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CALORIMETRIC STUDY OF THE DESORPTION CYCLES OF DIOXYGEN FROM TITANIUM DIOXIDE

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ABSTRACT

The energetics of dioxygen desorption on pure and doped titanium dioxide has been studied at 305 K by adsorption microcalorimetry.

Differential heats of desorption ranging from 9 to 4 kJ/mol have been determined. The examination of the thermokinetics parameters shows the existence of different desorption mechanisms.

Desorption cycle from an hydrogen covered sample indicates the onset of a chemical interaction.

INTRODUCTION

Heterogeneous catalytic reactions involving dioxygen are acquiring increasing importance in chemical and bio-technology (ref. 1). Much work has been performed on the interaction of molecular oxygen with semiconductor oxides using I.R. and E.S.R. techniques (for a review see ref. 2). A few studies have investigated the thermodynamical properties of the surface phase, to which the catalytic activity may be somehow correlated (ref. 3).

Here we give some results concerning the energetics of dioxygen desorption cycles on pure and doped titanium dioxide; the aim is to study the influence of controlled ions loading on the catalytic and photocatalytic behaviour of this semiconductor oxide (ref. 4).

EXPERIMENTAL

The material used was: i) a P-25 sample (72% anatase, 28% rutile,surface area 55 m^2/g; ii) a P-25 sample loaded with 1% of RuO_2 (sample indicated hereafter as P-25/Ru; iii) a TiO_2 sample prepared as elsewhere described (ref. 4), with anatase structure, a high surface area 220 m^2/g, loaded with 8% Pt, 0.4% Nb_2O_5, 0.1% RuO_2 (sample indicated as TiO_2/Pt,Nb,Ru). All the samples were heated in vacuum at 423 K for 1 hour before the first adsorption run.

A Tian Calvet microcalorimeter connected to a greaseless vacuum-line allowed the simultaneous determinations of calorimetric and volumetric isotherms (ref. 5). The measurements were performed at 305 K and were repeated at least twice to check reproducibility.

RESULTS AND DISCUSSION

In Fig. 1 we show the general trend of the desorption process for the three samples.

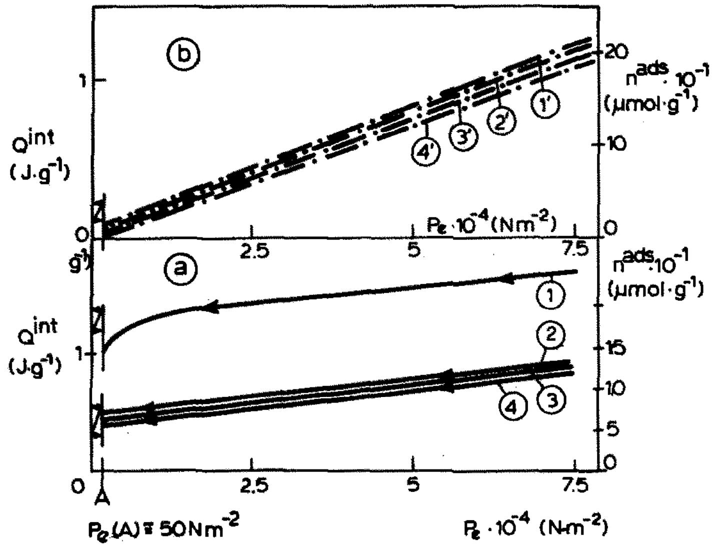

Fig. 1. The trends of successive desorption runs (calorimetric or volumetric isotherms, i.e., the integral heats (Q^{int}, scale on the left) or the reversibly adsorbed amounts (n^{ads}, scale on the right) as a function of equilibrium pressure) on:

a) TiO_2/Pt,Ru,Nb or P-25/Ru
b) P-25
1, 1' - desorption after the first adsorption run
2, 2' - desorption after the second adsorption run
3, 3' - desorption after the third adsorption run
4, 4' - desorption after the fourth adsorption run

The curves of Fig. 1 result from a deeper examination of preceding data (refs. 6-7) and on the ground of further adsorption-desorption cycles in the higher pressures range. We may note that P-25/Ru and TiO_2/Pt,Nb,Ru release down to 50 Nm^{-2} about 35 and 30% respectively of the oxygen amounts adsorbed in the first run. For all the desorption runs of P-25 and for the second and successive desorption runs on P-25/Ru and on TiO_2/Pt,Nb,Ru we have almost complete reversibility. But there is a small fraction (0.5-1%) that is irreversibly adsorbed in each run. Later, we will discuss the possible mechanism associated with such a phenomenon which becomes more important after a great number of cycles.

In Table 1 we report the differential heats of desorption and the corresponding released amounts for the first cycle from an equilibrium pressure of 7.10^4 N/m^2 down to about 50 N/m^2.

TABLE 1

Sample	Differential heats of desorption ($kJ.mol^{-1}$)	Oxygen desorbed amounts ($\mu mol.g^{-1}$)
P-25	4.5	265
P-25/Ru	5.3	160
P-25/Ru	9.1	20
TiO_2/Pt,Nb,Ru	3.8	436
TiO_2/Pt,Nb,Ru	8.5	52

The small magnitude of these heats would suggest a similar desorption process for all three samples. However, it must be remembered that oxygen adsorption on n-type semiconductors like TiO_2 follows an ionosorption mechanism which implies the formation of the superoxide ion (O_2^-) and the monoatomic ion (O^-) as a thermodynamically stable species, even if other routes of adsorption involving lower activation energy cannot be excluded (ref. 8)

The examination of the thermokinetics parameter, deduced by a semiquantitative procedure from the calorimetric peaks (ref. 9), show that different desorption mechanisms are implied on the three samples at the same equilibrium pressures (see Fig. 2a).

