Kinetics and Catalysis, Vol. 42, No. 2, 2001, pp. 275–280. Translated from Kinetika i Kataliz, Vol. 42, No. 2, 2001, pp. 306–311.

Kinetics of the Thermal Desorption of Atomic Oxygen during Transformations $BiO_{2-x} \longrightarrow \beta\text{-}Bi_2O_3 \longrightarrow \alpha\text{-}Bi_2O_3$

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Received January 18, 1999

Abstract—The thermal desorption of atomic oxygen during the transformations $BiO_{2-x} \longrightarrow \beta\text{-}Bi_2O_3 \longrightarrow \alpha\text{-}Bi_2O_3$ is shown to be due to the removal of overstoichiometric oxygen from the bulk of $\beta\text{-}Bi_2O_3$. Oxygen formed at the first stage is desorbed in a molecular form. The maximum desorption rate of atomic oxygen is found before the phase transformation $\beta\text{-}Bi_2O_3 \longrightarrow \alpha\text{-}Bi_2O_3$. The activation energy of the diffusion of excess oxygen in the $\beta\text{-}Bi_2O_3$ lattice is ≈30 kcal/mol.

INTRODUCTION

"Active" oxygen is given special attention in the mechanistic studies of the selective oxidation of hydrocarbons on mixed-oxide catalysts, and the nature of this species is still under discussion. Various oxygen species on the surface of metal oxides are known: O^-, O^{2-}, O_2^{ads}, O_2^-, O_2^{3-}, O_3^-, and O_4^- [1]. When oxygen desorbs, the species become less diverse. The desorption of the O, O_2, $^1\Delta_g O_2$, and O_3 species was found under different conditions [2–4]. The nature of desorbed oxygen species should be taken into account in studies of heterogeneous–homogeneous catalytic processes. This is also important for the so-called remote-control mechanism that was suggested to account for the effect of synergism on multiphase catalysts for partial oxidation. This effect manifests itself in that active species are formed on some regions of a catalyst and react on other regions.

It was found in a series of studies that some oxides (for example, Bi_2O_3, Sb_2O_4, etc.) play a role of active oxygen donors, whereas other oxides are oxygen acceptors, and the catalytic process occurs on the latter oxides (see, for instance, [5]). It was shown in [6] that active oxygen, which participates in the reaction, comes from the bulk of the donor oxide and the gaseous oxygen becomes active only after passing through the volume of a grain of the donor oxide. Therefore, the study of the properties of active oxygen and the conditions of its diffusion from the grain bulk to the surface and migration to catalytic sites is especially important. In our previous study [7], we carried out a simulation of oxygen migration from the grain bulk to the surface and proposed a model to determine the diffusivity. It was found that the oxygen atom is a possible species of active oxygen, which can be monitored as O_3 when O_2 is present in the gas phase. O_3 is formed from O via the fast reaction $2O_2 + O \longrightarrow O_3 + O_2$. The reaction $O_2^g + O^{ads} \longrightarrow O_3^g$ was ruled out for the following reason. According to the reported data [1], a precursor of O_3^- decomposes on the oxides under study at $T > 150$°C. In our experiments, desorption occurs at $T > 300$°C and reaches a maximum in the range 400–500°C, and this likely eliminates the possibility of the above reaction.

This work is intended to find a relationship between the genesis of bismuth oxide, a component of multicomponent catalysts for the partial oxidation of hydrocarbons, and the kinetics of oxygen thermal desorption in both molecular and atomic forms. To our knowledge, such studies were not carried out earlier.

EXPERIMENTAL

Samples of BiO_{2-x} were prepared by the oxidation of bismuth hydroxide with sodium persulfate (sample 1) or potassium ferricyanide (sample 2) in an alkali solution.

