Supplementary information

Optimizing Citrate Combustion Synthesis of A-Site-Deficient La,Mn-Based Perovskites: Application for Catalytic CH_4 Combustion in Stoichiometric Conditions

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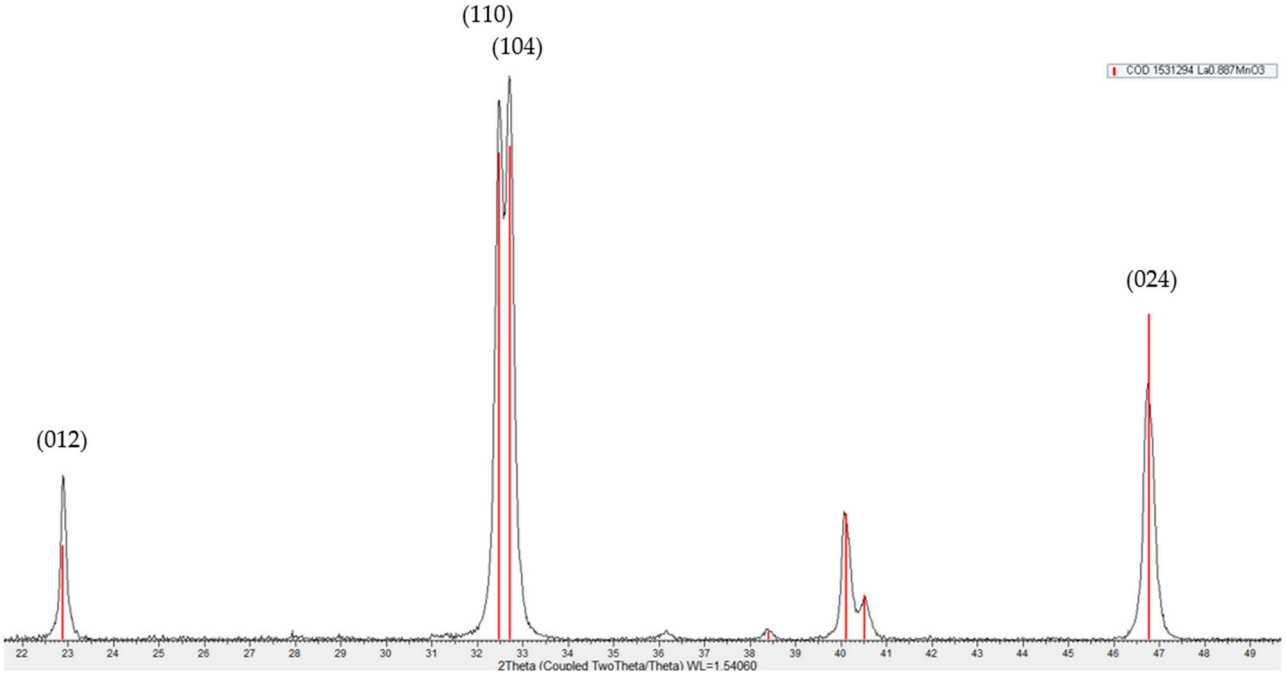

Figure S1. Extract of the XRD pattern of $La_{0.8}MnO_3$-NH_3-CA1.1 sample as example, showing the good matching with hexagonal $La_{0.887}MnO_3$ phase (COD reference 1531294). The reported (hkl) indexes are relative to the reflections fitted to obtain crystallite size by Williamson-Hall method, according to Equation S1:

$$\beta \cos\theta = \frac{K\lambda}{d} + 4\varepsilon \sin\theta \qquad \text{(S1)}$$

where β is the full width at half maximum of each reflection (obtained by gaussian fitting), θ is the reflection angle (radians), K a constant assumed 0.90, λ the irradiation wavelength (0.154 nm, Cu Kα), d the average crystallite size (nm) and ε the crystal strain. By linear fitting of $\beta \cos\theta$ as function of $4\varepsilon \sin\theta$, the crystallite size d is obtained from the intercept and the strain ε from the slope.

