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THE KINETICS OF WATER DESORPTION FROM POROUS GLASSES

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The kinetics of water desorption from porous glasses silica gel and porous aluminosilicates were followed through the TG and DTG methods.

In all cases only one thermodesorption peak appeared.

The kinetic parameters were determined by standard nonisothermal methods. The activation energy is constant and independent of the coverage degree and pore diameter in the system porous glass-water. The function E (θ) were determined for the silica gel and porous aluminosilicates $E = E_0 + a \exp(-b\theta)$. The parameters E_0, a and b depend on the SiO_2/Al_2O_3 ratio and on the distribution of active centers on the surface.

Desorption kinetics is most commonly presented by the equation:

$$-\frac{d\theta}{dt} = \theta^n A \exp(-E/RT) \tag{1}$$

in which n is the reaction order, A the pre-exponential factor and E the activation energy. In the general case, kinetic parameters depend upon the degree of coverage [1].

Such an equation can be applied to high-energy chemisorbed states and to low-energy physisorbed states. Silicate and aluminosilicate are typical examples of systems on which there exist physisorbed and chemisorbed molecules at the same time [2]. It is known that surface hydroxyl groups act as primary centres in the physical adsorption of water [3–5]. Zettlemoyer [5] considers the hydroxyl groups to be donors and water molecules to be acceptors of hydrogen-bonds. According to the results of Kiselev [6], an adsorptive complex is formed in which approximately two hydroxyl groups correspond to one molecule of water. Dehydroxylation (associative desorption) is preceded by the desorption of physically adsorbed water and, due to the considerable difference in bond energy, it can be expected that these processes take place as two independent consecutive stages. It is probable that

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primary surface heterogeneity influences both processes. On the basis of IR spectroscopic results [4, 7, 8], this influence is not clearly distinguished.

The desorption kinetics of physisorbed water on this type of surface have not been investigated in a wide temperature range, so the influence of surface heterogeneity on the kinetic parameters is not known. In this paper the kinetic parameters of the thermodesorption of water from some silicate surfaces have been determined.

Experimental

The kinetics of desorption from various silicates under isothermal and nonisothermal conditions have been investigated. Porous glasses manufactured by SERVA, Pfaltz Bauer silica gel and porous aluminosilicates made in our laboratories were applied. The porous aluminosilicates were synthesized by the precipitation procedure at room temperature. Dilute solutions of sodium aluminate and sulphuric acid were simultaneously added dropwise to a dilute solution of sodium silicate. The precipitate was washed with a solution of ammonium chloride until the Na_2O concentration in the precipitate had dropped below 0.5%. The washed precipitate was then heated at 500°. Samples prepared in this fashion have specific surfaces of 400–600 m^2/g. The samples were dehydrated at 400° for 1 h and water was then adsorbed at room temperature for 24 h. A DuPont 990 thermal analyser was used to follow the kinetics of isothermal and nonisothermal desorption. TG and DTG methods were applied simultaneously, in a dry nitrogen flow of 15 ml/min (dew point below -70°C). The necessary calculations were performed on a Hewlett–Packard 931 computer system. The integral heat of desorption was measured on a DuPont 1090 by using a DSC cell.

Results

The thermodesorption of water from porous glasses, silica gel and some porous aluminosilicates was followed in the range of lower temperatures, below 600 K. Up to that temperature, all the observed systems have only one thermodesorption peak and no change in mass was detected after 500 K. A relative degree of coverage was used, calculated according to mass change for the given temperature interval.

