THERMALLY STIMULATED RELEASE OF LABELLED H₂S
FROM LEACHED BASALT FIBERS

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Thermally stimulated release of labelled H_2S from basalt fibers treated in two steps by HCl solutions is studied using radioactive tracers. The experiments were conducted on an apparatus for combined emanation—thermal analysis. It was found that the shape of the thermal desorption spectrum of $H_2{}^{35}S$ depends essentially on the presence of traces of water in the fiber adsorbent. The formal order and activation energy of the thermal desorption of labelled H_2S are determined. It is demonstrated that the porous structure of the adsorbents based on leached basalt fibers is considerably nonuniform.

Thermally stimulated gas release (TSGR) is widely used to characterize the surface of adsorbents and to measure gas—solid interaction parameters [1—3]. The method consists of adsorbing a specially chosen gas (probe) at constant temperature and then subjecting the sorbent to programmed (as a rule linear) heating. During the course of the experiment the flux of probe evolved from the sample is measured. Plots of the dependence of the gas-release flux on temperature, so-called thermal desorption spectra (TD spectra) provide a direct readout of the principal features of the initial energy spectrum of the atomic states of the adsorbate and adsorbent.

The gases evolved are detected by mass spectrometry, chromatography, etc. Radiometric detection has been used to investigate thermal desorption of heavy radioactive inert gases [1]. The high sensitivity of labelled atoms, the versatility, and the possibility of measuring the activity of both the gas and solid suggest that this method will be expanded to various adsorbate—adsorbent systems.

The goal of the present study was to develop radiochemical thermal desorption spectroscopy for application to the investigation of H_2S desorption from leached basalt fibers [4]. The main attention was focused on investigating the uniformity of the porous structure of the sorbent and on determining the formal order and activation energy of thermal desorption of labelled H_2S.

MATERIALS

New sorbents prepared from basalt fibers treated in two steps were used in the investigation [4]. In the first step the fibers were treated for 20—50 min with 2—5 M HCl at 92—95°C with stirring, washed with distilled water, again treated with 0.25—3 M HCl for 4—8 h under the same conditions, and again washed with distilled water. This produced a leached fibrous material with a high adsorption capacity for H_2O, SO_2, and H_2S.

The lack of sensitive, selective, and reliable detectors for H_2S made it necessary to use radioisotope methods for recording the desorption kinetics. The adsorbate was H_2S labelled with ^{35}S that was prepared by the literature method [6] from aluminum sulfide with the calculated amount of radioactive $Ba^{35}S$ added.

EXPERIMENTAL

The experimental apparatus for recording the kinetics of thermally stimulated desorption was assembled based on a differential-thermal analysis apparatus [3, 7]. The apparatus enabled detection of labelled H_2S evolved from a sample in a

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TABLE 1. Measurement Conditions of TD Spectra of H_2S from Leached Basalt Fibers

Sample No.	Curve No.	Heating rate, K/min	Flow rate, ml/min	Peak temperature, K	Width, K	Asymmetry
1	1	4.8	420	290	47	1.2
	2	7.8	420	306	50	0.6
2	1	3.03	120	266	47	0.7
	2	4.8	120	285	35	1.6
3	1	9.6	300	306	40	1.5
4	1	5.4	300	298	54	1.4
	2	4.8	300	290	24	0.6
5	1	6.0	420	298	44	0.87
	2	4.8	420	294	34	1.0
6	1	5.4	300	306	48	0.8
	2	8.1	300	302	34	0.7

TABLE 2. Calculated Parameters of the Desorption Equation for Experimental TD Peaks

Sample No.	Curve No.	Activation energy, kcal/mol	Frequency factor, min	Coverage	Order	Root mean-square deviation
1	1	7.8	$0.12 \cdot 10^6$	1.0	1.0	$0.20 \cdot 10^{-5}$
	2	7.8	$0.12 \cdot 10^6$	1.0	1.0	$0.63 \cdot 10^{-6}$
2	1	7.8	$0.54 \cdot 10^6$	1.0	1.2	$0.10 \cdot 10^{-5}$
	2	12.0	$0.42 \cdot 10^9$	0.85	1.0	$0.11 \cdot 10^{-5}$
		20.36	$0.88 \cdot 10^{14}$	0.15	1.0	
3	1	17.9	$0.50 \cdot 10^{13}$	0.6	1.0	$0.27 \cdot 10^{-5}$
		26.2	$0.40 \cdot 10^{18}$	0.4	1.0	
4	1	11.55	$0.10 \cdot 10^9$	0.55	1.0	$0.16 \cdot 10^{-5}$
		14.00	$0.10 \cdot 10^{10}$	0.45	1.0	
	2	16.36	$0.10 \cdot 10^{13}$	1.0	1.0	$0.60 \cdot 10^{-5}$
5	1	10.37	$0.12 \cdot 10^8$	1.0	1.0	$0.12 \cdot 10^{-5}$
	2	11.60	$0.12 \cdot 10^9$	1.0	1.0	$0.20 \cdot 10^{-5}$
6	1	8.9	$0.57 \cdot 10^6$	1.0	1.1	$0.64 \cdot 10^{-6}$
	2	11.72	$0.11 \cdot 10^9$	1.0	1.0	$0.50 \cdot 10^{-5}$