Samples of $\beta\text{-}Bi_2O_3$ were prepared by three procedures: the heating of BiO_{2-x} (sample 1) at 350°C for 10 min (sample 3), the heating of basic bismuth carbonate ($Bi_2O_2CO_3$) at 380°C for 20 min (sample 4), and the treating of a solution of bismuth nitrate with excess 2 mol/l solution of sodium hydroxide at 100°C for 3 min followed by fast filtration of a precipitate and thorough washing (sample 5). The latter sample differs from more fine-crystalline samples 3 and 4 by stability on exposure to H_2O and CO_2. For more detailed data on the preparation of these samples, see [8].

Hydrated $\beta\text{-}Bi_2O_3$ (sample 6) was prepared by storing fine-crystalline $\beta\text{-}Bi_2O_3$ (samples 3 and 4) in wet air for several days or by the impregnation of the samples with water followed by fast drying at 120°C.

0023-1584/01/4202-0275$25.00

The thermal desorption of atomic oxygen (ozone) was measured by chemiluminescence in an air flow as described in [9]. A signal from a selective amplifier was recorded using a Pentium-based PC via a 12-bit analog-to-digital converter using original software for recording and treating the signals.

The thermal desorption of molecular oxygen was studied in a helium flow under the conditions of a linear increase in temperature at a rate of 10°C/min. Desorbing water and CO_2 were collected in a silica gel trap. Evolved oxygen was recorded with a thermal-conductivity detector.

X-ray diffraction analysis was performed using a DRON-3 instrument (CuK_α-irradiation).

DTA and DTG curves were recorded using an MOM analyzer (Hungary).

The experiments in an isothermal regime were carried out as follows: a sample was introduced into the reactor preheated to a specified temperature; purging with air and O_3 recording were not interrupted during these experiments.

The experimental thermal desorption curves obtained in the isothermal regime were approximated by the $\exp(-kt)$ or $\exp(-k\sqrt{t})$ functions. Experimental data fit was worse if other functions were used. A criterion for the best fit was the minimum root-mean-square deviation of the experimental data from the calculated curve. The desorption rates thus calculated at different temperatures obey the Arrhenius equation, from which the activation energy of the process was found.

RESULTS

The X-ray diffraction study showed the correspondence of the spectra for BiO_{2-x} and β-Bi_2O_3 to the tabulated values for these substances. Samples 1 and 2 prepared by different procedures were crystalographically identical (fluorite-type cubic lattice).

The thermogravimetric measurements revealed a marked weight change in the range of 340–380°C and a small endothermic peak at 380°C, which, according to the reference data, indicates the decomposition of BiO_{2-x} to β-Bi_2O_3. A small exothermic peak at ≈530°C appeared on further heating at almost constant weight, which we attributed to the β-$Bi_2O_3 \longrightarrow \alpha$-$Bi_2O_3$ transition.

Essential weight variations were not found on the DTA curve of the β-Bi_2O_3 sample. The DTA curve has a small exothermic peak at 420°C, which corresponds to the β-$Bi_2O_3 \longrightarrow \alpha$-$Bi_2O_3$ transition and is in good agreement with the reported data. The origin of the somewhat enhanced temperature of the phase transition in the case of β-Bi_2O_3 prepared by the decomposition of BiO_{2-x} remains unclear. In this case, β-Bi_2O_3 is likely stabilized by the hydroxyl groups that were introduced into BiO_{2-x} during preparation in an aqueous solution or by excess lattice oxygen, which was not removed completely upon dioxide decomposition.

Figure 1 presents the experimental thermal desorption curves both for O_2 and O, which was monitored as O_3 for the BiO_{2-x} and β-Bi_2O_3 samples. The maximum temperature of O_2 thermal desorption from the BiO_{2-x} sample coincides with that for BiO_{2-x} decomposition to β-Bi_2O_3. In addition, two small peaks at ≈445 and 560°C appeared with an increase in temperature. The thermal desorption of atomic oxygen during the BiO_{2-x} decomposition is at the background level, then it sharply increases after passing through maximum of decomposition, and reaches a maximum (437°C) somewhat earlier than the second maximum at 445°C appears on the thermal desorption curve for O_2.

