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TG AND DTA STUDY OF OXYGEN DEPLETION AND REOXIDATION OF BISMUTH MOLYBDATES (2:1; 2:3)

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Oxygen depletion and reoxidation of bismuth molybdates (2:1; 2:3) have been studied by means of isothermal thermogravimetry and DTA measurements. From the isothermal curves, Arrhenius energies were obtained between 411 and 683 K. The activation energies for oxygen depletion from $Bi_2O_3 \cdot MoO_3$ were lower than those for $Bi_2O_3 \cdot 3\,MoO_3$. Two kinetically different types of oxygen release were identified for both molybdates. Arrhenius plots were also obtained from reoxidation experiments: $Bi_2O_3 \cdot MoO_3$ was more easily reoxidable than $Bi_2O_3 \cdot 3\,MoO_3$. The substantial closeness of the respective activation energies suggests that depletion and reoxidation follow the same mechanistic steps.

Some DTA measurements confirm the existence of at least two types of reoxidation sites for both oxysalts.

Bismuth molybdates are extensively used as catalysts of the oxidation and ammoxidation of olefins. The literature on this subject is quite abundant and several studies have been performed with the aim of achieving a better activity for this catalytic system [1, 2]. It seems quite clear that lattice oxygen plays an important role in the reaction mechanism [3], although there is no general agreement about the nature of the active catalytic sites [4, 5].

This work is part of a general investigation into these catalytic oxides, and it employs thermal analysis methods (TG, DTA and adsorption calorimetry measurements) [6, 7].

Oxygen depletion by simple outgassing is a well-known property of these molybdates [8]: in this study we compare the oxygen loss under vacuum and the reoxidation of bismuth molybdates (2:1; 2:3), which are usually considered to have different oxygen diffusion coefficients.

Experimental

$Bi_2O \cdot 3\,MoO_3$ (α-phase) and $Bi_2O_3 \cdot MoO_3$ (γ-phase) were prepared according to Batist's method [9]. X-ray analysis of both samples before and after each redox treatment gave spectra diffraction corresponding to the structures cited in the literature [2].

Oxygen depletion measurements at different temperatures were made by means of a Sartorius microbalance (sensitivity 0.1 μg), connected to a vacuum apparatus (10^{-4} Pa).

The samples were standardized in an oxygen atmosphere at 673 K before each outgassing treatment.

The reoxidation process was studied by both the isothermal thermogravimetric method and DTA measurements. The reoxidation isotherms were determined in a static atmosphere of oxygen (6650 Pa); the DTA curves were obtained by oxidizing the outgassed samples with an air flux (0.5 ml s^{-1}) directly into the calorimeter (Rigaku, Japan; sensitivity 2 J s^{-1}).

Results and discussion

a) Oxygen depletion: isothermal experiments

In Figs 1 and 3 we give thermogravimetric data on oxygen depletion under vacuum at the indicated temperature for $Bi_2O_3 \cdot MoO_3$ (γ-phase) and $Bi_2O_3 \cdot 3\ MoO3$ (α-phase). The trends of the isotherms are quite similar, and it is possible to apply Barret's method of curve analysis to both sets of data to show that these isotherms belong to a family of kindred curves which obey the same kinetic law [10].

It therefore seems reasonable to apply the Arrhenius law to obtain the activation energies. It is well known that the Arrhenius equation has been submitted to several mathematical and physical criticisms [11, 12], but here we wish only to make a comparison between the reactivities of the two molybdate phases. The Arrhenius plots are given in Figs 2 and 4, and the activation energies in Table 1. From a qualitative point of view, the results in Table 1 are in agreement with the common knowledge that the γ-phase is more easily reducible than the α-phase [13, 14]. It is also quite reasonable that these activation energies are smaller than those corresponding to the reduction by hydrogen we obtained before [6]: the phenomenon in that case was much more complex, implying water formation and desorption. We note the existence of two kinds of oxygen release for each sample: the former characterized by a higher rate and lower energy, and the latter by a lower rate and higher energy. Two types of reduction site were also found in the previous study with hydrogen on the same catalytic oxide [6].

On the other hand, the values of E_a we have here are much smaller than those calculated by Dadyburjor and Ruckenstein [15] for the removal of various kinds of oxygen from bismuth molybdate. However, as those authors themselves argue, a "real" bismuth molybdate lattice, containing ion vacancies, could show different energy paths. A proof of a vacancy mechanism in the oxygen depletion process might come from the analysis of our data in Fig. 1. If one applies the logarithmic transform to these data, the reduction rate (α_{red}) seems to follow a cubic law ($\alpha_{red} = k\ t^{1/3}$) as concerns the time-dependence; this is typical of a vacancy diffusion mechanism in semiconductor oxides [10].

