Kinetic analysis of nicotine desorption from silicon dioxide under non-isothermal conditions

Natasa Lazarevic [a], Borivoj Adnadjevic [b,*], Jelena Jovanovic [b]

[a] Nuclear Facilities of Serbia, Mike Petrovica Alasa 12–14, 11351 Belgrade, Vinca, Serbia
[b] Faculty of Physical Chemistry, Studentski trg 12-16, 11001 Belgrade, Serbia

ARTICLE INFO

ABSTRACT

The non-isothermal kinetics of nicotine desorption from precipitated silicon dioxide was investigated. The non-isothermal thermogravimetric curves of nicotine desorption at different heating rates (β = 5, 10 and 20 K/min) were recorded. The kinetics model of non-isothermal kinetics of nicotine desorption was determined by using the model-fitting and master-plot methods. It was found that non-isothermal nicotine desorption can mathematically describe by the theoretical kinetics model of phase – boundary controlled reaction (contracting volume, i.e., three dimensional shape) – R3. By applying the method of Kissinger and method of invariant kinetic parameters the values of kinetic parameters were determined. It was established that both applied method give almost identical kinetic parameters regardless their theoretical limitations. The dependence of activation energy on the degree of nicotine desorption was determined using the KAS method. It was found that the value of activation energy is independent on the degree of nicotine desorption. The effect of heating mode on the kinetic of nicotine desorption was analyzed. It was established that the type of heating mode (isothermal and non-isothermal) does not influence the mechanism of the formation of the activation complex nor the kinetics model of desorption. The increase in the values of kinetic parameters obtained for non-isothermal heating in comparison to the isothermal ones are explained with the Larson's model of selective transfer of energy.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Nicotine, the principal alkaloid in tobacco, along with small amounts of 12 other alkaloids, is emitted in the side stream and exhaled in the mainstream smoke of cigarettes. In small quantities, nicotine acts as a stimulus and causes adrenaline secretion, but in larger quantities, it becomes a highly toxic substance which is harmful for human health because it acts as a nerve toxin that causes general paralysis [1]. Nicotine is a highly toxic compound: 40–60 mg (0.5–1 mg/kg) can be a lethal dose for adult, and it is more toxic than many other alkaloids [2].

Traditional cigarettes cause an undeniable hazard to human health. It is widely accepted that inhaling nicotine by electronic cigarette is allegedly safer [3]. Nowadays electronic cigarettes is based on solution of nicotine in glycerin and propylene glycol. Nicotine evaporates and release desirable dose of nicotine. In order to enhance the efficiency of nicotine transfer to gas phase a novel type of electronic cigarettes which is based on the nicotine adsorbed on various types of adsorbent are developed. Material used as a nicotine carrier in electronic cigarettes has to be efficient nicotine adsorbent which can desorbs nicotine at low temperatures. However, it is also necessary for the material to be an adsorbent of desorbed nicotine to ensure that sufficient nicotine is retained so that at least about 1 μg is dispensed in response to each puff of the user [4].

Nicotine desorption from Teflon and cotton surfaces in the presence of ozone were investigated in dry and humid air [5]. Mihranyan and co-workers investigated nicotine desorption from cellulose powder samples and the influence of the crystallinity, surfaces area and pore volume of cellulose powders on the loading, nicotine desorption into an airstream, nicotine release into water and stability of nicotine. It was found that highly porous cellulose matrices could be useful as nicotine carriers in nicotine products used as smoking substitutes [6].

The isothermal kinetic of the release of nicotine from a poly(acrylic acid) (PAA) hydrogel into water solution was investigated at temperature range from 299 K to 318 K [7]. By applying the "model fitting" method it was established that the kinetic model of release of nicotine from the PAA hydrogel was $[1 - (1 - \alpha)^{1/3}] = k_M t$. The limiting stage of the kinetics release of nicotine was found

Table 1
Basic physico-chemical properties of the silicon dioxide.

Physical and chemical properties	Value
Surface area-BET (m^2/g)	160
Average primary particle size (nm)	18
Average aggregate size (μm)	10
DBP adsorption (mL/100 g)	230
pH of 5% aq. suspension	6.8
Residue on 40, μm screen (%)	0.1
Compacted bulk density (kg/m^3)	160
Bulk density as packaged (kg/m^3)	200
Moisture loss (2 h/373 K)	4
Loss on ignition (1 h/1273 K)	5
SiO_2 (%)	99
Al_2O_3 (% max)	0.2

to be the contracting volume of the interaction interface (nicotine bonded to hydrogel and external solution). The activation energy of nicotine release from the PAA hydrogel changes with the changes in the degree of nicotine release. The shape of the distribution function of the activation energies, which showed two peaks with most probable values of the $E_{a,\alpha.} = 26$ kJ/mol and $E_{a,\alpha.} = 35$ kJ/mol, were established. Energetically heterogeneity of the interaction interface was explained by the existence of the two different modes of bonding the nicotine molecules onto the hydrogel network by hydrogen bond and electrostatic forces.

