Photochemical and Photophysical Processes on the Surface of Wide Band Gap Insulator Particulates: Gas/Solid System Involving Scandia (Sc_2O_3) Particles

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Surface photochemical processes and the interconnected photophysical events taking place in the bulk and at the surface of a wide band gap insulator material, e.g. scandia (Sc_2O_3), have been examined to ascertain the role of intrinsic defects (e.g. anion and cation vacancies) on surface processes such as photoadsorption of electron acceptor (O_2) and donor (H_2 and CO) molecules. The influence of surface processes on the formation and destruction of photoinduced defects (i.e. electron F-type color centers and hole V-type color centers) in scandia and the role that color defect centers play in the overall efficiency of surface reactions have been explored spectroscopically. Photoadsorption of gases on the scandia particle surface and the resulting effect on photocoloration and photobleaching have been used to identify the type of color centers produced on photoexcitation with UV light in the fundamental absorption edge (intrinsic) and in the extrinsic absorption region of powdered scandia specimens. Formation of color centers red-shifts the spectral limits of surface photoreactions. Formation of F and V color centers decreases the quantum yield of surface photochemical processes because of recombination of charge carriers through color centers, but increases the overall efficiency of these processes through photobleaching of the color centers on irradiation at appropriate UV wavelengths.

Introduction

Exploration of photocatalytic and photochemical surface reactions in heterogeneous systems has dealt mostly with semiconductor photocatalysts.[1−3] The dominant reason for this is the correspondence that exists between the photocatalysts' band gap energy and the energies of available sunlight photons. However, the wider the band gap of a semiconductor is, the greater is the difference between the quasi-Fermi levels of electrons and holes upon irradiation and thus the greater is the driving force for redox processes at the surface of such photocatalysts. For these very reasons, titania TiO_2, an n-type (quasi-) semiconductor, has been one of the more popular photocatalysts employed in a variety of applications.[4−7] At the same time, TiO_2 also possesses some insulator properties because of its wide band gap energy (3.2 eV for the anatase polymorph). Properties of wide band gap solids can be very different relative to those of true semiconductors, as for example Si and GaAs. In particular, the role of lattice defects in wide band gap solids is sufficiently enhanced in excitation and recombination processes. Studies of photochemical processes on the surface of wide band gap photocatalysts have principally implicated metal oxides.[8−11]

Scandium oxide (Sc_2O_3) is a wide band gap insulator ($E_{bg} = 6.0$ eV) having a cubic crystal lattice belonging to the $T_h{}^7$ space group; lattice constant $a = 9.845$ Å.[12] The uppermost levels of the valence band originate from 2p states of the oxide ions, whereas the lowest energy levels of the conduction band are formed from the 3d states of scandium. No excitonic absorption band is observed in the absorption spectra of scandia;[13] hence,

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light absorption at the fundamental absorption edge of scandia generates free electrons and free holes. Charge carrier decay in these metal oxide insulators occurs predominantly by recombination through defect centers accompanied by luminescence; an emission band for Sc_2O_3 is displayed at 3.6 eV (i.e., 344 nm).[13,14] Carrier trapping by preexisting defect centers in scandia particulates generates the color centers: electron F-type centers with absorption maximum at ~3.54 eV (ca. 350 nm) and hole V-type centers with maximum absorption at about 2.75 eV (i.e. 450 nm).[15,16] Preliminary studies on the photoadsorption of hydrogen, methane, and oxygen on powdered scandia have been reported by Basov and co-workers[9] and by Kotova;[17] initial studies of the influence of surface photochemical processes on the formation of photoinduced defects in Sc_2O_3 have been carried out by Burukina[18] and Emeline.[19]

To get a better handle and achieve a better understanding of surface photochemical processes and their interconnection with photophysical processes taking place in the bulk and at the particle surface, together with the role that intrinsic defects [anion (V_a) and cation (V_c) vacancies] and photoinduced electron F-type and hole V-type color centers have on the overall efficiency of surface reactions, we examined the influence of a simple (at least phenomenologically) surface process, e.g. photoadsorption of O_2, H_2, and CO, on the formation (photocoloration) and destruction (photobleaching) of these photoinduced defects in scandia.

Experimental Section

Powdered Sc_2O_3 ("o.s.ch.", IREA) was used in the present study; the specific surface area of the sample determined by the Brunnauer−Emmet−Teller BET method with nitrogen was ~9 $m^2\ g^{-1}$. Ubiquitous organic impurities and adsorbed adventitious molecules on the specimen surface were removed by thermal pretreatment ($T = 900$ °K) in an O_2 atmosphere ($P = 100$ Pa) and then in vacuo for a few days. Reproduction of the original state of the specimens between the various experiments was achieved by heating the samples in oxygen for ca. 1 h. Experimental errors in either the spectral or the kinetic measurements that may have been caused by the nonreproducibility of the original state of the specimen are less than 10%.