Table 1 lists the main parameters of oxygen thermal desorption for the samples under study. Note the amount of oxygen that evolved during BiO_{2-x} decomposition and was estimated from the thermal desorption data is in good agreement with the DTA findings for the oxygen-deficient BiO_{2-x} dioxide (parameter x depends on the preparation procedure and achieves values up to 0.25). The amount of atomic oxygen evolved during the $BiO_{2-x} \longrightarrow Bi_2O_3$ transition is $\approx 10^{-6}$ of the amount of desorbed molecular oxygen.

The preparation procedure for the BiO_{2-x} samples does not actually affect the experimental results. Only slight differences were found in the temperatures of phase transition and the amount of desorbed oxygen (because of different oxygen concentration in the nonstoichiometric BiO_{2-x}).

In the case of preliminarily prepared β-Bi_2O_3, the low-temperature peak (375°C) due to the evolution of molecular oxygen via the reaction $BiO_{2-x} \xrightarrow{-O_2} \beta$-$Bi_2O_3$ is absent but the high-temperature maxima at 445 and 560°C are still present. These peaks on the thermal desorption curve are likely due to the removal of overstoichiometric lattice oxygen from the β-Bi_2O_3 lattice rather than the decomposition of bismuth dioxide. Apparently, these processes also produce atomic oxygen during thermal desorption (the maximum of evolution is seen at ~540°C). β-Bi_2O_3 prepared by bismuth dioxide decomposition contains a significant amount of overstoichiometric oxygen. The results of thermal desorption measurements show that the oxygen concentration corresponds to the β-$Bi_2O_{3.16}$. Meanwhile, the data of X-ray diffraction study of nonstoichiometric samples are the same as the data for usual β-Bi_2O_3. This fact is due to the presence of oxygen vacancies in the β-Bi_2O_3 lattice, which are capable of accepting excess oxygen without reconstruction of the crystal lattice.

To study desorption kinetics in more detail, we performed experiments in the isothermal regime. Measurements were conducted at various temperatures with a fresh sample in each run. Table 2 presents the results of experiments on atomic oxygen desorption in the isothermal regime. The exponential kinetics for thermal

