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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+}

$$LaMnO_{3+\delta(s)} + \delta(H^+,Cl^-)_{aq} \rightarrow (Mn^{2+},2Cl^-)_{aq} + (La^{3+},3Cl^-)_{aq} + (\frac{\delta-5}{2})Cl_2(g) + \delta/2\ H_2O_{lq}$$

$$(\frac{\delta-5}{2})Cl_{2(g)} + 2(\frac{\delta-5}{2})\ I_3^-{}_{aq} \rightarrow (\frac{\delta-5}{2})\ Cl^-{}_{aq} + 3(\frac{\delta-5}{2})\ I_{2aq}$$

$$(\frac{\delta-5}{2})\ I_{2aq} + 2\ (\frac{\delta-5}{2})\ S_2O_3^{2-}{}_{aq} \rightarrow (\frac{\delta-5}{2})\ S_4O_6^{2-}{}_{aq} + 2\ (\frac{\delta-5}{2})\ I^-{}_{aq}$$

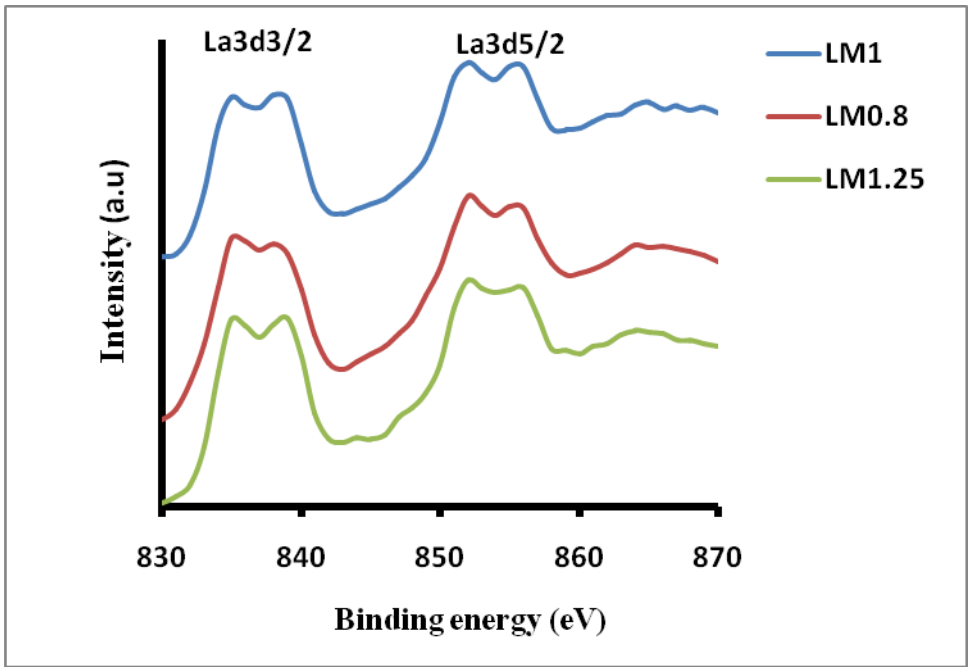
The statistical error calculated on 4-6 experiments did not exceed 0.01 in δ (oxygen excess), which corresponds to ±2% absolute error on Mn^{4+} content.

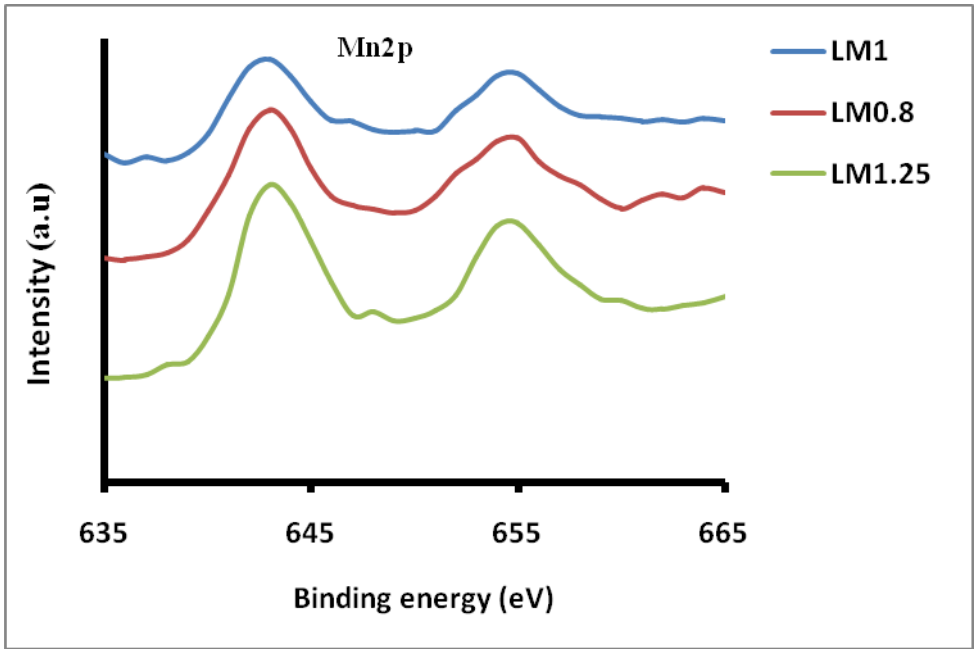
S2: Experimental details for CO_2 adsorption

