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TEMPERATURE-PROGRAMMED DESORPTION MASS SPECTROMETRY

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Abstract

Temperature-programmed desorption mass spectrometry (TPD MS) is discussed with reference to studies of modified pyrogenic oxides. Simple theoretical models are presented in order to allow an approximate analytical treatment of TPD MS data. The formulae for rate constant are presented for first-, second- and third-order reactions. Products of thermal decomposition of carbonized surface layer are observed and identified. The different pathways of uni- and bimolecular desorption were investigated by temperature-programmed desorption mass spectrometry. The rate constants of reactions were derived from TPD MS measurements. Applications of TPD MS to investigation of endocrine disruptors fate and formations on the solid aerosol surface are discussed.

Keywords: carbonized oxides, disperse oxides, endocrine disruptors, non-isothermal kinetics, temperature-programmed desorption

Introduction

Oxide microparticles carbonized by the products of combustion are the main dust pollutant of the atmosphere in industrial areas using coal as a fuel. Though the effect of dust microparticles of such a kind on the human organism has not been studied in detail, it is clear that chemical reactions of biologically neutral compounds on the surface of carbonized oxide particles may result in their catalytic transformations into toxic compounds. Those compounds may be delivered to the human organism with the respirable fraction of aerosols or through drinking water. It is known that adsorption of drugs on enterosorbents cause their prolonged action; in the same vein, adsorption of the toxic compounds on the surface of dust microparticles may lead to prolonged exposure of toxins. Anyway, presence of incomplete combustion products known as strong toxins, carcinogens and mutagens on the surface of disperse oxides may result in serious hazard to human health.

Carbonization appears as complex, multi-stage process resulting in formation and growth of cluster-like germs of carbon phase. Under effect of temperature and duration of carbonization process the three-dimensional carbon lattice is formed, the number of hydrogen atoms decreases and the decrease of the number of sp^2 hybridized atoms in condensed polyaromatic systems is observed [1–3].

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The surface layer may also include a large amount of chemisorbed molecules formed on the early stages of pyrolysis. Those surface complexes are the main source of polycyclic aromatic molecules, potential toxins, carcinogens and mutagens, which may appear as a result of catalytic reactions in the surface layer of carbonized disperse oxide. Heating of the carbon-mineral samples in vacuum is expected to destroy existing surface complexes and to release chemisorbed molecules. The composition of products and kinetics of thermal decomposition of surface layer of a carbon-mineral sorbent is a source of valuable information about mechanism of carbonization of oxide surface. The temperature-programmed desorption mass spectrometry is a reliable method of investigation the chemisorbed carbon-containing compounds [4, 5]. The method allows to find out not only the composition of chemisorbed molecules but also to estimate non-isothermal kinetic parameters of surface reactions, such as pre-exponential factors and activation energies.

Desorption models

For the interpretation of temperature dependencies of mass spectra we assume that the desorption equation may be expressed as

$$\mathrm{d}\Theta/\mathrm{d}t=-k\Theta^{n} \tag{1}$$

where Θ is the surface coverage varying in the interval $0<\Theta<1$, n the reaction order (assumed to be known from experimental data) and the desorption rate is

$$k=k_0\exp(-E_\mathrm{d}/KT) \tag{2}$$

where E_d is the activation energy of desorption and k_0 the pre-exponential factor (both parameters assumed to be known from experiments). At the initial condition $\Theta_{t=0}=1$ we have the following solutions of equation (1):

$$\begin{aligned}\Theta(t)&=\exp[-\Phi(t)] \quad \text{for} \quad n=1\\ \Theta(t)&=1/[1+\Phi(t)] \quad \text{for} \quad n=2\\ \Theta(t)&=1/[1+2\Phi(t)]^{1/2} \quad \text{for} \quad n=3\end{aligned} \tag{3}$$

where

$$\Phi(t)=\int_0^t k\mathrm{d}t \tag{4}$$

In Fig. 1 formulae (3) are illustrated for reaction orders n=1,2,3; linear law $T=T_0+\beta t$ of temperature upon time dependence; and parameters of the model $\beta=0.1$ K s^{-1}; $k_0=10^{13}$ s^{-1}; E=200 kJ mol^{-1}; $K=8.31\cdot10^{-3}$ kJ K^{-1}. As it is illustrated by the Fig. 1, the less is reaction order, the steeper is the temperature dependence. More detailed information may be derived from the differential form of the dependence. In TPD MS experiment, due to uninterrupted pumping of desorbed compounds, the ion current of chosen component of mass specter is proportional to desorption rate of chosen product. According to Eqs (3), the desorption rate which is directly proportional to the ion current can be obtained as

$$\begin{aligned} d\Theta(t)/dt &= -k\exp[-\Phi(t)] \quad \text{for} \quad n=1 \\ d\Theta(t)/dt &= -k\{1/[1+\Phi(t)]\} \quad \text{for} \quad n=2 \\ d\Theta(t)/dt &= -k\{1/[1+\Phi(t)]\}^2 \quad \text{for} \quad n=3 \end{aligned} \tag{5}$$

Formulae (5) are illustrated by Fig. 2 in which desorption rates (proportional to derivatives of surface coverage) are presented as a function of the same parameters as were used in calculations of Fig. 1.

