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A Computational Approach for Selection of Optimal Catalyst Shape for Solid-Catalysed Gas-Phase Reactions

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Supplementary information

1. A kinetic model for methane steam reforming over a $Ni/\alpha - Al_2O_3$ catalyst[1]

$$r_1 = \frac{k_1\Big(\frac{P_{CH_4}P_{H_2O}^{0.5}}{P_{H_2}^{1.25}}\Big)\Big(1-\Big(\frac{P_{CO}P_{H_2}^3}{K_{eq1}P_{CH_4}P_{H_2O}}\Big)\Big)}{\Big(1+K_{CO}P_{CO}+K_HP_H^{0.5}+K_{H_2O}\Big(\frac{P_{H_2O}}{P_{H_2}}\Big)\Big)^2} \quad \Big[\frac{kmol}{kg_{cat}.s}\Big] \tag{1}$$

$$r_2 = \frac{k_2\Big(\frac{P_{CO}P_{H_2O}^{0.5}}{P_{H_2}^{0.5}}\Big)\Big(1-\Big(\frac{P_{CO_2}P_{H_2}}{K_{eq2}P_{CO}P_{H_2O}}\Big)\Big)}{\Big(1+K_{CO}P_{CO}+K_HP_H^{0.5}+K_{H_2O}\Big(\frac{P_{H_2O}}{P_{H_2}}\Big)\Big)^2} \quad \Big[\frac{kmol}{kg_{cat}.s}\Big] \tag{2}$$

$$r_3 = \frac{k_3\Big(\frac{P_{CH_4}P_{H_2O}}{P_{H_2}^{1.75}}\Big)\Big(1-\Big(\frac{P_{CO_2}P_{H_2}^4}{K_{eq3}P_{CH_4}P_{H_2O}^2}\Big)\Big)}{\Big(1+K_{CO}P_{CO}+K_HP_H^{0.5}+K_{H_2O}\Big(\frac{P_{H_2O}}{P_{H_2}}\Big)\Big)^2} \quad \Big[\frac{kmol}{kg_{cat}.s}\Big] \tag{3}$$

$$K_{eq1} = 1.198\times10^{17}\, exp\Big(\frac{-26830}{T}\Big) \quad \Big[(kPa)^2\Big] \tag{4}$$

$$K_{eq2} = 1.767\times10^{-2}\, exp\Big(\frac{4400}{T}\Big) \quad [\,] \tag{5}$$

$$K_{eq3} = 2.117\times10^{15}\, exp\Big(\frac{-22430}{T}\Big) \quad \Big[(kPa)^2\Big] \tag{6}$$

$$k_1 = 5.922\times10^{8}\, exp\Big(\frac{-209.2}{RT}\Big) \quad \Big[\Big(\frac{kmol}{kg_{cat}.s}\Big)(kPa)^{-0.25}\Big] \tag{7}$$

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$$k_2 = 6.028 \times 10^{-4}\ exp\Big(\frac{-15.4}{RT}\Big) \quad \Bigg[\Big(\frac{kmol}{kg_{cat}.s}\Big)(kPa)^{-1}\Bigg] \tag{8}$$

$$k_3 = 1.093 \times 10^{3}\ exp\Big(\frac{-109.4}{RT}\Big) \quad \Bigg[\Big(\frac{kmol}{kg_{cat}.s}\Big)(kPa)^{-0.25}\Bigg] \tag{9}$$

$$K_{CO} = 5.127 \times 10^{-13}\ exp\Big(\frac{140.0}{RT}\Big) \quad \Big[(kPa)^{-1}\Big] \tag{10}$$

$$K_{H} = 5.68 \times 10^{-10}\ exp\Big(\frac{93.4}{RT}\Big) \quad \Big[(kPa)^{-0.5}\Big] \tag{11}$$

$$K_{H_2O} = 9.251 \times exp\Big(\frac{-15.9}{RT}\Big) \quad [\,] \tag{12}$$

$T : Temperature\ [K]$

$R : Universal\ gas\ constant\ \Bigg(8.314\ \Big[\frac{kJ}{mol.K}\Big]\Bigg)$

$P_i : Partial\ pressure\ of\ component\ i\ [kPa]$

2. A kinetic model for water gas shift reaction over a $Cu/ZnO/Al_2O_3$ catalyst[2]

$$r_1 = k_1\Bigg(P_{CO}P_{H_2O} - \Big(\frac{P_{CO_2}P_{H_2}}{K_{eq1}}\Big)\Bigg) \quad \Big[\frac{mol}{g_{cat}.h}\Big] \tag{13}$$