Adsorption and desorption processes in this temperature interval are completely reversible. The adsorption-desorption equilibrium influences the rate of thermodesorption. In Fig. 1, a comparison is given of the results obtained for water desorption from porous glass with a pore diameter of 75 Å in a flow of dry nitrogen (curve *a*)

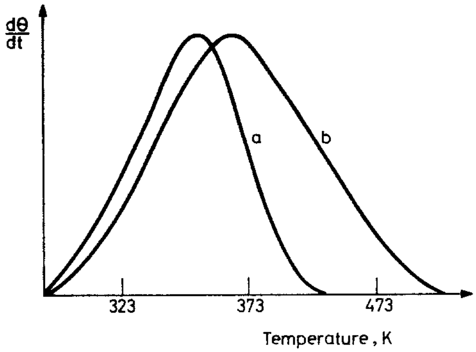

Fig. 1 DTG desorption curves of water from porous glass of 75 Å pore diameter at a heating rate of 20 deg/min a) in a stream of nitrogen, and b) in static atmosphere

and in a static atmosphere (curve *b*). It is evident that the peak which corresponds to desorption in static atmosphere is shifted towards higher temperatures ($\Delta T_m = 15$ deg) and that it is considerably broader than the nitrogen flow peak. Readsorption leads to deceleration of the desorption process.

Water desorption from porous glasses was followed as a function of pore diameter and degree of coverage. The thermodesorption results given in Fig. 2a show that at the maximum degree of coverage an increase in pore diameter leads to desorption acceleration, and the peaks shift towards lower temperatures. For a pore diameter increase from 75 to 500 Å, the shift is about 20 deg. A change in the initial degree of coverage does not influence the position and shape of the thermodesorption peaks. The results obtained for porous glass with a pore diameter of 75 Å are presented in Fig. 2b. The Coats–Redfern [9] method was applied to the thermodesorption results and the kinetic parameters are presented in Table 1. The high regression coefficient indicates that the reaction is a first-order one. The pre-exponential factors are of the order of 10^4 s^{-1} and the activation energies are 45 ± 3 kJ/mol. Kinetic analysis of the curves obtained for various initial degrees of coverage (porous glass with a pore diameter of 75 Å) yielded kinetic parameters with similar values (Table 1). The equation which included readsorption was applied to results obtained in the static atmosphere [10, 11]. These kinetic parameters are also given in Table 1. The other porous glasses yielded similar results.

Water desorption from silica gel was also accompanied by the appearance of only one thermodesorption peak. Figure 3 shows the experimentally obtained curves at a heating rate of 10 deg/min and at various initial degrees of coverage. For small degrees of coverage ($\theta = 0.25$), T_m shifts toward higher temperatures. All the peaks are almost symmetrical, which differs considerably from the shape of the peaks obtained in desorption from porous glass.

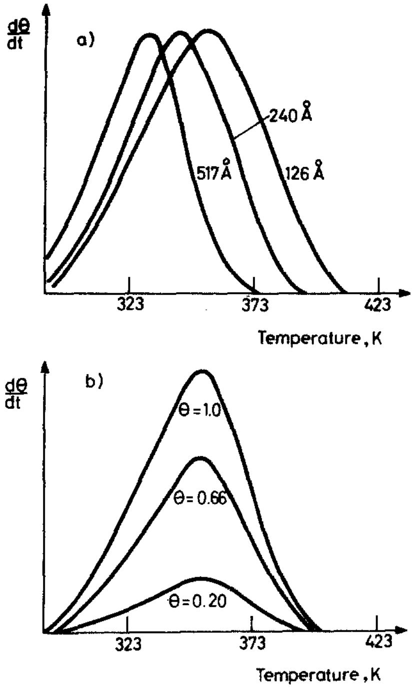

Fig. 2 Thermodesorption of water from porous glasses: a) of various pore diameter; b) desorption from 75 Å porous glass with various initial values of the degree of coverage

Table 1 Kinetic parameters of the process of water desorption from porous glasses

System	S, m^2/g	ΔQ, kJ/mol	E, kJ/mol	A, s^{-1}	R
517 Å	52	46.2	43.0	4.9×10^4	0.999
368 Å	86		47.8	0.79×10^4	0.998
240 Å	126		42.7	3.2×10^4	0.998
176 Å	160		44.3	2.1×10^4	0.999
120 Å	170		43.7	1.9×10^4	0.998
75 Å	220				
θ max		45.6	44.1	3.0×10^4	0.999
$\theta = 0.66$		45.0	46.3	7.0×10^4	0.999
$\theta = 0.25$		44.8	42.9	1.7×10^4	0.998
75 Å θ_{max} Readsorption[11]			$\Delta H = 44.4$	1.4×10^4	0.998

ΔQ is integral heat of desorption measured by DSC method.

