

Electronic Supplementary Information (ESI)

Cobalt-based Layered Double Hydroxides Revisited: evidence for an oxidizing radical generation

Rafael dos Santos Macedo,^{a#} Rodrigo Boni Fazzi,^a Ana Maria da Costa Ferreira,^a and Vera Regina Leopoldo Constantino^{a*}

^a Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo-USP, Av. Prof. Lineu Prestes 748, CEP 05508-000, São Paulo - SP, Brazil. E-mail: vrlconst@iq.usp.br

Current address: Departamento de Engenharia de Minas e de Petróleo, Escola Politécnica da Universidade de São Paulo- USP, Av. Prof. Mello Moraes 2373, CEP 05508-030, São Paulo – SP, Brazil. E-mail: rafaelmacedo@usp.br

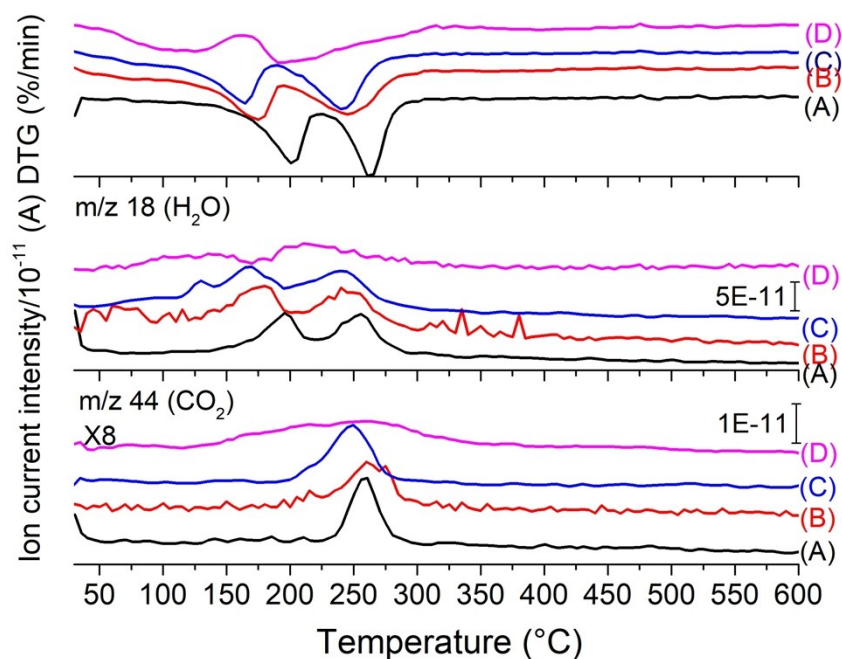


Fig. 1S DTG (superior) and MS (inferior) curves of $\text{Co}_R\text{Al-CO}_3$ materials: (A) $\text{Co}_2\text{Al-CO}_3$, (B) $\text{Co}_3\text{Al-CO}_3$, (C) $\text{Co}_4\text{Al-CO}_3$, and (D) $\text{Co}_5\text{Al-CO}_3$.

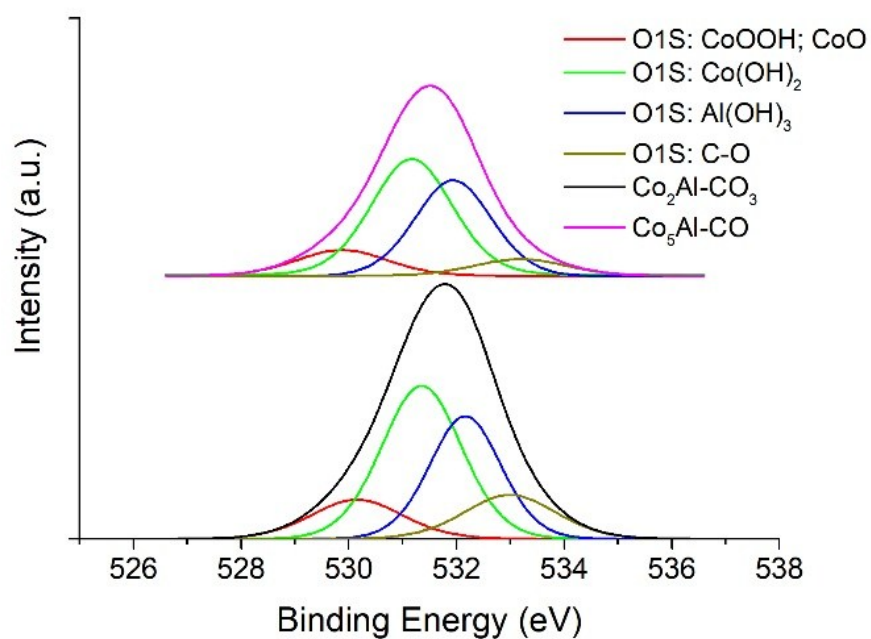


Fig. 2S High-resolution XPS O1S of $\text{Co}_2\text{Al-CO}_3$ and $\text{Co}_5\text{Al-CO}_3$ materials.

