Effects of spillover and particle size in a kinetic model of catalyzed reactions

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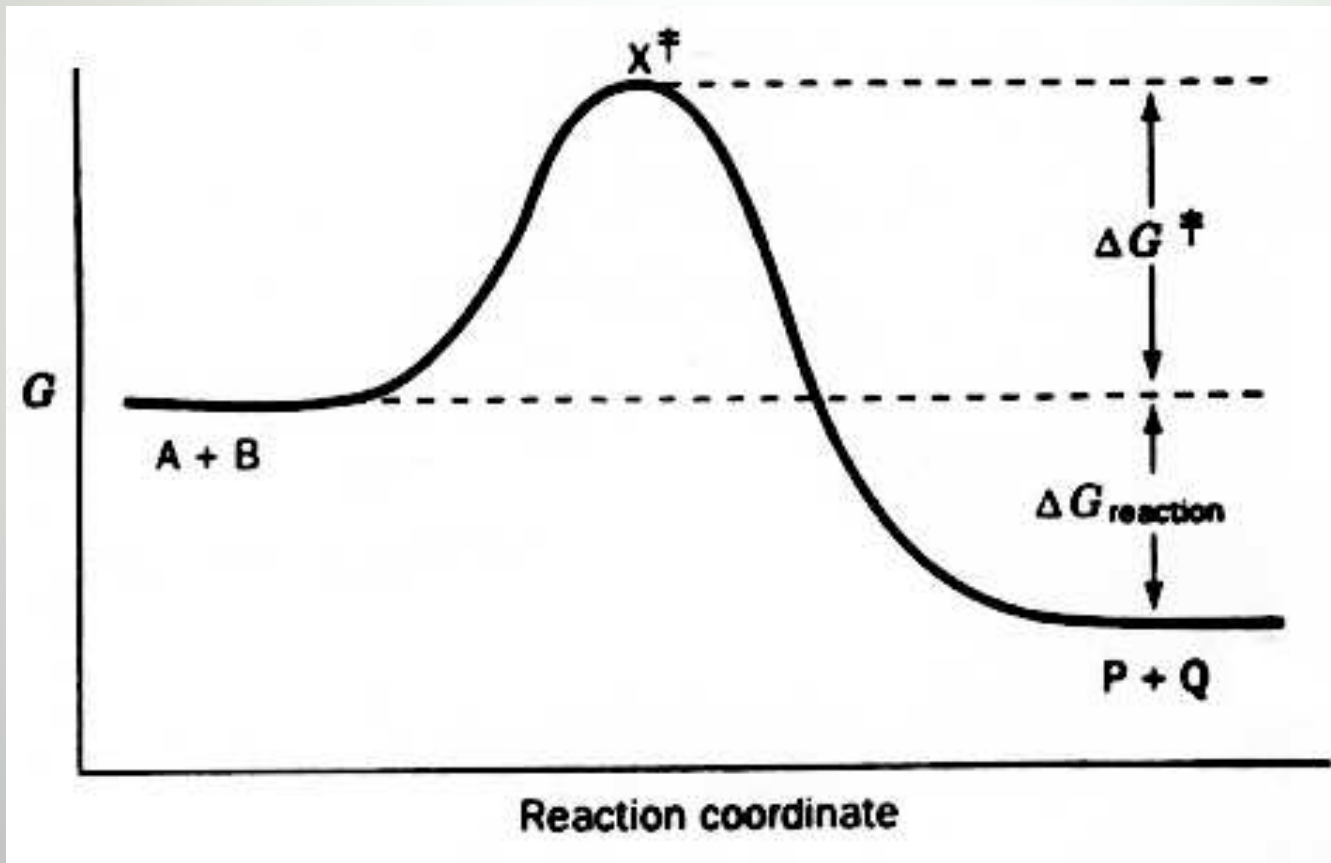
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Outline

- ✓ **Introduction**
- ✓ **Goal**
- ✓ **The Model**
- ✓ **Reactant Mobility and Catalyst Geometry**
- ✓ **Temperature**
- ✓ **Conclusions**
- ✓ **Perspectives**
- ✓ **References**

Introduction

transition state theory

Introduction

supported catalysts

✓ *metal particles deposited on the internal surface of a porous support*

✓ *designed to maximize the active surface area per unit mass and volume of the catalyst*

✓ *porous pellets (2 – 20 nm in diameter) or monoliths with a porous "washcoat"*

✓ *pores diameter: 1 – 2 nm (micropores)*
        2 – 50 nm (mesopores)
        ≥ 50 nm (macropores)

Introduction

supported catalysts

- ✓ *size of metal particles: few atoms*

  1 – 20 nm (more typical)

  10 – 100 nm (car exhaust)

- ✓ *fabrication of real/model catalysts: impregnation, evaporation, chemical vapor deposition, vesicle-mediated deposition, spin-coating technique, electron beam lithography, electrochemical fabrication etc.*

Introduction

heterogeneous catalysis

- ✓ *particle structure: geometric shape, exposed crystal planes, size, properties of the support (e.g. metal-support interaction), temperature and method of fabrication*

- ✓ *reaction mechanisms: prescription of elementary steps (adsorption, desorption, reaction and diffusion) and ratios of the rate constants*

- ✓ *spillover and back spillover effects*

Introduction

heterogeneous catalysis

- ✓ *rate equations (mean-field)*

- ✓ *distribution of catalytic sites in lattices (CO oxidation), with simplified diffusion and adsorption of some species*