stream of inert carrier gas, linear heating at 1—20 K/min in the range 200—400 K, and measurement of the differential temperature difference of the investigated sample and a reference (DTA).

The apparatus for studying thermal desorption of H_2S from leached adsorbents with detection of gaseous S-labelled H_2S consists (Fig. 1) of a working cell (4) with a heater (5), a water-cooled gas line (9) and a stopcock for connecting the vacuum pump or a H_2S cylinder, and a SI-3B radiometric window counter with a recorder (10) and a carrier-gas flow-rate meter (11). Tubes (2) with the sample (6) and reference (7) are inserted into the cell (4). These are sealed with cover nuts (3). Thermocouples (1) are placed in the tubes in order to perform differential-thermal analysis of the sample. The principal parts of the apparatus are made of stainless steel.

The TD spectra of labelled H_2S were recorded as follows. Tubes with a sample of leached sorbent and a reference, powdered quartz, were placed in the heating cell. The sample was then regenerated in a stream of inert gas (He, Ar) at 130°C for 30 min. The cell was cooled to room temperature. The flow of inert gas was stopped. The cell was connected to a cylinder of labelled H_2S and placed in a Dewar flask over liquid nitrogen vapor for 40 min. After the sample was completely saturated at low temperature, the H_2S cylinder was disconnected. The inert-gas flow was started and passed through the cell.

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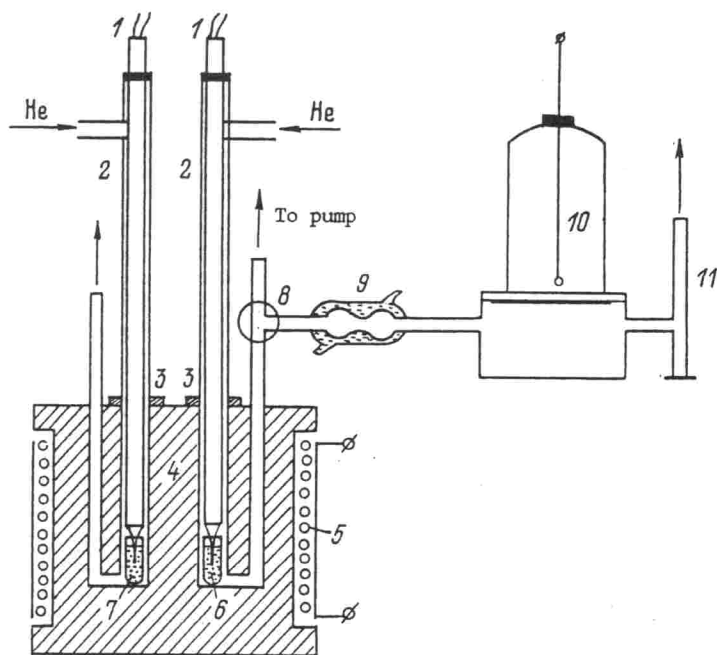
Fig. 1. Block-diagram of the experimental apparatus for studying thermal desorption of labelled H_2S. Thermocouples (1), tubes (2), sealing nuts (3), working cell (4), programmed heater (5), sample (6), DTA reference (7), gas stopcock (8), water-cooler (9), SI-3B window counter (10), bubble flow-rate meter (11).
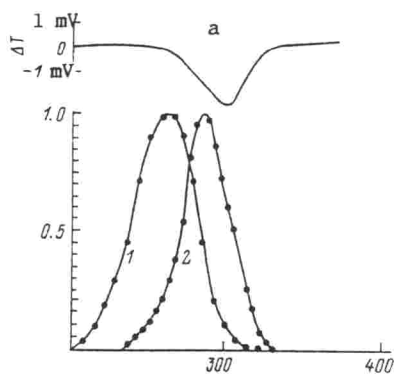

