Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information for

Understanding of binding energy calibration in XPS of lanthanum oxide by in situ treatment

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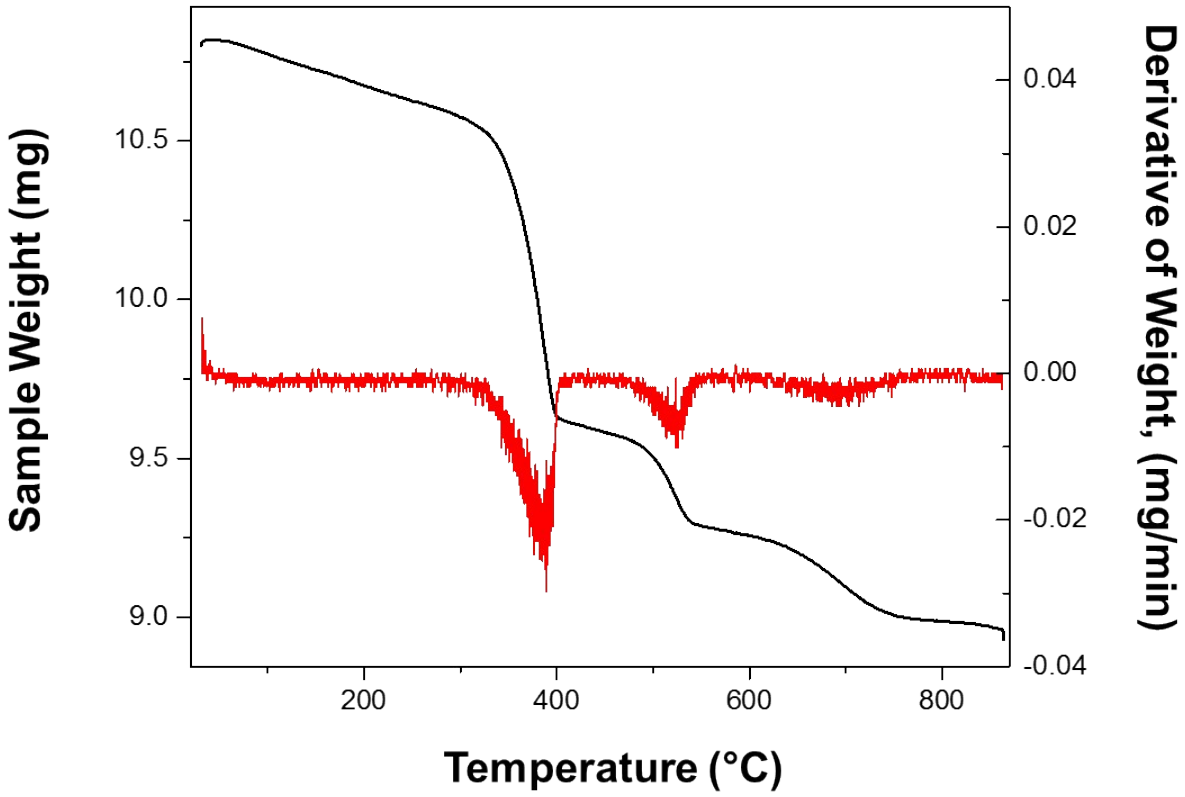

Figure S1. Thermogravimetric analysis (TGA) (black) and derivative weight loss curves (red) of La_2O_3 ample under N_2 flow

TGA results show that 3 steps of mass change are observed after 100°C. In the 1st step, a 10 % mass loss was observed at ~380°C identified as H_2O desorption. In the 2nd step, a 2.7 % mass loss was observed at ~510°C identified as additional H_2O desorption. Finally, in the 3rd step, a 2.7 % mass loss was observed at ~700°C identified as CO_2 desorption. As the he desorption species are confirmed with the MS signal obtained. The results are also in line with the literature [1, 2]. It has been reported that in the 1st step, a mixture of $La_2(OH)_4(CO_3)$ and $La(OH)_3$ phases are decomposed to form $La_2O_2CO_3$ and LaOOH respectively, both yielding H_2O as desorbed product. The 2nd step is the subsequent LaOOH decomposition to La_2O_3, yielding additional H_2O as desorbed product. The 3rd step is $La_2O_2CO_3$ phase being decomposed to La_2O_3 yielding CO_2 as the desorbed product [3].