- ✓ *simple models emphasizing scaling properties*

Goal

discuss the interplay of various physico-chemical quantities and conditions in systems where spillover is present
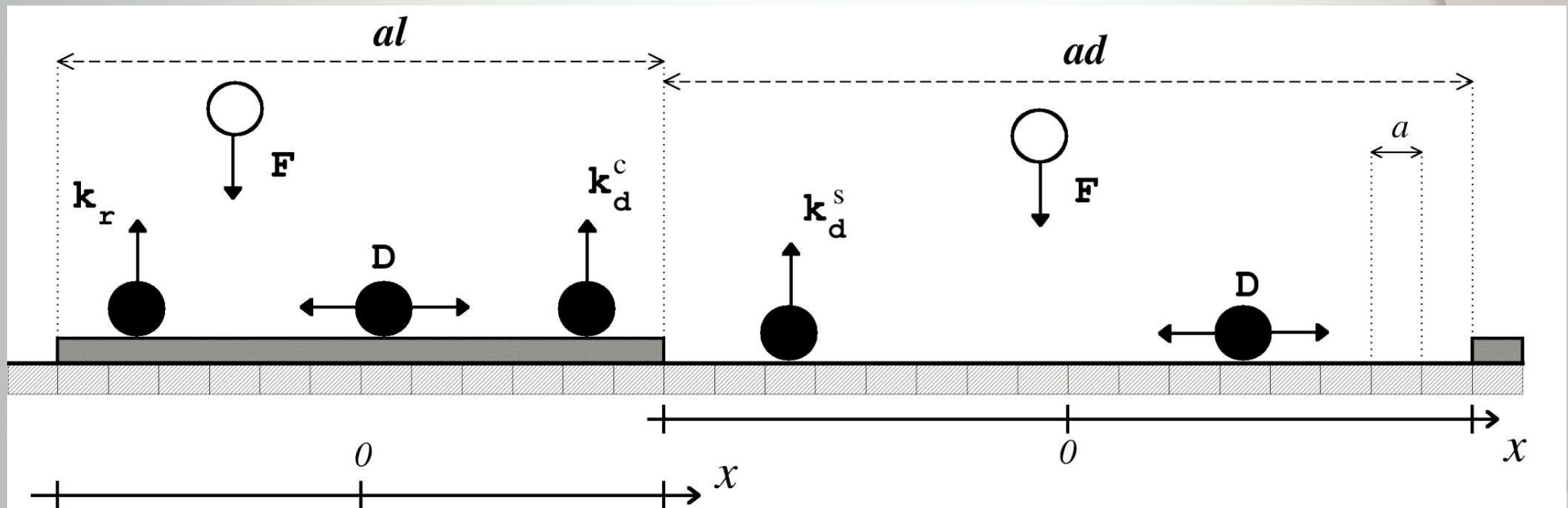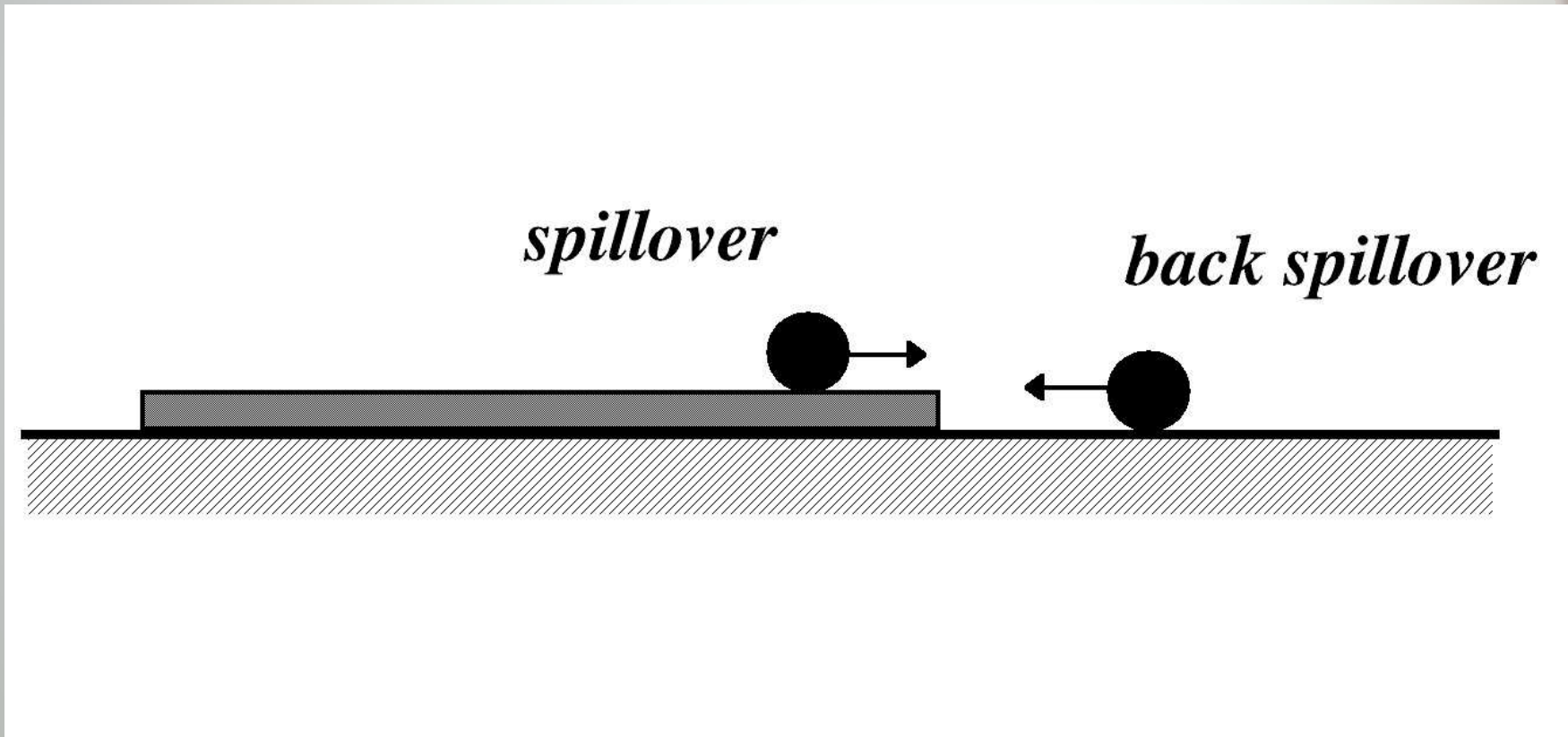
The Model