Fig. 2. Thermal desorption spectra of H_2S from leached basalt fibers No. 2 and the differential temperature difference (DTA) curve (a) for spectrum 2. The rate $\beta = 3.1$ (1) and 4.8 K/min in the presence of water (2). Along the vertical: flow, rel. units; along the horizontal: T, K.
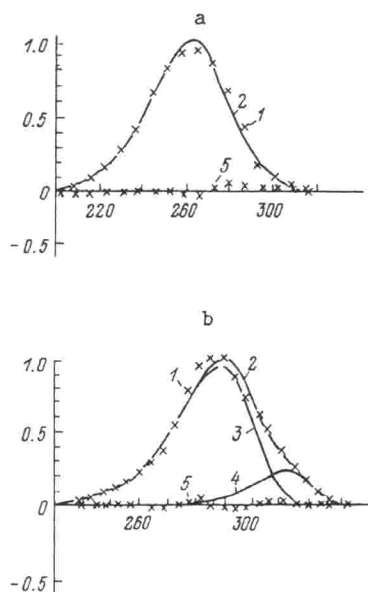
Fig. 3. Experimental TD spectra, the corresponding theoretical curves, and the difference between the experimental and theoretical curve. Release of labelled H_2S in the absence of water (*a*), release of labelled H_2S in the presence of water (*b*). Experimental data (1), theoretical curve (2), contributions of separate components (3, 4), difference between curves 1 and 2 (5). Along the vertical: flux, rel. units; along the horizontal: T, K.

the water-cooled gas line, and the ^{35}S β-detector. The gas flow rate was recorded using a bubble meter and was held constant during the whole experiment. The temperature of the working cell was increased at a given linear rate by turning on the heater. The count rate (radioactivity) of H_2S evolved, the sample temperature, and the differential temperature difference were continuously and simultaneously recorded during the course of the experiment.

During saturation with the adsorbate at low temperature, a some of the samples were contacted with atmospheric humidity. This caused co-adsorption of H_2S and H_2O.

RESULTS AND DISCUSSION

Gas-release plots were obtained from the study of thermally stimulated desorption of labelled H_2S from leached adsorbents. These were plotted in coordinates $I(T)/I(T_{max}) - T$, where $I(T)$ is the count rate recorded by the gas detector, I/T_{max} is the count rate at the maximum in the gas-release curve, and T is the temperature. The characteristics of the experimental TD peaks and the measurement conditions are presented in Table 1.

All experimental curves can be divided into two groups owing to the difference in saturation conditions, the presence or absence of water in the studied samples. For samples with a significant amount of water, the DTA curves recorded during thermally stimulated desorption contained a distinct endotherm due to loss of water. Loss of H_2S from anhydrous samples was not accompanied by thermal effects. All experimental TD spectra were unimodal poorly resolved peaks.

As an example of the experimental TD spectra, plots for sample No. 2 measured in two successive experiments and differing by the absence (curve 1) and presence (curve 2) of significant amounts of water are presented in Fig. 2. Experimental curve 1 is located at lower temperatures than curve 2, which is measured in the repeat experiment.

The maximum of curve 1 is broader and its temperature was $T_{max} = 265.9$ K whereas for curve 2 $T_{max} = 285.6$ K. The width at half-height for the first peak is $\Delta T = 47$ K whereas for the second $\Delta T = 34$ K. The ascending branch of curve 1 is steeper than this branch in the curve of the repeat experiment. However, the descending branches of both peaks follow parallel paths with a small difference between them. The peak asymmetry coefficient calculated from the formula $\delta t = (T_{1/2} -$

$T_{max}/(T_{max} - T_{1/2})$, where $T_{1/2}$ and $T_{1/2}$ are the temperatures of the peak half-height on the descending and ascending branches of the peak, respectively, is $\delta T_1 = 0.7$ for curve 1 and 1.6 for curve 2.

The DTA curve is plotted in Fig. 2. Only during the repeat experiment was an endotherm detected, the maximum of which follows after the gas-release peak.

The TSGR curves over the whole TD spectrum can only be treated by nonlinear least squares (LS). Preliminary treatment of the TD spectra to determine the energy spectrum of the adsorbate states in the sorbent, a possible model, and an estimate of its parameters have been discussed [8, 9].