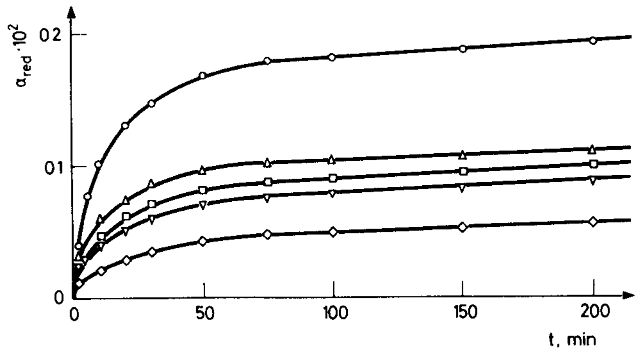

Fig. 1 Isothermal experiments: weight loss (percentage desoxidation) by outgassing of $Bi_2O_3 \cdot MoO_3$ at: ◇ 423 K, ▽ 523 K, □ 573 K, △ 623 K, ○ 679 K

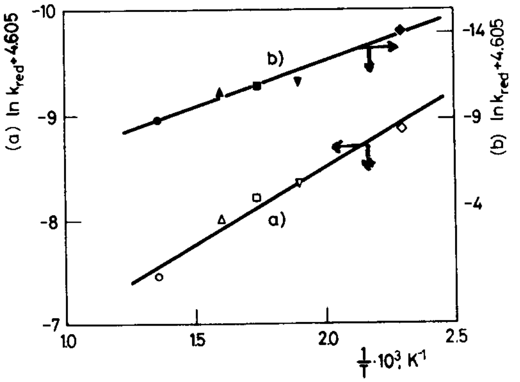

Fig. 2 Arrhenius plots for oxygen depletion of $Bi_2O_3 \cdot MoO_3$ (symbols as in Fig. 1); curve a) initial rate, curve b) final rate

Table 1 Activation energies for oxygen depletion from bismuth molybdates by outgassing

Phase	Desoxidation E_a, kJ/mol	Reduction rate	Temperature range, K
$Bi_2O_3 \cdot MoO_3$	13.6	initial	423–679
	46.8	final	
$Bi_2O_3 \cdot 3\,MoO_3$	41.8	initial	523–683
	63.6	final	

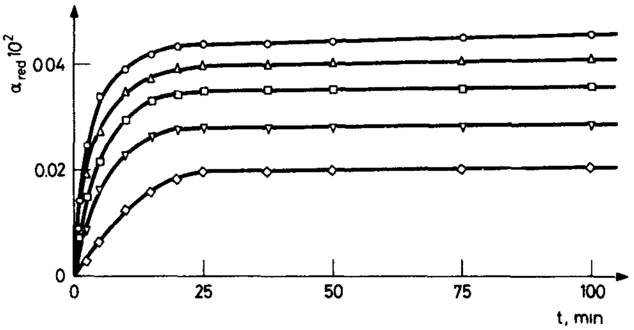

Fig. 3 Isothermal experiments: Weight loss (percentage desoxidation) by outgassing of Bi_2O_3 • • 3 MoO_3 at: ◇ 523 K, ▽ 573 K, □ 623 K, △ 653 K, ○ 683 K

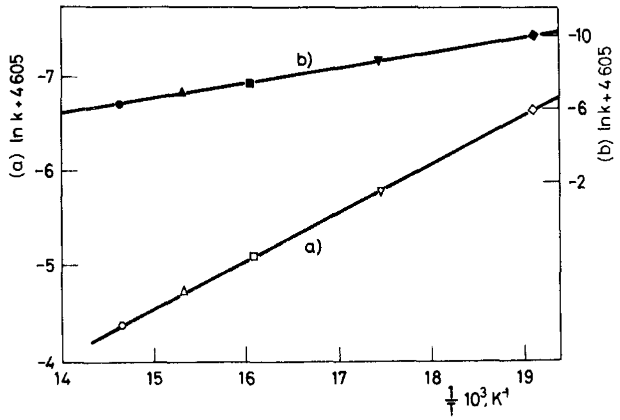

Fig. 4 Arrhenius plots for oxygen depletion of Bi_2O_3 • 3 MoO_3 (symbols as in Fig. 3): curve a) initial rate, curve b) final rate

b) Reoxidation experiments: isothermal thermogravimetry and DTA measurements

It is commonly recognized that the reoxidation of reduced bismuth molybdates is very fast [1, 2] and shows a marked dependence on the initial reduction state [14]. We have not been able to carry out isothermal determination of the reoxidation rates for the samples that were reduced by vacuum outgassing, as this process is practically instantaneous at a pressure of 6650 Pa of oxygen and over 473 K. We have performed some measurements on the reoxidation kinetics of the two samples reduced by about 0.4%. The results obtained are given in Figs 5 and 7, with the corresponding Arrhenius plots in Figs 6 and 8, and the activation energies in Table 2.