reaction mechanism

$$R_{gas} \leftrightarrow R_{ads}$$

$$R_{ads} + C \rightarrow P_{gas}$$

$$R_{ads} + R'_{gas} + C \rightarrow P_{gas}$$

The Model

definition

catalyst coverage: $\varepsilon = \dfrac{l}{l+d}$

The Model

definition

The Model

continuum limit

$$l \gg 1$$

$$d \gg 1$$

$$1 - 50 \, nm \quad \Rightarrow \quad 3 \leq l \leq 150$$

$$50 - 200 \, nm \quad \Rightarrow \quad 100 \leq d \leq 500$$

The Model

reactant coverage

$$\theta_c(x,t) \implies -\frac{la}{2} \leq x \leq \frac{la}{2}$$

$$\theta_s(x,t) \implies -\frac{da}{2} \leq x \leq \frac{da}{2}$$

The Model

reactant coverage

$$\frac{\partial}{\partial t}\theta_c(x,t) = \frac{D}{2}\frac{\partial^2}{\partial x^2}\theta_c(x,t) + F[1-\theta_c(x,t)] - \left(k_r + k_d^c\right)\theta_c(x,t)$$

$$\frac{\partial}{\partial t}\theta_s(x,t) = \frac{D}{2}\frac{\partial^2}{\partial x^2}\theta_s(x,t) + F[1-\theta_s(x,t)] - k_d^s\theta_s(x,t)$$

The Model

stationary state

$$\frac{\partial}{\partial t}\theta_c(x,t) = \frac{\partial}{\partial t}\theta_s(x,t) = 0$$

$$\theta_c(x,t) = \theta_c(x)$$

$$\theta_s(x,t) = \theta_s(x)$$

The Model

stationary state

$$\frac{D}{2}\frac{d^2\theta_c}{dx^2} + F(1-\theta_c) - \left(k_r + k_d^c\right)\theta_c = 0$$

$$\frac{D}{2}\frac{d^2\theta_s}{dx^2} + F(1-\theta_s) - k_d^s\theta_s = 0$$

The Model

solution

$$\theta_c(x) = r_c + \alpha_c \cosh(x/\lambda_c)$$

$$r_c = \frac{1}{1 + k_r/F + k_d^c/F} \qquad \lambda_c = \sqrt{\frac{D/F}{2\left(1 + k_r/F + k_d^c/F\right)}}$$

The Model

solution

$$\theta_s(x) = r_s + \alpha_s \cosh(x/\lambda_s)$$

$$r_s = \frac{1}{1 + k_d^s/F}$$

$$\lambda_s = \sqrt{\frac{D/F}{2\left(1 + k_d^s/F\right)}}$$

The Model

balance

$$\left(\Delta\theta_c\right)_{loss}=\left(\Delta\theta_c\right)_{lass}=\frac{2D}{d^2}\left(1-\frac{2D}{a^2}\right)\left(\theta^\dagger-\theta^*\right)\theta\frac{1}{a}\int_{-la/2}^{la/2}\left(kl\left(kk_r^c+k_d\right)\theta_d^c\right)\overline{\theta}_c\,dx'$$

$$\theta^* \equiv \theta_s\!\left(\frac{da}{2}\right) = r_s + \alpha_s \cosh\!\left(\frac{da}{2\lambda_s}\right)$$

$$\theta^\dagger \equiv \theta_c\!\left(\frac{la}{2}\right) = r_c + \alpha_c \cosh\!\left(\frac{la}{2\lambda_c}\right)$$

$$\overline{\theta}_c \equiv \frac{1}{la}\int_{-la/2}^{la/2}\theta_c(x')\,dx'$$

The Model

balance

$$\left(\Delta\theta_c\right)\left(\Delta\theta_c\right)\frac{2D}{gain\;c}\,d = \theta^*\left(1-\frac{2D}{a^2}\right) + \theta^\dagger\left(\frac{1}{a}\right)\int_{-la/2}^{la/2} F\left[F - \left(\theta_c - \overline{\theta}_c'\right)\right]\,dx'$$

$$\theta^* \equiv \theta_s\left(\frac{da}{2}\right) = r_s + \alpha_s \cosh\left(\frac{da}{2\lambda_s}\right)$$

$$\theta^\dagger \equiv \theta_c\left(\frac{la}{2}\right) = r_c + \alpha_c \cosh\left(\frac{la}{2\lambda_c}\right)$$