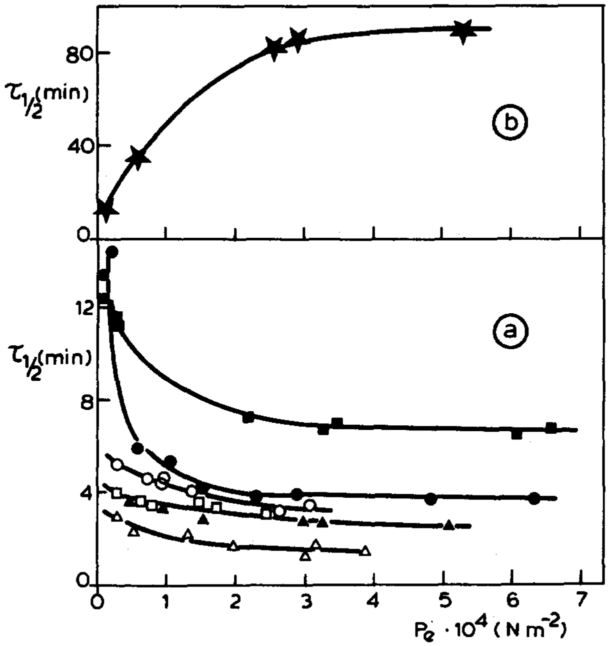

Fig. 2. Thermokinetics of oxygen adsorption-desorption cycles on various samples (the peak breadth parameter, $\tau_{1/2}$, as a function of equilibrium pressure):

a) ■ adsorption on TiO_2/Pt,Ru,Nb
□ desorption on TiO_2/Pt,Ru,Nb
● adsorption on P-25/Ru
○ desorption on P-25/Ru
▲ adsorption on P-25
△ desorption on P-25

b) oxygen interaction with preadsorbed hydrogen on P-25/Ru.

In particular from Fig. 2a the following may be deduced: i) for all the samples the rate of desorption is less than the rate of adsorption, as is to be expected from the theory of ionosorption, and is in agreement with the results obtained with another semiconductor oxide (ref. 10); ii) the apparent discrepancy between thermodynamics and kinetics (similar adsorption heats, different kinetics) may be explained if we assume that distinct surface complexes may be found with similar heats but different activation energy: in other words, in this case we would have some overlapping between physisorption and non equilibrium chemisorption (ref. 8).

Another indication of a non equilibrium distribution of adsorbed species may come from the curves a, b, c of Fig. 3 that shows the surprising exothermic peak obtained by the outgassing of the samples. These calorimetric data do not allow this exothermic path to be assigned to a recombination of atomic surface oxygen or to a rearrangement of surface complexes with rehybridisation of bonding orbitals.The formation of a more stable phase might also explain the small fraction of irreversible adsorbate which is detected by reiterating adsorption-desorption cycles.

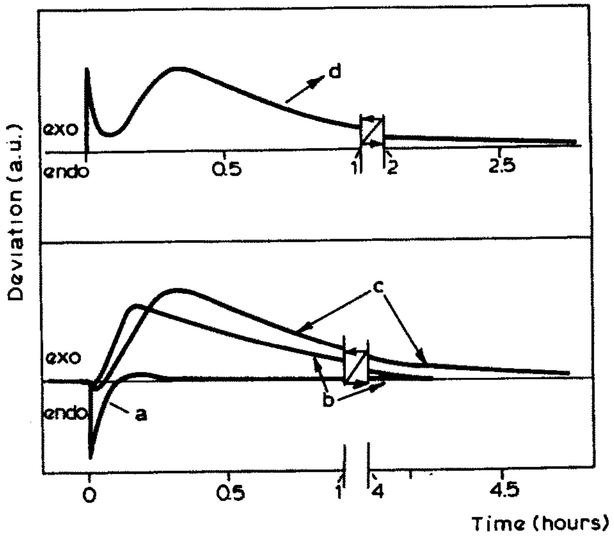

Fig. 3. Typical heat emission peak (calorimetric deviation versus time) for oxygen desorption by direct outgassing:
a) of P-25
b) of P-25/Ru
c) of TiO_2/Pt,Nb,Ru
d) of hydrogen and oxygen coadsorbed on P-25/Ru.

The existence of a surface oxygen species that appears after evacuation at R.T. is confirmed by E.S.R. and I.R. spectra (refs. 11-12).

The kinetics of heat emission is completely different when dioxygen is adsorbed and desorbed from an hydrogen covered TiO_2 surface. The kinetic trend in the adsorption run (Fig. 2b) indicates the onset of a chemical interaction, whose apparent activation energy seems to increase during the process. The outgassing of H_2 and O_2 covered TiO_2 surface gives a complex thermogram (curve d, Fig. 3) that might be the combination of at least two sharp calorimetric peaks of opposite sign where the exothermic path has higher energy but slower rate than the endothermic one.

The calorimetric data of Fig. 2b and 3 appear in fair agreement with the conclusions of Thermal (ref. 13) and Electron Stimulated (ref. 14) Desorption measurements, that indicated the existence at R.T. of reactive hydrogen with the co-adsorbed oxygen on a TiO_2 surface.

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