, F.; Geantet, C.; Innovative low temperature regenerable zinc based mixed oxide sorbents for synthesis gas desulfurization, *Fuel* **2015**, 140, 453–461.