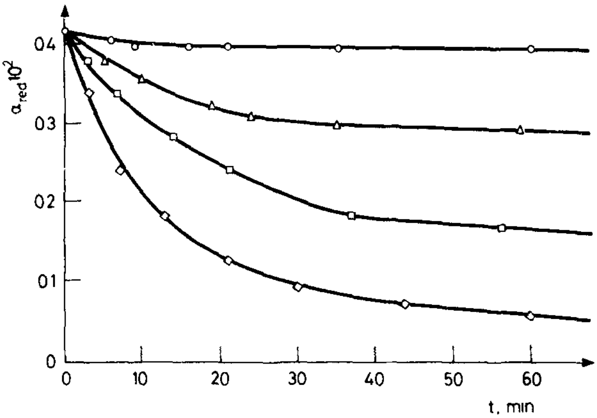

Fig. 5 Weight recovery (percentage reduction decrease) during reoxidation of previously reduced (0.4%) $Bi_2O_3 \cdot MoO_3$ at: ○ 411 K, △ 424 K, □ 456 K, ◇ 475 K

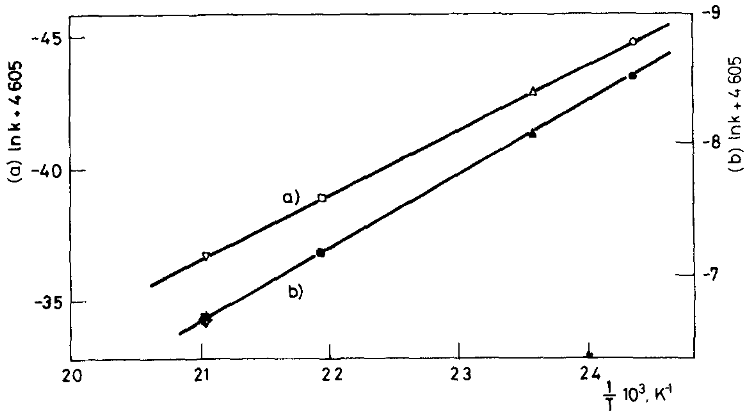

Fig. 6 Arrhenius plots for reoxidation of previously reduced (0.4%) $Bi_2O_3 \cdot MoO_3$ (symbols as in Fig. 5); curve a) initial rate, curve b) final rate

Table 2 Activation energies for reoxidation of previously reduced bismuth molybdates

Phase	Reoxidation E_a, kJ/mol	Reoxidation rate	Temperature range, K
$Bi_2O_3 \cdot MoO_3$	20.1 46.4	initial final	411–475
$Bi_2O_3 \cdot 3\,MoO_3$	47.7 55.2	initial final	387–450

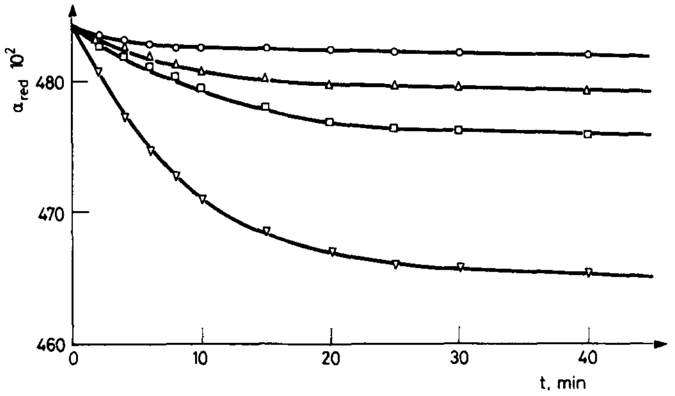

Fig. 7 Weight recovery (percentage reduction decrease) during reoxidation of previously reduced (0.484%) $Bi_2O_3 \cdot 3\,MoO_3$ at: ○ 387 K, △ 401 K, □ 418 K, ▽ 450 K

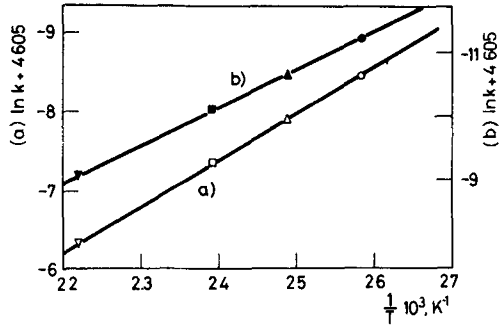

Fig. 8 Arrhenius plots for reoxidation of previously reduced (0.484%) $Bi_2O_3 \cdot 3\,MoO_3$ (symbols as in Fig. 7): curve a) initial rate, b) final rate

From a qualitative point of view these results are in agreement with some common knowledge: i) the γ-phase is more easily reoxidized than the α-phase; ii) in both phases there are two reoxidation processes, the former characterized by a higher rate and lower activation energy, and the latter by a lower rate and higher activation energy [14]. Furthermore, it may be noted (see Tables 1 and 2) that the oxygen depletion and reoxidation display very close, Arrhenius energies, bearing in mind all the sources of errors and all the criticisms of the Arrhenius method. This substantial agreement suggests that the two processes (depletion and reoxidation) follow essentially the same mechanistic steps. In the case of $Bi_2O_3 \cdot MoO_3$, a cubic law is also obtained for the kinetics of the reoxidation process, adding evidence for the vacancy diffusion mechanism.