$$K_{eq1} = exp\Big(\frac{4577.8}{T} - 4.33\Big) \quad [\,] \tag{14}$$

$$k_1 = 2.96 \times 10^{5}\ exp\Big(\frac{-47400}{RT}\Big) \quad \Bigg[\Big(\frac{mol}{g_{cat}.h}\Big)(atm)^{-2}\Bigg] \tag{15}$$

$T : Temperature\ [K]$

$R : Universal\ gas\ constant\ \Bigg(8314\ \Big[\frac{J}{mol.K}\Big]\Bigg)$

$P_i : Partial\ pressure\ of\ component\ i\ [atm]$

3. A kinetic model for methanol synthesis over a $Cu/ZnO/Al_2O_3$ catalyst[3]

$$r_1 = \frac{k_1K_{CO}\Big[P_{CO}P_{H_2}^{1.5} - \frac{P_{CH_3OH}}{P_{H_2}^{0.5}K_{eq1}}\Big]}{(1 + K_{CO}P_{CO} + K_{CO_2}P_{CO_2})\Bigg[P_{H_2}^{0.5} + \Big(\frac{K_{H_2O}}{K_{H_2}^{0.5}}\Big)P_{H_2O}\Bigg]} \quad \Big[\frac{mol}{kg_{cat}.s}\Big] \tag{16}$$

$$r_2 = \frac{k_2 K_{CO_2}\Big(P_{CO_2}P_{H_2} - \dfrac{P_{H_2O}P_{CO}}{K_{eq2}}\Big)}{(1 + K_{CO}P_{CO} + K_{CO_2}P_{CO_2})\left[P_{H_2}^{0.5} + \Big(\frac{K_{H_2O}}{K_{H_2}^{0.5}}\Big)P_{H_2O}\right]} \quad \Big[\frac{mol}{kg_{cat}.s}\Big] \tag{17}$$

$$r_3 = \frac{k_3 K_{CO_2}\Big[P_{CO_2}P_{H_2}^{1.5} - \dfrac{P_{CH_3OH}P_{H_2O}}{P_{H_2}^{1.5}K_{eq3}}\Big]}{(1 + K_{CO}P_{CO} + K_{CO_2}P_{CO_2})\left[P_{H_2}^{0.5} + \Big(\frac{K_{H_2O}}{K_{H_2}^{0.5}}\Big)P_{H_2O}\right]} \quad \Big[\frac{mol}{kg_{cat}.s}\Big] \tag{18}$$

$$K_{eq1} = 10^{\left(\frac{5139}{T} - 12.621\right)} \quad \Big[(bar)^{-2}\Big] \tag{19}$$

$$K_{eq2} = 10^{\left(\frac{-2073}{T} + 2.029\right)} \quad [\,] \tag{20}$$

$$K_{eq3} = K_{eq1} \times K_{eq2} \tag{21}$$

$$k_1 = 2.69 \times 10^7 \; exp\Big(\frac{-109900}{RT}\Big) \quad \left[\Big(\frac{mol}{kg_{cat}.s}\Big)(bar)^{-1}\right] \tag{22}$$

$$k_2 = 7.31 \times 10^8 \; exp\Big(\frac{-123400}{RT}\Big) \quad \left[\Big(\frac{mol}{kg_{cat}.s}\Big)(bar)^{-0.5}\right] \tag{23}$$

$$k_3 = 4.36 \times 10^2 \; exp\Big(\frac{-65200}{RT}\Big) \quad \left[\Big(\frac{mol}{kg_{cat}.s}\Big)(bar)^{-1}\right] \tag{24}$$

$$K_{CO} = 7.99 \times 10^{-7} \; exp\Big(\frac{58100}{RT}\Big) \quad \Big[(bar)^{-1}\Big] \tag{25}$$

$$K_{CO_2} = 1.02 \times 10^{-7} \; exp\Big(\frac{67400}{RT}\Big) \quad \Big[(bar)^{-1}\Big] \tag{26}$$

$$\frac{K_{H_2O}}{K_{H_2}^{0.5}} = 4.13 \times 10^{-11} \; exp\Big(\frac{104500}{RT}\Big) \quad \Big[(bar)^{-0.5}\Big] \tag{27}$$