$$\overline{\theta}_c \equiv \frac{1}{la}\int_{-la/2}^{la/2}\theta_c(x')\,dx'$$

The Model

final solution

$$\alpha_c = \frac{\lambda_c (r_s - r_c) \tanh\left(\dfrac{da}{2\lambda_s}\right)}{\lambda_c \cosh\left(\dfrac{la}{2\lambda_c}\right) \tanh\left(\dfrac{da}{2\lambda_s}\right) + \left[\lambda_s + a \tanh\left(\dfrac{da}{2\lambda_s}\right)\right] \sinh\left(\dfrac{la}{2\lambda_c}\right)}$$
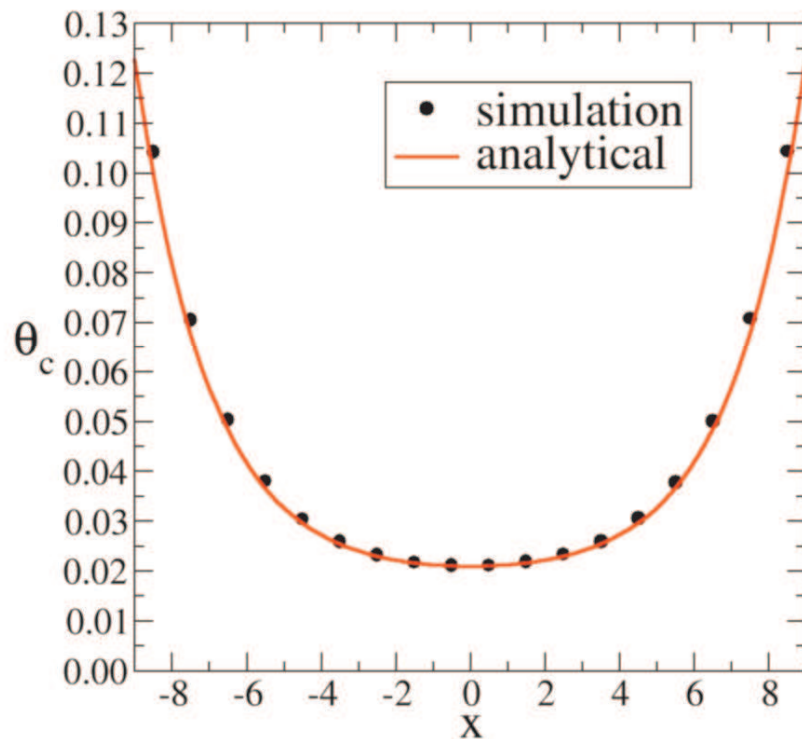
The Model

final solution

$$\alpha_s = \frac{\lambda_s (r_c - r_s)\tanh\left(\dfrac{la}{2\lambda_c}\right)}{\lambda_s \cosh\left(\dfrac{da}{2\lambda_s}\right)\tanh\left(\dfrac{la}{2\lambda_c}\right) + \left[\lambda_c + a\tanh\left(\dfrac{la}{2\lambda_c}\right)\right]\sinh\left(\dfrac{da}{2\lambda_s}\right)}$$

The Model

turnover frequency

$$TOF = k_r \overline{\theta}_c$$

The Model

comparison with simulations

Mobility and Geometry

diffusion lengths

$$L_c = \sqrt{\frac{D_c}{k_r + k_d^c}}$$

$$L_s \equiv \sqrt{\frac{D_s}{k_d^s}}$$

Mobility and Geometry

a few assumptions

✓ *setting the time unit* $\implies$ $F = 1s^{-1}$

$$TOF / F \leq 1$$

✓ *low desorption on the catalyst* $\implies$ $\dfrac{k_d^c}{F} << 1$
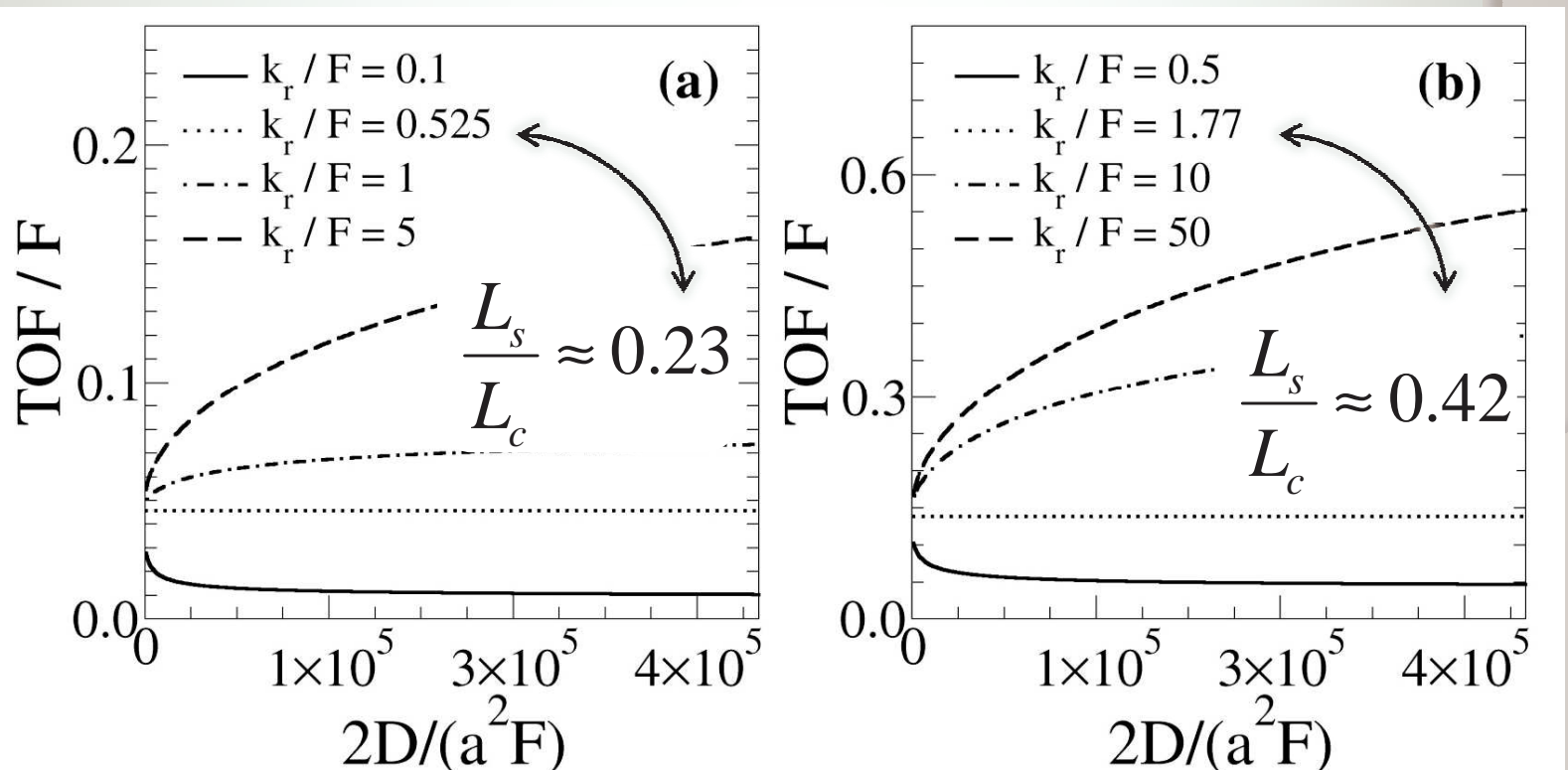
Mobility and Geometry

