Surface characterization of zirconium titanate ($ZrTiO_4$) powder by measurements of electrical photoconductance and photoassisted oxygen isotope exchange

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The photosensitivity of a $ZrTiO_4$ sample (33 m^2/g) prepared by a sol–gel method has been assessed in the presence of O_2 by both photoconductance and oxygen isotope exchange (OIE) measurements at room temperature at wavelengths >290 nm. For oxygen pressures $P_{O_2} <$ ca. 13.3 Pa, the steady-state photoconductance σ of $ZrTiO_4$ was unaffected by P_{O_2}, which indicated that the direct recombination of the photoproduced charges played the dominant role. At higher pressures, σ varied as the reciprocal of P_{O_2}, which was consistent with the fact that the electronic equilibrium was then governed by $O_2 + e^- \rightarrow O_2^-$. OIE over $ZrTiO_4$ occurred predominantly via the overall mechanism which involves the exchange of two surface oxygen atoms for each exchange act. It was very slow as compared with OIE over photocatalytically active anatase samples which, in addition, occurs via another mechanism. These results allow one to predict that this $ZrTiO_4$ sample is a poorly active photocatalyst for oxidations involving gaseous oxygen, and further illustrate the interest of σ and OIE measurements to evaluate the photosensitivity of semiconductor oxide samples.

Keywords: Photoconductivity; photocatalysis; oxygen isotope exchange; zirconium titanate; $ZrTiO_4$

1. Introduction

The binary system TiO_2–ZrO_2 provides efficient acid–base bifunctional catalysts [1–3]. Polycrystalline zirconium titanate, $ZrTiO_4$, which has been investigated as a high-dielectric material, has not been used in heterogeneous photocatalysis as yet. In this study, its photosensitivity in the presence of oxygen has been assessed by measurements of the conductance and the oxygen isotope exchange (OIE) under UV-irradiation and at room temperature. Both measurements have been successfully used previously to probe other semiconductor oxides [4–8].

The sample we used was synthesized by the sol–gel technique and calcined at 913 K [9]. This method yields an almost pure phase, unlike other methods which yield either low surface area solids because of the use of temperatures in the range 1273–1773 K or solids including various phases when lower temperatures are employed [10].

We first present the results of the photoconductance measurements which show that at low oxygen pressures, the direct recombination of charges dominates the capture of electrons by oxygen. The slow rate of OIE indicates the weak photoinduced lability of $ZrTiO_4$ surface oxygen. These results are briefly compared with those previously obtained with anatase TiO_2 samples to predict the photocatalytic activity of $ZrTiO_4$ in oxidation reactions which involve gaseous oxygen.

2. Experimental

2.1. APPARATUS AND MATERIAL

Photoconductivity cell. The photoconductivity cell has been described previously [4]. It was connected to a grease and mercury-free vacuum system (residual pressure ca. 10^{-3} Pa) and a gas line. The powder sample was lightly compressed to form a pellet inserted into a frame perpendicular to the UV beam. This frame comprised two gold electrodes which were found photoinactive in an oxygen atmosphere.

OIE photoreactor. OIE was carried out in a static cell which had the shape of a cylinder box, 1 cm high, closed by two parallel optical windows of 6 cm diameter and made of pyrex transmitting wavelengths >290 nm. A thin layer of sample was deposited onto the horizontal lower optical window. This cell was connected to a vacuum system (residual pressure 10^{-5}–10^{-6} Pa) equipped with a Datametric Dresser barocel pressure sensor and a Riber QMM17 quadruple analyzer.

Irradiation. UV-light was provided by a Philips HPK-125W mercury lamp whose output was filtered by a water-circulating cuvette and pyrex optical windows, so that $ZrTiO_4$ received photons of energy higher than that of its band gap (3.3 eV, as was determined by diffuse reflectance spectroscopy). The radiant flux reaching the sample in either the photoconductivity cell or the photoreactor, was measured by use of a radiometer (United Detector Technology, model 21 A) and maintained constant by appropriate adjustments.

$ZrTiO_4$ preparation. Powder zirconium titanate was prepared by sol–gel technique [9]. It was obtained by first hydrolyzing equimolar amounts of titanium tetra-

chloride (Merck) and zirconyl chloride (Fluka) in methanol in the presence of hydrogen peroxide. After washing, the precipitate was dried, then calcined at 923 K. The resulting solid had the structure of $ZrTiO_4$, as was shown by X-ray diffraction patterns, and a specific area of 33 m^2/g [9].

2.2. PROCEDURES

Photoconductance measurements. The sample was first air-dried at 383 K for 45 min. This facilitated the formation of a pellet that adhered well to the measurement frame. The pellet was evacuated under dynamic vacuum for 15 h.

