



A unified kinetic model for adsorption and desorption – Applied to water on zeolite



Marco Gaulke*, Viktor Guschin, Sebastian Knapp, Sandra Pappert, Wilhelm Eckl

Fraunhofer Institute for Chemical Technology, Pfinztal, Germany

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ABSTRACT

A kinetic model for reversible adsorption and desorption processes under non-isothermal conditions based on reaction kinetics is deduced. This is done by explicit temperature dependence of all equations of the model. However in the performed experiments the coupling with the thermal bath was strong enough to neglect thermal conductivity and set the temperature as a timely-varying and spacial-constant parameter. Furthermore adsorption- and desorption-mechanisms of higher order and diffusion are considered. The formulation with partial differential equations is adaptable to the geometry of the adsorbent. To solve the system of coupled differential equations numerical methods of Wolfram Mathematica® are used. This model is applied to water on zeolite 3A. Beside the non-isothermal thermogravimetric analysis and the differential scanning calorimetry an isothermal experiment for the time-dependent measurement of the adsorption is used to evaluate the model. The sorption isotherms of a commercial zeolite manufacturer serve as a further source of comparison. The parameters are fitted numerically with the χ^2 -method to the experimental data. As a result of this paper a unified sorption model is introduced.

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1. Introduction

In adsorption and desorption-processes, an adsorptive is bound to the large inner surface of a porous material. If a molecule is adsorbed, energy is released. If the material is heated up, the adsorbate is set free in a desorption process. Modeling reactions kinetics is broadly used in semiconductor physics [1,2], biological systems [3,4] process engineering [5] and chemistry [6,7]. Detailed kinetic reaction mechanisms with several hundred steps can be described. In few cases these approaches are extended by considering diffusion because transport-limitations are significant [6]. In the given case of zeolite 3A, both reaction and diffusion need to be considered because the diffusion rate is similar to the rate of adsorption [8].

In contrast most of the existing sorption models are analytically solvable with the need of simplifying assumptions, e.g. isothermal conditions. An often used kinetic adsorption model is the “Linear Driving Force” [9–11]. Dawoud describes non isothermal adsorption kinetics with heat- and mass-transfer equations but no explicit

reactions [12]. In addition, desorption kinetics is described by Hahn [13]. Kinetic models for ad- and desorption are rarely utilized. Other sorption models are only capable of being applied to the thermodynamic equilibrium [14–16].

This paper introduces a unified approach to describe adsorption and desorption with one model. It combines reversible reaction kinetics of three components with diffusion of the adsorptive. The components here refer to the different sorption mechanisms. The solving of differential equations are conducted with numerical methods, which allows a broad and detailed simulation of kinetics without working with common approximations. This leads to the numerical simulation of sorption on single grains.

2. Theory

Our model describes a multi-stage reaction of higher order of an adsorptive in a porous material including the temperature dependencies. Adsorption- and desorption-kinetics are considered to be coupled with diffusion. Equilibrium states are the stationary-solutions of this model. The assumptions are:

- The reaction is completely reversible.

* Corresponding author.

E-mail address: Marco.gaulke@ict.fraunhofer.de (M. Gaulke).

- Sorption happens as a localized reaction. Hence, there is no further transport mechanism in the adsorbed phase.

Diffusion is described via Fick's laws with additional sinks and sources for the reactions [17] with D being the diffusion coefficient in m^2s^{-1} . In the following each R_i stands for one adsorption mechanism and each G_i for a desorption mechanism out of l possible mechanisms. We find

$$\frac{\partial c}{\partial t}(\vec{r}, t) = D \Delta c(\vec{r}, t) - \sum_{i=1}^l R_i(\vec{r}, t) + \sum_{i=1}^l G_i(\vec{r}, t), \quad (1)$$

where $c(\vec{r}, t)$ is the adsorptive concentration in mol/m^3 and Δ denotes the Laplacian.

With the relative loading of the adsorbents of the i th mechanism $\theta_i \in [0, 1]$ and the conversion factor to water concentration n_i , which is closer determined in Equation (9), the reaction terms are written as

$$n_i \frac{\partial \theta_i}{\partial t}(\vec{r}, t) = R_i(\vec{r}, t) - G_i(\vec{r}, t). \quad (2)$$

Equations (1) and (2) form a system of $l + 1$ coupled differential equations.

