Supporting Information : Atomistic Mechanisms for the Nucleation of Aluminium Oxide Nanoparticles

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SI.1 Isomer data

For each molecular formula Al_xO_y, geometries along with point-zero energies for all the selected isomers are reported in the supplementary material attached to the Letter in a xyz format where the number of atoms and the point-zero energy [Hartree] are given in the commentary line. The positions are given in Angstrom. The name $i\_j.xyz$ of each files denotes the molecular formula Al_iO_j.

SI.2 Gas composition

From the dissociation energy, the vibrational and rotational constants, the Gibbs free energy of formation $\Delta_f G_{Al_xO_y^{(i)}}$ of each $Al_xO_y^{(i)}$ is computed as a function of the temperature (T) and the pressure ($P_\circ$). i denotes the Al_xO_y isomer considered. For each isomer i of each Al_xO_y, the Gibbs free energy G was calculated using the electronic energy E_0 (calculated at MP2/6-311++G(3df,3pd) level of theory), the entropy S_{total}, and the energy E_{total} resulting from translational, vibrational and rotational motion :

$$G = E_0 + E_{total} + RT - TS_{total}$$

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where R is the gas constant. S_{total} and E_{total} were calculated using the geometries and the harmonic frequencies computed at B3LYP/6-311+G(3df,3pd) level of theory. They are defined as follow:

$$E_{total} = E_{trans} + E_{vib} + E_{rot}$$

$$S_{total} = S_{trans} + S_{vib} + S_{rot}$$

where $trans$, vib and rot must be understood as translation, vibration and rotation. The energies were calculated as follow. $E_{rot} = RT$ for linear molecules and $\frac{3}{2}RT$ for non linear molecules.

$$E_{trans} = \frac{3}{2}RT$$

$$E_{vib} = R\sum_{p=0}^{N} \Theta_p \left(\frac{1}{2} + \frac{1}{exp(\Theta_p/T) - 1}\right)$$

where $\Theta_p = h\nu_p/k_B$, ν_p is the harmonic frequency of mode number p, $N = 3 \times (number\ of\ atoms) - 5$ for linear molecules and $3 \times (number\ of\ atoms) - 6$ for non linear molecules .
The entropy was calculated as follow:

$$S_{trans} = R\left[ln\left(\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\frac{k_B T}{P_\circ}\right) + \frac{5}{2}\right]$$

$$S_{vib} = R \sum_{p=0}^{N} \left[\frac{\Theta_p/T}{exp(\Theta_p/T) - 1} - ln\left(1 - exp\left(\frac{-\Theta_p}{T}\right)\right) \right]$$

$S_{rot} = R\left[ln\left(\frac{T}{\Theta_r}\right) + 1\right]$ for linear molecules, and $R\left[ln\left(\frac{1}{2}\sqrt{\frac{\pi T^3}{\Theta_{rx}\Theta_{ry}\Theta_{rz}}}\right) + \frac{3}{2}\right]$ for non linear molecules. $\Theta_{rx} = h^2/8\pi^2 I_x k_B$ where I_x is the moment inertia with respect to x axis (respectively y and z).

From the set of $\Delta_f G_{Al_xO_y^{(i)}}$, we can compute the composition of a gas feed with aluminium and oxygen atoms as a function of the temperature, the initial proportion of elements ($\lambda \equiv N_{Al}/N_O$) and the pressure. We considered a set of reactions which correspond to the formation of the $Al_xO_y^{(i)}$ molecules from an atomic gas:

$$xAl + yO \rightleftarrows Al_xO_y^{(i)} \qquad (1)$$
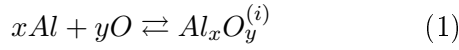
The gibbs free energy of reactions $\Delta_r G_{Al_xO_y^{(i)}}$ are deduced from the $\Delta_f G_{Al_xO_y^{(i)}}$.[1] The composition in the equilibrium state is driven by the dissociation constants :

$$K_{Al_xO_y^{(i)}} = \frac{P_{Al_xO_y^{(i)}} P_\circ^{(x+y)-1}}{P_{Al}^x P_O^y} \qquad (2)$$

where $P_{Al_xO_y^{(i)}}$, P_{Al} and P_O are respectively the partial pressure of the $Al_xO_y^{(i)}$ molecule, the partial pressure of aluminium atoms and the partial pressure of oxygen atoms. Each $K_{Al_xO_y^{(i)}}$ is expressed using the Van't Hoff law:

$$K_{Al_xO_y^{(i)}} = \exp\left(-\frac{\Delta_r G_{Al_xO_y^{(i)}}(T, P_\circ)}{k_B T}\right) \qquad (3)$$