OIE. The $ZrTiO_4$ layer was heated at 723 K under 13.3 kPa $^{16}O_2$ for 3 h. Then it was UV-irradiated at room temperature under 133.3 Pa $^{16}O_2$ for 12 h to saturate the surface in photoadsorbed oxygen species and therefore to minimize the photoadsorption of $^{18}O_2$ during the OIE. Finally, $^{16}O_2$ was evacuated in the dark and replaced by $^{18}O_2$ (ca. 98.15 at% ^{18}O; Yeda R.&D. Co., Israel) at a pressure of 6.67 Pa.

3. Results and discussion

3.1. ELECTRICAL PHOTOCONDUCTANCE OF $ZrTiO_4$

3.1.1. Under vacuum

Fig. 1 shows the differences in the conductance of the $ZrTiO_4$ pellet in the dark or under UV-irradiation. With the exception of the first irradiation period, the electrical equilibrium under irradiation was reached within the time-scale of our measurements (seconds). The delay to attain the equilibrium when irradiating the sample for the first time can be attributed to the photodesorption of negatively charged oxygen species [4,5,11], in particular O_2^-,

$$(ZrTiO_4) + h\nu \rightarrow e^- + p^+ , \qquad (1)$$

$$O_2^-(ads) + p^+ \rightarrow O_2(g) . \qquad (2)$$

This hypothesis is based on the electrical behavior of $ZrTiO_4$ in an oxygen atmosphere (see below). However, the photodesorption of oxygen was not important since the concentration in electrons that cannot recombine because of the consumption of holes (eq. (2)) was negligible with respect to the total concentration in photogenerated electrons as shown by the reversibility of the successive equilibria. When the irradiation was stopped, electrons and holes recombined and the dark conductivity could not be measured. When the irradiation was resumed, the photoconductance σ recovered its steady-state value.

The electrical behavior of $ZrTiO_4$ is quite different from that of TiO_2 [4,5], but

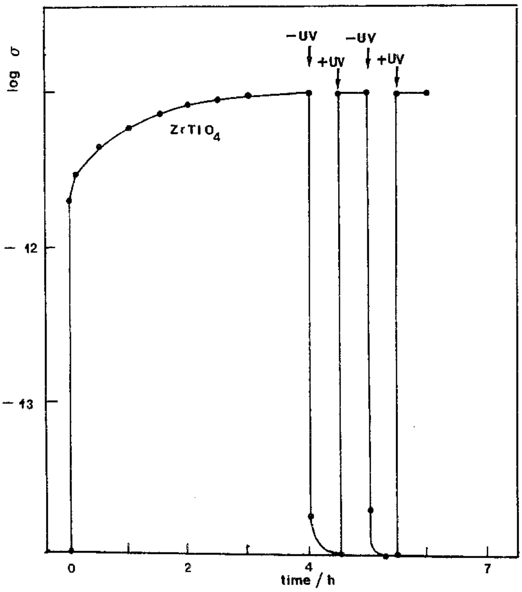

Fig. 1. Kinetic variations of the logarithm of the conductance σ (in ohm^{-1}) of the $ZrTiO_4$ sample which was alternatively UV-irradiated or nonirradiated.

is similar to that of CdS [11]. The amount of oxygen initially photodesorbed in the case of $ZrTiO_4$ is much smaller than in the case of TiO_2.

3.1.2. Under an oxygen atmosphere

The log–log plot of fig. 2, obtained for increasing oxygen pressures P_{O_2}, shows that below ca. 13.3 Pa P_{O_2} had no significant influence upon σ. By contrast, for $P_{O_2} > 13.3$ Pa, σ varied as the reciprocal of P_{O_2}.

These phenomena were quasi-reversible on decreasing P_{O_2}. They showed that $ZrTiO_4$ is a photoconductor of type n. Therefore the contribution of electrons to σ may be supposed to prevail as usually suggested in that case [12], although the respective mobilities of electrons and holes in this material are unknown. It is worth noting that in the parent material, TiO_2, a higher mobility of electrons was estimated from time-resolved microwave conductivity measurements [13]. By further assuming that the adsorption of oxygen on UV-irradiated $ZrTiO_4$ occurs according to

