Supporting Information
Morphology control of metallic nanoparticles supported on carbon substrates in catalytic conditions

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We show how the Young-Dupré equation can be derived at the nanoscale from the free energy of a system consisting in a nanoparticle supported on a carbon template. The free energy is described as the sum of the different energy contributions in the system, (Eq. 1). The first term corresponds to the particle energy, the second and third terms are respectively the substrate energy and his surface energy. The next two terms are the nanoparticle surface energy and the metal-carbon interface energy. Finally the last term is the line energy at the edge of the metal-substrate interface. In (Eq. 1), $G_M(x_c)$ denotes the energy of metal atoms at a C concentration x_c, $\gamma_m(x_c)$ and γ_{m-c} are respectively the surface energy of the NP and the interface energy corresponding to bonds between the NP and the substrate. τ_{m-c} denotes the line energy between the NP and the substrate. The line energy is usually neglected and we will not consider it in the following calculation. All terms describing the metal-carbon interface will be consider independent of x_c. Indeed, we have shown that a C depletion area

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is formed at the vicinity of the metal-carbon interface on a wide range of x_c. For a sake of simplicity, we assume that x_c above the liquidus line of the phase diagram presented in the article, does not depend on x_c. This approximation induce a deviation at high carbon concentration, (seen on Figure 2 in article). R_{NP} corresponds to the radius of an isolated NP (with a volume Ω), R_s is the radius of the wetting NP and r_s the radius of the disk corresponding to NP-substrate interface, Figure 1.

We show how the Young-Dupré equation can be derived at the nanoscale from the expression of the free energy of a system composed of a nanoparticle supported on carbon. The free energy is described as the sum of the different energy contributions of the system, (Eq. 1). In this expression, the first term corresponds to the volume energy of the particle, the second and third terms are respectively the energy of the substrate and its surface energy. The next two terms correspond to the surface energy of the nanoparticle and the interface energy between metal and carbon. Finally, the last term corresponds to the line energy at the edge of the metal-substrate interface.

In (Eq. 1), $G_M(x_c)$ refers to the energy of metal atoms at a concentration x_c, $\gamma_m(x_c)$ and γ_{m-c} are respectively the surface energies of NP and the binding energy corresponding to the bonds between metal and carbon. τ_{m-c} is the line energy between NP and substrate. The line energy is a still debated question that does not make consensus. To simplify this problem, we will not take it into account in the following calculation.

All terms describing the metal-carbon interface will be considered independent of x_c. Indeed, we have shown that a C-depletion area is formed at the metal-carbon interface bellow the liquidus concentration. For simplicity, we assume that x_c above the liquidus of the phase diagram (see Figure 1 of the article), does not depend on x_c. Obviously, this approximation induces a deviation at a high carbon concentration (see Figure 2 of the article). In the following equations, R_{NP} is the radius of an isolated NP (with a volume Ω), R_s is the radius of the wetting NP and r_s the radius of the disk corresponding to the NP substrate

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interface, Figure 1.

$$G = \frac{4\pi}{3} \ R_{NP}^3 \ \rho_{NP} \ G_{NP}(x_c) \ + \ V_{sub} \ \rho_{sub} \ G_{sub} \ + S_{sub}\gamma_{sub}$$
$$+ \ R_s^2 \ \gamma_m(x_c) \int_0^\theta \int_0^{2\pi} \sin(\theta)d\theta \ d\varphi + \ \pi r_s^2 \ (\gamma_{m-c} - \gamma_c) + \ 2\pi r_s \tau_{m-c} \tag{1}$$

$$\Omega = \frac{4\pi}{3} \ R_{NP}^3 \ = \ \frac{\pi R_s^3}{3} \ \left[2 - 3\cos(\theta) + \cos(\theta)^3\right] \tag{2}$$

$$R_s = R_{NP} \left(\frac{4}{2 - 3\cos(\theta) + \cos(\theta)^3}\right)^{1/3} \quad \text{and} \quad r_s = R_s \tag{3}$$

