

Supplemental Information

for

Chemical and Thermal Sintering of Supported Metals with Emphasis on Cobalt Catalysts During Fischer-Tropsch Synthesis

Mahmood Rahmati,[†] Mohammad-Saeed Safdari,[†] Thomas Fletcher, Morris D. Argyle,[†] Calvin Bartholomew*,[†]

[†] Department of Chemical Engineering, Brigham Young University, Provo, UT 84602, United States

Supplemental information includes:

- (i) This Word document with basic equations and a brief explanation of their derivations with important references and specific reference to figures, tables, and calculations in the Excel file.
- (ii) Excel document with calculations and fits of data compiled in figures and tables.
- (iii) Short movies of Ostwald Ripening, Nanocrystal Migration and Coalescence, and CO-induced OR

1. Calculation of Co NCs surface energy versus d_{NC} (see Excel sheet S1):

(i) Using simplified broken bond (SBB) model:

Cobalt surface energy (γ_{Co}) for fcc nanocrystal (NC) phase was calculated using equation (S1). This equation is the basis for the simple broken bond (SBB) model which was first introduced by Tyson and Miller.¹

$$\gamma_{NC} = N_s \Delta E_{coh.bulk} \left(1 - \frac{Z_{cs}}{Z_{cb}}\right) \quad (S1)$$

In equation (S1), Z_{cb} is the coordination number of a bulk atom which is 12 for fcc Co and N_s is the atomic surface density (atoms/cm²) which is 14.6 atoms/nm². $\Delta E_{coh.bulk}$ was assumed to be equal to bulk sublimation enthalpy for enough large NCs. ΔH_{sub} is 425 kJ/mol² and using equation (S2) d_{NC} was found to be about 100 nm for Co NC to reach 425 kJ/mol as bulk cohesive energy. Also assuming N_s of 14.6 atoms/nm², $\Delta E_{coh.bulk}$ with units of J/m² was calculated using equation (S2)³ to be 10.3 J/m².

$$\Delta E_{coh.NC} = \Delta E_{coh.bulk} \times \left(1 - \frac{D}{\eta d_{NC}}\right) \quad (S2)$$

Z_{cs} represents the average coordination number of atoms in the fcc NC structure which changes with NC size. Z_{cs} was obtained via three methods:

(a) From section 3.4 in the dissertation by Swart⁴ it is indicated that a free Co atom with 12 broken bonds has surface energy (SE) of 4.4 eV and the SE has linear relation with number of broken bonds (NBB). Equation (S3) and (S4) were used to calculate the SE of a Co atom per broken bond:

$$\gamma_{Co \text{ atom}} \left(\frac{J}{nm^2}\right) = 4.4 \left(\frac{eV}{atom}\right) * 1.6022E-19 \left(\frac{J}{atom}\right) * 14.6 \left(\frac{atom}{nm^2}\right) * 1E18 \left(\frac{nm^2}{m^2}\right) = 10.3 \quad (S3)$$

$$\text{Gain in surface energy/broken bond} = 10.3/12 = 0.858 \text{ J/NBB} \quad (S4)$$

Figure 3.9 in the dissertation of Swart⁴ reports the SE of cuboctahedron Co NCs versus d_{Co} . The units used in this figure are kJ/mol and therefore a conversion factor of 14.6 atoms/nm² was used to calculate γ_{Co} with units of J/m² after which equation (S3) was used to get NBB versus d_{Co} . Finally, values of Z_{cs} versus d_{Co} were calculated using equation (S5); calculations of NBB, Z_{cs} , and SE values calculated using the SBB model are summarized in the Excel file, sheet S1_CalcCoSe, Table S1.

$$Z_{cs} = 12 - \text{NBB} \quad (S5)$$

The number of broken bonds

(b) Figure 2 from van Steen et al⁵ was used to obtain the average number of broken bonds on Co NC surface versus number of atoms in Co fcc NC; Table 3 in van Helden et al.² lists number of atoms in fcc Co NC versus d_{Co} . Therefore, using these data^{2,5} the average NBBs versus d_{Co} for Co fcc NC were calculated. These data are summarized in the same Excel sheet, Table S3.