The dependence of the gas-release flux J on T with linear heating $T = T_0 + \beta t$, where T_0 is the initial temperature and β is the heating rate assuming kinetic gas release and a monoenergetic spectrum of adsorbate initial states is described by

$$J(T) = -\frac{d\theta}{dt} = K \cdot \theta^{pow},$$ (1)

where pow is the formal order of the desorption reaction (as a rule $0 < pow < 3$) and k is the desorption constant. Taking into account the temperature dependence of the desorption constant $k = k_0 \cdot \exp(-E/RT)$ for reaction order $pow - 1$, the solution of Eq. (1) with the initial condition $\theta(t = 0) = \theta_0$ can be written as [1]:

$$J(T) = k_0 \theta_0 \exp(-E/RT) \exp(\tau),$$ (2a)

where

$$\tau = \frac{k_0 \cdot E}{\beta \cdot R} \left[-\frac{\exp(\xi)}{\xi} + E_i(\xi) \right] \Bigg| \begin{array}{l} \xi = -E/RT \\[4pt] \xi = -E/RT_0 \end{array}$$

and $E_i(z) = \int_{-\infty}^{z} \frac{\exp(t)}{t} dt$

$$J(T) = k_0 \cdot \exp(-E/RT) \cdot \theta_0^{1-pow} + (1 - pow) \cdot \tau^{pow/(1-pow)}.$$ (2b)

For a discrete adsorption center energy spectrum, the flux from the sample is determined by [8]

$$J(T) = \sum_{i=1}^{n} \Phi_i J_i(T),$$ (3)

where φ_i is the flux J_i from the i-th type of adsorption centers.

The program ATEGREC (Analysis of the ThErmostimulated Gas RElease Curve) was written in FORTRAN to process the experimental TD spectra of labelled H_2S from leached adsorbents. The program was run on an IBM PC/XT personal computer. The program operates using a main menu where the subprogram numbers and types of operations carried out by them are listed. The program requests the number of the operation and transfers into the appropriate subprogram. After completing the subprogram, one is returned to the main menu.

The programs enables:

— from a data file, calculation of the experimentally obtained count rates I, the uncertainty of the measurement ΔI and T, symbolic data (sample name and number, date, etc.), experimental conditions (heating rate, carrier-gas flow rate);

— on the basis of a selected gas-release model, construction of the corresponding functional scale, a graphic representation of the linearized experimental curve and, on the basis of any portion of the curve using linear LS, calculation of the parameters and their uncertainties in addition to the sum of squares of the deviation of the model curve from the experimental data;

— calculation of the dependence of $\ln[I(T)/\theta(T^{pow})]$ on $1/T$, graphic display of it and, from any part of the curve obtained using linear LS, calculation of the activation energy, the frequency factor, and their uncertainties;

— nonlinear optimization of the parameters of the model selected from the list, determination of the uncertainties of these parameters, calculation of the discrepancy, graphic display of the experimental curve and theoretical curve with optimized parameters, and, for the additive model, determination of the separate contributions of components and graphic display of the residuals (difference between experimental data and model curve).

Six adsorbent samples prepared from leached basalt fibers were investigated by TD spectroscopy. The samples differed in preparation method. Sorbent samples were saturated with labelled H_2S at low temperature and part of the samples jointly with labelled H_2S and water for the TD experiments.

Treatment of the TD curves revealed a satisfactory description of the desorption mechanism by an n-th order chemical kinetic equation or the sum of two such equations. For most of the samples, the order of the TD reaction was about 1.

Experimental TD spectra and the corresponding theoretical curves and drifts of residuals for adsorbent No. 2 are plotted in Fig. 3. The saturation conditions of the adsorbent in these two experiments was different. The presence of an endotherm on the DTA curve is consistent with the presence of water in the sample during the second experiment. Apparently this condition distorted the shape of the H_2S release curve. Whereas the desorption activation energy for the anhydrous sample (one peak of gas-release) was 7.8 kcal/mol with frequency factor $-0.84 \cdot 10^6$ min^{-1}, two poorly resolved peaks are observed for the sample with water. The principal peak has energy 12 kcal/mol and $k_0 = 0.42 \cdot 10^9$ min^{-1}; the minor one, 20.4 kcal/mol and $k_0 = 0.88 \cdot 10^{14}$ min^{-1}.

On the basis of the treatment of the experimental TD spectra, it can be concluded that the TD spectra of H_2S in the absence of water are described well by a theoretical curve with a single activation energy, which agrees well with the differential heat of adsorption [5]. The presence of water in the sample complicates the TD spectrum of H_2S for the samples, where two poorly resolved peaks appear. This can be explained by the fact that H_2S dissolves well in water and is desorbed with the latter. Thus, the activation energy calculated on the basis of the TD peak can be portrayed as desorption of H_2S itself (in the absence of water) and joint release of water and H_2S. In the second instance the calculated activation energies have substantially greater values than in the first (Table 2).

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