$$O_2(g) \rightleftharpoons O_2(ads)\,, \tag{3}$$

$$O_2(ads) + e^- \rightarrow O_2^-(ads)\,, \tag{4}$$

and by taking into account the recombination of electrons and holes,

$$e^- + p^+ \rightarrow N \quad (N = \text{neutral center})\,, \tag{5}$$

the steady state of σ is expressed by

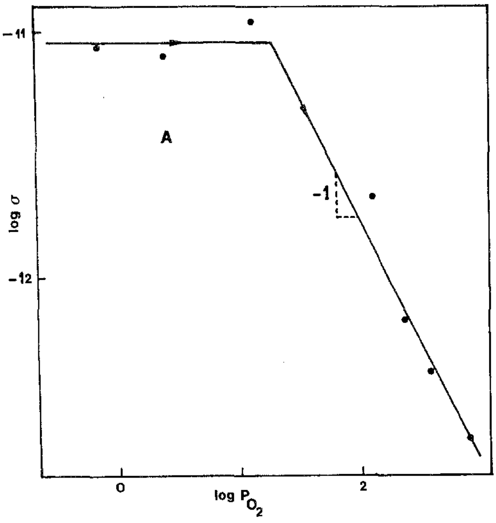

Fig. 2. Log–log plot of the photoconductance σ (in ohm^{-1}) of the $ZrTiO_4$ sample at equilibrium as a function of the oxygen pressure (in Pa).

$$\begin{aligned} d\sigma/dt &= A d[e^-]/dt = A(r_1 - r_4 - r_5) \\ &= A(G - k_4[e^-][O_2(ads)] - k_5[e^-][p^+]) = 0 \\ &= A(G - k_4 K_3 P_{O_2}[e^-] - k[e^-][p^+]) = 0\,, \end{aligned} \tag{6}$$

where A is a coefficient which includes the electron charge and mobility, as well as textural parameters of the solid, G is the generation rate of electrons and holes (eq.(1)) which depends on the constant radiant flux, r_1, r_4, r_5, K_3, k_4 and k_5 are the reaction rates, the equilibrium constant and rate constants of the corresponding reactions, respectively. From eq. (6), the steady state value of σ is given by

$$\sigma = A[e^-] = \frac{AG}{k_4 K_3 P_{O_2} + k_5[p^+]}\,. \tag{7}$$

Eq. (7) implies that the contribution of the non-illuminated part of the pellet to the overall conductance was negligible. This was demonstrated by switching off the irradiation in the P_{O_2} range where $\sigma = k/P_{O_2}$; the dark conductivity was, as expected, beyond the measurement capabilities of our apparatus and the steady-state σ value was recovered when the irradiation was switched on.

According to the model symbolized by eqs. (3)–(7), the experimental results indicate that the first term in the denominator of eq. (7) was negligible with respect to the second term at oxygen pressures below ca. 13.3 Pa, whereas it was the reverse at higher oxygen pressures. In other words, when P_{O_2} was higher than ca. 13.3 Pa, the electrical equilibrium was controlled by O_2^- species, at least up to the highest pressure used (667 Pa).

3.2. OIE BETWEEN $^{18}O_2$ AND $ZrTi^{16}O_4$

OIE over a solid oxide can occur via three mechanisms [14,15]. In the case symbolized by eq. (8), all the isotopically exchanged species originate from the gas phase and the solid catalyzes the OIE without participation of its surface oxygen atoms,

$$^{18}O^{18}O(g) + {}^{16}O^{16}O(g) \rightarrow 2\,{}^{16}O^{18}O\,. \tag{8}$$

If OIE involves isotopic species from both phases, the following mechanisms of heteroexchange are distinguished, depending on whether one or two surface oxygen atoms are involved in each act of exchange:

$$^{18}O_2(g) + {}^{16}O(s) \rightarrow {}^{16}O^{18}O(g) + {}^{18}O(s)\,, \tag{9}$$

$$^{18}O_2(g) + 2\,{}^{16}O(s) \rightarrow {}^{16}O_2(g) + 2\,{}^{18}O(s)\,. \tag{10}$$

These equations stand for the overall exchanges without any assumption on the elementary steps.

The UV-irradiation of $ZrTiO_4$ in the presence of gaseous $^{18}O_2$ produced a decrease in the fraction C_{36} of gaseous $^{18}O_2$ molecules and corresponding increases in the fractions C_{32} and C_{34} of gaseous $^{16}O_2$ and $^{16}O^{18}O$ molecules; the latter growth was comparatively very slow (fig. 3).

A kinetic model has been developed in ref. [8] according to which the variation rates of C_{36} and C_{34} are

$$-\mathrm{d}C_{36}/\mathrm{d}t = (k_9 + k_{10})C_{36}\,, \tag{11}$$

$$\begin{aligned} \mathrm{d}C_{34}/\mathrm{d}t = {} & k_8[2\alpha(1-\alpha) - C_{34}] + k_9[\alpha(1-\alpha_s) + (1-\alpha)\alpha_s - C_{34}] \\ & + k_{10}[2\alpha_s(1-\alpha_s) - C_{34}]\,, \end{aligned} \tag{12}$$

where k_9 and k_{10} are the rate constants corresponding to eqs. (9) and (10), respectively, α_s is the fraction of ^{18}O atoms in the oxygen of the solid surface and α is the fraction of ^{18}O atoms in the gas phase which varies in accordance with

$$\mathrm{d}\alpha/\mathrm{d}t = (k_9/2 + k_{10})(\alpha_s - \alpha)\,.$$

In the particular case where α_s remains close to zero, the constants k_8, k_9 and k_{10} can be determined, since all these equations become simpler.

