Electronic Supplementary Information

Thermal stability of PMMA-LDH nanocomposites: Decoupling the physical barrier, radical trapping, and charring contributions using XAS/WAXS/Raman time-resolved experiments

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Sample	LDH nominal composition (M")(M"")	Calculated anionic exchange capacity (mEq/100g)	Basal distance (Å)		
			LDH-	LDH-	PMMA-
			Cl	DS	LDH
ZA	(Zn _{2.0})(Al)	301	7.61	26.35	27.78
ZCA	(ZnCu)(Al)	303	7.66	26.35	29.12
ZAF	(Zn _{2.0})(Al _{0.75} Fe _{0.25})	295	7.73	25.96	26.96
ZCAF	(ZnCu)(Al _{0.5} Fe _{0.5})	291	7.65	24.52	28.57

 Table S1. Basal distances measured by WAXS for LDH-Cl, LDH-DS, and PMMA-LDH.

MCR-ALS analysis of the data for the nanocomposites

In several recent studies, multivariate analysis based on the MCR-ALS method (multivariate curve resolution with alternating least squares) has been used for the qualitative and quantitative interpretation of time-resolved XAS data recorded during solid-state reactions.¹⁻⁸ The purpose of this chemometric approach is to extract the spectra of components whose sum constitutes the experimental spectra and to determine the concentrations of each of these components in the mixture.⁹

The set of normalized XAS experimental spectra recorded during thermal decomposition of the nanocomposites was defined as a matrix **D** resulting from the combination of three matrices: **C** (concentrations of the pure components); S (normalized XAS spectra of the pure components); and E (experimental uncertainties). This could be described by the following equation: $D = C S^T + E$, where S^{τ} is the transposed matrix of **S**. The basis of the MCR-ALS technique is the mathematical determination of a likely set of concentrations C (varying along the series) and spectra S that can explain the whole set of **D**, by iteration and least-squares minimization of the **E** matrix. For this purpose, physically and chemically meaningful constraints on the *C* and *S* matrices are used in order to assist convergence of the multivariate curve resolution. In the present work, for all the samples investigated, the concentrations matrix \boldsymbol{c} contained only positive values, with each species being described by a single maximum in its concentration profile (unimodality) and the sum of the species concentrations being equal to 100% at any time of the reaction (closure relation). Additionally, the S matrix contained 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**, in order to provide an initial estimate of either the concentration matrix or the component spectra matrix.

The number of components involved in a given XAS data point obtained during thermal decomposition, recorded at a specified K-edge of an element of interest belonging to the LDH structure, was determined using the singular value decomposition (SVD) method. Scree plots, displaying the eigenvalues determined by SVD for each component, arranged in descending order as a function of the number of spectra in **D**, or scores plots for each component, as a function of the spectrum number, were used for estimation of the number of chemical components to include in the MCR-ALS minimization. An example of this type of SVD-derived plot is shown in Figure S0. In the scree plot analyses (Figure SO(a)), the numbers of components to be retained considered those in the steep section of the curve, before the first point that started the asymptotic line trend. The results of the SVD analysis shown in Figure S0, which concerns the XAS data recorded at the Cu Kedge for the thermal decomposition of PMMA-ZCA, indicated that the variance of the experimental XAS data, D, could be described considering 5 components. In the case of the scores plots for the components, as a function of the reaction coordinates (here, this was the increase of temperature), smooth trajectories (without noise) were expected. In the case of the thermal decomposition of PMMA-ZA, monitored at the Zn K-edge, smooth trajectories were obtained for the first three components (Figure S0(b)). Detailed descriptions of the SVD and MCR-ALS methods applied to XAS data can be found in earlier publications.^{2, 5, 7-8}

The MCR-ALS minimization of the Quick-XAS data presented here was carried out using the MCR-ALS GUI 2.0 software developed by Roma Tauler and his group, on the Matlab[®] platform.¹⁰ An initial estimate of the spectra used in the ALS minimization was performed using the SIMPLISMA (SIMPLe to use Interactive Self-modeling Mixture Analysis) method.¹¹



(b)



Figure S0. (a) Scree plot representation used to determine the number of components to be retained for description of the variance associated with the XAS data set recorded at the Cu K-edge during the thermal decomposition of PMMA-ZCA. (b) Scores plot representation used to determine the number of components to be retained for description of the variance associated with the XAS data set recorded at the Zn K-edge during the thermal decomposition of PMMA-ZA.