The structure of the reaction terms is determined through the microphysics of the sorption processes. The reaction is assumed to be

$$j m + z \rightarrow j m_A,$$

where z stands for a vacant bonding site and the index A implies that the adsorptive molecule m is adsorbed. Thus, for the adsorption-terms $R_i(\vec{r}, t)$ and the desorption-terms $G_i(\vec{r}, t)$ it is assumed

$$R_i(\vec{r}, t) = k_{A_i} n_i c(\vec{r}, t)^{j_i} (1 - \theta_i(\vec{r}, t)) \theta_{i-1}(\vec{r}, t) \quad (3)$$

$$G_i(\vec{r}, t) = k_{D_i} n_i \theta_i(\vec{r}, t)^{j_i} (1 - \theta_{i+1}(\vec{r}, t)), \quad (4)$$

where

- k_{A_i} is the reaction constant of the adsorption,
- $k_{A_i} \cdot c(\vec{r}, t)^{j_i}$ has the dimension s^{-1} and can be understood as generalization of an inverse time constant,
- k_{D_i} is the reaction constant of the desorption,
- and j_i is the order of the reaction.

The adsorption speed is proportional to the percentage of free bonding sites and the amount of free adsorptive molecules to the power of the reaction order j_i . The reactions are carried out successively not simultaneously because it is assumed to have several adsorption layers. This physical phenomenon is taken into account by multiplying with the covered bonding sites θ_{i-1} for the adsorption, and the free bonding sites at the desorption $1 - \theta_{i+1}$ for the neighboring layer. Furthermore the desorption speed is proportional to the relative loading to the power of the reaction order.

The sorption reactions strongly depend on temperature. This is taken into account by explicit temperature dependence of the equations. However in the performed experiments the coupling with the thermal bath is strong enough to neglect thermal conductivity. Therefore the temperature is regarded as a timely-varying and spacial-constant controlled parameter.

The temperature dependence for the reaction constant of the desorption is according to collision theory [18] assumed to be

$$k_{D_i} = \tilde{k}_{D_i} \sqrt{T} \underbrace{e^{-\frac{E_{B_i}}{k_B T}}}_{\text{Arrhenius-Law}}, \quad (5)$$

where k_B is the Boltzmann-constant. The temperature-independent part of a parameter is denoted with a tilde in the following. The activation-energy is equal to the binding energy because there are no transition states taken into account. For the diffusion coefficient D and the reaction constant of the adsorption k_{A_i} a dependence $k_{A_i} \propto \sqrt{T}$ and $D \propto \sqrt{T}$ is assumed. This can be motivated in case of the reaction constant of the adsorption with a higher root mean square speed [18].

In general the model can be applied to any geometry, however the spherical symmetry is used in the following paragraphs. Equation (1) can be transformed to spherical coordinates and the angle terms can be dropped in the isotropic case because of symmetry reasons. For an ideal adsorption experiment one receives

$$c(r, t) = \begin{cases} 0, & r < r_0, t = 0 \\ C_A, & r = r_0, t \geq 0; \end{cases} \quad \theta_i(r, 0) = 0, \quad \frac{\partial c}{\partial r}(0, t) = 0 \quad (6)$$

where r_0 denotes the radius of a zeolite sphere. It is assumed that there remains no adsorptive inside the sphere at all after a heating process. At the edge of the sphere there is constant adsorptive concentration C_A during the whole experiment. The last boundary condition says that there is no gradient i.e. flux of adsorptive, in the origin. For a desorption experiment one finds analogical initial- and boundary-conditions.

In order to describe sorption processes equilibrium-isotherms are often analyzed. These specify the loading in the equilibrium in relation to the partial pressure of the adsorptive. Mathematically the time derivatives in Equation (2) vanish and $\theta_i(\vec{r}) = \theta_i$ becomes constant in space. Since the reaction terms cancel out each other pairwise Equation (1) becomes a Laplace's equation. For the given boundary conditions from Equation (6) the solution is $c(r, t \rightarrow \infty) = C_A$. One finds a system of l coupled algebraic equations of the form

$$0 = K_i C_A^{j_i} (1 - \theta_i) \theta_{i-1} - \theta_i^{j_i} (1 - \theta_{i+1}), \quad (7)$$

where the quotient of the reaction constants $K_i := k_{A_i}/k_{D_i}$ is combined to the equilibrium-constant. In the case that there is only one sorption mechanism $l = 1$ with reaction order $j = 1$, Equation (7) corresponds to the adsorption model of Langmuir [15].

The loading is measured with temporal but not with spatial resolution. Thus, the average over the spherical grain is calculated via

$$\theta_{\text{total}}(t) = \frac{4\pi}{V_0} \int_0^{r_0} dr r^2 \sum_{i=1}^l \frac{g_i}{g_\Sigma} \theta_i(r, t), \quad (8)$$

with $V_0 = \frac{4\pi}{3} r_0^3$. Here, g_i is a weighting factor based on the number of water molecules in the i th layer. $g_\Sigma = \sum_i g_i$ normalizes the sum. Therefore, $\theta_{\text{total}}(t)$ corresponds to a normalized signal that can be read out from a scale. The product $n_i \theta_i$ is equal to the water molecules per volume where n_i is determined with the structure of zeolite. It can be calculated with the concentrations

$$n_i = \frac{g_i}{g_\Sigma} C_A = g_i \frac{\rho_Z}{M_Z}. \quad (9)$$

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