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Adsorption and Desorption of Water on Tin Dioxide

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Abstract—Adsorption isotherms were obtained for water on SnO_2 samples subjected to heat treatment at various temperatures. The monolayer capacity and adsorption constants were determined by Langmuir equation. The enthalpy and entropy of adsorption were determined using the isobar equation.

The dependences of the concentration ($\bar{C}$, mol g^{-1} SnO_2) and “strength” ($\bar{K}_{dis}$) of acid centers of the SnO_2 surface on the temperature of the preliminary heat treatment of the samples (T_{ht} 100, 200, 300, 500, 700°C) were found in [1] by pH-metric heterogeneous titration of aqueous suspensions of tin dioxide powders with alkali.

It was of interest to find whether there is a correlation between the parameters found in [1] and the corresponding parameters of water vapor adsorption, and also to calculate the enthalpy (ΔH) and entropy (ΔS) of water desorption.

The adsorption experiments involved measuring the weight gain of SnO_2 samples kept in a desiccator over sulfuric acid. Preliminarily heat-treated SnO_2 samples were kept in a desiccator over 90% sulfuric acid (P_{H_2O} 0.005 mm Hg at 20°C [2]). Then they were placed in desiccators over 75, 70, 60, and 40% sulfuric acid (i.e., with a certain partial pressure of water vapor at a given temperature), after which the SnO_2 samples were weighed. The results are given in Table 1.

Adsorption of water vapor on SnO_2 samples is reversible, since the adsorption isotherms coincide with the desorption isotherms.

The adsorption isotherms have a shape typical for monomolecular adsorption [3]. Hence, we treated them using Langmuir equation [4] to determine the numbers of adsorption centers and the adsorption constants.

$$m_{H_2O} = m_{max}\frac{K_{ads}P_{H_2O}}{1 + K_{ads}P_{H_2O}}. \qquad (1)$$

Here m_{H_2O} is the weight of adsorbed water (g H_2O/g SnO_2), m_{max} is the monolayer capacity (g H_2O/g SnO_2), P_{H_2O} is the water vapor pressure in a desiccator (mm Hg), and K_{ads} is the equilibrium constant of adsorption (Henry constant).

The expression for K_{ads} can be written as

$$K_{ads} = \frac{m_{H_2O}}{(m_{max} - m_{H_2O})P_{H_2O}}, \qquad (2)$$

Table 1. Experimental data on water vapor adsorption on SnO_2 samples[a]

W, % H_2SO_4	P_{H_2O}, mm Hg	T_{ht} 100°C			T_{ht} 200°C			T_{ht} 300°C		
		$m^{exp}_{H_2O} \times 10^2$	$(P/m) \times 10^{-1}$	$m^{calc}_{H_2O} \times 10^2$	$m^{exp}_{H_2O} \times 10^2$	$(P/m) \times 10^{-1}$	$m^{calc}_{H_2O} \times 10^2$	$m^{exp}_{H_2O} \times 10^2$	$(P/m) \times 10^{-1}$	$m^{calc}_{H_2O} \times 10^2$
75	0.3	4.5	0.67	4.55	2.8	1.07	2.80	1.4	2.14	1.41
70	0.8	6.2	1.29	6.21	4.4	1.82	4.39	2.6	3.08	2.26
60	2.8	7.4	3.78	7.37	5.8	4.83	5.81	3.9	7.18	3.91
40	9.8	7.8	12.6	7.78	6.4	15.3	6.41	4.6	21.3	4.60

[a] m_{H_2O} is given in g H_2O/g SnO_2.

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Table 2. Parameters derived from experimental data on water vapor adsorption on the SnO_2 surface

T_{ht}, °C	$m_{max} \times 10^{-2}$, g H_2O/g SnO_2	$C_{max} \times 10^3$, mol H_2O/g SnO_2	K_{ads}, (mm Hg)$^{-1}$	S_{sp}, m^2/g SnO_2	$S_{sp}^{T=100}/S_{sp}^{T}$	$C_{max}^{T=100}/C_{max}^{T}$
100	7.96 ± 0.05	4.4	4.45 ± 0.18	200	1.00	1.00
200	6.68 ± 0.05	3.7	2.40 ± 0.05	175	1.14	1.19
300	4.95 ± 0.05	2.7	1.34 ± 0.05	120	1.67	1.61

$$\frac{P_{H_2O}}{m_{H_2O}} = \frac{1}{K_{ads} m_{max}} + \frac{1}{m_{max}} P_{H_2O}. \qquad (3)$$

Equation (3) gives a linear plot of P_{H_2O}/m_{H_2O} vs. P_{H_2O}.