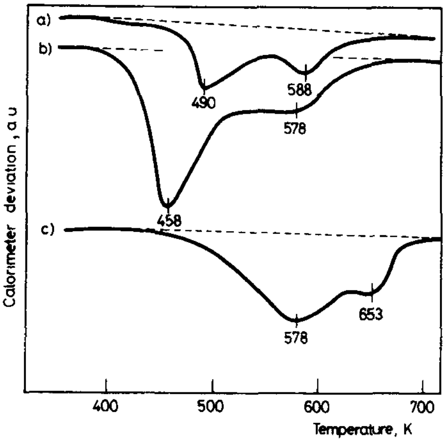

Fig. 9 DTA curves of reoxidation with air flux (0.5 mol sec^{-1}) of previously reduced bismuth molybdates: curve a) $Bi_2O_3 \cdot MoO_3$ (reduction percentage $\alpha_T \cdot 100 = 0.1$), curve b) $Bi_2O_3 \cdot MoO_3$ (reduction percentage $\alpha_T \cdot 100 = 0.6$), curve c) $Bi_2O_3 \cdot 3\,MoO_3$ (reduction percentage $\alpha_T \cdot 100 = 0.04$)

We have also made some DTA measurements on the reoxidation of γ and α samples that had previously been submitted to oxygen depletion by outgassing. Typical DTA curves are given in Fig. 9, and they suggest the following remarks:

i) there is no evidence of an endothermic peak corresponding to the melting of Bi as was observed for more drastically reduced samples [6];

ii) the γ-phase is more easily reoxidized than the α-phase, as may be deduced by the lower temperature of the maxima in the DTA curve: this is also well stated the literature [16, 17];

iii) from the comparison of curve a) with b) it is deduced that the reoxidation process is strictly dependent on the degree of reduction;

iv) the existence of at least two types of different sites of reoxidation is confirmed for both samples [17].

* * *

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Zusammenfassung — Deoxygenierung und Reoxydation von Wismutmolybdaten — 2:1; 2:3 — wurden mittels isothermer TG und DTA untersucht. Aus den isothermen Kurven wurden im Temperaturbereich von 411 bis 683 K die Arrhenius-Energien ermittelt. Die Deoxygenierung von $Bi_2O_3 \cdot MoO_3$ erfordert eine geringere Aktivierungsenergie als die von $Bi_2O_3 \cdot 3\,MoO_3$. Zwei sich kinetisch unterscheidende Arten der Sauerstoffabspaltung wurden bei beiden Molybdaten festgestellt. Auch die Daten der Reoxydation wurden in Arrhenius-Diagrammen dargestellt: $Bi_2O_3 \cdot MoO_3$ ist leichter als $Bi_2O_3 \cdot 3\,MoO_3$ zu reoxydieren. Die nahe beeinander liegenden Werte der betreffenden Aktivierungsenergien lassen auf gleiche Teilschritte im Mechanismus der Deoxygenierung und Reoxydation schließen. Einige DTA-Messungen bestätigen das Vorliegen von zumindest zwei Typen von Reoxydationszentren bei beiden Oxysalzen.

Резюме — Методом изотермической термогравиметрии и ДТА изучено уменшенние кислорода и повторное окисление молибдатов висмута состава 2:1 и 2:3. Исходя из изотермических кривых получены аррениусовские энергии в интервале 411 и 683 K. Энергии активации уменьшения кислорода для $Bi_2O_3 \cdot MoO_3$ были ниже, чем для $Bi_2O_3 \cdot 3\,MoO_3$. Для обоих молибдатов были идентифицированы два кинетически различных типов высвобождения кислорода. Из опытов по повторному окислению были получены аррениусовские графики. Система $Bi_2O_3 \cdot MoO_3$ была более легко окисляемой по сравнению с $Bi_2O_3 \cdot 3\,MoO_3$. Близость значений соответствующих энергий активации предполагает, что уменьшение кислорода и повторное окисление следуют тем же самым механистическим стадиам. Некоторые измерения ДТА подтвердили существование, по крайней мере, двух типов участков повторного окисления для обоих оксисолей.