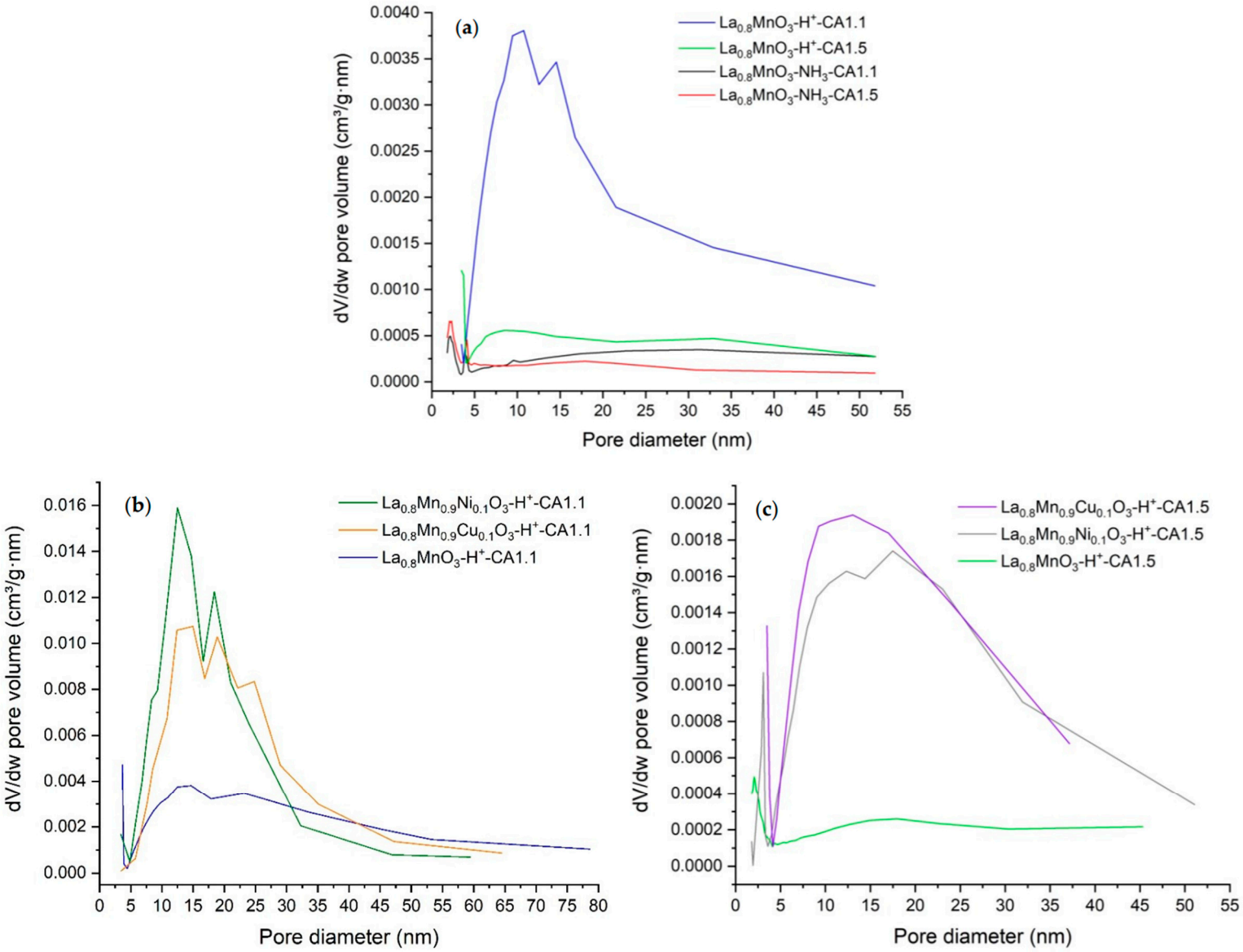

Figure S2. Pore size distribution of the prepared catalysts, according to BJH model, obtained from the desorption branch of N_2 isotherms: (**a**) the four $La_{0.8}MnO_3$ samples, (**b**) Ni- and Cu-doped samples with CA1.1, compared to $La_{0.8}MnO_3$-H^+-CA1.1, (**c**) Ni- and Cu-doped samples with CA1.5, compared to $La_{0.8}MnO_3$-H^+-CA1.5.