reactant mobility

$k_d^c = 10^{-3}$

$k_d^s = 10$

$l = 75$

$\varepsilon = 0.05$
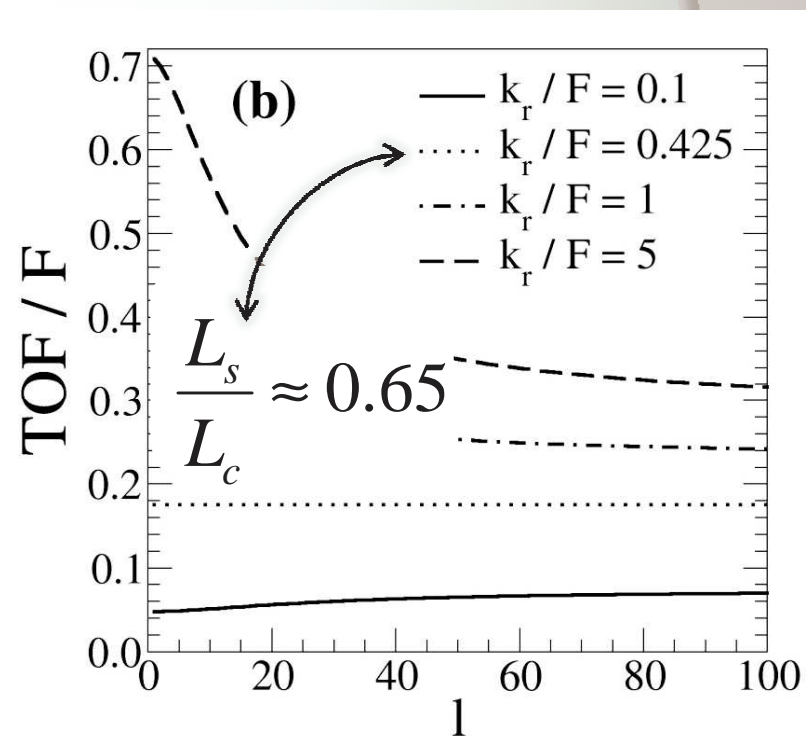
$\varepsilon = 0.15$
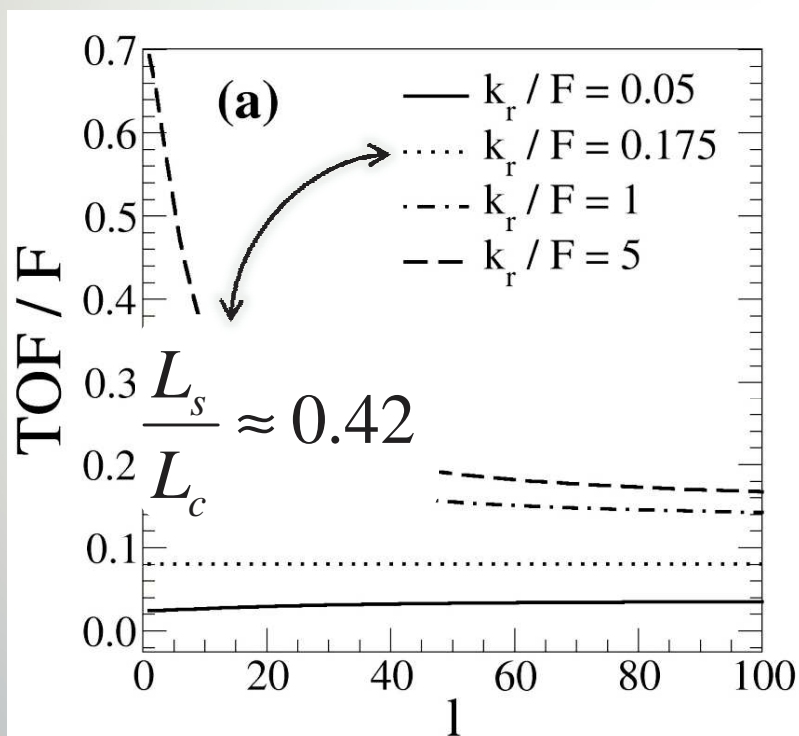
Mobility and Geometry

catalyst particles size

$D/a^2 = 500$

$k_d^c = 10^{-3}$

$k_d^s = 1$

$\varepsilon = 0.15$

$\varepsilon = 0.3$

(a) TOF / F vs. l; legend: $k_r/F = 0.05$, $k_r/F = 0.175$, $k_r/F = 1$, $k_r/F = 5$; $\dfrac{L_s}{L_c} \approx 0.42$