In equation (1), $G_{NP}(x_c)$ depends on the carbon concentration via the solubility factor λ and entropy with the following expression:

$$G_{NP} = G_{M_0} \ n_M + \mathcal{G}_C \ n_C +$$
$$(n_M + n_C) \left(\lambda \ x_c(1 - x_c) + k_B T \left[x_c \ln(x_c) + (1 - x_c)\ln(1 - x_c)\right]\right) \tag{4}$$

G_{M_0} and G_C correspond respectively to the energy of one metal atom in a bulk, n_M and n_C are the number of metal and carbon atoms inside the nanoparticle.
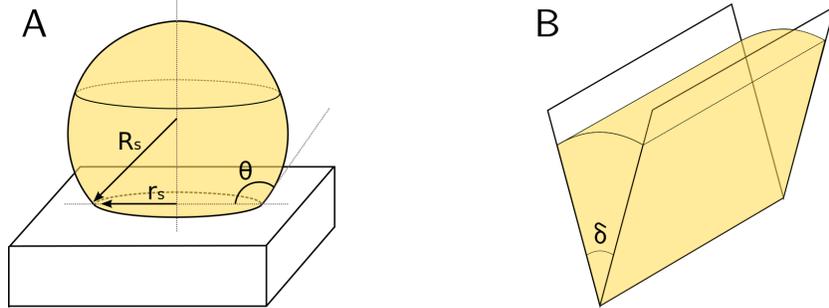
Figure 1: Schematic representation of a nanoparticle wetting: A. a flat substrate, B. a curve substrate

We approximate the shape of the NP as a sphere and we do not consider explicitly the core-shell state of the nanoparticle. C depletion area is only accounting

in NP-substrate and the surface energy γ_{m-c} does not depend on x_c.

$$
\begin{aligned}
G \; &= \Omega \; \rho_{NP} \; G_{NP}(x_c) \; + \; V_{sub} \; \rho_{sub} \; G_{sub} \; + \; S_{sub}\gamma_{sub} \\
&+ \; 2\pi\gamma_m(x_c)R_{NP}^2 \; \left(\frac{4}{2 - 3\cos(\theta) + \cos(\theta)^3} \right)^{2/3} (1 - \cos(\theta)) \\
&+ \; \pi \; (\gamma_{m-c} - \gamma_m)R_{NP}^2 \; \left(\frac{4}{2 - 3\cos(\theta) + \cos(\theta)^3} \right)^{2/3} \left(1 - \cos(\theta)^2\right)
\end{aligned}
\tag{5}
$$

For a carbon concentration x_c, we minimize the free energy. For a sake of simplicity, we note $\cos(\theta) = \sigma$.

$$
\begin{aligned}
\left.\frac{\partial G}{\partial \sigma}\right|_{x_c} &= \gamma_m(x_c) \; \frac{\partial \left(\frac{1}{2-3\sigma+\sigma^3} \right)^{2/3}}{\partial \sigma}(1 - \sigma) \\
&- \gamma_m(x_c) \; \left(\frac{1}{2 - 3\sigma + \sigma^3} \right)^{2/3} \\
&+ \frac{(\gamma_{m-c} - \gamma_m)}{2} \; \frac{\partial \left(\frac{1}{2-3\sigma+\sigma^3} \right)^{2/3}}{\partial \sigma}(1 - \sigma^2)
\end{aligned}
\tag{6}
$$

Free energy derivation give naturally the Young-Dupré equation,

$$
\gamma_m(x_c)\cos(\theta) + (\gamma_{m-c} - \gamma_c) \; = \; 0
\tag{7}
$$

Table 1: Parameters used in this model.

$\mathcal{G}_{m_0}[1]$	-4.44	eV/at
$\mathcal{G}_C[2]$	-7.32	eV/at
$\lambda[1]$	-0.05	eV/at
$\gamma_m(x_c) = \gamma_{m0} - \gamma_{m1}x_c$		
$\gamma_{m0}[3]$	0.11	eV/Å^2
$\gamma_{m1}[4]$	0.372	eV/Å^2
$\gamma_c[5]$	0.003	eV/Å^2
$\gamma_{m-c}[6]$	0.033	eV/Å^2
$x_c^{sat}[4]$	0.25	

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