We determined m_{max} and K_{ads} by solving this equation graphically. Below are given $m_{max} \times 10^2$ (g H_2O/g SnO_2), $C_{max} \times 10^3$ (mol H_2O/g SnO_2), and K_{ads} (T_{ht}): 8.0, 4.4, 4.5 (100°C); 6.7, 3.7, 2.4 (200°C); 5.0, 2.7, 1.3 (300°C).

We also calculated m_{max} and K_{ads} by the least-squares method (Table 2); they agree with the values found graphically.

Samples with T_{ht} 500 and 700°C, in contrast to samples with T_{ht} 100, 200, and 300°C, have the specific surface area smaller by a factor of ~10; therefore, the amount of adsorbed water cannot be determined with a high accuracy. To estimate K_{ads} for these samples, we assumed that m_{max} is equal to the weight of adsorbed water at a maximal water vapor pressure (P_{H_2O} 9.8 mm Hg); thus, it is $\sim 6 \times 10^{-3}$ g H_2O/g SnO_2 for samples with T_{ht} 500°C and $\sim 2 \times 10^{-3}$ g H_2O/g SnO_2 for samples with T_{ht} 700°C.

At P_{H_2O} 0.8 mm Hg, m_{H_2O} is $\sim 1/2 m_{max}$. Therefore, according to Eq. (3), K_{ads} (for samples with T_{ht} 500 and 700°C) can be estimated as $1/P_{H_2O}$, and, consequently, $K_{ads} \approx 1.25$.

We tested the reliability of m_{max} and K_{ads} found for the samples with T_{ht} 100, 200, and 300°C by calculating $m_{H_2O}^{calc}$ using Eq. (1) and comparing them with $m_{H_2O}^{exp}$ (Table 1).

Figure 1 gives a plot of the monolayer capacity (C_{max}, mol H_2O/g SnO_2) vs. the specific surface area (S_{sp}, m^2/g SnO_2) of the samples with T_{ht} 100, 200, and 300°C, found from nitrogen adsorption [4]. This dependence is linear, which allows the landing surface area for a water molecule to be calculated as δ_{H_2O} 8.3 Å^2. This value is comparable with the value calculated by the BET equation [4, 5]: δ_{H_2O} 1.091 $(M_{H_2O}/N_A \rho_{H_2O})^{2/3} \times 10^{16}$ (where M_{H_2O} is the molar weight of water, N_A is the Avogadro number, and ρ_{H_2O} is the density of liquid water). With regard to a 20% error, it comprises 10.5 ± 2.1 Å^2, supporting the results of determining C_{max} for water adsorption on SnO_2 samples.

We emphasize that the ratios $S_{sp}^{T=100}/S_{sp}^{T}$ and $C_{max}^{T=100}/C_{max}^{T}$ (T 100, 200, and 300°C) virtually coincide (Table 2).

We studied the desorption of water from the surface of air-dry SnO_2 samples with T_{ht} 100, 200, and 300°C by derivatography with simultaneous recording of DTG, DTA, and TG curves in the temperature range 20–350°C (Fig. 2). The resulting DTA and DTG curves suggest that the desorption is endothermic with the peaks at ~130°C for T_{ht} 100°C, ~70°C for T_{ht} 200°C, and ~55°C for T_{ht} 300°C.

The desorption process can be described by Eq. (4):

$$H_2O_{ads} \overset{K_{des}}{\rightleftarrows} H_2O_{vap}. \qquad (4)$$

Here K_{des} is the desorption constant.

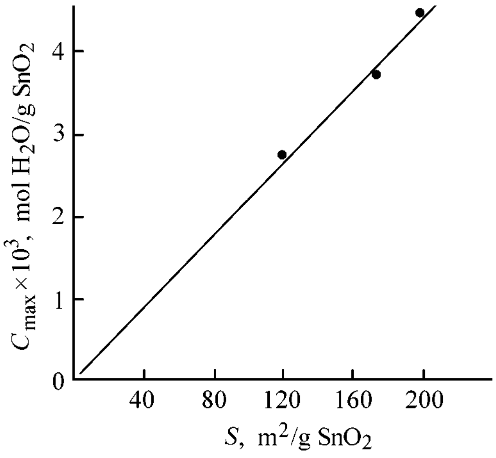

Fig. 1. Plot of C_{max} vs. S_{sp} for SnO_2 samples with T_{ht} 100, 200, and 300°C.