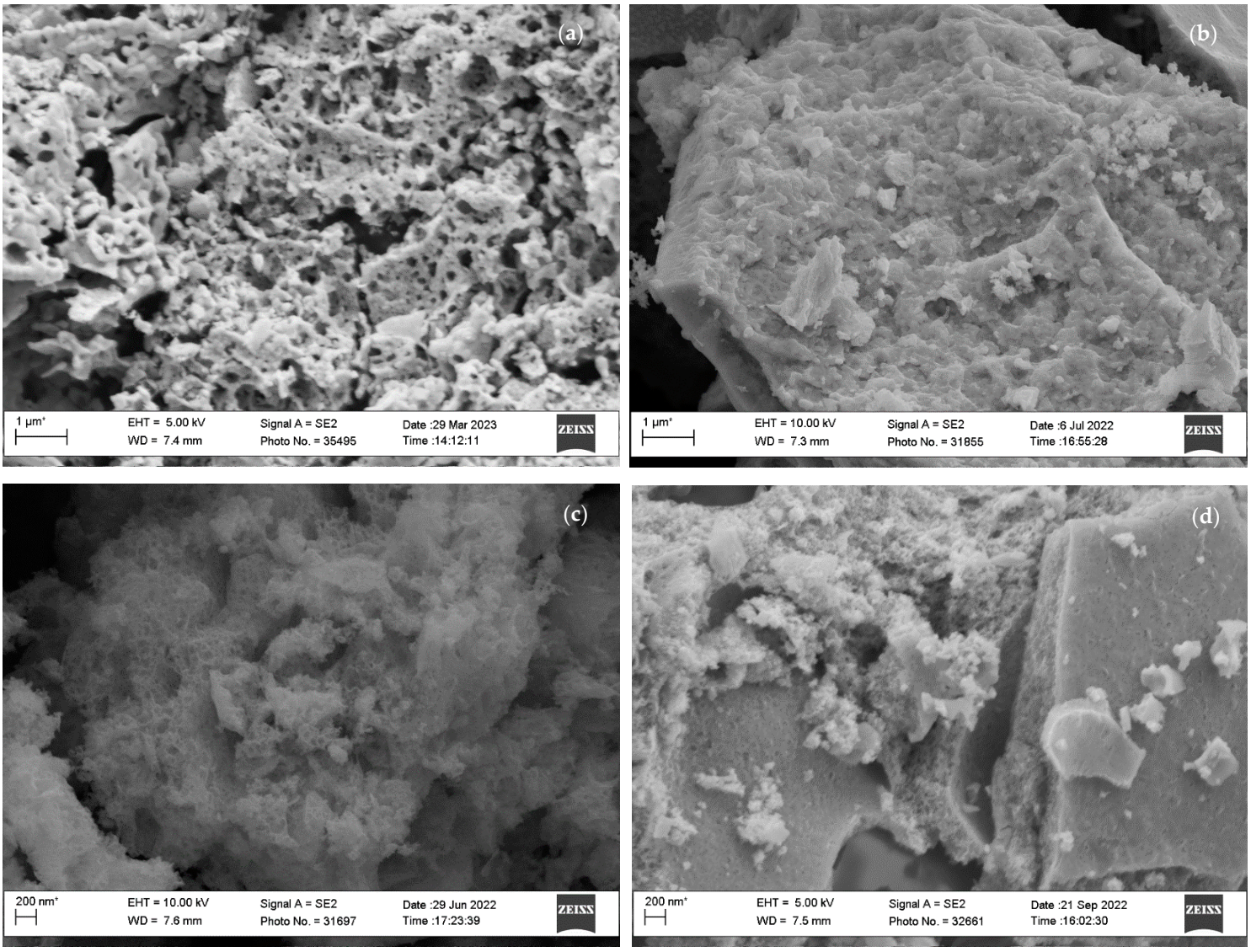

Figure S3. SEM micrographs of: (**a**) $La_{0.8}MnO_3$-NH_3-CA1.5; (**b**) $La_{0.8}MnO_3$-H^+-CA1.5; (**c**) $La_{0.8}Mn_{0.9}Cu_{0.1}O_3$-$H^+$-CA1.1; (**d**) $La_{0.8}Mn_{0.9}Cu_{0.1}O_3$-$H^+$-CA1.5. Images (**a**,**b**) are taken at 25000× magnification, images (**c**,**d**) at 50000× magnification.

