catalysts

Supplementary Materials: Heteropolyacid Salt Catalysts for Methanol Conversion to Hydrocarbons and Dimethyl Ether: Effect of Reaction Temperature

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1. Testing criteria: exclusion of heat and transport limitations

Mass and heat limitations were calculated according to the criteria below, the detailed calculation process can refer to the SI file of reference [1].

(a) Internal mass transfer limitations

The effect of internal mass transfer limitations can be evaluated by the Weisz-Prater criterion, see eq. (R1) [2]:

$$N_{WP} = \frac{r_p^2 \cdot r_{obs,V}}{D_e \cdot C_s} \leq 0.3 \tag{R1}$$

where N_{WP} is the Weisz-Prater number, r_p is the catalyst particle diameter (m), $r_{obs,V}$ is the observed reaction rate per volume of solid catalyst (mol·m^{-3}·s^{-1}), D_e is the effective diffusion coefficient (m^2·s^{-1}) and C_s is the concentration of the limiting reactant (mol·m^{-3}) at the outside catalyst surface.

Experimental conditions: Reaction temperature T = 473.15 K, WHSV=2.0 h^{-1}, Partial pressure of MeOH [P_{MeOH}] = 0.48 bar, $r_{obs,v}$= 34.7 mol·m^{-3}·s^{-1}, r_p = 3.75·10^{-5} m.

Calculation of *Cs* and *De* can according to the SI file of the reference [1].

Cs = 12.3 mol·m^{-3}, *De* = 1.22·10^{-6} m^2·s^{-1}.

$$N_{WP,particle} = \frac{(3.75 \cdot 10^{-5}\ m)^2 \cdot\ 34.7 \frac{mol}{m^3 \cdot s}}{1.22 \cdot 10^{-6} \frac{m^2}{s} \cdot 12.3 \frac{mol}{m^3}} = 3.25 \cdot 10^{-5} \leq 0.3$$

(b) External mass transfer limitations

The Mears criterion was used to determine the influence of external mass transfer limitations, see eq. (R2) [3].

$$\omega = \frac{r_{obs} \cdot \rho_b \cdot r_p \cdot n}{k_c \cdot C_{M,b}} \leq 0.15 \tag{R2}$$

where, r_{obs} is the observed rate of methanol conversion in mol·kg$_{cat}^{-1}$·s^{-1}, ρ_b is the density of catalyst bed in kg·m^{-3}, r_p is the particle radius in m, n is the order of the reaction, k_c is the mass transfer coefficient in m·s^{-1}, and $C_{M,b}$ is the concentration of methanol in the bulk phase in mol·m^{-3}.

The density of catalyst bed ρ_b is 2000 kg·m^{-3}, superficial gas velocity u 0.0127 m·s^{-1}. Since the Rep value is 1.37, the correlation [4] used to estimate j_D is:

$$\varepsilon_B j_D = 0.010 + \frac{0.863}{\mathrm{Re}_p^{0.68} - 0.483} \quad \text{(R3)}$$

r_{obs} = 0.0174 mol·kg^{-1}·s^{-1}, kc = 0.0414 m·s^{-1}, $C_{M,b}$ = 12.3 mol·m^{-3}.

$$\omega = \frac{0.0174\, mol/(kg \cdot s) \cdot 2000\, kg/m^3 \cdot 3.75 \cdot 10^{-5} m \cdot 1}{0.0414\, m/s \cdot 12.3\, mol/m^3} = 2.55 \cdot 10^{-3} < 0.15$$

(c) External heat transfer limitations

The Mears criterion was used to determine the influence of external heat transfer limitations, see Equation (R4) [3].

$$\chi = \left| \frac{\Delta H_r \cdot r_{obs} \cdot \rho_b \cdot r_p \cdot E_{app}}{h_p \cdot T^2 \cdot R} \right| < 0.15 \quad \text{(R4)}$$

where, ΔH_r is the heat of reaction in J·mol^{-1}, E_{app} is the apparent activation energy of the reaction in J·mol^{-1}, and h_p is the gas to particle heat transfer coefficient in W·m^{-2}·K^{-1}.

ΔH_r = -2.156·10^4 *J/mol*, E_{app} = 1.02·10^5 *J/mol*, h_p = 7.36·10^2 W·m^{-2}·K^{-1}.

$$\chi = \left| \frac{-2.156 \cdot 10^4\, J/mol \cdot 0.0173\, mol/(kg \cdot s) \cdot 2 \cdot 10^3\, kg/m^3 \cdot 3.75 \cdot 10^{-5} m \cdot 1.02 \cdot 10^5\, J/mol}{7.36 \cdot 10^2\, W/(m^2 \cdot K) \cdot (473.15 K)^2 \cdot 8.314\, J/(mol \cdot K)} \right|$$

$$\chi = 2.08 \cdot 10^{-3} < 0.15$$

(d) Internal heat transfer limitations

Internal heat transfer limitations were evaluated via the Anderson's criterion, shown in eq. (R5) [5].

$$Da_{IV} = \left| \frac{\Delta H_r \cdot r_{obs,V} \cdot r_p^2}{\lambda_{p,eff} \cdot T} \right| < 0.75 \left(\frac{R \cdot T}{E_a} \right) \quad \text{(R5)}$$

$\lambda_{p,eff}$, the effective thermal conductivity of the particle (J·m^{-1}·s^{-1}·K^{-1}).

$$\lambda_{p,eff} = \lambda_f^{\varepsilon_{pellet}} \cdot \lambda_s^{1-\varepsilon_p} \quad \text{(R6)}$$

$\lambda_{p,eff}$ = 0.257 W·m^{-1}·K^{-1}.

$$\left(\frac{E_a}{R \cdot T} \right) \left| \frac{\Delta H_r \cdot r_{obs,V} \cdot r_p^2}{\lambda_{p,eff} \cdot T} \right|$$

$$= \left(\frac{1.02 \cdot 10^5\ J/mol}{8.314\ J/(mol \cdot K) \cdot 473.15\ K} \right) \left| \frac{-2.156 \cdot 10^4\ J/mol \cdot 34.7\ mol/(m^3 \cdot s) \cdot (3.75 \cdot 10^{-5}\ m)^2}{0.257\ W/(m \cdot K) \cdot 473.15\ K} \right|$$

$$= 2.24 \cdot 10^{-4} < 0.75$$

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