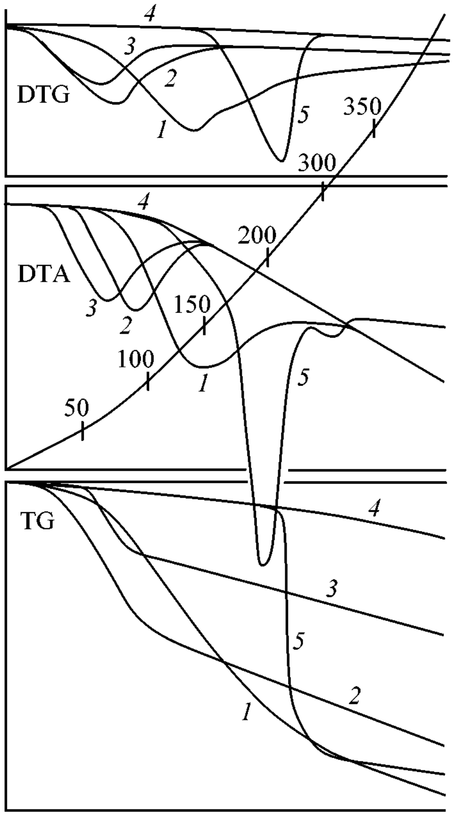

Fig. 2. Derivatograms of SnO_2 samples: (*1*) 100°C, (*2*) 200°C, (*3*) 300°C, and (*4*) 500°C; (*5*) CaC_2O_4.

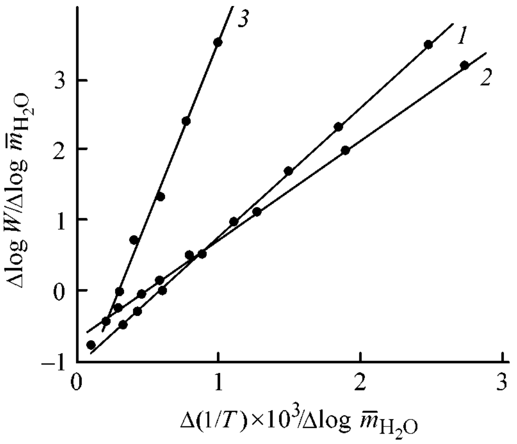

Fig. 3. Plot of $\Delta\log W/\Delta\log \bar{m}_{H_2O}$ vs. $\Delta(1/T)/\Delta\log \bar{m}_{H_2O}$ for SnO_2 samples. (*1*) 100°C, (*2*) 200°C, and (*3*) 300°C.

$$K_{des} = \frac{[H_2O]_{vap}}{[H_2O]_{ads}} = \frac{\Delta\bar{m}_{H_2O}}{(\bar{m}_{max} - \Delta\bar{m}_{H_2O})}. \qquad (5)$$

Here $\Delta\bar{m}_{H_2O}$ is the weight loss of an SnO_2 sample at the temperature T, and $\Delta\bar{m}_{max}$ is the maximal weight loss of an SnO_2 sample.

The desorption rate depends on both the heating rate and the activation energy of desorption.

We calculated the activation energy of water vapor desorption (E_a) by graphic solution of Eq. (6) [6, 7] (Fig. 3).

$$\frac{\Delta\log W}{\Delta\log \bar{m}_{H_2O}} = \frac{\Delta E_a}{2.3RT}\,\frac{\Delta(1/T)}{\Delta\log \bar{m}_{H_2O}} - n. \qquad (6)$$

Here $W = \Delta\bar{m}_{H_2O}/\Delta t$ is the desorption rate, and n is the reaction order of water vapor desorption, equal to ~1.

At relatively slow heating (~5 deg min^{-1}), relatively high desorption rate owing to low activation energy (E_a 7–8 kcal mol^{-1}) of desorption, and low rate of water vapor diffusion from the inner volume of pores, we can suggest that the equilibrium (4) of water distribution between the surface and the vapor is attained at every temperature T [3]. Hence, it appears possible to calculate K_{des} for every temperature T and to use isobar equation (7) for graphic determination of ΔH_{des} [8] and for subsequent calculation of ΔS_{des}.

$$\log K_{des} = -\frac{\Delta H_{des}}{2.3R}\,\frac{1}{T} + \frac{\Delta S_{des}}{R}. \qquad (7)$$

The calculated values of ΔH_{des} and ΔS_{des} are given below.

	ΔH, kcal mol^{-1}	ΔS, cal mol^{-1} deg^{-1}
T_{ht} 100°C	11.0	28
T_{ht} 200°C	11.4	33
T_{ht} 300°C	13.7	40
Water–vapor	9.6	48
Ice–vapor	11.4	55

The obtained ΔH and ΔS values suggest that the state of water adsorbed on the SnO_2 surface does not differ from its state in liquid and crystalline phases. However, as the heat-treatment temperature increases, ΔH_{des} and ΔS_{des} vary in parallel: an increase in ΔS_{des} corresponds to an increase in ΔH_{des}.

EXPERIMENTAL

Samples of SnO_2 were weighed on a VLR-200g analytical balance with the accuracy of $\pm2\times10^{-4}$ g. The derivatograms were recorded on a Paulik–Paulik–Erdey derivatograph with 0.2-g samples at a heating rate of 5 deg min^{-1}.

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