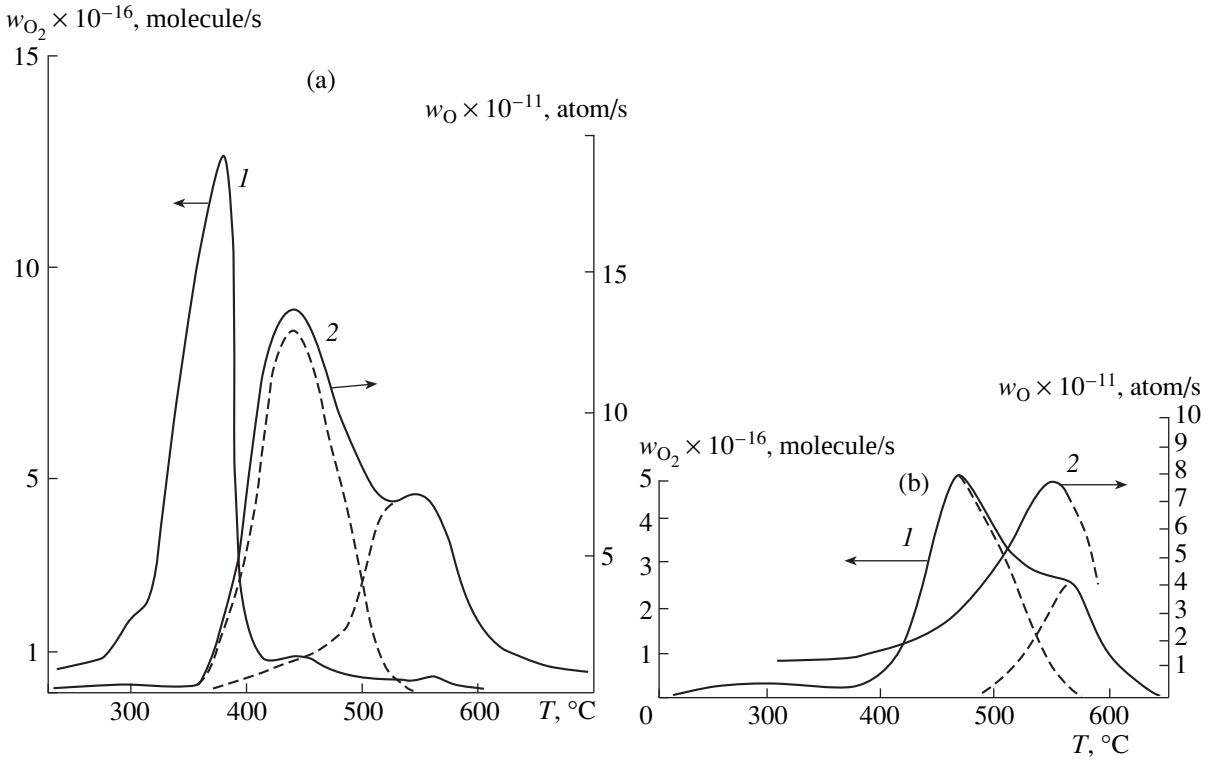

Fig. 1. Thermal desorption of (*1*) O_2 and (*2*) O from (a) BiO_{2-x} (sample 2) and (b) β-Bi_2O_3 (as-prepared sample 3). *w* is the thermal desorption rate. The dashed line shows deconvolution to distinct peaks.

desorption decay was found for two samples, hydrated bismuth oxide (sample 6) and fine-crystalline β-Bi_2O_3 (sample 4). A more complicated time profile of the rate of atomic oxygen evolution was found for sample 5 prepared by precipitation with alkali. This fact will be discussed below.

Figure 2 shows the decay curves for atomic oxygen desorption at different temperatures. The two-peak pattern is clearly seen, which can be explained by the desorption of the surface oxygen (the first peak) and the subsequent desorption of oxygen, which diffuses from the bulk (the second peak).

We also studied ozone decay both on the reactor walls and on the oxide samples. The concentrations of atomic species and ozone presented in the table are underestimated because of the decay on both the samples and reactor walls. Nevertheless, different samples and the concentrations in two peaks for the same sample can be compared semiquantitavely.

DISCUSSION

The experimental results for the thermal decomposition of BiO_{2-x} (Table 1, samples 1 and 2) provide evidence that atomic oxygen is formed beginning from $T > 360$°C and up to the temperature of β-$Bi_2O_3 \longrightarrow$ α-Bi_2O_3 phase transition. Because only β-Bi_2O_3 exists in this temperature range during decomposition, atomic oxygen is likely formed from overstoichiometric lattice oxygen of the β-phase, which diffuses from the bulk to the surface. After the removal of excess lattice oxygen (which stabilizes β-Bi_2O_3), the β-$Bi_2O_3 \longrightarrow$ α-Bi_2O_3 transition occurs.

Table 1. Thermal desorption of molecular and atomic oxygen from bismuth oxides

Sample	S_{sp}, m^2/g	O_2		O	
		amount of desorbed molecules, g^{-1}	temperature of the desorption maximum, °C	amount of desorbed atom, g^{-1}	temperature of the desorption maximum, °C
1	3.5	3×10^{20}	365	1.7×10^{14}	470
		–	475	2.0×10^{14}	510
2	4.3	4.2×10^{20}	375	4.4×10^{14}	437
		9.5×10^{17}	445	5.0×10^{14}	545
		$\approx 10^{17}$	560	–	–
3	15.6	1.4×10^{20}	445	2.0×10^{15}	540
		–	560	–	–
4	3.8	–	–	4.4×10^{13}	545
5	0.7	–	–	1.8×10^{13}	340

The chemical reaction $BiO_{2-x} \longrightarrow \beta\text{-}Bi_2O_3$, which produces the main amount of molecular oxygen, does not lead to the additional desorption of atomic oxygen.

