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Supporting Information

Thermal decomposition and recovery properties of ZnAl-CO₃ layered double hydroxide for anionic dye adsorption: Insight of the aggregative nucleation and growth mechanism of LDH memory effect.

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Multivariate Curve Resolution with Alternating Least Square fitting (MCR-ALS)

Several recent works have proven the efficiency and power of the MCR-ALS procedure (Multivariate Curve Resolution - Alternating Least Squares) in the qualitative and quantitative investigation of time-resolved evolving XAS data recorded during solid-state reactions.¹⁻⁵ This statistical approach allows one to extract the components whose sum constitute the experimental spectra without introducing biases, such as resorting to hypotheses on the species involved during the reaction or using reference spectra that may not be appropriate.⁶

A series of normalized XAS experimental spectra D, recorded upon reaction whose relative concentrations vary with time, temperature... 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 (constant along the series) 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, the matrix of concentrations C (unimodality) 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 pure components describing the matrix D to provide an initial guess either of the concentration matrix or of the component spectra

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Singular Value Decomposition (SVD) method which describes D into orthogonal vectors is first used for the rank analysis of the C and S^{T} matrices. A Scree plot, which displays the eigenvalues determined by SVD for each component arranged in descending order as a function of number of spectra in D, can be used for the estimation of the number of chemical components to include in the MCR-ALS minimization. The number of components to be retained using such Scree plot (Fig. S1) are those in the steep curve before the first point that starts the asymptotic line trend. Herein SVD analysis indicates that the variance of the D XAS experimental matrix recorded upon thermal decomposition of the pristine LDH is described considering only 3 components whereas only 2 components are necessary for explaining the variance of the XAS data recorded upon recovery of the Calc-LDH in contact with aqueous or dye solutions. A detailed description of the SVD and MCR-ALS methods applied to XAS data can be found in references.^{2, 5}



Fig. S1 Scree plot for determination of components to be retained in (a) LDH thermal decomposition and (b) LDH recovery in presence of dye.

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.⁷ An initial guess of the spectra in the ALS minimization was done using the SIMPLISMA (SIMPLe to use Interactive Self-modeling Mixture Analysis) method.⁸ Fig. S2 displays the results of the minimization obtained for the thermal decomposition of the pristine LDH and for the recovery of the Calc-LDH in presence of dye. For the latter data set resolution (Fig. S2b), an additional constraint has been added with the addition of RT spectra of pristine LDH to the data set recorded during LDH recovery. This explains why the data with spectrum number higher than 2022 correspond to 100% of the component associated to the pristine LDH.



Fig. S2 Results of the minimization obtained for: (a) the thermal decomposition of pristine LDH and (b) LDH recovery in presence of AB dye solution.

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Fig. S3 Characteristic Zn K edge Quick-XANES spectra recorded at different temperatures during the LDH thermal decomposition. The spectra of nano-ZnO and nano-ZnAl₂O₄ are also presented for comparison purpose.



Fig. S4 Comparison of the EXAFS spectra measured at RT and corresponding FT of the Calc. LDH with the ones of a crystalline ZnO reference.

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Fig. S5 Evolution of FT of the Zn K edge EXAFS signals measured *in situ* during the LDH recovery at room temperature (\approx 25 °C) after: (a)water and (b) 1000 mg·L⁻¹ AB dye solution addition on the Calc-LDH.



Fig. S6 Percentages of Zn based species determined by MCR-ALS analysis of the Quick-XAS recorded at room temperature (≈25°C) during recovery of LDH phase after addition of water and AB dye solution to Calc-LDH.



Fig. S7 Van't Hoff plot.



Fig. S8 Recyclability of the adsorbent Calc-LDH after AB adsorption.

_values. $E_0 = 9663 \text{ eV}$ and $S_0^2 = 0.87$						
Sample	Ν	R (Å)	σ² (Ų)	ΔE_0 (eV)	R _f (%)	
Bulk ZnO	<i>4</i> O	1.96 ± 0.03	0.0044 ± 0.0021	0 72 + 3 9	1 0	

Bulk ZnO	4 O 12 Zn	1.96 ± 0.03 3.23 ± 0.03	0.0044 ± 0.0021 0.0094 ± 0.0011	0.72 ± 3.9	1.9
Pristine LDH	6.2 O ± 0.6 4.1 Zn ± 0.3 1.9 Al	2.05 ± 0.01 3.11 ± 0.01 3.09 ± 0.04	0.0100 ± 0.0012 0.01054 ± 0.0010 0.01164± 0.0077	-0.77 ± 2.3	0.9
Calc_Zn	3.9 O ± 0.5 12.1 Zn ± 0.8	1.96 ± 0.01 3.24 ± 0.01	0.0056 ± 0.0012 0.0182 ± 0.0025	1.00 ± 1.2	0.5

Table S1 Best fitted EXAFS parameters of the LDH and Calc-LDH samples measured at RT. Italic parameters are fixed values. $E_0 = 9663 \text{ eV}$ and $S_0^2 = 0.87$

 Table S2 Pseudo-second order kinetic model fitted parameters, and correlation coefficients for AB dye adsorption on LDH and Calc-LDH at 25 °C.

Pseudo-second order model						
Adsorbent	k _{2,1} (g∙mg ⁻¹ ∙h ⁻¹)	k _{2,2} (g∙mg ⁻¹ ∙h ⁻¹)	q _{e1} (mg·g⁻¹)	q _{e2} (mg·g⁻¹)	R_1^2	R_2^2
LDH	$1.3 \cdot 10^{-2} \pm 9.9 \cdot 10^{-4}$	-	278.5 ± 3.340	-	0.997	-
Calc-LDH	$1.8 \cdot 10^{-2} \pm 4.5 \cdot 10^{-3}$	1.9·10 ⁻³ ± 9.2·10 ⁻⁵	1177±11.02	1351±5.334	0.994	0.989

Table S3 Langmuir isotherm model fitted parameters, q_{max} and k_L , and correlation coefficients, R_L^2 , for AB dyeadsorption on LDH and Calc-LDH at different temperatures.

Adsorbent	Т. (°С)	q _{max} (mg⋅g⁻¹)	k _L 10 ⁻³ (L∙mg ⁻¹)	RL ² *
LDH	25	261.8	39	0.998
Calc-LDH	25	1587	5.8	0.997
Calc-LDH	30	1615	7.3	0.998
Calc-LDH	35	1677	7.9	0.999
Calc-LDH	40	1693	9.8	0.999

Supplementary References

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