Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Colloid and Interface Science 291 (2005) 334–344

JOURNAL OF
Colloid and
Interface Science

www.elsevier.com/locate/jcis

New approach to determination of surface heterogeneity of adsorbents and catalysts from the temperature programmed desorption (TPD) technique: One step beyond the condensation approximation (CA) method

Piotr Kowalczyk [a], Katsumi Kaneko [a], Artur P. Terzyk [b,*], Hideki Tanaka [a],
Hirofumi Kanoh [a], Piotr A. Gauden [b]

[a] *Department of Chemistry, Faculty of Science, Chiba University, 1-3 Yayoi, Chiba 263, Japan*
[b] *Physicochemistry of Carbon Materials Research Group, Department of Chemistry, N. Copernicus University, Gagarin Street 7, 87-100 Toruń, Poland*

Received 25 January 2005; accepted 10 May 2005

Available online 29 June 2005

Abstract

Recovery of the desorption activation energy distribution from the experimental temperature programmed desorption (TPD) spectra is among the most difficult problems of adsorption science. Since the heterogeneity effects strongly influence on transport, diffusion, and catalytic reaction time, the estimation of their magnitude is very important for practical purposes. Up to the present, several theories have been used for the interpretation of the TPD results. Almost all advanced theoretical approaches take into account the effect of surface disorder (heterogeneity in desorption activation energy); however, they ignore the numerical difficulties coming from the “ill-posed” character of the linear Fredholm integral equations appearing in the theoretical description of the TPD results. Thus, there is a growing interest in developing novel methods supported by powerful numerical algorithms taking this into account. In the current study we propose a new approach and consider the theoretical aspect as well as numerical problems appearing in the TPD analysis. Our modeling is based on the well-known and generally accepted “absolute rate theory,” which has been used extensively for the interpretation of TPD results. We propose and verify (applying computer simulations) the new advanced numerical hybrid type algorithms taking into account the heterogeneity effects. They seem to be very promising in TPD spectra analysis. The stability of the proposed advanced numerical methods is confirmed by the computer simulation experiments, and the results are compared with those obtained from the condensation approximation (CA) method.

Keywords: Temperature programmed desorption; Adsorption rate theory; Computer simulations

---

1. Introduction

Temperature-programmed desorption (TPD) techniques are important methods for the determination of the kinetics and thermodynamic parameters of desorption processes or decomposition reactions [1–4]. In a TPD experiment a sample is heated with a linear temperature increase and the partial pressures of desorbed molecules evolving from the sample are measured, usually by gas chromatography or mass spectrometry (Fig. 1). This is a simple view of much more complicated real processes associated with the TPD experiment. In reality the interpretation of the TPD spectrum (i.e., the desorption profile) is very difficult since diffusion and readsorption effects may influence the observed rate of desorption [5,6]. Moreover, most real systems are energetically heterogeneous and therefore they show a very complex TPD spectrum characterized by multiple peaks and shoulders [7]. These peaks are ascribed to various sites characterized by different activation energies for desorption. Obviously, heterogeneity effects are very important for practical

---

* Corresponding author.
E-mail address: aterzyk@chem.uni.torun.pl (A.P. Terzyk).

0021-9797/$ – see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2005.05.029

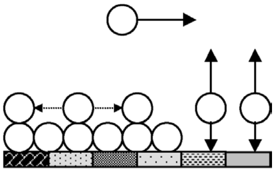

Fig. 1. Schematic presentation of the TPD experiments from the heterogeneous surface. Open circles—preadsorbed molecules; dotted arrows—nearest-neighbor adsorbate–adsorbate interactions; solid line—desorption/readsorption from a homogeneous patch of the surface.

application of adsorbents, catalysts, and other materials [8]. In other words, it is important to obtain information about the strength and the composition of adsorption sites distributed on real solid surfaces [9]. So far, almost all theoretical studies of TPD have been based on the absolute rate theory (ART); however, the ART formulation for real existing more or less heterogeneous surfaces leads to a very difficult problem known in the literature as the "ill-posed" one [10–14]. Moreover, contrary to classical adsorption equilibrium theory, the TPD theory is more complicated since we have no explicit formula describing the rate of desorption from a homogeneous patch of a surface. Consequently, a theoretical development with advanced numerical algorithms should be proposed for the proper interpretation of the TPD results. Recently, Rudziński and co-workers [15] concluded that the so-called simplified condensation approximation (CA) methods, usually used on the ground of adsorption equilibrium theory, are in practice the only approximation methods leading to stable evaluation of the desorption activation energy from the TPD spectrum. It will be shown below that the CA gives only a general view of the real desorption activation energy and CA-type methods seem to be perfect as an initial approximation (i.e., trial function). It can be mentioned here that the CA method is often applied as the starting one in some advanced numerical algorithms [16,17] (for example in the HILDA algorithm) to evaluate the initial energy distribution function from the adsorption data.