(b) TOF / F vs. l; legend: $k_r/F = 0.1$, $k_r/F = 0.425$, $k_r/F = 1$, $k_r/F = 5$; $\dfrac{L_s}{L_c} \approx 0.65$

Temperature

Arrhenius

$$D = a^2 \nu_D \exp\left(-\frac{E_D}{k_B T}\right)$$

$$k_d^s = \nu_d \exp\left(-\frac{E_d}{k_B T}\right)$$

$$k_r = \nu_r \exp\left(-\frac{E_r}{k_B T}\right)$$

Temperature

a few assumptions

$$a^2\nu_D = \nu_r = 2 \times 10^{12} \, s^{-1}$$

$$a = 5 \times 10^{-10} \, m$$

$$F = 1s^{-1}$$

$$E_D < E_d$$

$$k_d^c << 1$$

$$10 \leq \frac{\nu_d}{\nu_r} \leq 1000$$

$$\varepsilon = 0.15$$

Temperature

activation of a process

- ✓ *exceeding the external flux*

- ✓ *excluded volume effects*

- ✓ *low temperature* → *surface poisoning*

- ✓ *reaction activation* → *other processes activation*

Temperature

$$L_s \sim \exp\left(\frac{E_d - E_D}{2k_B T}\right)$$

activation energies

$E_D = 5\,\text{kcal/mol}$

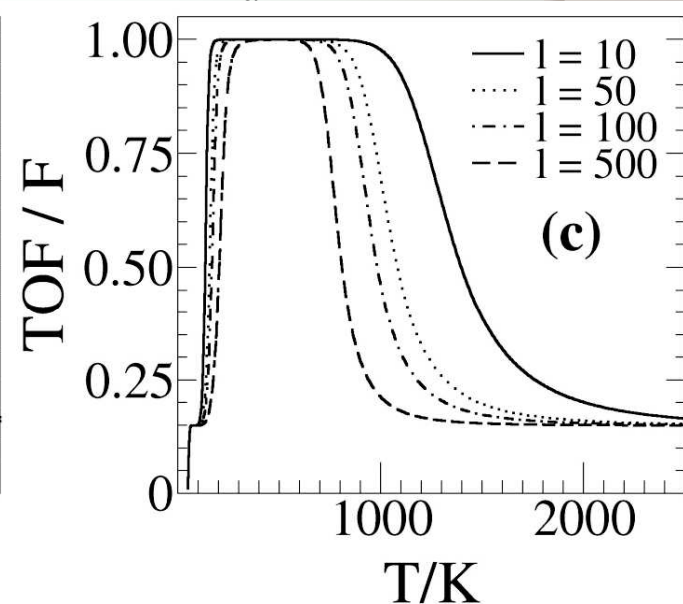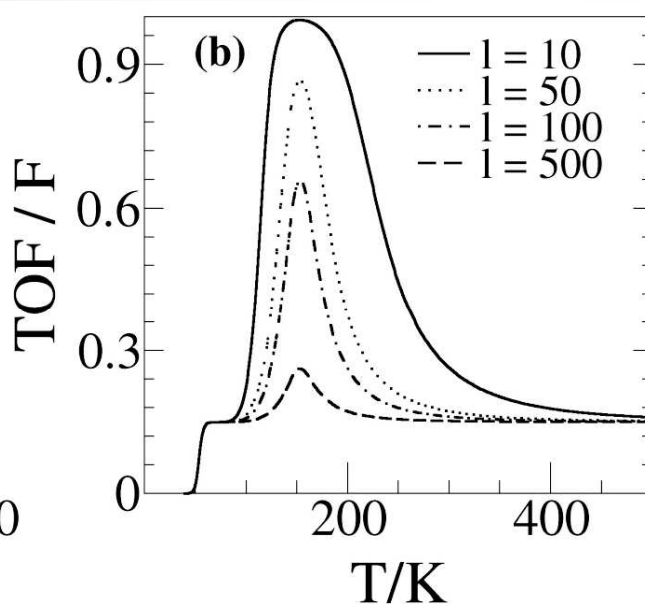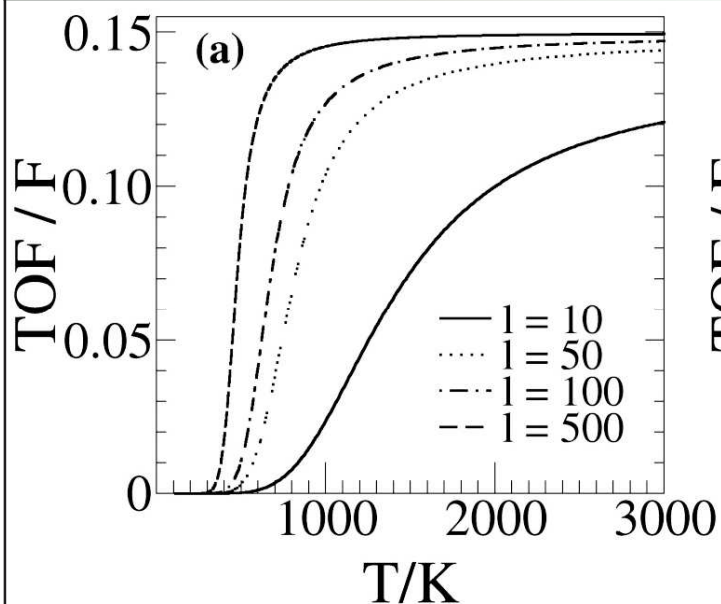$E_r = 15\,\text{kcal/mol}$

