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ENERGETICS OF THE ADSORPTION-DESORPTION CYCLES OF OXYGEN ON DOPED TITANIUM DIOXIDE

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ABSTRACT

The adsorption-desorption cycles of dioxygen on doped TiO_2 have been investigated at 305 K by means of a microcalorimetric technique. O_2 chemisorption occurs at low equilibrium pressure, while at higher pressure the process goes through physically adsorbed molecules. Interaction energies ranging from 5 to 40 kJ/mol were detected for the chemisorbed species. The oxygen adsorption in the second and in the successive cycles is reversible.

INTRODUCTION

Titania based catalysts find major applications in a range of technically significant processes. Numerous investigations have been performed, in recent years, of the use of this semiconductor oxide in photocatalytic and photosynthetic reactions (ref. 1). Interesting results in the photocleavage of water in H_2 and O_2 have been obtained with a bifunctional redox catalyst based on TiO_2 particles loaded with RuO_2 and Pt (ref.2).

The interactions of differently prepared TiO_2 samples with hydrogen or oxygen have been extensively studied by using IR and other spectroscopic techniques (ref. 1), but few attempts have been made to quantify the effects of the metal-support interaction or of the ions loading in terms of thermodynamic properties such as the enthalpies and entropies of adsorption.

This paper is a part of a study, using a microcalorimetric technique, of the energetics of dioxygen adsorption-desorption cycles on pure and doped TiO_2 (ref. 3).

The calorimetric measurements were performed at 305 K employing a Tian-Calvet microcalorimeter, according to an experimental procedure

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already described (ref. 3). The samples of TiO_2, characterized by a very high surface area (220 m^2/g) (anatase structure, loaded with 8% Pt, 0.4% Nb and 0.1% RuO_2) were heated in vacuum at 423 K for 1 hour as these seem to be the best experimental conditions for photoadsorption (ref. 4).

RESULTS AND DISCUSSION

The calorimetric adsorption isotherms (i.e. the plots of the integral heats of adsorption ($J.g^{-1}$) versus the equilibrium pressure) for dioxygen at 305 K on the doped titania sample are shown in Fig. 1; the corresponding volumetric isotherms, not reported here for simplicity are quite similar.

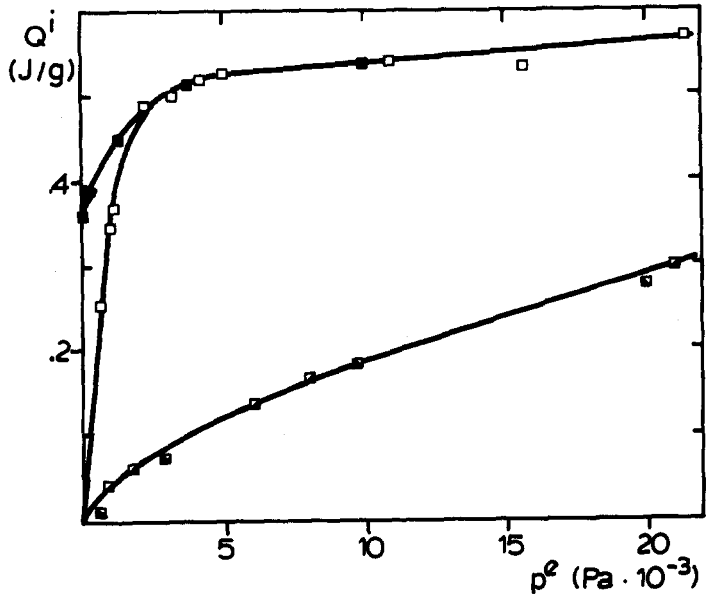

Fig. 1. Calorimetric adsorption isotherm for oxygen on doped TiO_2 at 305 K: □ first adsorption run; ■ desorption after the first adsorption run; ◪ second adsorption run after desorption of the first run; ◩ third adsorption run after desorption of the second run.

From Fig. 1 the following may be observed;

i) approximately 70% of the oxygen employed in the first run is adsorbed irreversibly

ii) the second and successive adsorption-desorption cycles of oxygen seem to be, within the experimental errors, reversible from 1 to 20 KPa.

It is well known that by differentiation of the curves of the integral heats of adsorption it is possible to obtain the differential heats of adsorption and these are shown in Fig. 2: this type of plot provides a satisfactory description of the evolution of the interaction energies between adsorbent and adsorbate.

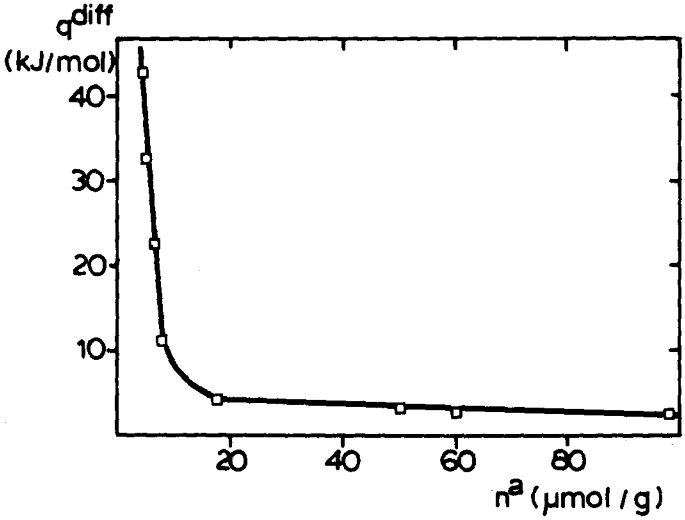

Fig. 2. Differential heats of adsorption ($J.g^{-1}$) versus the amounts adsorbed ($\mu mol.g^{-1}$) of oxygen on doped TiO_2.

The adsorption of dioxygen on the surface of n-type oxides is a very complex phenomenon which seems to follow the scheme: $O_2(ads) \rightarrow O_2^-(ads) \rightarrow O^-(ads) \rightarrow O^{2-}(lattice)$. It must be also reminded that titania-supported catalysts are well known to exhibit the SMSI (strong metal-support interaction) effect which can modify the electronic properties of the metal.

The data in this work indicate essentially three types of interaction, assuming no overlap between the different family sites:

a) a strong interaction ($q^{diff} \geq$ 30 kJ/mol) with a very small fraction of very active sites (about 6-7 μmol/g)

b) an energy spectrum from 5 to 30 kJ/mol is shown by a more populated (about 20 μmol/g) family site: however this quantity roughly corresponds to one tenth of a complete surface monolayer of dioxygen

c) a final weak interaction ($\leq$5 kJ/mol) corresponding to physically adsorbed molecules, as this heat of adsorption is of the same order of magnitude of the heat of condensation of oxygen.

The nature of the more active sites on our doped titanium dioxide cannot be definitely authenticated by this preliminary work: the formation of RuO_x surface complexes has already been suggested to explain the chemisorption of oxygen on a similarly loaded titania (ref. 3). Moreover a contribution from the SISM effect, which is well established in the case of Pt/TiO_2 (ref. 5), cannot be neglected.

Additional investigations including calorimetric IR and EPR measurements are needed to have more detailed information about the nature of the site involved in the donating electronic levels and about the corresponding chemisorbed oxygen species.

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