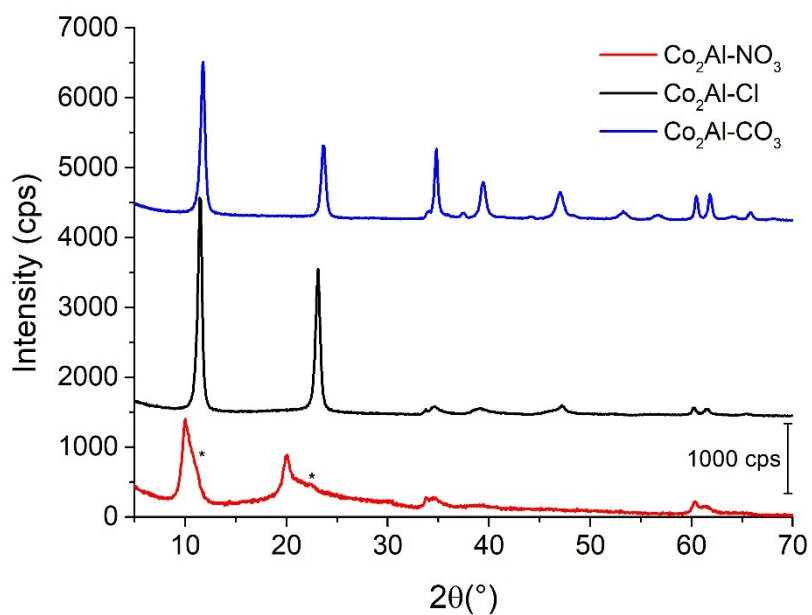


Fig. 3S XRD patterns of cobalt-based LDH. (*) carbonate phase.

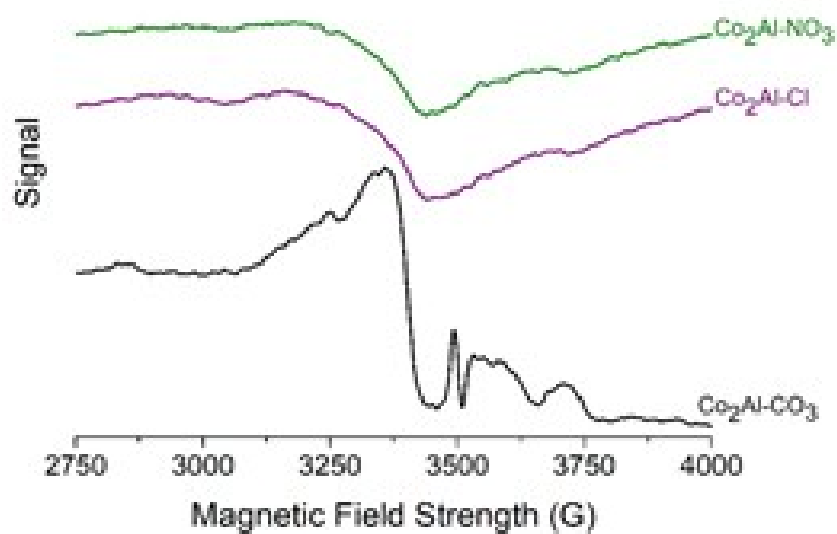


Fig. 4S EPR spectra of $\text{Co}_2\text{Al-CO}_3$ (black line), $\text{Co}_2\text{Al-Cl}$ (purple line) and $\text{Co}_2\text{Al-NO}_3$ (green line).

Table 1S Metal analysis (ICP OES) of nitrate and chloride cobalt-based LDH materials.

LDH samples	Molar ratio (Co/Al)
$\text{Co}_2\text{Al-NO}_3$	2.10 ± 0.00
$\text{Co}_2\text{Al-Cl}$	2.21 ± 0.02

Table 2S Reduction potential for some oxygen, carbon and cobalt species.

Reaction condition	Reaction	Potential (V x SHE)	Ref.
pH = 0	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229	1
	$O_2 + H^+ + e^- \rightarrow HO_2^-$	-0.105	1
	$\bullet OH + H^+ + e^- \rightarrow H_2O$	2.85	1
	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.695	1
	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.776	1
	$H_2O_2 + H^+ + e^- \rightarrow H_2O + \bullet OH$	0.71	1
	$Co^{3+} + e^- \rightarrow Co^{2+}$	1.92	1
pH = 7	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	0.815	2
	$O_2 + e^- \rightarrow O_2^{\bullet -}$	-0.16	2
	$O_2^{\bullet -} + 2H^+ + e^- \rightarrow H_2O_2$	0.89	2
	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.28	2
	$H_2O_2 + H^+ + e^- \rightarrow H_2O + \bullet OH$	0.38	2
	$\bullet OH + H^+ + e^- \rightarrow H_2O$	2.32	2
	$H_2O_2 + 2e^- \rightarrow 2OH^-$	1.349	2
	$CO_3^{\bullet -} + e^- \rightarrow CO_3^{2-}$	1.57	3
pH = 14	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.401	1
	$O_2 + e^- \rightarrow O_2^{\bullet -}$	-0.563	1
	$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	-0.076	1
	$HO_2^- + H_2O + e^- \rightarrow \bullet OH + 2OH^-$	-0.245	1
	$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$	0.878	1
	$\bullet OH + e^- \rightarrow OH^-$	2.02	1
	$Co(OH)_3 + e^- \rightarrow Co(OH)_2 + OH^-$	0.17	1

References

- 1 W. M. Haynes, D. R. Lide and T. J. Bruno, CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, 97th ed., 2017.
- 2 P. M. Wood, *Biochem. J.*, 1988, **253**, 287-289.
- 3 D.A. Armstrong, R.E. Huie, W.H. Koppenol, S.V. Lymar, G. Merényi, P. Neta, B. Ruscic, D. M. Stanbury, S. Steenken and P Wardman, *Pure Appl. Chem.*, 2015, **87**, 1139–1150.