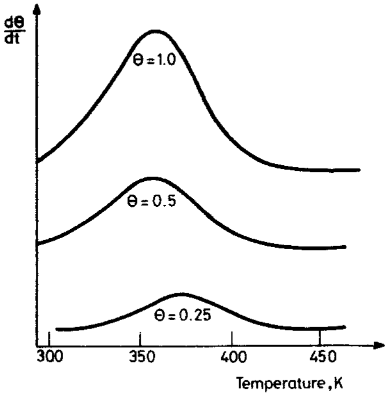

Fig. 3 Thermodesorption of water from silica gel with various degrees of coverage

Table 2 Kinetic parameters of the process of water desorption from silica gel

	Coats–Redfern [9]		Redhead [12]		$E = E_0 + a\exp(-b\theta)$			
	E, kJ/mol	A, s^{-1}	E, kJ/mol	A, s^{-1}	E_0, kJ/mol	a	b	A, s^{-1}
θ_{max}	46.2	4.1×10^4	47.3	4.0×10^4	45	8	22	4.0×10^4
$\theta = 0.25$	48.8	3.8×10^4						

The process parameter were determined by the methods of Coats–Redfern and Readhead [12]. The results are given in Table 2. Agreement between the methods is good and the determined kinetic parameters are similar. In both cases the reaction order is $n = 1$. There is a difference between the activation energies: for a degree of coverage θ_{max}, $E=46.2$, and for $\theta=0.25$ $E=48.8$. In Fig. 4 the experimentally obtained curves (full lines) are compared with the computer ones (kinetic parameters by the Readhead method). The experimental curves are always more disperse than the calculated ones, and for a heating rate of 20 deg/min the deviation of the experimental curves from the calculated ones is considerable. These results, and also the curve shifts toward higher temperatures with θ decrease, indicate that the silica gel surface could be energetically heterogeneous. An attempt was made to explain the process kinetics by means of a constant pre-exponential factor and an activation energy which changes with the degree of coverage. The function $E(\theta)$ was determined in the same way as in paper [13]. The best ageeement between the calculated and experimental curves was obtained for the exponential type of function $E(\theta)$; the kinetic parameters are given in the third column of Table 2. These kinetic parameters describe the experiment better, as is shown in Fig. 5. The deviations of the computer curves from the experimental ones are now

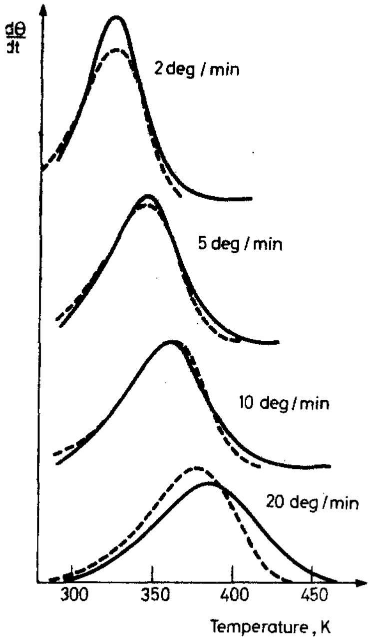

Fig. 4 Comparison of the calculated and experimental desorption curves for E = const for various heating rates

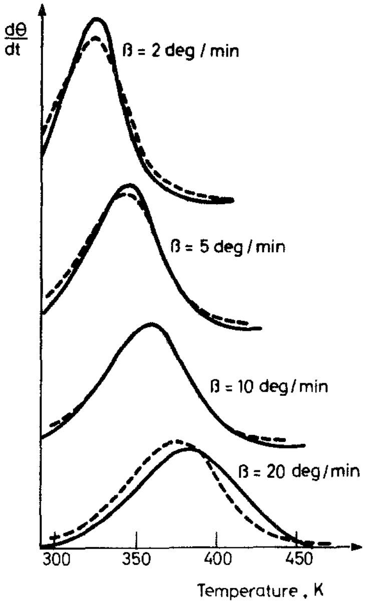

Fig. 5 Comparison of the calculated and experimental desorption curves of water from silica gel for $E = E_0 + a\exp(-b\theta)$