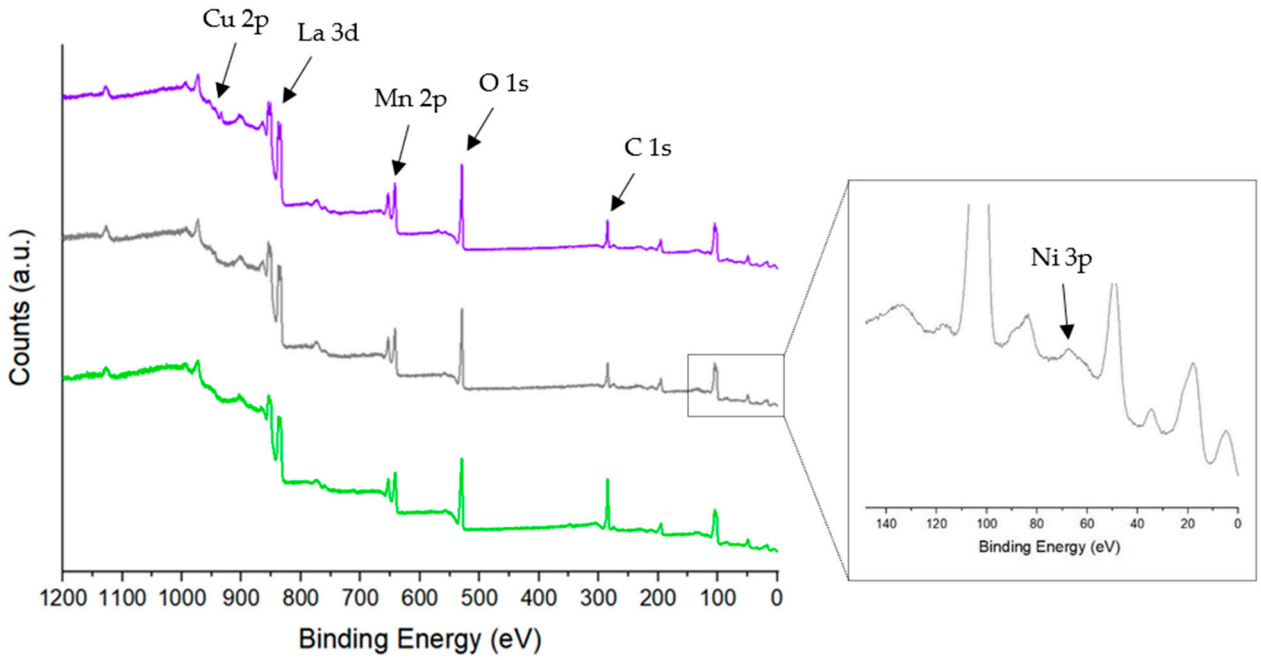

Figure S4. Representative XPS survey spectra of H^+-CA1.5 samples and identification of the main photopeaks: $La_{0.8}MnO_3$ (green); $La_{0.8}Mn_{0.9}Ni_{0.1}O_3$ (grey), with zoom on the low binding energy region to highlight Ni3p photopeak; $La_{0.8}Mn_{0.9}Cu_{0.1}O_3$ (violet).

Table S1. EDX and XPS composition of the prepared perovskites, also considering the oxygen content (nominal amounts according to stoichiometry are reported in brackets).

Sample		O (at%)	La (at%)	Mn (at%)	Ni or Cu (at%)
$La_{0.8}MnO_3$-NH_3-CA1.1	EDX	64.6	17.0	18.4	/
	XPS	72.9	12.2	14.9	/
	(nominal)	(62.5)	(16.7)	(20.8)	/
$La_{0.8}MnO_3$-NH_3-CA1.5	EDX	72.7	12.6	14.7	/
	XPS	69.3	13.2	17.5	/
	(nominal)	(62.5)	(16.7)	(20.8)	/
$La_{0.8}MnO_3$-H^+-CA1.1	EDX	66.1	17.0	16.9	/
	XPS	71.6	11.8	16.6	/
	(nominal)	(62.5)	(16.7)	(20.8)	/
$La_{0.8}MnO_3$-H^+-CA1.5	EDX	65.0	16.3	18.7	/
	XPS	74.4	10.7	14.9	/
	(nominal)	(62.5)	(16.7)	(20.8)	/
$La_{0.8}Mn_{0.9}Ni_{0.1}O_3$-$H^+$-CA1.1	EDX	67.0	16.1	15.3	1.6
	XPS	66.5	12.7	20.1	0.7
	(nominal)	(62.5)	(16.7)	(18.8)	(2.1)
$La_{0.8}Mn_{0.9}Ni_{0.1}O_3$-$H^+$-CA1.5	EDX	63.3	17.7	16.8	2.2
	XPS	66.5	13.3	18.8	1.4
	(nominal)	(62.5)	(16.7)	(18.8)	(2.1)
$La_{0.8}Mn_{0.9}Cu_{0.1}O_3$-$H^+$-CA1.1	EDX	67.7	15.5	15.6	1.2
	XPS	63.5	13.6	18.8	4.1
	(nominal)	(62.5)	(16.7)	(18.8)	(2.1)
$La_{0.8}Mn_{0.9}Cu_{0.1}O_3$-$H^+$-CA1.5	EDX	64.9	16.9	16.0	2.2
	XPS	65.5	12.3	18.5	3.7
	(nominal)	(62.5)	(16.7)	(18.7)	(2.1)