Powdered samples were contained in a 5-mm quartz cell (illuminated area, 10 cm^2) connected to a high-vacuum setup equipped with an oil-less pump system; the ultimate gas pressure in the reaction cell was ca. 10^{-7} Pa. Kinetic measurements were carried out with a Pirani-type manometer (sensitivity, 18 mV Pa^{-1} for O_2 and 24 mV Pa^{-1} for H_2). Control of gas composition was obtained using the mass spectrometer MX-7301. Irradiation of the solid sample was carried out using a 120-W high-pressure mercury lamp (DRK-120; MELZ); the incident light irradiance E_o at wavelengths below 400 nm was 6 mW cm^{-2}, measured through a water filter using a thermoelement (IOFI; sensitivity, 1.5 V W^{-1}). The photon fluence at wavelengths below 250 nm was ~10^{15} photons $cm^{-2}\ s^{-1}$. Cutoff filters from a standard set of colored glass filters (Vavilov SOI) were used to select the spectral regions for sample excitation.

Diffuse reflectance spectra ($BaSO_4$ was the reference standard) were recorded with a Specord M-40 (Karl Zeiss, Jena) spectrophotometer equipped with an integrating sphere assembly; data processing was carried out using the "Data Handling I" package. Measurement of diffuse reflectance spectra, ΔR, for the temperature dependence of thermoannealing of the hole color centers was carried out using the following procedure. The original state of the scandia specimen was prepared by heating the sample for 1 h in an oxygen atmosphere at 900 °K, followed by cooling to room temperature; subsequently, the specimen was irradiated in vacuo for ~15 min with all the UV/visible wavelengths of the light source to obtain the maximum coloration possible to within ca. ±5% for each temperature used. The specimen was then heated to the desired temperature in the linear heating regime at a rate of 0.3 K s^{-1} also in vacuo, following which the sample was rapidly quenched back to ambient temperature and the ΔR ($= R_o - R_{h\nu}$) measured. This procedure was repeated to obtain the ΔR of the specimen at a different annealing temperature.

In our experiments, the moveable high-vacuum setup/quartz cell system was moved as a whole unit between the position of irradiation and of thermal treatment of the sample to a position for recording spectra; both positions were fixed with high-precision instruments.

The following system of notation is herein used to denote[11] the diffuse reflectance spectra (DRS) and the "difference diffuse reflectance spectra" (DDRS):

R_o = original DRS spectra of the original state of the sample

$R_{h\nu}$ = original DRS spectra of the preirradiated sample

$R_{h\nu(\mathrm{vac})}$ = original DRS spectra of the sample preirradiated in vacuo

$R_{h\nu(H_2)}$ = original DRS spectra of the sample preirradiated in a hydrogen atmosphere

$R_{h\nu(O_2)}$ = original DRS spectra of the sample preirradiated in an oxygen atmosphere

$R_{h\nu(\mathrm{CO})}$ = original DRS spectra of the sample preirradiated in a carbon monoxide atmosphere

$R_{\mathrm{post}(H_2)}$ = original DRS spectra of the sample after hydrogen postadsorption

$\Delta R = R_1 - R_2$ DDRS spectra; here R_1 and R_2 refer to one of the original spectra defined above

$\delta R = \Delta R_1 - \Delta R_2$ DDRS spectra; here ΔR_1 and ΔR_2 are the DDRS spectra defined above

In an earlier study[20] we showed that UV light induces changes in the reflectance coefficient: $\Delta R_{h\nu} = (\mathrm{const})\ \Delta\alpha$ where $\Delta\alpha$ is the change in the absorption coefficient of the solid at a given energy $h\nu$, so that $\Delta R_{h\nu}$ spectra denote actual absorption spectra of the photoinduced color centers.

Results

Photoadsorption of Oxygen and Hydrogen. Simple photochemical processes on the surface of scandia, e.g. photoadsorption of oxygen, hydrogen, methane,

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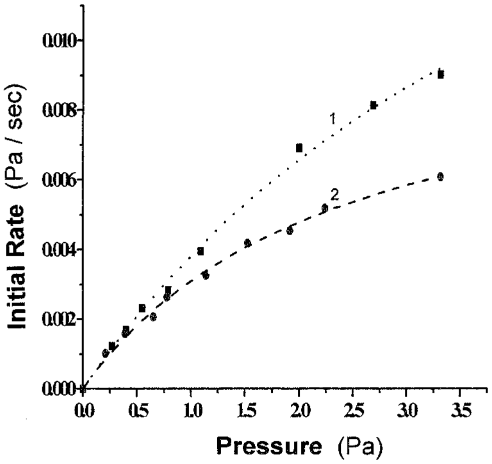

Figure 1. Plots depicting the dependencies of the initial rate of photoadsorption of oxygen (curve 1) and hydrogen (curve 2) on the gas pressure.