(c) In present study, values of Z_{cs} were also calculated by taking the average SE from values obtained via methods (a) and (b). Equation (S1) was then used to calculate γ_{Co} using the SBB model.

(ii) Using the modified broken bond (MBB) model:

This model is used to modify the values obtained via SBB based on the decrease in cohesive energy E_{coh} with decreasing d_{Co} , since SBB model assumes bulk value for E_{coh} regardless of NC size. Yaghmaee and Shokri³ proposed equation (S6) to calculate the decrease in E_{coh} with NC size. For a spherical NC, cohesion energy per bond can be estimated as:

$$\Delta E_{coh.NC} = \Delta E_{coh.bulk} \times \left(1 - \frac{D}{\eta d_{NC}}\right) \quad (S6)$$

In this equation D is the atomic diameter, η is the atomic packing factor (i.e volume of atoms in a unit cell divided by the volume of a unit cell) which for face centered cubic (fcc) crystals is 0.74, and d_{NC} is the NC diameter. Therefore, calculation of the NC surface energy, that accounts for changes in cohesion energy, is possible by multiplying equation (S1) by $\left(1 - \frac{D}{\eta d_{NC}}\right)$, assuming a constant packing factor η . Values of γ_{Co} using SBB and MBB models are listed in the same Excel sheet, Tables S1, S2, S3, S4. Values of SE for a cubo-octahedron are plotted versus NC diameter in Figure S1 based on SBB and MBB models using the approach of Swart. In Tables S1 through S4 SE vs d_{Co} are fitted to a three parameter model of the form $\gamma_{Co} = SE_{bulk} [1 + (a/d_{Co}) + (b/d_{Co}^2)]$ originally reported by van Steen.⁵ Data fits based on MBB models using the approaches of Swart and van Steen and the average of these data are plotted in Figure S2 in the form of Co NC SE versus d_{Co} . The fit of the average SE vs d_{Co} from this study shown in Table S4 is $\gamma_{Co} = 2.43 [1 + (0.322/d_{Co}) + (.046/d_{Co}^2)]$. A simpler and more accurate fit listed in equation (3) of the review on p. 24: $\gamma_{Co} = 2.416 (1 + 0.894/d_{Co})$. This fit was obtained using Minitab to evaluate an 8-term function to determine which terms were significant to within a 95% confidence interval. It was found that the p-value for more than 2 terms were significantly larger than 0.05 indicating that presence of those terms are not required in the model.

Calculation of E_{adh} versus d_{NC} for Co NCs supported on $\gamma\text{-Al}_2\text{O}_3$:

Values of E_{adh} versus d_{NC} for Co NCs supported on $\gamma\text{-Al}_2\text{O}_3$ were calculated using equation (S6) with three important assumptions: (i) constant values of support surface energies (γ_{Supp}) for (a) dry and (b) wet alumina at constant FT reaction conditions⁶ (Figure 11 of the paper and Excel sheet S2). (ii) a constant, bulk value, for Co-support interfacial energy ($\gamma_{NC-Supp}$) calculated as explained in section 3.2 to be 2.72 J/m². Assumption of constant $\gamma_{NC-Supp}$ is probably reasonable for NC diameters larger than about 0.5 nm (i.e., after formation of the first three atomic layers). This is because upon formation of two or three atomic layers the nature of the bond between the NC and the support remains constant. In fact, this assumption is in accordance with the Stranski-Krastanov (SK) NC growth model,⁷ which assumes formation of metal NCs begins with formation of a monolayer of partially oxidized metal atoms on the oxide support.⁸ The assumption of constant $\gamma_{NC-Supp}$ has also been reported by other researchers.^{7,9} (iii) the NC SE γ_{NC} does not change measurably with the extent of water adsorbed at either wet or dry FT reaction conditions. This last assumption is approximate since adsorption of water on Co during wet FT reaction conditions can cause a slight decrease in its NC SE and thus in E_{adh} , although the coverage of water during reaction is very small because of its weak adsorption and because of high CO and H coverages. γ_{Co} used in equation (S6) was adapted from Table S4.