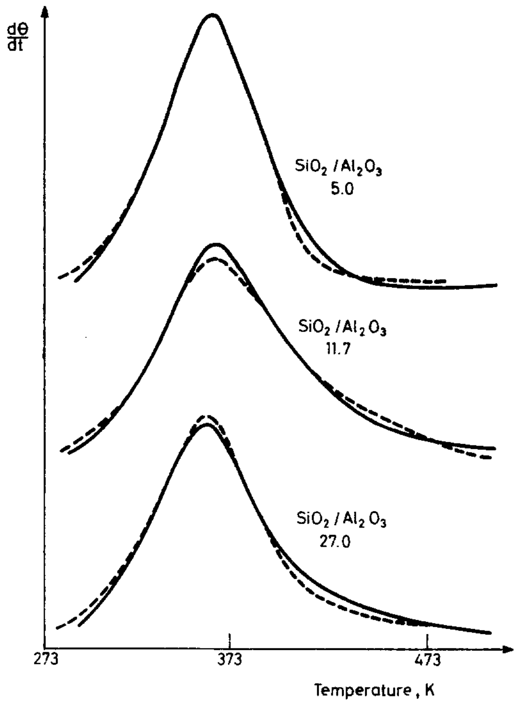

Fig. 6 Comparison of the calculated and experimental desorption curves of water from porous aluminosilicates

considerably less and lie within the limits of experimental error. The only exception is at the heating rate of 20 deg/min, where the deviations are still noticeable.

Porous aluminosilicates have very disperse peaks, with maxima temperatures close to that for silica gel. In Fig. 6 the DTG results of some typical porous aluminosilicates are presented with a full line. For the system with a SiO_2/Al_2O_3 ratio = 11.7, the desorption is decelerated and in the region of high temperatures a very long tail appears. It is not possible to apply classical methods of nonisothermal kinetics to such systems. The Coats–Redfern function is not linear, which is also the case with the other methods. It was necessary to introduce the function $E(\theta)$ to the expression for the reaction rate.

The process for the exponential function $E(\theta)$ with A = const and $n = 1$ was computer-simulated; the results are presented in Table 3. The kinetic parameters determined in this way describe the experiment well; the calculated curves are in good agreement with the experimental ones (Fig. 6). A certain dispersion appears if the experimental curves at various heating rates are fitted. For all porous aluminosilicates the determined pre-exponential factors are of the order of 10^4 s^{-1}

Table 3 Kinetic parameters of the process of water desorption from porous aluminosilicates A = const. $E = E_0 + a \exp(-b\theta)$

SiO_2/Al_2O_3	A, s^{-1}	E_0, kJ/mol	a	b
27	5×10^4	46.8	7.5	20
11.7	1×10^4	46.3	11.5	4
5	4×10^4	46.2	9.3	13

and the activation energy of E_0 for high degrees of coverage is the same for all systems. Parameters a and b defining the energetic heterogeneity of the surface differ from one another.

Discussion

The presented results show that water desorption from porous glasses, silica gel and porous aluminosilicates is a slow desorption process. In all cases the desorption is a first-order reaction.

The calculated activation energies for the system porous glass-water (Table 1) are in reasonable agreement with the integral heats of desorption evaluated with the DSC method. The errors are below 10%. The activation energies and differential heats of desorption are independent of the initial coverage degree. It is obvious that the porous glass surface is energetically homogeneous. The rate of water desorption from porous glasses (Fig. 2) decreases with decrease of the pore diameter. The calculated activation energies for different pore diameters are very close to one another (±2.5 kJ/mol). The calculated values correspond to approximately two hydrogen-bonds per water molecule. According to the obtained kinetic parameters (E and A), the rate of desorption increases in the sequence (517 Å)<(240 Å)<(120 Å) = (75 Å). The glasses with pore diameters of 368 Å and 176 Å are exceptions. These results are in accordance with the NMR results [17]. The mobility of the water molecules in the self-diffusion measurements decreases with decrease of the pore diameter.