In our previous investigations the isothermal kinetics of nicotine desorption from silicon dioxide was investigated [8]. The kinetic parameters (E_a, ln A) of nicotine desorption were determined by applying various methods (stationary point, model fitting method, differential-isoconversion). It was found that the kinetic of desorption process of nicotine from silicon dioxide is a complex, multi-stage process with two independent desorption stages with the values of the kinetic parameters, a higher activation energy ($E_a = 50$ kJ/mol) and a lower ($E_a = 36$ kJ/mol) activation energy.

The main objectives of this study were: (a) to examine the kinetics of non-isothermal desorption of adsorbed nicotine at precipitated SiO_2 and to determine kinetic triplet – kinetic model and the values of the kinetic parameters for the desorption of nicotine by application the most frequently used methods recommended by the Committee ICTAC, (b) to determine the possibility of using the recommended methods and reliability of the obtained results, keeping in mind the limitations of the various methods known in literature, (c) made an objective critical analysis of the kinetics of non-isothermal and isothermal desorption of nicotine, and (d) make a solid basis for the analysis of the influence of reaction conditions on the kinetics the investigated process.

2. Materials and methods

2.1. Materials

Nicotine (p.a.) was purchased from Merck, Darmstadt, Germany. Silicon dioxide, used in the form of precipitated SiO_2 (SIL-1), was purchased from TG-Birac, R. Bosnia and Herzegovina. The physico-chemical properties of the used SiO_2 are summarized in Table 1.

2.2. Sample preparation

Nicotine was absorbed onto silicon dioxide as follows. To 1 g of thermally activated SiO_2 ($T = 393$ K for 2 h) in a porcelain mortar, nicotine was added drop wise from a buret, whereby the powder was kneaded with a pestle until all the powder was wetted with nicotine and it began to separate from the wall of the mortar.

2.3. Thermogravimetric measurements

The non-isothermal thermogravimetric curves were recorded using a TA Instruments-SDT simultaneous TGA-DSC thermal analyzer model 2960. These experiments were performed with samples weight (20 ± 5) mg of SiO_2-nicotine absorbed. The samples were placed in platinum pans under nitrogen (99.9995 vol.%) flowing at a rate of 20 mL/min. The three different heating rates ($\beta = 5$, 10 and 20 K/min) were used in this study. All experiments are conducted in the temperature range from an ambient one up to 473 K.

The original mass loss vs. temperature (TG) curves obtained at constant heating rate were transformed into the degree of desorption (α) vs. temperature curves by means of the following equation:

$$\alpha = \frac{m_0 - m}{m_0 - m_f} \tag{1}$$

where m_0, m and m_f refer to the initial, actual and final mass of the sample.

2.4. Methods for the determination of kinetics parameters

Assuming that the reaction rate of a thermally stimulated solid-state reaction, under non-isothermal conditions, can be described:

$$\frac{d\alpha}{dT} = \frac{A}{v_h} \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \tag{2}$$

v_h is heating rate, where α is the conversion degree, T the temperature, E_a is the activation energy, A is the pre-exponential factor, R is the gas constant and $f(\alpha)$ is the reaction model associated with a certain theoretical reaction mechanism [9] and does not change with changing α.

2.4.1. Kissinger method

The method of Kissinger [10] belongs to the kinetic methods developed for n-order reaction models. For the $n = 1$ the Kissinger equation is given by the expression:

$$\ln \frac{v_h}{T_{max}^2} = \ln \frac{AR}{E} - \frac{E_a}{R}\left(\frac{1}{T_{max}}\right) \tag{3}$$

where T_{max} is the temperature for the maximal reaction rate.

2.4.2. Kissinger–Akahira–Sunose (KAS) method

The Kissinger–Akahira–Sunose method [11,12] is the isoconversional integral method which uses Coats-Redfern approximation of the temperature integral that leads to equation:

$$\ln\left(\frac{v_h}{T^2}\right) = \ln\left(\frac{AR}{E_a g(\alpha)}\right) - \frac{E_a}{RT} \tag{4}$$

where $g(\alpha)$ is the integral form of the selected kinetic model. For $\alpha = const.$, the plot $\ln(v_h/T^2)$ vs. $1/T$ should be a straight line whose slope can be used to evaluate the apparent activation energy.

2.5. Model-fitting method

Though the model-fitting methods are known for their simplicity in providing the kinetic triplet (i.e. frequency factor A, activation energy E_a and the reaction model $f(\alpha)$), they suffer from several problems such as their inability to establish a unique reaction model. On the other hand, it is difficult to get an idea about the reaction model with the help of the model-free isoconversional methods which provide accurate estimates of E_a. It has been recently demonstrated that the complementary use of the model-free method with the isoconversional methods is very useful to understand the solid-state reaction kinetics [13]. One of the most