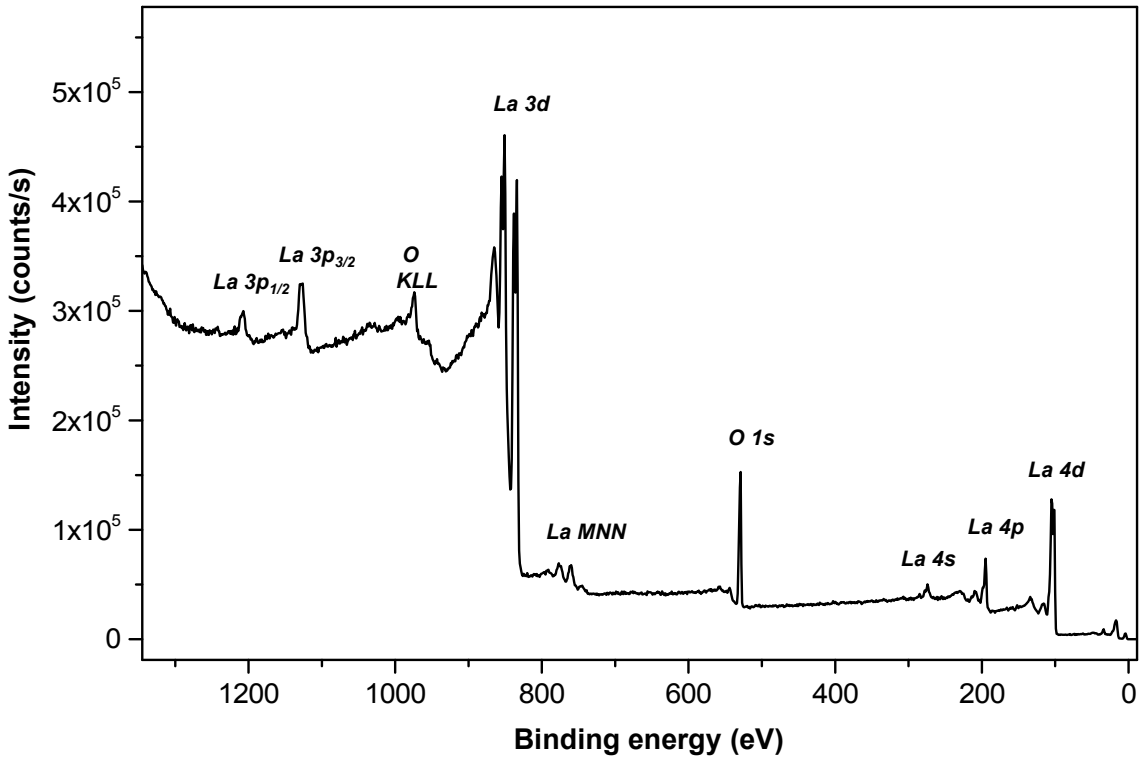

Figure S2. XPS survey scan of clean La_2O_3 surface (after 800°C calcination in HPGS of XPS spectrometer).

La $4p_{3/2}$ spectra of La_2O_3 sample taken after different treatments are shown in Figure S3. The binding energy scale is calibrated to La $4d_{5/2}$ peak at 102.2 eV as described in the main text. On treatments La $4p_{3/2}$ peak (195.7 eV) demonstrates no variation (±0.05 eV) which makes this peak an alternative internal standard for calibration even if it two times less intense than La $4d_{3/2}$ peak.