It was established that ART does not explicitly give the coverage and temperature dependence necessary to predict TPD spectra in several systems. Thus an alternative model called statistical rate theory (SRT) was formulated [7, 18–21]. This theory was successfully developed mainly by Rudziński and Pańczyk [20,22]. Moreover the ART was criticized by Rudziński and Pańczyk [23], who showed, base on data on kinetics of CO_2 adsorption on scandia, that some of the ART parameters always exhibit a nonphysical meaning. On the other hand, different authors still prefer ART and this theory is still being developed [24–26]. Thus, in the present study we limit our considerations to the ART due to its simplicity.

Consequently, we propose a theoretical background and numerical algorithms for the proper estimation of desorption activation energy from TPD experiments. By analogy, in the developed algorithms the desorption activation energy obtained by means of the CA method is used as an initial approximation of the real one. Next, the real desorption activation energy is obtained from the Tikhonov's iterative regularization method (TIRM) [27–31] and from the weighted successive substitution algorithm (WSSA) [17–22]. The validity of the proposed theoretical approaches and numerical algorithms is confirmed by the simulation experiments. The proposed theoretical background, as well as the numerical hybrid-type methods, seem to be very excellent in the analysis of real surface heterogeneity by means of TPD experiments.

2. Problem formulation

According to the absolute rate theory (ART), the change of the surface coverage with time can be described as follows [32,33]:

$$\begin{aligned}\frac{\mathrm{d}\theta(t)}{\mathrm{d}t} &= \Omega_\mathrm{a} - \Omega_\mathrm{d}\\ &= A_\mathrm{a}(\theta)p(1-\theta)^n \exp[-E_\mathrm{a}/RT]\\ &\quad - A_\mathrm{d}(\theta)\theta^n \exp[-E_\mathrm{d}/RT]. \end{aligned} \tag{1}$$

Here the first term describes the adsorption whereas the second describes the desorption rates. Both the adsorption and desorption preexponential factors (i.e., $A_\mathrm{a}(\theta)$, $A_\mathrm{d}(\theta)$, respectively) should be surface-coverage-dependent [34]. However, such dependence is not known exactly and probably its real formula is not simple. In Eq. (1) T is the temperature, p is the bulk pressure, R is the universal gas constant, and n denotes the number of adsorption sites in an elementary adsorption/desorption process. In other words, n describes the order of Eq. (1). As usual, $n = 1$ (i.e., one molecule occupies one adsorption site), at equilibrium $\mathrm{d}\theta(t)/\mathrm{d}t = 0$, and Eq. (1) with the assumption that $A_\mathrm{d}(\theta) \equiv A_\mathrm{d}$ and $A_\mathrm{a}(\theta) \equiv A_\mathrm{a}$ leads to the classical Langmuir isotherm [35]. Clearly, it is possible to introduce lateral interactions between adsorbed molecules by (for example) the Bragg–Williams approximation; however, in practice it is rather difficult to estimate the nearest-neighbor interaction energy [36,37]. For this reason Eq. (1) is usually assumed by the simplest Langmuir approximation.

Let us next assume that readsorption can be neglected and as a result the first term in Eq. (1) tends to zero:

$$A_\mathrm{a}(\theta)p(1-\theta)^n \exp[-E_\mathrm{a}/RT] \cong 0. \tag{2}$$

Moreover, as in the majority of papers dealing with the TPD results, we assume that the preexponential desorption factor slightly depends on the surface coverage and can be approximated by a constant value, $A_\mathrm{d}(\theta) \cong A$ [38]. Finally, we are introducing a linear increasing of desorption temperature, $T = T_0 + \beta t$, and we transform Eq. (1) to the following final form:

$$\frac{\mathrm{d}\theta(T)}{\mathrm{d}T} = -\frac{A}{\beta}\theta^n \exp(-E_\mathrm{d}/RT). \tag{3}$$

The nonlinear first-order differential equation given by Eq. (3) is known as the Polanyi–Wigner expression [39–41].