$E_d = 10\,\text{kcal/mol}$

$\nu = 100\,\nu$

$E_D = 5\,\text{kcal/mol}$

$E_r = 3\,\text{kcal/mol}$

$E_d = 10\,\text{kcal/mol}$

$E_D = 6\,\text{kcal/mol}$

$E_r = 3\,\text{kcal/mol}$

$E_d = 35\,\text{kcal/mol}$

Temperature
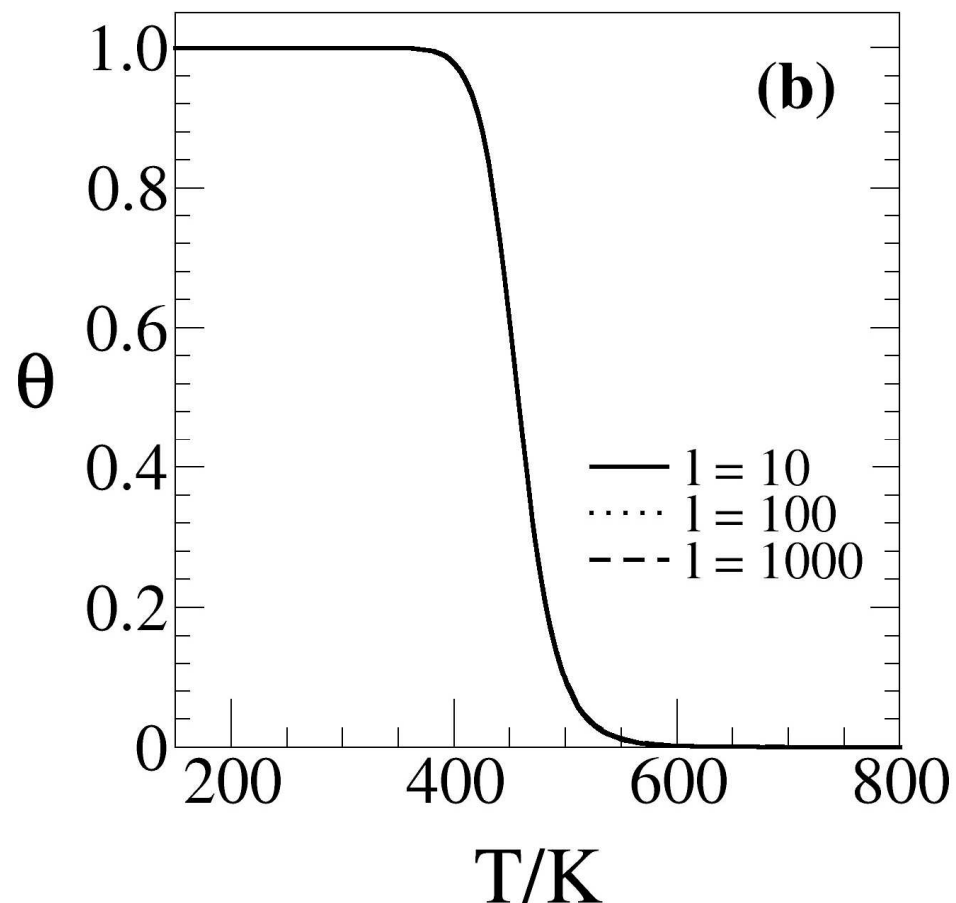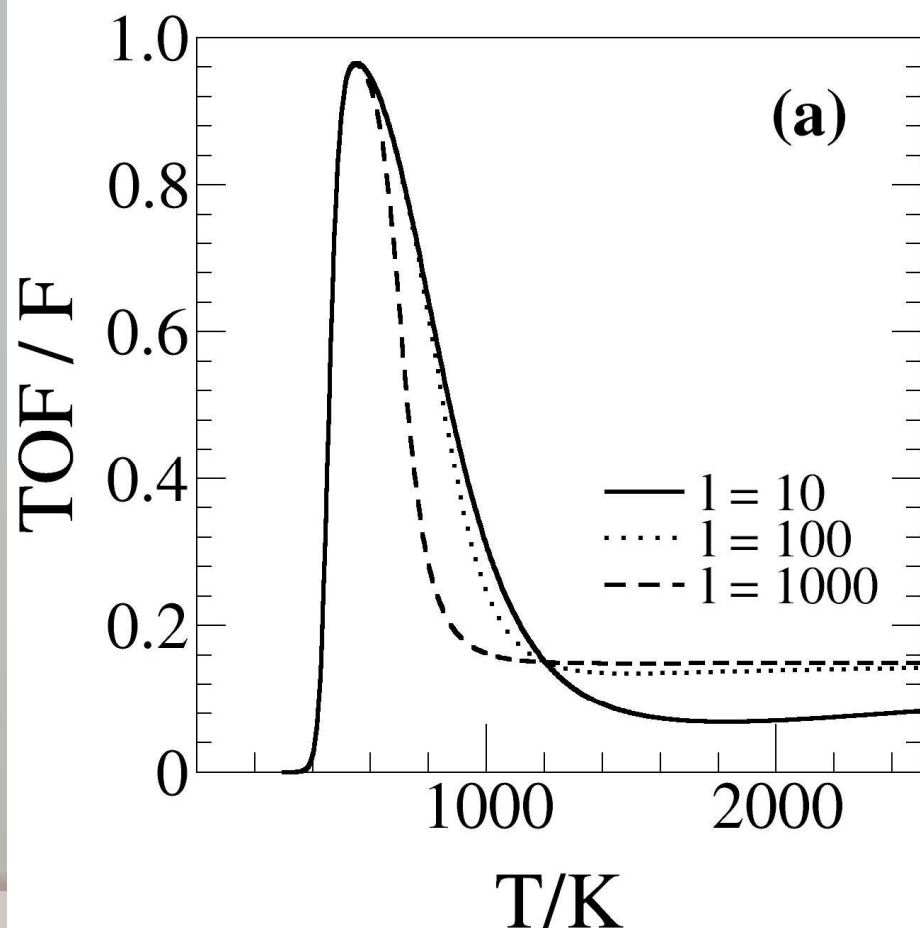
$E_D = 6 \, \text{kcal/mol}$