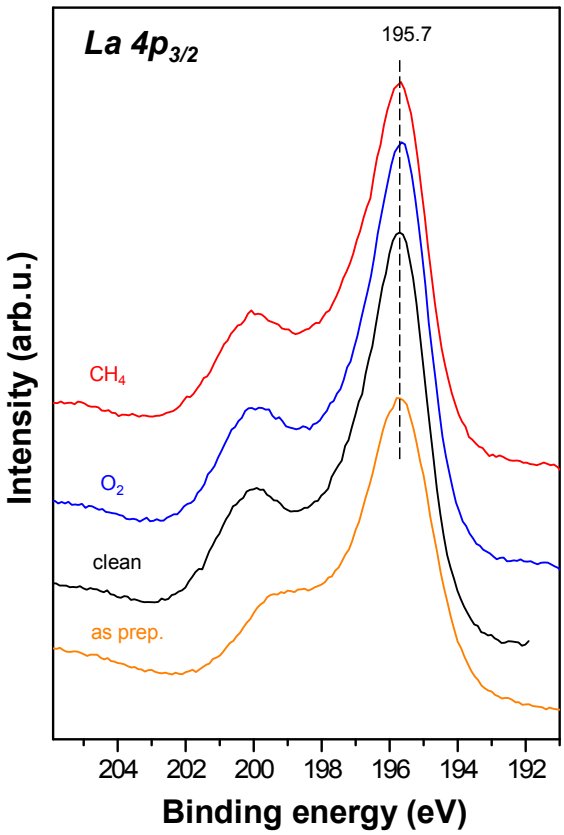

Figure S3. La $4p_{3/2}$ core level spectra of as prepared La_2O_3 surface (brown), clean surface after 800°C in situ calcination (black), and after interaction with O_2 (blue) and CH_4 (red).