The model of a "black sphere" developed by us [7] predicts the following time profile of the thermal desorption rate for the isothermal thermal desorption of excess oxygen from the bulk of the grain, when chemical reactions and phase transitions are absent (the rate-determining step is the diffusion of excess oxygen to the surface):

$$w(t) \approx (N_0/\pi^2\tau_D)(t/\tau_D)^{1/2} \exp(-t/\tau_D)^{1/2}, \qquad \tau_D = a^2/4\pi^2 D, \tag{1}$$

where N_0 is the average amount of excess oxygen atoms in the oxide grain, a is the average radius of the oxide grain, and D is the diffusivity of excess oxygen in the oxide lattice.

However, the actual kinetics of atomic oxygen thermal desorption from the $\beta\text{-}Bi_2O_3$ samples depends on their preparation procedure and history. A simple exponential character of the decay of the desorption intensity in the isothermal regime (Table 2, sample 4) was found for the fine-crystalline $\beta\text{-}Bi_2O_3$. As mentioned above [10], the hydration of $\beta\text{-}Bi_2O_3$ powder by storing in a wet air or wetting the sample with distilled water followed by drying at $T \approx 120$°C results in a substantial increase in the amount of desorbed atomic oxygen. The kinetics of thermal desorption decay under isothermal conditions is also exponential and the activation energy is extremely high (Table 2, sample 6). This fact can be explained by the possible recombination of a fraction of the hydroxyls introduced by hydration according to the following scheme as it shown in our previous work [10]

$$2OH^- \longrightarrow H_2 + 2O^- \tag{I}$$

followed by the reaction

$$2O^- \longrightarrow O^{2-} + O\uparrow. \tag{II}$$

In both cases (fine-crystalline $\beta\text{-}Bi_2O_3$ or hydrated sample), the simple exponential kinetics of the thermal desorption decay that does not correspond to Eq. (1) was found. It follows that diffusion is likely complicated by a chemical side reaction of the first (or pseudofirst) order, which is the rate-determining step of the whole process (it is this chemical side reaction that is characterized by the activation energy obtained for these samples). This conclusion is also confirmed by experimental data on the linear heating of fine-crystalline and hydrated $\beta\text{-}Bi_2O_3$ samples. We have shown previously [10] that a weight loss of the sample occurs at temperatures up to 500°C, which are significantly higher than the temperature of the $\beta \longrightarrow \alpha$ transition (420°C). This weight loss is due to the removal of the structural OH^- groups (removal of excess oxygen from these samples of $\beta\text{-}Bi_2O_3$ does not manifest itself on the DTA curves). Hence, the structural OH^- groups are maintained in the hydrated samples up to ~500°C. Therefore, a small flow of O atoms, which is due to the desorption of excess oxygen from $\beta\text{-}Bi_2O_3$ and accompanied by phase transition, is completely masked by a flow of oxygen atoms formed by reactions (I) and (II) over a wide temperature range.

The only sample on which the desorption flow in the isothermal regime obeyed Eq. (1) was $\beta\text{-}Bi_2O_3$ prepared by precipitation from an aqueous solution (sample 5). After examining the thermal desorption kinetics for atomic oxygen from this sample, we attributed the first peak to the thermal desorption of atomic oxygen, which is located on the surface of oxide granules. The second peak concerns the thermal desorption of atomic oxygen, which diffuses from the granule bulk. A decrease in atomic oxygen desorption at high temperatures (Table 2, sample 5) is likely due to the concurrent recombinative desorption of atoms.

