SUPPLEMENTARY MATERIAL

Structure, Chemical Composition and Catalytic Behavior of Stoichiometric and Non-Stoichiometric LaMnO$_3$ Toward Deep Oxidation of Ethanol

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S1: Redox titration of Mn$^{3+}$ and Mn$^{4+}$

LaMnO$_{3+\delta}$(s) + δ(H$^+$,Cl$^-$)$_{aq}$ $\rightarrow$ (Mn$^{2+},2$Cl$^-$)$_{aq}$ + (La$^{3+},3$Cl$^-$)$_{aq}$ + ($\frac{\delta-5}{2}$)Cl$_2$(g) + 2H$_2$O$_{aq}$

($\frac{\delta-5}{2}$)Cl$_2$(g) + 2($\frac{\delta-5}{2}$)I$_3$$_{aq}$ $\rightarrow$ ($\frac{\delta-5}{2}$)Cl$^-$$_{aq}$ + 3($\frac{\delta-5}{2}$)I$_2$$_{aq}$

($\frac{\delta-5}{2}$)I$_2$$_{aq}$ + 2($\frac{\delta-5}{2}$)S$_2$O$_5^{2-}$$_{aq}$ $\rightarrow$ ($\frac{\delta-5}{2}$)S$_4$O$_6^{2-}$$_{aq}$ + 2($\frac{\delta-5}{2}$)I$^-$$_{aq}$

The statistical error calculated on 4-6 experiments did not exceed 0.01 in δ (oxygen excess), which corresponds to ±2% absolute error on Mn$^{4+}$ content.

S2: Experimental details for CO$_2$ adsorption

A mass of 0.6 g of lanthanum manganite oxide was used for adsorption experiments. In order to determine the extent of CO$_2$ adsorption, the adsorbate was left in the cell, at a given temperature and long enough to reach equilibrium before the isotherm of total adsorption was determined. The sample was pumped of under a vacuum pressure of 1.3 $10^{-6}$ mbar and a second isotherm of CO$_2$ was determined (this measurement corresponds to reversible adsorption (Q$_{rev}$). The difference between the results was taken as the irreversible adsorption (Q$_{irrev}$). To avoid changes in specific surface area, the final heating temperature of the
sample under vacuum was kept at 100°C below the maximum temperature used for sample preparation.

S3: Comparison of XPS spectra of LM1, LM1.25 and LM0.8

![Image of XPS spectra comparison for La3d3/2 and La3d5/2 binding energy](image1)

![Image of XPS spectra comparison for Mn2p binding energy](image2)