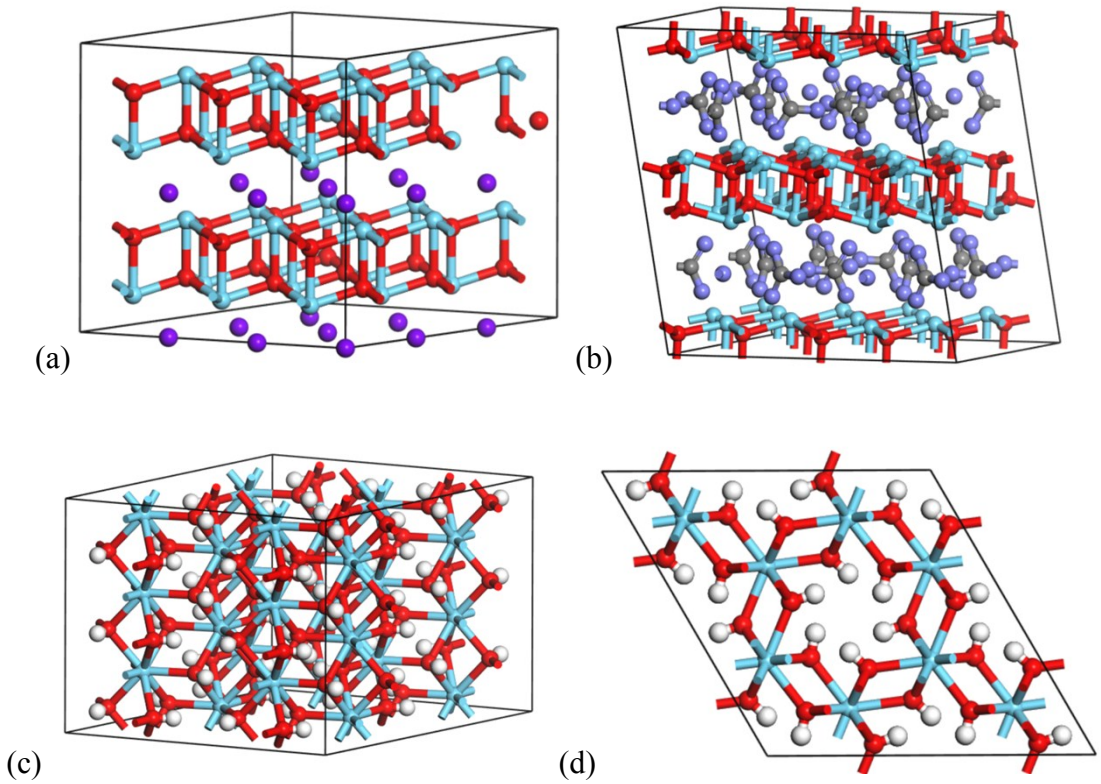

Figure. S4. (a) The (3x3x3) supercell of bulk La_2O_3. Blue: lanthanum atom; Red: four-coordinated oxygen (O_{4c}); Purple: six-coordinated oxygen (O_{6c}). (b) The (2x2x1) supercell of bulk $La_2O_2CO_3$. Blue: lanthanum atom; Grey: carbon atom; Light purple: oxygen atom in the carbonate species; Red: non-carbonate oxygen atom (O_{4c}). (c) The (2x2x3) supercell of bulk $La(OH)_3$. Blue: lanthanum atom; Red: oxygen atom in the hydroxyl species; White: hydrogen atom. (d) An alternative view of the $La(OH)_3$ supercell.

The above figure shows the relaxed structures used in our first principles predictions of the O 1s binding energies. The primitive unit cells of the bulk structures of La_2O_3, $La_2O_2CO_3$, and $La(OH)_3$ are first relaxed, and the relaxed structures are then used to build the (3x3x2) supercell for bulk La_2O_3, the (2x2x1) supercell for bulk $La_2O_2CO_3$, and the (2x2x3) supercell for bulk $La(OH)_3$. These supercells are sufficiently large, which are required for the reliable predictions of the O 1s binding energies. A Γ-centered Monkhorst-Pack [4] k-point mesh of (2x2x2) is used in these calculations.

The O 1s binding energies are usually calculated using the ΔSCF method with a well-defined reference, here the experimental value of 529.8 eV for the surface lattice oxygen site of the *in situ* prepared La_2O_3 sample, which is assigned to the La_2O_3 (001) surface due to its stability. The 1s binding energies for other types of oxygen sites are then calculated from

$$O_{1s} = \Delta O_{1s} + O^{ref,exp}_{1s} \quad (1)$$

where $O^{ref,exp}_{1s}$ is the reference O_{1s} binding energy, here 529.8 eV for the surface lattice oxygen on the La_2O_3 (001) surface, and ΔO_{1s} is calculated from

$$\Delta O_{1s} = (E_f - E_0) - \left(E^{ref}_f - E^{ref}_0\right) \quad (2)$$

where E_f and E_0 are the electronic energies of the system of interest with and without a core hole on the probed O atom, respectively (i.e. the final and initial states during the core hole formation). E_f calculation use a special pseudopotential with a core hole on the ionized atom. The superscript *ref* denotes the values for the reference.

Table S1. XPS peaks parameters: binding energy, FWHM value and La $3d_{5/2}$ spectral component separation. Energy scale is calibrated to La $4d_{5/2}$ peak maximum, 102.2 eV.

Sample	Binding energy, eV (FWHM, eV)			
	C 1s	O 1s	La $3d_{5/2}$	Δ La 3d, eV
as prepared	284.5 (1.6) 285.9 (1.6) 287.9 (1.6) 289.5 (1.7)	528.5 (1.2) 531.0 (1.9) 532.3 (1.9)	835.2, 838.8	3.6
clean La_2O_3	285.9 (2.1) 287.9 (2.3) 290.6 (2.3)	529.9 (1.3) 531.5 (2.4)	834.8, 839.1	4.3
O_2 treated	286.1 (2.2) 287.7 (2.2) 290.1 (2.6)	529.8 (1.4) 531.7 (2.7) 533.5 (2.3)	834.5, 839.1	4.6
CO_2 treated	286.2 (2.5) 288.3 (2.5) 290.6 (1.5) 291.9 (1.5)	529.7 (1.4) 530.7 (1.4) 532.6 (2.6)	834.6, 839.0	4.4
CH_4 treated	284.9 (1.3) 286.0 (1.4) 287.4 (2.1)	529.9 (1.2) 531.4 (2.0)	834.4, 839.1	4.7
H_2O treated	286.2 (2.5) 288.4 (1.5) 290.6 (1.7)	529.8 (1.2) 531.8 (2.6)	835.6, 839.4	3.8

References

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