$E_{rd} = 24 \, \text{kcal/mol}$

$E_r = 100 \, \text{k}$

$E_d = 35 \, \text{kcal/mol}$

Temperature

$$E_D = 5 \, \text{kcal/mol}$$

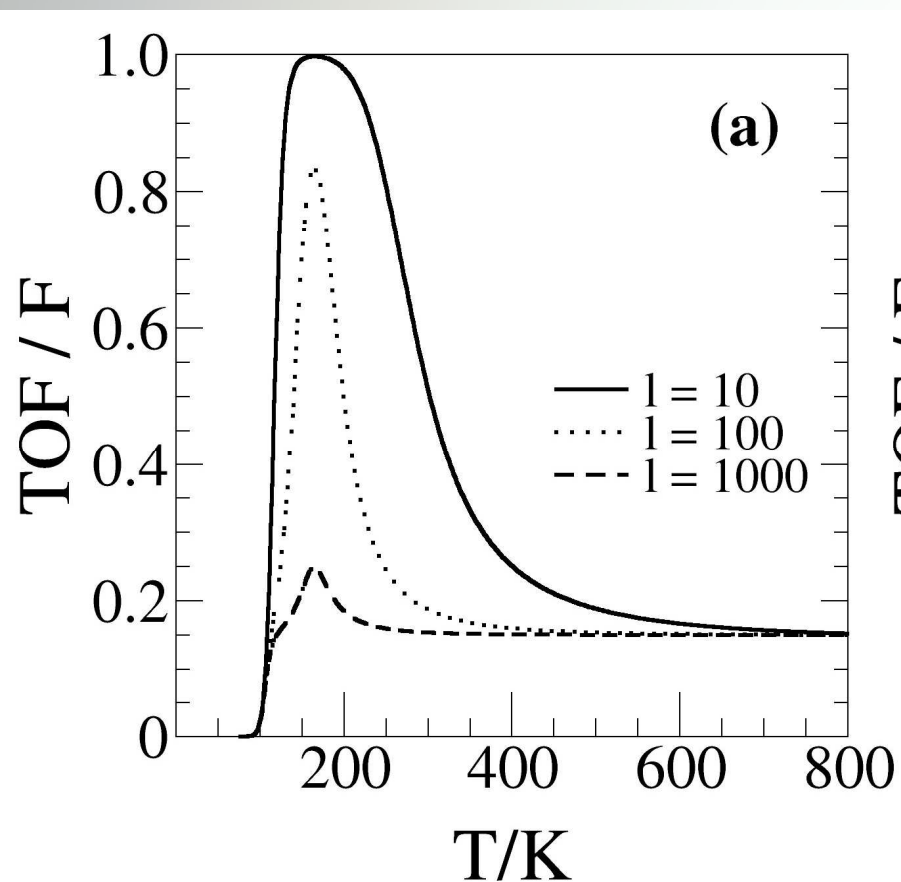$$E_r = 6 \, \text{kcal/mol}$$

$$E_d = 10 \, \text{kcal/mol}$$

$$\nu_d = 10 \, \nu_r \qquad\qquad \nu_d = 1000 \, \nu_r$$

Conclusions

- ✓ *for rapid reactions, enhancing surface diffusion or increasing catalyst particle size favors back spillover and thus increases the turnover frequency*

- ✓ *for slow reactions, spillover-dominated regime: enhancing surface diffusion or increasing catalyst particle size slows down the convertion*

- ✓ *catalyst coverage dependent critical ratio of diffusion lengths separates these regimes*

Conclusions

- ✓ *a peak in the turnover frequency as function of temperature is observed when $E_d > E_D$ and $E_r < E_d$*

- ✓ *significant particle size dependece in the peaks for small gaps between the activation energies*

- ✓ *for fixed amount of catalytic material, small particle sizes allow the turnover frequency to attain high peak values (beneficial effect of back spillover)*

Conclusions

- ✓ *for slow reactions, i.e. $E_r > E_d$, the turnover frequency monotonically increases with temperature*

- ✓ *in that case, large particle sizes are more efficient to avoid negative effects of spillover*

Perspectives

- ✓ ***catalyst deactivation by poisoning (trapping problems):***

  T. G. Mattos and F. D. A. Aarão Reis

  J. Chem.Phys. (accepted)

- ✓ ***anodic corrosion of metals: formation of patterns with nanotube shapes:***

  in colaboration with Prof. J-P Badiali and D. Di Caprio (CNRS - Paris)

References

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