The experimental kinetic variations of C_{36} and α for OIE over $ZrTiO_4$ fitted the exponential laws:

$$C_{36} = 0.965\exp(-k't) \quad \text{and} \quad \alpha = 0.978\exp(-Rt)\,,$$

with

$$k' = k_9 + k_{10} = 2.93\ \mathrm{h}^{-1} \quad \text{and} \quad R = k_9/2 + k_{10} = 2.68\ \mathrm{h}^{-1}\,,$$

from which

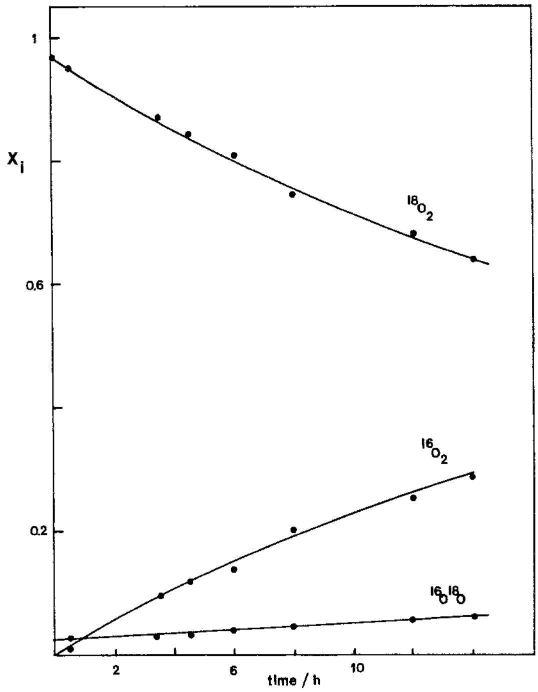

Fig. 3. Kinetic changes in the isotopic composition of gas-phase oxygen over the UV-irradiated $ZrTiO_4$ sample.

$$k_9 = 5.03 \times 10^{-3}\ h^{-1} \qquad \text{and} \quad k_{10} = 2.43 \times 10^{-2}\ h^{-1}\,.$$

These results indicate first that α_s remained close to zero, since $\alpha = \alpha_0 \exp(-Rt)$, which means that the rate of exchange of surface oxygen atoms with bulk oxygen atoms was much higher than that of the former with gaseous oxygen. Secondly, eq. (8) was not involved. Thirdly, the ratio of the rate constants k_{10}/k_9 shows that eq. (10) accounted for about 80% of OIE.

3.3. COMPARISON OF $ZrTiO_4$ WITH ANATASE

Anatase is the most commonly used photocatalyst because of the highest photocatalytic activity exhibited by some of its samples. Therefore these samples were taken as references. OIE over Degussa P-25 TiO_2 (50 m^2/g) and other nonporous anatase specimens prepared from titanium tetrachloride in a flame reactor occurs at a much higher rate [6] than over the present $ZrTiO_4$ sample; for example, k_9 was $8.16 \times 10^{-1}\ h^{-1}$ for Degussa P-25 under conditions similar to those employed for $ZrTiO_4$. As a correlation was observed between the OIE rate and the rate of photocatalytic oxidation reactions by use of oxygen [6], we predict that the $ZrTiO_4$ sample will display low photocatalytic activity in these reactions as compared with

Degussa P-25 TiO_2. Similarly, the rate of photoassisted OIE over a nonporous zirconium oxide (37 m^2/g) was greater than over $ZrTiO_4$ [7]. It may be worth noting that OIE takes place almost uniquely via eq. (9) over these anatase [6] and ZrO_2 [7] samples. These differences in OIE activity and mechanism may be caused by the structure of $ZrTiO_4$. However, the texture may also play an important part.

A similar conclusion can be drawn from the photoconductance measurements. As already mentioned, the photodesorption of oxygen from $ZrTiO_4$, when this sample was UV-irradiated under vacuum for the first time, was so low that it did not produce a dark conductivity measurable by our instrumentation in contrast with the case of Degussa P-25 TiO_2 [4]. Furthermore, in an oxygen atmosphere, the σ steady-state value of this latter sample depended on the oxygen pressure even at the lowest pressure investigated (ca. 0.1 Pa) [4]; in other words, the direct recombination rate of the photoproduced charges was never the phenomenon that governed the electronic equilibrium in the presence of gaseous oxygen, by contrast with what occurred for the $ZrTiO_4$ sample (fig. 2; eq. (7)).

The present results further show the potential of photoconductance and oxygen isotope exchange measurements to estimate the photosensitivity of new semiconductor oxide samples in the presence of gaseous oxygen.

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