The fitting with a first-order reaction and constant activation energy shows deviations in the other systems (silica gel and porous aluminosilicates). The fitting by exponential functions $E(\theta)$ gives better results.

The fitting does not significantly improve in the system silica gel-water on using the exponential function $E(\theta)$. The fitting errors decrease slightly for heating rates of 2, 5 and 10 deg/min, but do not change for 20 deg/min. On the basis of the obtained results, it is not clear to which type of surface silica gel belongs; both models are possible.

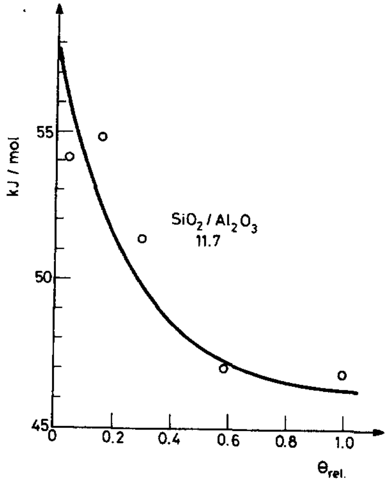

Fig. 7 Calculated activation energy and differential heat of desorption as function of coverage degree in the system porous aluminosilicate–water

The computer-simulated curves are in good agreement with the experimental ones for the system porous aluminosilicates-water (Fig. 6). The variation of the activation energy with coverage degree is approximated by an exponential function (Table 3). In Fig. 7, the computed function $E(\theta)$ is compared with the integral heats of desorption. The integral heat of desorption (dots in Fig. 7) increases with decrease of the initial coverage degree. An energetically heterogeneous surface is formed. It could be concluded that centres with different strengths exist on the porous aluminosilicate. It is possible that Lewis and Bronsted acid sites are formed, as on the amorphous silica-alumina catalysts [18].

In all cases, regardless of whether the surface is homogeneous or nonhomogeneous, very low values were obtained for the pre-exponential factors, of the order of 10^4 s^{-1}, which is considerably lower than the value given by the transition state theory [14–16] and which is commonly found. Several factors can influence the obtaining of low pre-exponential factor values. In this paper we have analysed only the influence of readsorption. The pre-exponential factor computed in the static atmosphere is half that calculated in the flow of nitrogen (Table 1). The corrections should be higher [14]. The problem of the corrective influence of readsorption in the observed system can so far not be considered as solved. The problem could be solved by following the desorption in high vacuum [19].

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Zusammenfassung — Die Kinetik der Desorption von Wasser von porösen Gläsern, Silikagel und Aluminosilikaten wurde mittels TG und DTG verfolgt. In allen Fällen erscheint nur ein Desorptionspeak. Die kinetischen Parameter wurden durch nichtisotherme Standardmethoden bestimmt. Die Aktivierungsenergie ist konstant und unabhängig vom Bedeckungsgrad und dem Porendurchmesser im System porösen Glas/Wasser. Für Silikagel und poröses Aluminosilikat wurden die Funktionen $E(\theta)$ bestimmt: $E = E_0 + a\exp(-b\theta)$. Die Parameter E_0, a und b hängen vom SiO_2/Al_2O_3-Verhältnis und der Verteilung der aktiven Zentralen an der Oberfläche ab. Die Desorptionskinetik ist gewöhnlich durch die Gleichung

$$-\frac{d\theta}{dt} = \theta^n A \exp(-E/RT)$$

zu schreiben.

Резюме — Методом ТГ и ДТГ изучена кинетика десорбции воды из пористых стекол, силикагеля и пористых алюмосиликатов. Во всех случаях наблюдался только один пик термодесорбции. Кинетические параметры определялись стандартными неизотермическими методами. Энергия активации системы пористое стекло — вода являлась постоянной и независимой от степени покрытия и диаметра пор. Для силикагеля и пористых алюмосиликатов была определена функциональная зависимость $E(\theta)$ как $E = E_0 + a\exp(-b\theta)$. Параметры E_0, a и b зависели от соотношения SiO_2/Al_2O_3 и от распределениа активных центров на поверхности.