Electronic Supplementary Information for :

Tortuosity and mass transfer limitations in industrial hydrotreating catalysts: effect of particles shape and size distribution

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Mean Molar Flux Radius evaluation (intraparticle mass transfer limitation)

Let's consider an ideal (perfectly mixed) stirred-tank reactor loaded with a liquid phase and porous particles (external mass transfer resistance is neglected). The molar balance on the reactor gives:

$$V_R \cdot \varepsilon_i \cdot \frac{dC_f}{dt} = - \sum_i n_T \cdot x_i \cdot V_i \cdot \varepsilon_p \cdot \frac{d\overline{C}_{i,p}}{dt}$$

(SI.1.)

Where V_R is the reactor volume, ε_i the extragranular porosity, C_f the concentration in the fluid phase, n_T the total number of particles, x_i the number fraction of particles of volume V_i, ε_p the intragranular porosity and $\overline{C}_{i,p}$ the average concentration in the pore volume.

Considering spherical particles:

$$\frac{d\overline{C}_{i,p}(t)}{dt} = \frac{3}{R_{pi}^3} \cdot \int_0^{R_{pi}} r^2 \cdot \frac{\partial C_{i,p}(r,t)}{\partial t} \cdot dr$$

(SI.2.)

For a Fickian diffusion, the mass balance in the particles provides the following expression:

$$\frac{\partial C_{i,p}(r,t)}{\partial t} = \frac{1}{r^2} \cdot \frac{\partial}{\partial r}(r^2 J_i(r,t))$$

(SI.3.)

with: $$J_i(r,t) = - D_{eff} \cdot \frac{\partial C_{i,p}(r,t)}{\partial r}$$

(SI.4.)

Replacing equations (SI.2.) to (SI.4.) in (SI.1.) gives

$$V_R \cdot \varepsilon_i \cdot \frac{dC_f}{dt} = - \sum_{i=1}^{m} n_T \cdot x_i \cdot V_i \cdot \varepsilon_p \cdot \left(\frac{3}{R_{pi}^3} \cdot \int_0^{R_i} \frac{\partial}{\partial r}(r^2 J_i(r,t)) \cdot dr \right)$$

(SI.5.)

For a spherical particle:

$$V_i^3/R_{pi}^3 = 4.\pi$$

(SI.6.)

By inserting (SI.6.) in (SI.5.) and carrying out the change of variable $\rho = r/R_{pi}$, we get:

$$V_R.\varepsilon_i.\frac{dC_f}{dt} = -\sum_i n_T.x_i.\varepsilon_p.4.\pi.R_{pi}.\int_0^1 \frac{\partial}{\partial\rho}\left(\rho^2 J_i(\rho,t)\right).d\rho$$

(SI.7.)

The total number of particles is:

$$n_T = \frac{V_S}{\overline{V}_n}$$

(SI.8.)

Where Vs is the total solid volume and $\overline{V}_n$ is the average particle volume, defined by :

$$\overline{V}_n = \sum_i x_i.V_i$$

(SI.9.)

$$V_S = (1 - \varepsilon_i).V_R$$

(SI.10.)

Inserting equations (SI.8.) to (SI.10.) into (SI.7.) and considering that the mean molar flux density

$$\overline{J} = \int_0^1 \frac{\partial}{\partial\rho}\left(\rho^2 J_i(\rho,t)\right).d\rho$$
is the same for all particles finally gives:

$$\frac{dC_f}{dt} = -\frac{(1 - \varepsilon_i)}{\varepsilon_i}.\varepsilon_p.3.\frac{\sum_{i=1}^m x_i.R_{pi}}{\sum_{i=1}^m x_i.R_{pi}^3}\cdot\overline{J}$$

(SI.11.)

For spherical particles that are homogeneous in size, the molar balance is:

$$\frac{dC_f}{dt} = -\frac{(1 - \varepsilon_i)}{\varepsilon_i}.\varepsilon_p.\frac{3}{R_p^2}\overline{J}$$

(SI.12.)

Comparing equations (SI.11.) and (SI.12.) enables to define the mean radius as:

$$R_{mmf} = R_p = \sqrt{\frac{\sum_{i=1}^m x_i.R_{pi}^3}{\sum_{i=1}^m x_i.R_{pi}}}$$