(a)



Figure S1. TG curves of pristine LDH-DS obtained under an air atmosphere.



Figure S2. DSC measurements under N_2 for the different PMMA-LDH nanocomposites.



Figure S3. Time-resolved WAXS patterns recorded for the PMMA-ZA (a), PMMA-ZAF (b), and PMMA-ZAF (c) nanocomposites.



Figure S4. (a) Experimental XANES spectra of the common intermediate Zn-based SPN species observed at ~355-365 °C during thermal decomposition of the PMMA nanocomposites, before the formation of ZnO and $ZnAl_2O_4$ species, and (b) fitting of the EXAFS spectrum of the SPN species isolated by MCR-ALS, in q space and in R space, for the decomposition of PMMA-ZA. The results obtained for the SPN species are summarized as follows:

Nanocomposite from which the SPN species were isolated	Atom	N	R (Å)	σ² (10 ⁻³ Ų)	ΔE ₀ (eV)	ρ (%)
PMMA-ZA	0	4.1±0.4	1.96±0.01	9.8±1.4	-0.5±1.3	0.03
PMMA-ZCA	0	4.1±0.3	1.95±0.01	9.4±1.3	-0.7±1.2	0.05
PMMA-ZAF	0	3.7±0.5	1.95±0.01	9.0±1.7	-1.1±1.7	0.05
PMMA-ZCAF	0	4.2±0.3	1.94±0.01	10.3±1.0	-1.1±0.9	0.08

 S_0^2 = 0.93 determined from a crystalline ZnO reference.



Figure S5. (a) Experimental XANES spectra measured at 450 °C for the different nanocomposites, and (b) Zn K-edge XANES spectra of the third species determined by MCR-ALS for the different PMMA nanocomposites, compared to spectra for nano-ZnAl₂O₄, nano-ZnO species, and ZnFe₂O₄. As reported previously,¹ the final component determined by MCR-ALS was a mixture of nano-ZnAl₂O₄ and nano-ZnO species, together with $ZnFe_2O_4$ when iron was present in the composition of the LDH (see Figure S10). Comparison between the spectra for nano-ZnO and the third MCR-ALS species extracted for the decomposition of PMMA-ZAF clearly evidenced that this species was mainly composed of nano-ZnO, while those determined for the other nanocomposites were mainly composed of spinel-like species, $ZnAl_2O_4$, and $ZnFe_2O_4$ (if present).



Figure S6. Zn K-edge Quick-EXAFS spectra recorded for the PMMA-ZA (a), PMMA-ZAF (b), and PMMA-ZCAF (c) nanocomposites during thermal decomposition.



Figure S7. Cu K-edge Quick-EXAFS spectra recorded for the PMMA-ZCA-0.14 (a) and PMMA-ZCAF (b) nanocomposites during thermal decomposition.



Figure S8. Fe K-edge Quick-EXAFS spectra recorded for the PMMA-ZCAF nanocomposite during thermal decomposition.





Figure S9. (a) Fe K-edge XANES spectra of the pure species determined by MCR-ALS during the thermal decomposition of PMMA-ZAF (top) and PMMA-ZCAF (bottom). Three species were involved during thermal decomposition of PMMA-LDH: the pristine LDH phase, an intermediate species with a rising edge position shifted by -2.6 eV compared to the LDH phase for PMMA-ZAF and by -3.4 eV for PMMA-ZCAF, and a third species identified as an iron(III) oxide, as detailed below.

