

Supporting information

Mechanistic modeling of cobalt-based catalyst sintering in a fixed bed reactor under different conditions of Fischer-Tropsch synthesis

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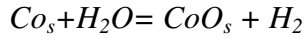
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This section gives the details of the sintering correlations proposed for cobalt-based crystallites. It is suggested that the first step of cobalt sintering in the presence of water could possibly involve reversible surface oxidation of cobalt nanoparticles:



The surface coverage by CoO in this case would be dependent on H_2O and H_2 pressures. The assumption that cobalt sintering is accelerated via particle surface oxidation would also explain why the sintering does not take place in the presence of either inert or reducing atmospheres, as they would inhibit the formation of surface CoO species. Eq. (5) allows calculation of CoO surface coverage θ_{CoO} as a function of operating conditions:

$$K_{CoO} = \frac{\theta_{CoO}}{1 - \theta_{CoO}} \left(\frac{P_{H_2}}{P_{H_2O}} \right)^{(\theta_{CoO} - 1)} \approx \theta_{CoO} \frac{P_{H_2}}{P_{H_2O}} \Rightarrow \theta_{CoO} = K_{CoO} \frac{P_{H_2O}}{P_{H_2}} \quad (4)$$

where for the sake of simplicity, the particle surface is assumed to be covered by either metallic or oxidized cobalt species.

Because of higher diffusivity of CoO relative to metallic cobalt we assume that particle diffusion is due to the presence of superficially oxidized cobalt particles¹.

$$D_i = 4.818 D_S^{CoO} \theta_{CoO} \left(\frac{2r}{d_i} \right)^4 = 4.818 D_S^{CoO} \left(\frac{2r}{d_i} \right)^4 K_{CoO} \frac{P_{H_2}}{P_{H_2O}} \quad (5)$$

where D_S^{CoO} is CoO surface diffusivity.

Once the particle surface is partially covered with cobalt oxide species, the particle growth occurs. Particle Migration and Coalescence occurs via a three-step (particle diffusion, collision, and coagulation) process. As already mentioned, the particles repartition measured during sintering² follows a *log normal distribution function (LNDF)*. Consequently the rate of collision, $d\Phi_i (s^{-1})$ for a particle i (with a diameter d_i) with *all* particles j (which have an average diameter d_j in the logarithmic size interval $d \ln(d_j)$) is calculated³ by:

$$d\Phi_i = \text{const} \cdot D_{ij} \cdot \frac{N}{A_{\text{support}}} \cdot f_{LN}(d_j) \cdot d \ln(d_j)$$

where *const.* is a time-independent constant, D_{ij} is the relative diffusion constant for particles of diameters d_i and d_j through the porous structure:

$$D_{ij} = D_i + D_j = 77.088 r^4 D_S^{CoO} K_{CoO} \frac{P_{H_2}}{P_{H_2O}} \left(\frac{1}{d_i^4} + \frac{1}{d_j^4} \right)$$

$f_{LN}(d_j)$ gives the fractional number of particles in the logarithmic size interval $d \ln(d_j)$, based on the *LNDF* while N/A_{support} gives the total number of Co particles per square meter of support:

$$\frac{N}{A_{\text{support}}} = \frac{6 X_{Co}}{\rho_{Co} (1 - X_{Co}) A_{m,\text{support}} \pi \bar{d}^3}$$

where ρ_{Co} is the cobalt mass density, X_{Co} is the cobalt loading in the catalyst, and $A_{m,\text{support}}$ is the specific support surface area. Therefore Φ_i the rate of collision of a particle j having a diameter d_i with all other particles is given by Ref. 4:

$$\Phi_i = \text{const} \cdot \frac{N}{A_{\text{support}}} \int_{-\infty}^{+\infty} D_{ij} f_{LN}(d_j) d \ln\left(\frac{d_j}{d}\right) = \text{const} \cdot \frac{N}{A_{\text{support}}} D_S^{CoO} K_{CoO} \frac{P_{H_2}}{P_{H_2O}} \left(\frac{1}{d_i^4} + \frac{e^{4 \ln^2 \sigma}}{\bar{d}^4} \right)$$

The total number of collisions per second Φ is calculated by:

$$\Phi = N \int_{-\infty}^{+\infty} \Phi_i f_{LN}(d_i) d \ln\left(\frac{d_i}{d}\right) = \text{const} \cdot \frac{N^2}{A_{\text{support}}} D_S^{CoO} K_{CoO} \frac{P_{H_2}}{P_{H_2O} \bar{d}^4}$$

The collision of two particles of diameters d_i and d_j results in a larger particle of diameter $(d_i^3 + d_j^3)^{1/3}$. The number of particles N is also reduced by one. The average increase in number-average diameter for the entire catalyst sample for one collision $\Delta(\bar{d})$ is then obtained from¹:

$$\Delta(\bar{d}) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \left(\frac{N\bar{d} - d_i - d_j + (d_i^3 + d_j^3)^{1/3}}{N-1} - \bar{d} \right) f_{LN}(d_i) d \ln\left(\frac{d_i}{d}\right) f_{LN}(d_j) d \ln\left(\frac{d_j}{d}\right)$$

Numerical integration gives:

$$\Delta(\bar{d}) = f(\sigma) \frac{\bar{d}}{N-1} \approx f(\sigma) \frac{\bar{d}}{N}$$

where $f(\sigma) = 1.36\ln^2\sigma - 0.13\ln\sigma + 0.28$ is a function of standard deviation of the lognormal distribution, σ .

The rate of increase in particle average diameter is then calculated by:

$$\frac{\partial(\bar{d})}{\partial t} = \Phi \Delta(\bar{d}) = \text{const.} f(\sigma) \frac{1.91 D_s^{CoO} X_{Co} K_{CoO}}{\rho_{Co} (1 - X_{Co}) A_{\text{support}} \bar{d}^6} \cdot \frac{P_{H_2O}}{P_{H_2}}$$

Reformulation yields the evolution of number-average Co particle diameter as a function of time and H_2O/H_2 partial pressure ratio during sintering:

$$\frac{\partial \bar{d}}{\partial t} = k_s \frac{P_{H_2O}}{P_{H_2}} \cdot \frac{1}{\bar{d}^6}$$

where sintering constant k_s , is the combination of all the parameters which are kept constant during sintering:

$$k_s = \text{const.} f(\sigma) \frac{13.38 D_s^{CoO} K_{CoO} X_{Co}}{(1 - X_{Co}) \rho_{Co} A_{\text{support}}}$$

In accordance with experimental data, a value of $29.68 \text{ nm}^7/\text{s}$ was used for k_s . An Arrhenius type of expression could be then employed for the sintering constant (k_s) to account for the variation with temperature⁴. As the *XRD* technique gives the surface-average diameter, Eq. (15) should be changed correspondingly. This is conducted using the correlation developed by Sehested⁴:

$$\bar{d}_s = \exp\left(\frac{5}{2} \ln^2 \sigma\right) \bar{d}$$

Fig. 1 suggests that the change in the standard deviation is small during sintering ($\sigma = 1.4$ for fresh catalyst, $\sigma = 1.45$ for sintered catalyst). Therefore one can neglect the change in the standard deviation for the particle diameters during sintering to convert the number-average diameter into surface-average diameter:

$$\frac{\partial \bar{d}_s}{\partial t} = k_s \frac{P_{H_2O}}{P_{H_2}} \cdot \frac{1}{\bar{d}_s^6} \quad (6)$$

Reference

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- (4) Sehested, J. Sintering of nickel steam-reforming catalysts. *J. Catal.* **2003**, 217, 417.