Isothermal adsorption kinetics on heterogeneous surfaces

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Abstract

Adsorption kinetics on energetically heterogeneous surfaces under isothermal conditions is analyzed using the uniform energy distribution model. Considering the quasi-equilibrium of surface diffusion between the adsorption sites with different energy, the kinetic equations $\frac{dQ}{dt} = \frac{k_a p}{C_0 A d K_{diff}} \left( \frac{1}{C_0 Q} \right)$ for first-order adsorption and $\frac{dQ}{dt} = k_a p \left( \frac{1}{C_0 Q} \right)^2$ for dissociative adsorption are obtained, where $K_{diff}$ is a coefficient describing the surface diffusion equilibrium, which depends on the coverage and the energy distribution. Under isochoric conditions with $p$ decreasing due to adsorption, surface diffusion accelerates the rate towards equilibrium significantly, as observed in static calorimetric adsorption experiments. An approximate solution in Langeren form is derived for this condition.

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1. Introduction

Compared with thermodynamics, the adsorption kinetics on heterogeneous surfaces is more complicated and far less studied. For a long time, it was evaluated mainly by temperature-programmed desorption (TPD) spectroscopy [1–5]. Several mathematical approaches, including the lattice-gas model [6], the Monte-Carlo method [7], fractal methods [8], and mean-field theory [9] have been applied to correlate the experimental data.

Similar to thermodynamic studies on heterogeneous surfaces, the realistic methodology to approach the kinetics on heterogeneous surfaces is to calculate the integral of the kinetics on local sites over different adsorption energies. Different kinetic equations have been used for this purpose considering local sites. The Elovich equation, in which the interaction between adsorbates is taken into account, was previously applied in both isothermal experiments [10] and in TPD [11]. In their comprehensive work on adsorption kinetics on heterogeneous surfaces, Rudzinski et al. [12–14] adopted the kinetic equation in the Statistical Rate Theory as the kernel equation, applied the “condensation approximation” and focused on a normal-like distribution of adsorption sites.

In this contribution, we present adsorption kinetics on heterogeneous surfaces based on the Wigner–Polanyi equation, which is the fundamental equation describing adsorption kinetics in transition state theory (TST), and on the uniform energy distribution model. It is shown that the energetic heterogeneity of surfaces can be well described within the TST theory, when a uniform energy distribution is considered, leading to simple mathematical approaches derived for different conditions. This work focuses on isothermal adsorption, as studied with static adsorption microcalorimetry under isochoric conditions, whereas the result of a corresponding TPD study will be presented elsewhere.

2. General theory for the adsorption on heterogeneous surfaces

2.1. Adsorption kinetics and surface heterogeneity

According to TST, the adsorption/desorption kinetics is described by the Wigner–Polanyi equation [15]:

$$\frac{d\theta}{dr} = k_a p (1 - \theta)^{v} - k_d \theta^{v}$$ (1)