Assuming a perfect gas, we define the quantities P_{Al}^{tot} and P_O^{tot} which respectively map the total number of aluminium atoms and oxygen atoms:

$$\begin{aligned} P_{Al}^{tot} &= \sum_{x,y,i} x P_{Al_xO_y^{(i)}} \\ &= \sum_{x,y,i} x K_{Al_xO_y^{(i)}} P_{Al}^x P_O^y P_\circ^{1-(x+y)} \\ P_O^{tot} &= \sum_{x,y,i} y P_{Al_xO_y^{(i)}} \\ &= \sum_{x,y,i} y K_{Al_xO_y^{(i)}} P_{Al}^x P_O^y P_\circ^{1-(x+y)} \end{aligned} \qquad (4)$$

The proportion of elements follows the ratio $\lambda = P_{Al}^{tot}/P_O^{tot}$. The mass conservation leads to $P_\circ = P_{Al}^{tot} + P_O^{tot}$. As a consequence, each $(P_\circ, \lambda)$ pair defines the quantities P_{Al}^{tot} and P_O^{tot}. The set of equations (4) is then solved numerically to obtain the partial pressures P_{Al} and the P_O. Finally, the partial pressures of all $Al_xO_y^{(i)}$ molecules composing the system are calculated from the equation (2).

SI.3 Calculation of λ_{min}

Assuming an α-Al_2O_3 density of 3.95 g.cm^{-3}, a molar mass of 101.96 g.mol^{-1}, we have obtained $7 \times 10^{15} \pm 70\%$ atoms ablated per pulse. Considering the size of the plasma, 2 mm in diameter,[2] and assuming an ideal gas, the number of O_2 molecules provided by the air is 2×10^{16}. λ_{min} corresponds to the ratio between the number of aluminium atoms provided by the target and the number of oxygen atoms provided by the target and the air.

$$\lambda_{min} = \frac{2/5 \times 7 \times 10^{15}}{3/5 \times 7 \times 10^{15} + 2 \times 2 \times 10^{16}} = 0.063$$

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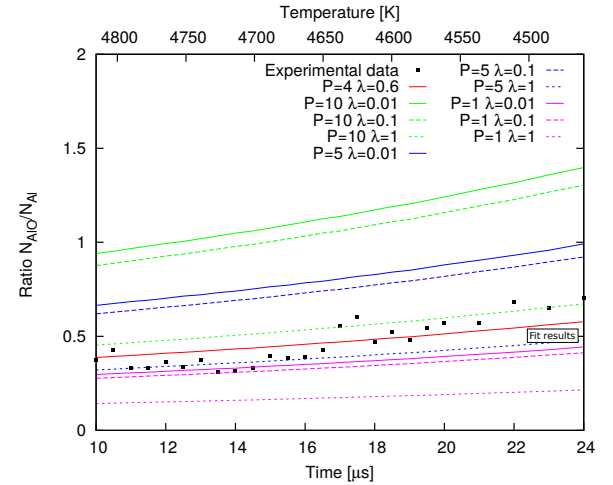# SI.4 Fit of the ration N_{AlO}/N_{Al}

Figure 1: Comparison between the experimental measurements (black dots) and the numerical calculations for different values of λ and $P_\circ$ at short time scale ($10\,\mu s$ - $24\,\mu s$).

In figure 1, corrected experimental measurements are plotted along with several theoretical curves in order to assess the quality of agreement between experimental measurements and theoretical calculations.
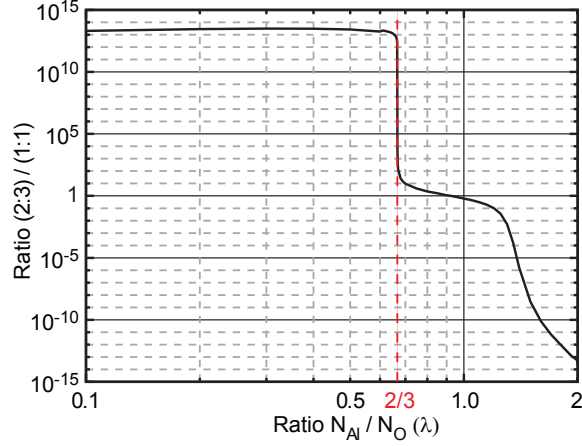
SI.5 Ratio (2:3)/(1:1)

Figure 2: Ratio in pressure between molecules following $(Al_2O_3)_n$ and those following $(AlO)_n$ as a function of λ calculated at 1500 K.

Figure 2 shows the ratio in pressure between molecules following $(Al_2O_3)_n$ and those following $(AlO)_n$ as a function of λ. The plateau observed for $\lambda < 2/3$ corresponds to the numerical error.

References

(1) McQuarrie, D. A.; Simon, J. D. *Molecular Thermodynamics*; University Science Books, 1999.

(2) Lam, J.; Motto-Ros, V.; Misiak, D.; Dujardin, C.; Ledoux, G.; Amans, D. Investigation of Local Thermodynamic Equilibrium in Laser-Induced Plasmas: Measurements of Rotational and Excitation Temperatures at Long Time Scales. *Spectroc. Acta Pt. B* **2014**, *101*, 86–92.