$$E_{adh} = \gamma_{NC} + \gamma_{Supp} - \gamma_{NC-Supp} \quad (S6)$$

Regarding the first assumption, for calculation of E_{adh} : (a) γ_{supp} for $\gamma\text{-Al}_2\text{O}_3$ at dry conditions was obtained from Castro and Quach⁶ to be 1.58 J/m²; (b) To calculate γ_{supp} for $\gamma\text{-Al}_2\text{O}_3$ at wet conditions during FT reaction following steps were taken: (i) van Rensburg et al.¹⁰ measured the OH adsorption capacity of $\gamma\text{-Al}_2\text{O}_3$ (100) and (110) surfaces, the dominant crystallite planes under typical FT reaction conditions ($T = 227^\circ\text{C}$ and $P_{H_2O} = 4$ bar), to be 8.5 and 17.7 OH/nm² respectively; (ii) If Boehmite is the source for preparation of a $\gamma\text{-Al}_2\text{O}_3$, the (110) plane is dominant, i.e., its percentage of the available planes ranges from 70 to 83%.^{6, 10-11} Therefore, for planar distribution during wet conditions an average of 76.5% for (110) and 23.5% (100) was considered. Then

the total OH adsorption on the γ -Al₂O₃ surface during FT conditions was estimated using equation (S7) to be 15.5 OH/nm²:

$$\text{OH/nm}^2 = 76.5\% \times 17.7 + 23.5\% \times 8.5 \quad (\text{S7})$$

(iii) Finally, based on concentration of OH groups and data provided by Castro and Quach,⁶ the surface energy of wet γ -Al₂O₃ during FT reaction conditions was calculated to be 0.63 J/m².

Calculation of contact angle for Co NCs supported on γ -Al₂O₃:

Equation (S8) was used to calculate the contact angle for bulk size (100 nm) Co NCs when supported on dry and wet γ -Al₂O₃.

$$(\gamma_{\text{Supp}} - \gamma_{\text{NC-Supp}}) / \gamma_{\text{NC}} = \cos\theta \quad (\text{S8})$$

Using previously calculated values of $\gamma_{\text{NC-Supp}} = 2.72 \text{ J/m}^2$ and $\gamma_{\text{NC}} = 2.44 \text{ J/m}^2$ and γ_{Supp} values of 1.58 and 0.63 J/m² for dry and wet γ -Al₂O₃ respectively values of contact angle θ of 118° and 153° were calculated from equation (S8) for bulk Co supported on dry and wet γ -Al₂O₃ respectively.

Calculation of diffusion length for Co NCs supported on γ -Al₂O₃:

To calculate the maximum diffusion length for Co NCs, equation (S9) from Wynblatt and Gjostein¹² was used:

$$L_D = \sqrt{4D_s t} \quad (\text{S9})$$

In this equation t is the sintering time which was selected to be 240 h,¹³ D_s is the diffusivity which was estimated from Figure S4 in the Excel file, sheet S3, to be 2.25E-12 cm²/s for a 10 nm NC and L_D was calculated from equation to be 2.79E-03 cm or 28 microns; the catalyst particle radius was about 25 microns on average.¹³ Thus, Co NCs could have easily diffused across the support surface to the pellet exterior during the 240 h of reaction during the study of Munnik et al.,¹³ especially considering the high concentration of steam at 80% conversion available to lower E_{adh} and increase D_s to a higher value than predicted from that in Figure S4.