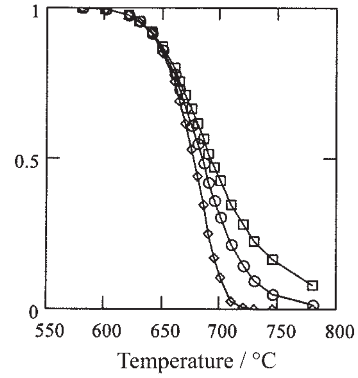

Fig. 1 Surface coverage Θ1, Θ2, Θ3 as functions of temperature T for reaction orders n=1, 2, 3 correspondingly

Equations (5) illustrate the typical temperature dependencies of the ion current, the second-order desorption curve being nearly symmetrical, the first-order curve decreasing faster on the high-temperature side and the converse being true for the third-order process. Taking into account the direct proportionality of $d\Theta/dt$ to the ion current, a simple procedure of treating the experimental data $I(t)$ may be proposed. The $\Theta(t)$ dependence on $I(t)$ may be written as $\Theta(t)=\Psi(t)/S$, or $d\Theta/dt=-I/S$, where

$$\Psi(t)=\int_t^\infty I dt; \quad S=\int_0^\infty I dt$$

Using Eqs (5) and (6) we obtain

$$\begin{aligned} \ln k &= \ln[\Psi(t)/I] \quad \text{for} \quad n=1 \\ \ln k &= \ln[\Psi^2(t)/IS] \quad \text{for} \quad n=2 \\ \ln k &= \ln[\Psi^3(t)/IS^2] \quad \text{for} \quad n=3 \end{aligned} \tag{6}$$

The deconvolution procedure proposed by Eqs (6) is illustrated by Fig. 3. A model dependence for third order reaction (dΘ3, Fig. 2) was chosen as an example of experimental curve. Three curves of desorption rate logarithm are presented as a function upon inverse temperature $\tau = (KT)^{-1}$ corresponding to three reaction orders n=1,2,3. Desorption rate parameters are the same as were used in calculations of Fig. 1.

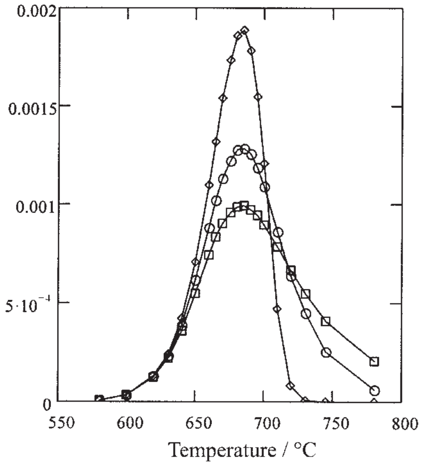

Fig. 2 Desorption rates dΘ1, dΘ2, dΘ3 as functions of temperature T for reaction orders n=1, 2, 3 correspondingly

If all the assumptions are allowable and the reaction order is a properly chosen whole number, n, then the function $\ln k = f(1/T)$ expressed according to Eqs (6) is linear over the full temperature range (in our case, $\ln k3$ in Fig. 3). The advantage of the procedure involving Eqs (6) is the utilization of all data obtained experimentally, including those in the high-temperature part of the curve which is most important in estimating the adequacy of the model and, in particular, the reaction order, n. Besides, as it can be seen from Fig. 3. Some additional simplifications are useful when operating with large amounts of TPD MS data. The key Eq. (4) may be expressed in an approximate analytical form for a slow temperature ramp ($\beta < 0.1$ K s^{-1}), high values of the pre-exponential factor ($k > 10^9$ s^{-1}) and high maximum temperatures ($T > 450$ K) as usually observed in experiments with chemisorbed organic molecules on a dispersed oxide surface.