$T : Temperature \; [K]$

$R : Universal \; gas \; constant \; \left(8314 \; \Big[\frac{J}{mol.K}\Big]\right)$

$P_i : Partial \; pressure \; of \; component \; i \; [bar]$

4. A kinetic model for dimethyl ether (DME) synthesis over a $CuO/ZnO/Al_2O_3$ catalyst[4]

$$r_1 = \frac{k_1 P_{CO} P_{H_2}^2 \Big(1 - \frac{P_{CH_3OH}}{K_{eq1} P_{CO} P_{H_2}^2}\Big)}{(1 + K_{CO}P_{CO} + K_{CO_2}P_{CO_2} + K_{H_2}P_{H_2})^3} \quad \Big[\frac{mol}{g_{cat}.h}\Big] \tag{28}$$

$$r_2 = \frac{k_2 P_{CO_2} P_{H_2}^3 \Big(1 - \frac{P_{CH_3OH} P_{H_2O}}{K_{eq2} P_{CO_2} P_{H_2}^3}\Big)}{(1 + K_{CO}P_{CO} + K_{CO_2}P_{CO_2} + K_{H_2}P_{H_2})^4} \quad \Big[\frac{mol}{g_{cat}.h}\Big] \tag{29}$$

$$r_3 = \frac{k_3 P_{CH_3OH} \Big(1 - \frac{P_{DME} P_{H_2O}}{K_{eq3} P_{CH3OH}^2}\Big)}{(1 + \sqrt{K_{CH_3OH} P_{CH_3OH}})^2} \quad \Big[\frac{mol}{g_{cat}.h}\Big] \tag{30}$$

$$K_{eq1} = 10^{\Big(\frac{5139}{T} - 12.621\Big)} \quad \Big[(bar)^{-2}\Big] \tag{31}$$

$$K_{eq2} = 10^{\Big(\frac{-2073}{T} + 2.029\Big)} \quad [\,] \tag{32}$$

$$K_{eq3} = K_{eq1} \times K_{eq2} \tag{33}$$

$$K_{eq3} = exp\Big(-9.76 + \frac{3.2 \times 10^3}{T} + 1.07\ log(T) - 6.57 \times 10^{-4}\ T + 4.9 \times 10^{-8}\ T^2 + \frac{6.05 \times 10^3}{T^2}\Big) \quad [\,] \tag{34}$$

$$k_1 = 7.38 \times 10^3\ exp\Big(\frac{-54307}{RT}\Big) \quad \Big[\Big(\frac{mol}{g_{cat}.h}\Big)(bar)^{-3}\Big] \tag{35}$$

$$k_2 = 5.059 \times 10^3\ exp\Big(\frac{-67515}{RT}\Big) \quad \Big[\Big(\frac{mol}{g_{cat}.h}\Big)(bar)^{-4}\Big] \tag{36}$$

$$k_3 = 1.062 \times 10^3\ exp\Big(\frac{-43473}{RT}\Big) \quad \Big[\Big(\frac{mol}{g_{cat}.h}\Big)(bar)^{-1}\Big] \tag{37}$$

$$K_{CO} = 3.934 \times 10^{-6}\ exp\Big(\frac{37373}{RT}\Big) \quad \Big[(bar)^{-1}\Big] \tag{38}$$

$$K_{CO_2} = 1.858 \times 10^{-6}\ exp\Big(\frac{53795}{RT}\Big) \quad \Big[(bar)^{-1}\Big] \tag{39}$$

$$K_{H_2} = 0.6716\ exp\Big(\frac{-6476}{RT}\Big) \quad \Big[(bar)^{-1}\Big] \tag{40}$$

$$K_{CH_3OH} = 3.48 \times 10^{-6}\ exp\left(\frac{54689}{RT}\right) \quad \left[(bar)^{-1}\right] \tag{41}$$

$T : Temperature\ [K]$

$R : Universal\ gas\ constant\ \left(8314\ \left[\frac{J}{mol.K}\right]\right)$

$P_i : Partial\ pressure\ of\ component\ i\ [bar]$

References

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