Figure S5 in the Excel file, sheet S4, illustrates the diffusivity for NC when deposited outside the pores. The higher values of diffusivity (i.e., 10 times) are due to the qualitative assumption that the mobility of the NCs deposit on the outside of pores are not hindered by the pore physical and chemical characteristics such as tortuosity and surface functional groups respectively.

Deconvolution of sintering deactivation from carbon deposition for FTS:

To deconvolute sintering from carbon deposition, following equations and assumptions were used (see Excel file, sheet S5 and S6):

$$f_{d,\text{tot}} = 1 - a_{\text{tot}} = (1 - ac) + (1 - a_{\text{sint}}) \quad (\text{S10})$$

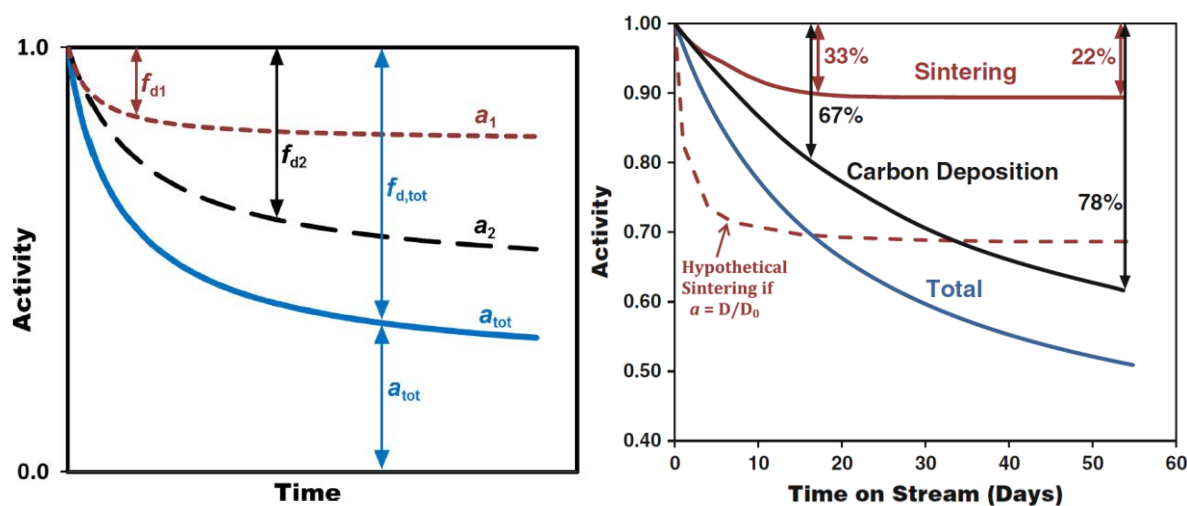
where f is the fractional deactivation, a_{tot} is the normalized rate (activity) as a function of the time on stream, ac is the remnant activity after deactivation by carbon deposition and $a_{\text{sint,ss}}$ is the remnant activity after

deactivation by sintering. Thus, $f = 1 - a_{\text{tot}}$ is the total fractional deactivation, and $f_{d2} = (1 - a_c)$, $f_{d1} = (1 - a_{\text{sint}})$ are the fractional deactivation by carbon deposition and sintering respectively.

$$1 - a_c = (1 - a_c) \times \exp(-k_{d,c} t) + a_{\text{sint,ss}} \quad (\text{S11})$$

Equation (S11) (i.e., first order GPLe) predicts the fractional deactivation if carbon deposition is the only deactivation mechanism. This equation was fitted to fractional deactivation data with the time on the stream for the time which deactivation by sintering was assumed to be complete and is represented by $a_{\text{sint,ss}}$ and for which carbon deposition was assumed to be the sole deactivation mechanism afterwards. This time for S6b was assumed to be 21 days. After fitting equation (S11) to the fractional deactivation, equation (S11) was then used to estimate the fractional deactivation by carbon deposition versus the time on stream for the whole duration of FT run. Then equation (S10) was used to calculate the values for $(1 - a_{\text{sint}})$ (i.e., fractional deactivation by sintering) and subsequently a second order GPLe equation (S12) was used to fit the values for $(1 - a_{\text{sint}})$ to estimate the deactivation by sintering as a function of the time on stream.

