Pulsed reactivity on $LaCoO_3$-based perovskites: a comprehensive approach to go inside CO oxidation mechanism and the effect of dopants.

Electronic supplementary information

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SI.1 Reaction rate

In order to understand the role of the doping in the catalytic oxidation, a kinetic analysis has been performed with the aim of collecting and comparing the activation energies values for the reaction. The need to acquire kinetic data from a single point conversion derived from a short pulse, has been satisfied by using the following expression for the reaction rate[1]:

$$r_{CO} = \frac{N_{CO} \cdot X_{CO}}{W}$$

where N_{CO} is the molar flow rate [mol/s], determined as the total mole of CO over the interaction time with the catalyst. For the scope of the present work, the interaction time has been defined as the width of the signal produced at the TCD detector. X_{CO} is the CO percentage conversion and W is the catalyst weight [g]. The reaction rate r_{CO} is expressed in $molg^{-1}s^{-1}$.

In analogy with Hueso et al.[2],a first reaction order respect to CO concentration has been considered. The Authors based the kinetic evaluation on the conditions of $[CO] << [O_2]$. In the present work, the reaction were performed in absence of gaseous oxygen with the aim of isolating the effect of the catalyst towards the CO oxidation. Then, the previous condition was fulfilled being the oxygen species supplied by the catalyst in large excess compared to the mole of reagent in the short reducing pulse.

SI.2 Arrhenius plots. Activation Energies.

The as-defined reaction rate has an Arrhenius dependency on temperature. An energy of activation for the CO oxidation reaction is then obtained from the slope of the Arrhenius plot. As shown in Figure S1, all the plots presented a change in the slope at temperatures around 350°C. A summary of the activation energies obtained at low and high temperature is reported in Table S1.

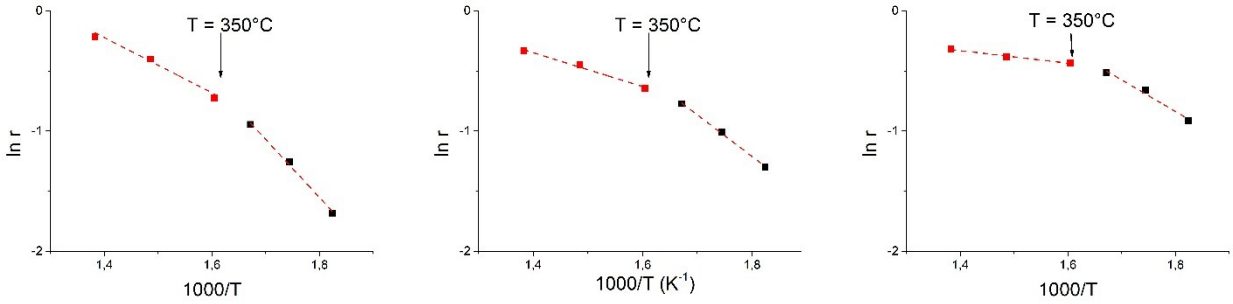

Figure S1. Arrhenius plot of the samples. From left to right: LC, LSC, LCC

Table S1: Activation Energies derived by results reported in Figure S1.

Sample	*EA (KJ/mol)* $T < 350$ °C	*EA (KJ/mol)* $T > 350$ °C
LC	40 ± 1	19 ± 1
LSC	29 ± 1	12 ± 1
LCC	27 ± 1	4 ± 1

References

1 A.-P. Jia, G.-S. Hu, L. Meng, Y.-L. Xie, J.-Q. Lu, M.-F. Luo, J. Catal. 2012, **289**, 199.

2 J.L. Hueso, D. Martínez-Martínez, A. Caballero, A.R. González-Elipe, B.S. Mun, M. Salmerón, Catal. Commun. 2009, 10, 1898.