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Analytical Model for Extrapolation of Experimental NMR Diffusion Studies to Reaction Conditions for Formulated Catalyst Particles

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1. Introduction

Formulated catalyst particles used in technical applications of heterogeneous catalysis are usually well characterized with respect to their catalytic and adsorption properties as well as with respect to the internal structure of their micro- and transport pores [1]. In the present work, pulsed field gradient (PFG) nuclear magnetic resonance (NMR) [1] is used to measure temperature-dependent diffusion coefficients of reactant molecules in formulated catalysts. A theoretical model is developed, which combines adsorption and pore structure parameters to extrapolate the measured diffusion data to reaction conditions. The only free parameter in this theoretical model is the tortuosity factor of the transport pore system, which we confirm in separate NMR diffusion experiments.

2. Theoretical approach and experimental results

The set of equations and experimental parameters necessary to model the effective diffusion (D_{eff}) of reactants in formulated catalyst particles is presented in Fig. 1. In comparison to earlier approaches to calculate the diffusion in loose beds of zeolites [1-3], we include a Langmuir-type adsorption isotherm (parameter K_{max}, $b(T)$) and the size of the transport pores d_{pore} as measured by mercury porosimetry into our model.

Fig. 2a compares the effective diffusion coefficients of an olefin measured by PFG NMR for two different loadings with those calculated using the above described model.

$$\boxed{\begin{aligned} D_{\mathrm{eff}} &= \frac{1}{\tau} a_{\mathrm{inter}} D_{\mathrm{inter}} \\ D_{\mathrm{inter}} &= \frac{1}{3} u d_{eff} \\ d_{eff} &= \left[\frac{1}{\lambda_{gas}} + \frac{1}{d_{pore}}\right]^{-1} \\ \lambda_{gas} &= \frac{kT}{\sqrt{2} p \pi \sigma^2} \\ u &= \sqrt{\frac{8RT}{\pi M}} \end{aligned}}$$

$$a_{\mathrm{inter}} = \frac{n_{\mathrm{pore}}}{n_{\mathrm{ads}} + n_{\mathrm{pore}}}, \ \text{loading}: \ n_{tot} = n_{\mathrm{ads}} + \frac{V_{\mathrm{gas}} p}{RT}$$

$$n_{\mathrm{ads}} = K_{\mathrm{max}} \frac{p}{b(T) + p} m_{\mathrm{cat}}, \ n_{\mathrm{pore}} = \frac{V_{\mathrm{pore}} p}{RT}$$

- adsorption isotherme, $n_{ads}(p)$: $K_{\mathrm{max}}, b(T)$
- porosity, pore size of catalyst: $\phi, \phi_{\mathrm{spec}}, d_{pore}$
- NMR sample geometry, loading: $V_{\mathrm{gas}}, m_{\mathrm{cat}}, n_{tot}$
- molecular mass, kinetic diameter: M, σ

fit parameter: tortuosity τ
variable: temperature T

Fig. 1: Equations to model the temperature dependence of the effective diffusivity D_{eff} of reactant molecules in formulated catalyst particles and the required experimental parameters from the adsorption isotherm, the pore structure and the (NMR) sample preparation.

Good agreement is observed between measured diffusivities and predicted data if one assumes a tortuosity of the transport pores of $\tau = 2.4$. This value could be confirmed by independent NMR diffusion measurements using liquid-saturated samples. Fig. 2b shows the time dependence of the mean square displacment ($\langle r^2(t) \rangle$) of water and cyclooctane in two different catalyst batches, which yield tortuosities of $\tau = 2.0 \pm 0.2$ and $\tau = 2.5 \pm 0.3$ for catalysts 01 and 02, respectively. With these tortuosities, the presented model for the effective diffusion coefficient was successfully applied to extrapolate the measured diffusion coefficients to the catalytically relevant elevated temperature and pressure conditions. These extrapolations are indicated by the high-temperature region in Fig. 2a.

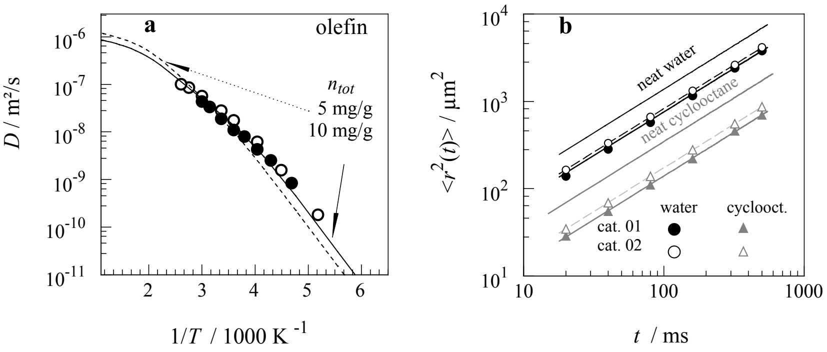

Fig. 2**a** (left): Arrhenius presentation of the effective diffusivity of an adsorbed gaseous olefin as measured by PFG NMR and predicted by the theoretical approach (solid and dashed lines) presented in Fig. 1. Fig. 2**b** (right): Results of PFG NMR studies of the time-dependence of the mean square displacement of water and cyclooctane in the neat liquid and in two catalyst samples. In this log-log plot, the parallel shift of the lines represents the tortuosity factor.

3. Conclusion

The combination of PFG NMR diffusion studies with adsorption isotherms and pore structure parameters of the catalysts were proved to be sufficient to develop a comprehensive model for transport diffusion in formulated porous catalysts. The model allows to reliably extrapolate the diffusion data, which are experimentally accessible by PFG NMR, to reaction conditions for the considered catalytic reaction. It is expected that the described approach to obtain diffusion data is also suitable for various other porous materials used in heterogeneous catalysis and separation processes.

References

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