$$a_{\text{sint}} = 1 / (k_d t + 1 / (1 - a_{\text{sint,ss}})) + a_{\text{sint,ss}} \quad (\text{S12})$$



Figures S6a terms involved in deconvolution of sintering from carbon deposition and S6b calculated values of sintering and carbon deposition along with total catalyst deactivation.¹⁴ ($a_1 = a_{\text{sint}}$, $a_2 = a_c$)

- (1) Tyson, W. R.; Miller, W. A. Surface free energies of solid metals: Estimation from liquid surface tension measurements. *Surf. Sci.* **1977**, 62, 267-276.
- (2) van Helden, P.; Ciobîcă, I. M.; Coetzer, R. L. J. The size-dependent site composition of FCC cobalt nanocrystals. *Catal. Today* **2016**, 261, 48-59.
- (3) Yaghmaee, M. S.; Shokri, B. Effect of size on bulk and surface cohesion energy of metallic nanoparticles. *Smart Mater. Struct.* **2007**, 16, 349.
- (4) Swart, J. C. W. A theoretical view on deactivation of cobalt-based Fischer-Tropsch catalysts. University of Cape Town, Department of Chemical Engineering, 2008.
- (5) van Steen, E.; Claeys, M.; Dry, M. E.; van de Loosdrecht, J.; Viljoen, E. L.; Visagie, J. L. Stability of Nanocrystals: Thermodynamic Analysis of Oxidation and Re-reduction of Cobalt in Water/Hydrogen Mixtures. *J. Phys. Chem. B* **2005**, 109, 3575-3577.
- (6) Castro, R. H. R.; Quach, D. V. Analysis of Anhydrous and Hydrated Surface Energies of gamma-Al₂O₃ by Water Adsorption Microcalorimetry. *J. Phys. Chem. C* **2012**, 116, 24726-24733.

- (7) Campbell, C. T. Ultrathin metal films and particles on oxide surfaces: structural, electronic and chemisorptive properties. *Surf. Sci. Rep.* **1997**, 27, 1-111.
- (8) Argile, C.; Rhead, G. E. Adsorbed layer and thin film growth modes monitored by Auger electron spectroscopy. *Surf. Sci. Rep.* **1989**, 10, 277-356.
- (9) I. Chorkendorff, J. W. N., *Concepts of Modern Catalysis and Kinetics, 2nd, Revised and Enlarged Edition*. 2 ed.; Wiley: 2007; p 477.
- (10) Janse van Rensburg, W.; van Helden, P.; Moodley, D. J.; Claeys, M.; Petersen, M. A.; van Steen, E. Role of Transient Co-Subcarbonyls in Ostwald Ripening Sintering of Cobalt Supported on γ -Alumina Surfaces. *J. Phys. Chem. C* **2017**, 121, 16739-16753.
- (11) Nortier, P.; Fourre, P.; Saad, A. B. M.; Saur, O.; Lavalley, J. C. Effects of crystallinity and morphology on the surface properties of alumina. *Appl. Catal.* **1990**, 61, 141-160.
- (12) Wynblatt, P.; Gjostein, N. A. Supported metal crystallites. *Prog. Solid State Chem.* **1975**, 9, 21-58.
- (13) Munnik, P.; de Jongh, P. E.; de Jong, K. P. Control and Impact of the Nanoscale Distribution of Supported Cobalt Particles Used in Fischer–Tropsch Catalysis. *J. Am. Chem. Soc.* **2014**, 136, 7333-7340.
- (14) Argyle, M. D.; Frost, T. S.; Bartholomew, C. H. Cobalt Fischer–Tropsch Catalyst Deactivation Modeled Using Generalized Power Law Expressions. *Top. Catal.* **2014**, 57, 415-429.