Assuming a linear law, $T = T_0 + \beta t$ and expanding the temperature dependence near the maximum T_m, we obtain an approximate equation

$$\Phi(t) = \frac{KT_m^2}{E\beta} k_0 \exp\left(-\frac{E}{KT}\right) \tag{7}$$

which, in most cases, is valid within experimental accuracy. According to Eq. (5), the condition of maximum value of $d\Theta/dt$ (or ion current $I(t)$), is

$$\Phi(t) = 1 \tag{8}$$

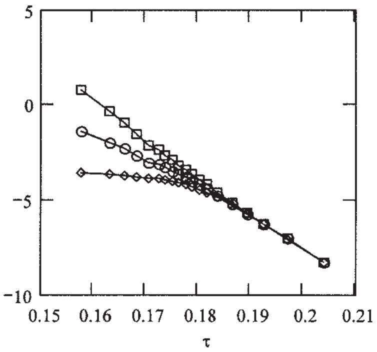

Fig. 3 Logarithm of desorption rate k for three values of reaction order as a function of inverse temperature $\tau=(KT)^{-1}$ calculated from Eqs (6)

$d\Theta/dt$ values calculated according to Eq. (7) for the first-order reaction with parameters $\beta=0.1$, $T=450$ K, $k_0=10^9$ s^{-1} provide deviations from exact solution not exceeding 0.04 throughout the whole temperature range. This is the upper limit of possible inaccuracy of Eq. (7) in comparison with exact solution. The deviation of exact value T_m for a second-order reaction from this derived from Eqs (5), (7) is of order $2(kT_m/E)^2$ which is less than 2 K for upper values of pertinent parameters.

If the special features of the structure of the adsorption complex make necessary the introduction of the distribution function for surface sites, $N(E)$, then the total desorption rate $(d\Theta/dt)_s$ (and the total ion current, I_s) must be calculated as an integral

$$(d\Phi/dt)_s=\int_0^\infty \frac{d\Phi(t)}{dt}N(E)dE$$

Practically important chemically modified dispersed ultrafine oxides as models of industrial dust microparticles demonstrate interesting and unexpected effects both in thermal desorption and in decomposition of surface complexes, including phase transitions in adsorption layer. The application of various known multi-parameter models to systems of this kind carries the implicit danger that they only provide an adjustment to the experimental data and foster the illusion of understanding, irrespective to adequacy of the model. So, the possibilities of any mathematical model, presented here in particular, are not to be overestimated. As was already emphasized by Menzel [6] an independent verification of the parameters obtained is always necessary which is not an easy task in the case of chemically modified dispersed systems. The advantage of our simple approach is that results are obtained in analytical form which facilitates the computer treatment of experimental thermal curves.

Treatment of experimental thermal curves

The temperature-programmed mass spectrometry techniques was used for analysis of volatile products of thermal decomposition of the carbon coated silica samples papers. The carbosil samples each of about 1 mg mass were placed in a quartz-molybdenum tube and evacuated at 10^{-1} Pa and then attached to the inlet system of a MI-1201 (Ukraine) mass spectrometer. The reactor-to-mass spectrometer interface included a high-vacuum valve with an orifice of diameter 5 mm and the inlet tube of 20 cm length, which was kept at 150°C. The reaction space is open in the ion-source direction, and at the heating rate used (about 0.1 K s^{-1}) the observed intensity of the ion current is expected to be proportional to the desorption rate so that diffusion inhibition may be neglected. We assumed quasi-stationary conditions when the shape and position of desorption peaks did not depend on the temperature of the spectrometer interface, the sample dispersity and/or its size. The TPD data were not considered further if these conditions were not fulfilled.

The desorption mass spectra were recorded in the 10–220 Dalton range and the temperature step was about 10 K. Mass spectra of decomposition products are presented in Fig. 4 for four temperatures.

The first mass-spectrum (Fig. 4a) corresponding to103°C includes the *m/z* lines at 43 and 58 as the main components except water (*m/z* at 18 and 17). Their origin can be easily explained from the availability of adsorbed acetone used upon sample pretreatment. Its TPD maximum lies at ca 100°C. It should be noted that the lines corre-