This is also confirmed by the experimental findings presented in Fig. 1. As can be seen, a decrease in atomic

Table 2. The results of the measurements of atomic oxygen thermal desorption from bismuth oxides in the isothermal regime

Sample	Temperature of desorption, °C	Amount of desorbed atoms O*, g^{-1}	Law of desorption rate decrease	Diffusivity, cm^2/s	Activation energy, kcal/mol
4	390	–	–	–	19.4
	425	1.7×10^{14}	Exponent	–	
	480	2.6×10^{14}	″	–	
5	390	–	–	1.2×10^{-13}	30
	430	3.6×10^{12}, 2.8×10^{13}	$\exp(-k\sqrt{t})$	3×10^{-13}	
	470	3×10^{12}, 7.2×10^{13}	″	1.4×10^{-12}	
	490	1.1×10^{12}, 1.3×10^{13}	″	1.8×10^{-12}	
6	480	–	–	–	40.7
	490	–	–	–	
	530	10^{16}	Exponent	–	

* Sample 5: two figures correspond to the oxygen amount in two desorption peaks (see Fig. 2).

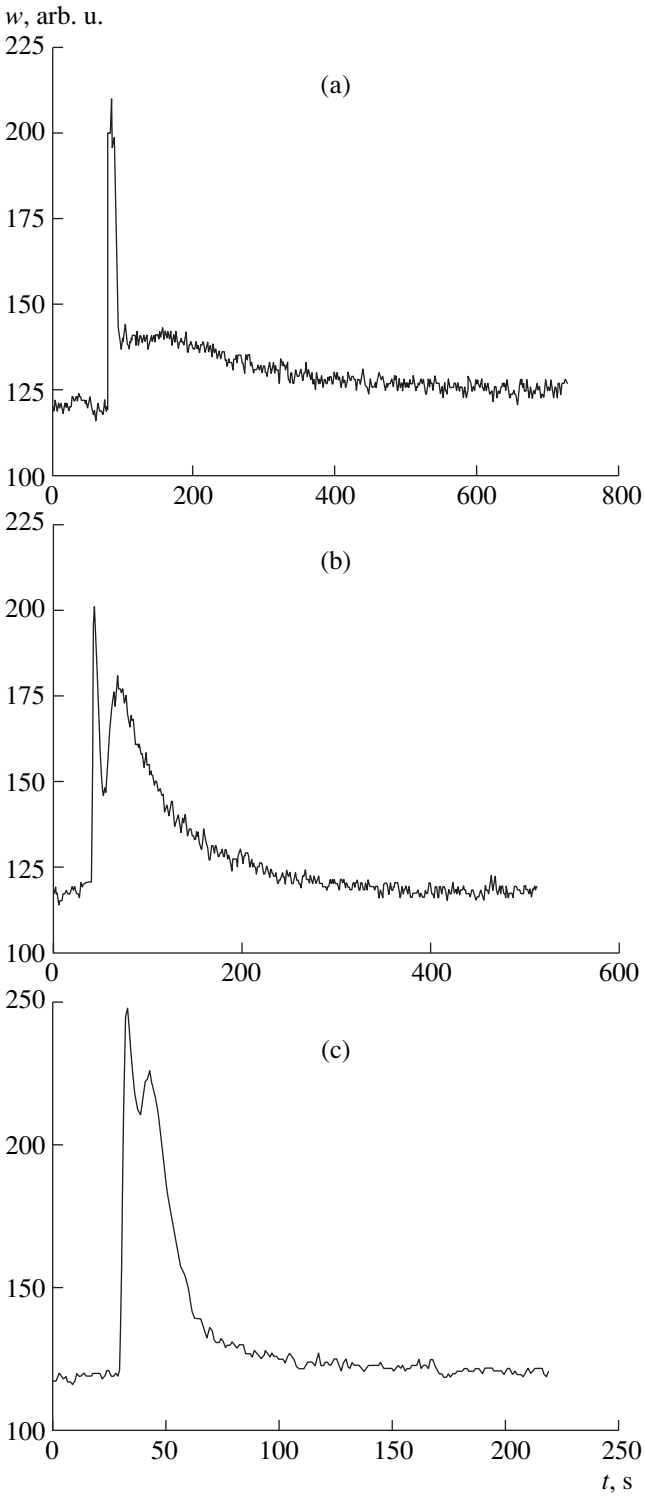

Fig. 2. Kinetics of atomic oxygen thermal desorption from β-Bi_2O_3 (sample 5) at temperatures, °C: (a) 390, (b) 430, and (c) 490.

