## Low-Temperature Atomic Layer Deposition Delivers More Active and Stable Pt-Based Catalysts

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## **Supporting Information**



Figure S1. Platinum loading vs deposition temperature after 10 ALD cycles and respective size distributions and representative TEM micrographs.



Figure S2. TGA curves obtained for untreated graphene, ozone-treated graphene, and Pt/GNP composites obtained at different temperatures.



**Figure S3.** Propene conversion as a function of temperature for the Pt/graphene composites obtained after 1, 3, and 10 ALD cycles at both 100 °C and 200 °C.



**Figure S4.** Extended results of the catalytic test plotted as propene conversion and temperature vs time obtained for (upper part) Pt/GNP/100 and Pt/GNP200 (bottom).



**Figure S5.** HRTEM image of the as-synthesized Pt/GNP/100 (center). The satellite images are zoomed-in views highlighting the crystalline structure and lattice constants of Pt NPs.



Figure S6. Determination of the lattice constants of the as-synthesized Pt NPs.



Figure S7. Growth of Pt NPs on untreated graphene at 150  $^{\circ}$ C (a) and 200  $^{\circ}$ C for 10 ALD cycles.



**Figure S8.** Surface-based size distribution (dS/dr vs d) of the Pt/GNP/100 and the Pt/GNP200 NPs after the catalytic test.



**Figure S9.** Simulation results of the sintering of Pt nanoparticles via simultaneous gas-phase-mediated Ostwald ripening and nanoparticle diffusion and coalescence. The initial conditions of the simulations were the experimental particle size distributions and nanoparticle density of the as-synthesized composites obtained after 1 and 3 cycles at both 100 °C and 200 °C. The parameters used for each simulation were: T=350 °C,  $p_{O2}=152$  torr,  $D_k=D_1k^{-0.1}$  (where  $D_k$  is the mobility of a nanoparticle of size k, that is the number of atoms comprising the nanoparticle) and  $D_1=0.01$  nm<sup>2</sup> s<sup>-1</sup>. From left to right, the plots show the evolution of: the number of nanoparticles per unit area normalized to to the initial value; the total number of facet sites divided by the total number of atoms; the total dispersion, that is the total number of surface atoms divided by the total number of atoms; the surface-averaged diameter of the ensemble; and the number-based particle size distribution.



**Figure S10.** Simulation results of the sintering of Pt nanoparticles via gas-phase-mediated Ostwald ripening and nanoparticle diffusion and coalescence. The initial conditions of the simulations were the experimental particle size distributions and nanoparticle density of the as-synthesized composites obtained after 10 cycles at both 100 °C and 200 °C. (a) shows the evolution of the number of nanoparticles per unit area normalized to the initial value in case of sintering via Ostwald ripening and sintering via simultaneous gas-phase-mediated Ostwald ripening (T=350 °C,  $p_{02}=152$  torr) and nanoparticle diffusion and coalescence ( $D_k=D_1k^{-2/3}$ ,  $D_1=0.1$  nm<sup>2</sup> s<sup>-1</sup>). (b) and (c) show the evolution of: the number of nanoparticles per unit area normalized to the initial value; the total number of facet sites divided by the total number of atoms; the total dispersion, that is the total number of surface atoms divided by the total number of atoms; the surface-averaged diameter of the ensemble; and the number-based particle size distribution (T=350 °C,  $p_{02}=152$  torr,  $D_k=D_1k^{-0.1}$ ,  $D_1=0.01$  nm<sup>2</sup> s<sup>-1</sup>).

## Evaluation of possible internal and external mass transfer limitations

In order to rule out possible mass transfer limitations we used the Wiesz-Prater criterion for internal mass transfer limitation:

$$C_{WP} = \frac{r_{obs}\rho_p R^2}{D_{eff}C_s} \ll 1$$

and the Mears criterion for external mass transfer limitations.

$$C_M = \frac{r_{obs}\rho_b R}{k_c C_s} \ll 1$$

Where  $r_{obs}$  is the observed reaction rate expressed in mol  $g_{cat}^{-1}s^{-1}$ ,  $\rho_p$  is the density of the catalyst particles, R is the volume-based radius of the catalyst particles,  $D_{eff}$  is the diffusion coefficient of the reactant within the catalyst particles,  $C_s$  is either concentration of reactant at outer surface of the catalyst particle for the Wiesz-Prater criterion or the concentration of reactant at the inlet of the reactor for the Mears criterion,  $\rho_b$  is the bulk density of the catalyst and,  $k_c$  is the external mass transfer coefficient.

 $\rho_b$  varies in the range of 0.03-0.1 g/cm<sup>3</sup> as reported by the supplier (Strem Chemicals) and it was thus approximated to an average value of 65 kg/m<sup>3</sup>. The volume-based radius was measured by means of a LS Beckman Coulter Particle Size Analyzer and it was found to be about 18.35  $\mu$ m. The density of the catalyst particle was estimated as follows:

$$\rho_p = \rho_{graphite} (1 - \epsilon_p) \sim 86 \text{ kg/m}^3$$

Where  $\rho_{graphite}$  is the density of graphite, which is about 2160 kg/m<sup>3</sup>, and  $\epsilon_p$  is the void fraction of the catalyst particle. The latter is assumed to be consisting of agglomerated graphene nanoplatelets, in other words  $\epsilon_p$  is the void fraction of the graphene nanoplatelets agglomerates.  $\epsilon_p$ , in turn, was estimated as follows:

$$\epsilon_p = 1 - \frac{(\rho_b / \rho_{graphite})}{(1 - \epsilon_{bed})} \sim 0.96$$

Here,  $(1 - \epsilon_{bed})$ , that is, the packing density of the catalytic bed, was assumed to be about 0.3 (close random packing for ellipsoids). Such a high value of the void fraction for the graphene nanoplatelets agglomerates ( $\epsilon_p > 0.9$ ) is consistent with typical values reported for agglomerates of nanostructured powders such as agglomerates of nanoparticles (0.95-0.99).

Given the high porosity of the graphene nanoparticle agglomerates,  $D_{eff}$  was assumed to be about  $10^{-5}$  m<sup>2</sup>/s, that is the typical value of the diffusion coefficient of a gas undergoing molecular diffusion at atmospheric pressure and room temperature (conservative estimate).

Given the low Reynolds number (~0.01, using average values for the viscosity and the density of helium in the temperature range of 100-450 °C and a superficial velocity of 0.04 m/s), we made a conservative estimate of  $k_c$  by approximating the Sherwood number to 2 (stagnant flow around a sphere). By doing so we found a  $k_c$  of about 5 m/s.

By using the aforementioned figures and calculating  $r_{obs}$  based on the maximum and the minimum value of  $k_{app}$  reported in this work, we obtain:

$$C_{WP} \sim 10^{-5} - 10^{-6} \ll 1$$

$$C_M \sim 10^{-6} - 10^{-7} \ll 1$$

Hence, we conclude that the influence of mass transfer on our results is negligible.