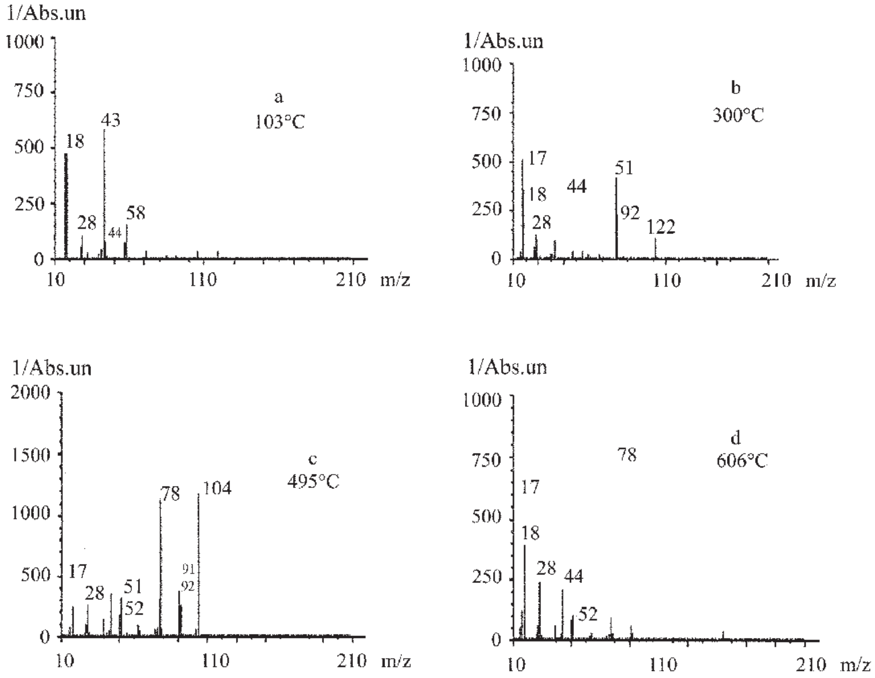

Fig. 4 TPD mass-spectra obtained upon decomposition reactions of phenylethanol bound to silica gel surface at: 103 (a), 300 (b), 495 (c) and 606°C (d)

sponding to N,N-dimethylformamide used in parallel with acetone upon sample preparation were not observed in any spectrum.

The next mass-spectrum (Fig. 4b) obtained at 300°C involves the *m/z* lines at 91, 92, and 122 caused by desorption of phenylethanol (this temperature corresponds to its maximal desorption). The main lines (*m/z* at 51, 78, 92, 91 and 104) in the spectrum obtained at 495°C (Fig. 4c) attest that phenylethylene and toluene desorb. The formation of phenylethylene is due to unimolecular decomposition of bound phenylethanol with H transfer from the CH_2 group (nearest to aromatic ring) to O from ≡SiOR group. Analogous mechanism of decomposition of butanol bound to the silica surface was studied in our previous work. However, kinetics of such processes for bound phenylethanol and butanol essentially differs.

The last mass-spectrum (Fig. 4d) obtained at 606°C includes the lines corresponding to benzene (*m/z* at 78) and biphenyl (*m/z* at 154). Inasmuch as the existence of these molecules in the surface layer at such temperature is improbable, they can be formed due to migration of phenyl radicals along the surface and their interaction with $H^{\bullet}$ or bound H (benzene formation) or bound C_6H_5 or free $C_6H_5^{\bullet}$ (biphenyl formation). At the temperatures above 600°C, the thermal transformations of bound organics have come to an end and only background lines are observed.

The temperature dependencies of the main components of the mass-spectra observed are shown in Fig. 5.

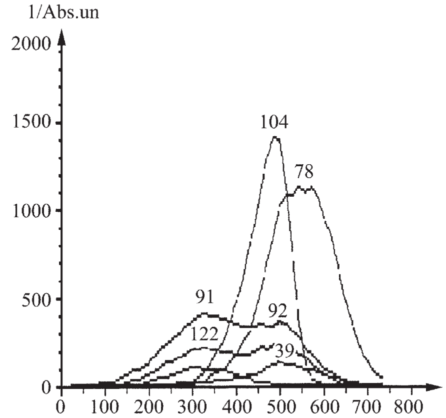

Fig. 5 Curves of desorption of phenylethanol (*m/z* at 122 and 91), phenylethylene (*m/z* at 104 and 91), toluene (*m/z* at 92, 91 and 39) and benzene (*m/z* at 78 and 39)

Phenylethanol desorption occurs in the 200–450°C range and it is maximal at ca 300°C. For phenylethylene, the temperature interval width of desorption is the same but it shifts to higher temperatures (300–550°C) with a maximum at 450°C. The curve of phenylethylene (*m/z* at 104) desorption has asymmetrical shape, which is typical for first order reactions. The curve of *m/z* at 91 has two maxima at 300 and 470°C that can be explained from the origin of the fragment $C_6H_5CH_2^+$ (responsible for *m/z* at 91) observed in the electron impact mass spectra for phenylethanol (*m/z* at 122), phenylethylene (*m/z* at 104), and toluene (*m/z* at 92); therewith, the first maximum of *m/z* at 91 corresponds to phenylethanol desorption. A benzene spectrum (*m/z* at 78) is observed in the 300–700°C range and its shape indicates that $C_6H_6^+$ ion is formed through to two mechanisms.