(b) Comparison of the Fe K-edge experimental XANES spectra recorded at RT after thermal decomposition of PMMA-ZAF and PMMA-ZCAF with the XANES spectra of $ZnFe_2O_4$ and γ -Fe₂O₃ references. The experimental XANES spectra for the decomposed nanocomposites were very similar to that for $ZnFe_2O_4$. In fact, linear combination fittings of the spectra for the decomposed nanocomposites resulted in the following composition: $13.5 \pm 1.5\%$ of γ -Fe₂O₃ and $86.5 \pm 1.5\%$ of $ZnFe_2O_4$.

(c) Comparison of the Fe K-edge experimental EXAFS spectra recorded at RT after thermal decomposition of PMMA-ZAF and PMMA-ZCAF with the EXAFS spectra of $ZnFe_2O_4$ and γ -Fe₂O₃ references.

(d) Corresponding Fourier transforms of the EXAFS signals. From comparison of the spectra for the samples and the references, it could be concluded that the Fe-based phase formed after thermal decomposition was mainly composed of $ZnFe_2O_4$.



Figure S10. Fitting of the EXAFS spectra, in k space, of the first (left) and second (right) species isolated by MCR-ALS for the thermal decomposition of PMMA-ZAF. The structural parameters obtained from the EXAFS simulations for the two species are summarized as follows:

Fit of species	Atom	Ν	R (Å)	σ² (10 ⁻³ Ų)	ΔE_0 (eV)	ρ (%)
PMMA-ZAF MCR1	0	6	2.01 ± 0.01	8.5 ± 0.9	1.3 ± 1.4	0.3
	Zn	6	3.07 ± 0.02	16 ± 2.1		
PMMA-ZAF MCR2	0	6	2.00 ± 0.02	16 ± 1.7	0.6 ± 2.4	0.7
	Zn	5.3 ± 1.1	3.00 ± 0.03	17 ± 2.7		

 S_0^2 = 0.72 determined from the fit of PMMA-ZAF MCR1.



Figure S11. Cu K-edge XANES spectra of the copper species determined by MCR-ALS analysis of the data acquired during the thermal decomposition of PMMA-ZCAF. Comparison with bulk crystalline reference Cu₂O, Cu(O), and Cu₂S, and with the solid resulting from the thermal decomposition at 450 °C of a ZnCuAl LDH with SO₄²⁻ anions in the interlayer galleries.

Supplementary References

- 1. H. W. P. Carvalho, S. H. Pulcinelli, C. V. Santilli, F. Leroux, F. Meneau, V. Briois. *Chem. Mater.* 2013, **25**, 2855.
- W. H. Cassinelli, L. Martins, A. R. Passos, S. H. Pulcinelli, C. V. Santilli, A. Rochet, V. Briois. *Catal. Today* 2014, 229, 114.
- 3. A. Voronov, A. Urakawa, W. Van Beek, N. E. Tsakoumis, H. Emerich. *Anal. Chim. Acta* 2014, **840**, 20.
- 4. J. Hong, E. Marceau, A. Y. Khodakov, L. Gaberová, A. Griboval-Constant, J.-S. Girardon, C. L. Fontaine, V. Briois. *ACS Catal.* 2015, **5**, 1273.
- 5. A. Rochet, B. Baubet, V. Moizan, C. Pichon, V. Briois. *Comptes Rendus Chim.* 2016, 19, 1337.
- 6. A. Rochet, A. R. Passos, C. Legens, V. Briois. Catal. Struct. Reactivity, 2017, 3, 33.
- 7. A. Rochet, B. Baubet, V. Moizan, E. Devers, A. Hugon, C. Pichon, E. Payen, V. Briois. J. Phys. Chem. C 2017, 121, 18544.
- 8. R. M. M. Santos, J. Tronto, V. Briois, C. V. Santilli. J. Mater. Chem. A 2017, 5, 9998.
- 9. A. de Juan, J. Jaumot, R. Tauler. Anal. Methods 2014, 6, 4964.
- 10. J. Jaumot, A. de Juan, R. Tauler. Chemom. Intel. Lab. Syst. 2015, 140, 1.
- 11. W. Windig, J. Guilment. Anal. Chem. 1991, 63, 1425.