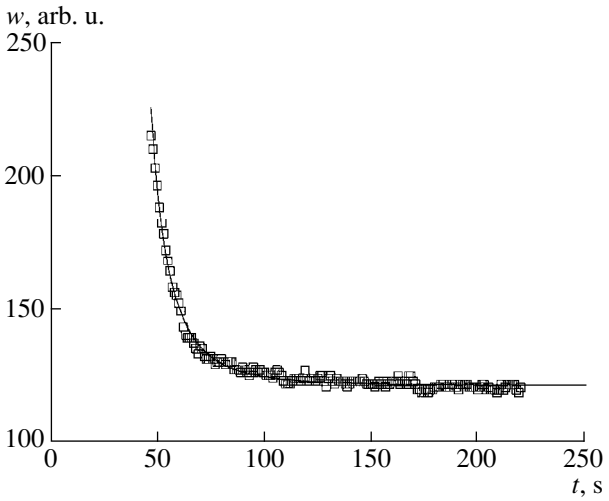

Fig. 3. Approximation of the kinetics of O thermal desorption at 490°C from sample 5 (β-Bi_2O_3) by theoretical Eq. (1). Points denote the experiment, and the curve denotes calculation.

oxygen desorption is accompanied by an increase in the desorption of molecular oxygen, that is, the competitive oxygen desorption both in atomic and molecular forms takes place because both processes originate from the diffusion of atomic oxygen from the grain bulk. The elucidation of a detailed mechanism requires additional experiments.

The above interpretation and the shape of curves (Figs. 2 and 3) follow from the "black sphere" model [7]. As it is seen from Fig. 3, the model satisfactorily describes the descending part of the second peak. The initial part of the second peak was ignored because the isothermal regime was not settled for such short times.

The problem on the rate-determining step of oxygen removal from the grain bulk is important because the use of the "black sphere" model suggests that the rate-determining step is oxygen diffusion from the bulk to the surface rather than the subsequent desorption. Let us consider this suggestion. A mathematical condition for the use of the "black sphere" model is the inequality

$$k_{des} > D/a^2,$$

where a is the average grain radius.

According to Frenkel:

$$k_{des} = 1/\tau = 10^{13}\exp(-Q/RT),\ s^{-1},$$

where k_{des} is the rate constant of desorption, τ is the lifetime of the adsorbed species, and Q is the heat of adsorption.

Taking the heat of adsorption of atomic oxygen on the surface of Bi_2O_3 equal to ~44 kcal/mol [11], we obtain at 390°C: $k_{des} = 10^{13}\exp(-22000/663) = 2.8 \times 10^{-1}\ s^{-1}$, where $Q/R = 22000$.

At the same time, at $D = 1.2 \times 10^{-13}\ cm^2/s$ at 390°C (see Table 2) and the average grain radius of $\sim 5 \times 10^3$ Å, $D/a^2 = 1.3 \times 10^{-6}\ s^{-1}$, that is, the inequality is fulfilled with a confidence.

Thus, the rate-determining step in the atomic oxygen desorption from the sample of large-crystalline

β-Bi_2O_3 is the diffusion of atomic oxygen and, hence, the activation energies estimated from thermal desorption concern the atomic oxygen diffusion. One can also assume that O_2 desorption is partially the result of the recombination of atomic oxygen. In this case, taking into account the process energy, one can suggest that a fraction of desorbed O_2 can be vibrationally excited.

CONCLUSIONS

(1) The main evolution of atomic oxygen from β-Bi_2O_3 occurs at the expense of overstoichiometric lattice oxygen and is accompanied by the lattice reconstruction β-$Bi_2O_3 \longrightarrow \alpha$-$Bi_2O_3$.

(2) The "black sphere" model proposed by us earlier is valid in the case of excess oxygen diffusion not complicated by chemical side reactions. These conditions are fulfilled only for the large-crystalline sample in the absence of CO_2 and H_2O, which form bismuth hydroxycarbonates by interaction with fine-crystalline samples.

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