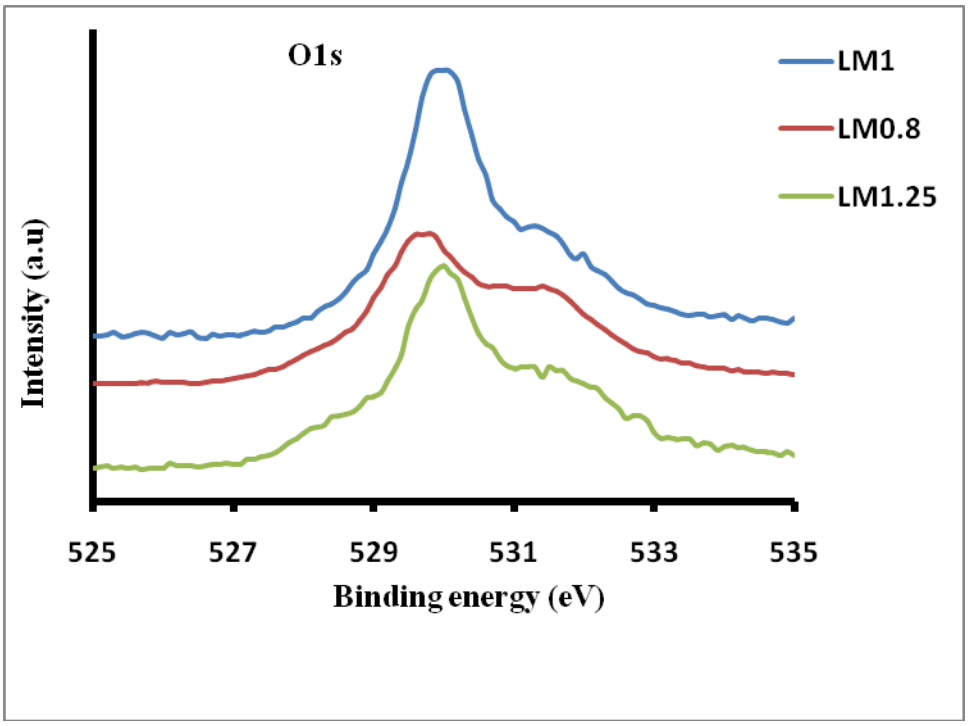
A mass of 0.6 g of lanthanum manganite oxide was used for adsorption experiments. In order to determine the extent of CO_2 adsorption, the adsorbate was left in the cell, at a given temperature and long enough to reach equilibrium before the isotherm of total adsorption was determined. The sample was 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 (Qrev). The difference between the results was taken as the irreversible adsorption (Qirrev). To avoid changes in specific surface area, the final heating temperature of the

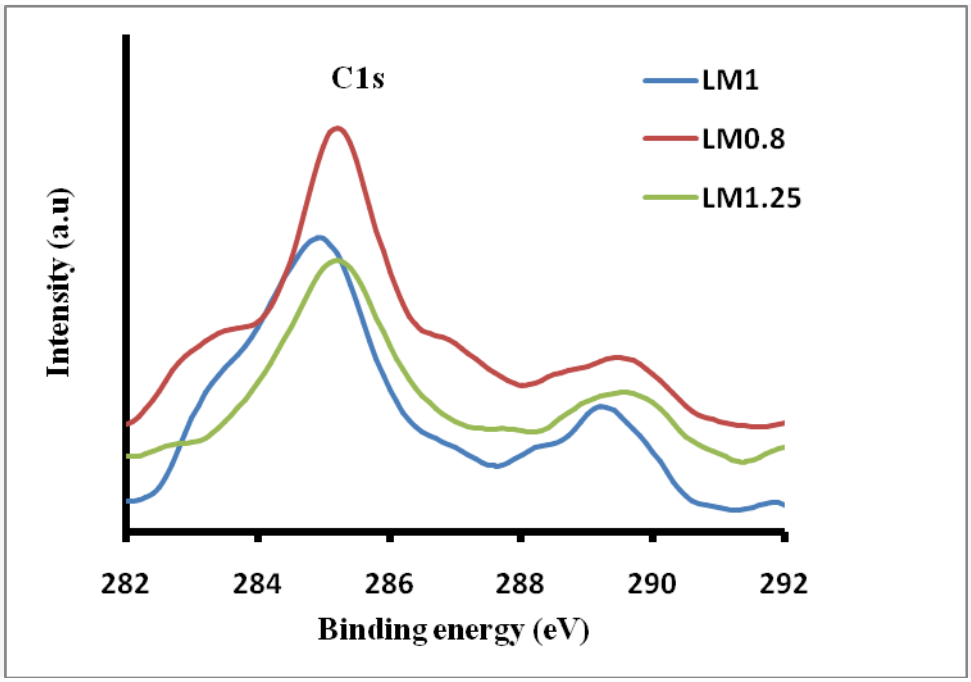
sample under vacuum was kept at 100°C below the maximum temperature used for sample preparation.

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






O1s
LM1
LM0.8
LM1.25
Intensity (a.u)
525
527
529
531
533
535
Binding energy (eV)


C1s
LM1
LM0.8
LM1.25
Intensity (a.u)
282
284
286
288
290
292
Binding energy (eV)