At low-temperatures (300–500°C), this ion is generated as a fragment of phenylethylene or phenylethanol and, at high-temperatures (500–700°C), it is obtained via ionization of benzene eliminated (Fig. 5). The deconvolution of the benzene TPD spectrum according the origin of $C_6H_6^+$ shows that its width after subtraction of the contribution by the decomposition of desorbed phenylethylene is close to that for phenylethanol and phenylethylene (about 250°C). Consequently, spectra broadening for these desorbed compounds is closely related, thereby implying that it is caused by similar features of the decomposition of groups bound to the surface of partially carbonized silica. It should be noted that the maxima of desorption of benzene and biphenyl coincide. This shows commonness of the origin of both compounds due to recombination or capture reactions at the surface with the participation of mobile phenyl radicals. Biphenyl desorbs in a more narrow high-temperature range (Fig. 4b).

Computation of kinetic parameters from this thermal curve, according to the technique described in previous section, gives the values depending on a curve portions used for the calculations of a pre-exponential factor k_o and activation energy E due to broadening of the spectra. The calculations of these parameters from the curve shape near the maximum give the k_o and E values ($4.4\cdot10^5$ s^{-1} and 85 kJ mol^{-1}, respectively) close for obtained for the total curve. Underestimated value of the pre-exponential factor (caused by spectrum broadening) attests that the observed width of the spectrum is determined not only by the mechanism of the bound group decomposition but also the dependence of the activation energy on the concentration of these groups and the surface heterogeneity.

Therefore for the determination of the real k_o and E values, additional information is needed, e.g. from theoretical modeling of these processes. However, we can use an initial slope of the TPD spectra, where the influence of broadening factors is small, for the calculations of kinetic parameters. The values obtained for this part of the TPD curve for *m/z* at 104 and 103 are closely related and we can assume that they are close to the real values of kinetic parameters for desorption of phenylethylene.

The deconvolution of the benzene TPD spectrum according the origin of $C_6H_6^+$ shows that its width after subtraction of a part caused by the decomposition of desorbed phenylethylene is close to that for phenylethanol and phenylethylene (about 250°C). Consequently, spectra broadening for these desorbed compounds is closely related, that is caused by similar features of the decomposition of groups bound to the surface of partially carbonized silica. It should be noted that the maxima of desorption of benzene and biphenyl coincide. This shows commonness of the origin of both compounds due to recombination or capture reactions at the surface with the participation of mobile phenyl radicals. Biphenyl desorbs in more narrow high-temperature range than other products that give the higher values of k_o and E.

As it was shown by Menzel in his fundamental review [6], the quantitative description of temperature-programmed desorption kinetics should be based on transition state theory. Unfortunately, the progress in the theory of thermal desorption during the last fifteen years has dealt mainly with lateral interactions in the surface layer. The results are summarized in the monograph by Tovbin [7]. Among recent publications, the models presented in papers by Tovbin [8], Tovbin and Votyakov [9] seem to be most impressive, all being directed at well-organized systems, i.e. simple molecules on monocrystalline surfaces. Progress in the application of TST to TPD MS studies has been much slower, largely because of computational difficulties. Support of the TST approach from the molecular dynamics point of view was presented recently by Tully [10]. The main idea of that work was that gas-phase and surface chemical reactions are controlled by many of the same factors, including the locations and energies of transition states, the rates and pathways of energy flow, the lifetimes of intermediates, etc.

Practically important chemically modified dispersed ultrafine oxides demonstrate interesting and unexpected effects both in thermal desorption and in decomposition of surface complexes, including phase transitions in the adsorption layer. The application of various known multi-parameter models to systems of this kind carries the implicit danger that they only provide an adjustment to the experimental data and foster the illusion of understanding, regardless of the adequacy of the model. Therefore, the mechanistic implication of any mathematical model, and in particular of the one presented here, are not to be overestimated. As was already emphasized by Menzel [6] an independent verification of the parameters obtained is always necessary but producing it is not an easy task in the case of chemically modified dispersed systems. The advantage of our simple approach is that the results are obtained in an analytical form which facilitates the computer treatment of experimental curves.

Further accumulation of experimental data concerning TPD MS of carbonized dispersed oxides is necessary for a detailed understanding of the chemisorption mechanism, the structure of chemisorbed biologically active molecules and the non-isothermal kinetics of their decomposition.

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