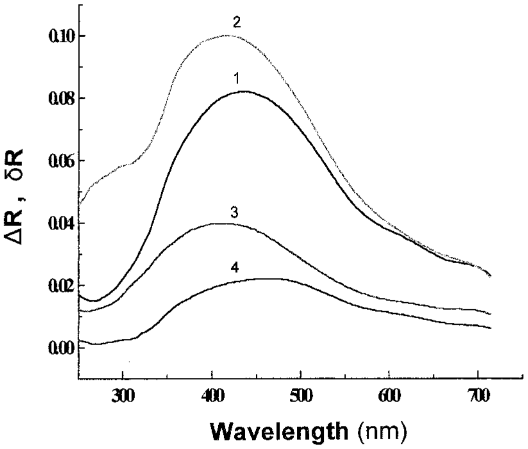

Figure 2. Difference diffuse reflectance spectra $\{\Delta R = R_o - R_{h\nu}\}$ of powdered scandia after 30 min of irradiation in vacuo (curve 1), in an oxygen atmosphere (curve 2), and in a hydrogen atmosphere (curve 3); difference diffuse reflectance spectrum, as δR (see text), of long-lived surface active centers postadsorption of hydrogen molecules (curve 4).

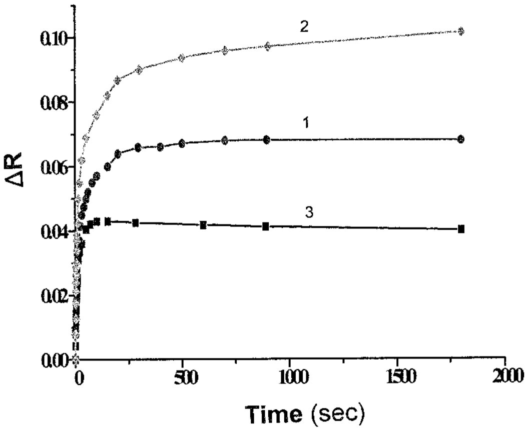

Figure 3. Kinetics of coloration (formation of color centers) at $\lambda = 436$ nm during sample irradiation at all UV wavelengths in vacuo (curve 1), in an oxygen atmosphere (curve 2), and in a hydrogen atmosphere (curve 3).

and carbon monoxide (among others), are also typical of other metal oxides. The results of our preliminary experiments dealing with the photoadsorption of H_2, CO, and O_2 showed that the spectral limit for all three processes occurred at about ~3.9 eV (320 nm). That is, the spectral limit is red-shifted by about 2 eV relative to the fundamental absorption edge of scandia (6.0 eV), which appears to be rather typical of other wide band gap adsorbers.[8-11]

The dependencies of the initial rates of photoadsorption of both hydrogen and oxygen on gas pressure P at constant light irradiance are illustrated in Figure 1 and can be described closely by the relationship expressed by eq 1:

$$\frac{dP}{dt}_{t\to 0} = k\frac{KP}{(1 + KP)} \tag{1}$$

These dependencies permit a determination of the lower limit of the lifetime of surface active centers for photoadsorption:[21] $\tau = k^{-1} = 0.7 \pm 0.2 \times 10^{-3}$ s for H_2 and $1.0 \pm 0.2 \times 10^{-3}$ s for O_2 for an assumed cross section of surface active centers of about 10^{-16} cm^2. Further, a postirradiation adsorption effect (i.e. adsorption of molecules after irradiation of the sample in vacuo) was also observed; this points to the existence of surface active centers with lifetimes longer than 10^2 s. The fraction of such centers determined from the postirradiation adsorption coefficient $K = N_{post}/N_{phot}$ (where N_{post} is the number of postadsorbed molecules and N_{phot} is the number of photoadsorbed molecules under light exposure, determined from thermal desorption spectra) does not exceed 10%. The absorption spectrum (ΔR) of long-lived hydrogen adsorption centers is portrayed in Figure 2 (curve 4). The latter spectrum was obtained as the difference between diffuse reflectance spectra recorded after and before postadsorption of hydrogen on the surface of the sample irradiated in vacuo for 30 min [$\Delta R = R_{post(H_2)} - R_{h\nu(vac)}$]. Thus, the changes in absorption are caused by interaction of hydrogen molecules with surface active centers (postadsorption of hydrogen). All subsequent experiments were carried out at pressures $P_{O_2} = 3.3$ Pa and at $P_{H_2} = 2.5$ Pa that provide the maximum rates of gas photoadsorption within the experimental region of gas pressures examined.

Photocoloration. UV irradiation of scandia powder leads to formation of color centers. The difference diffuse reflectance spectrum $\Delta R = R_o - R_{h\nu(vac)}$ recorded after 30 min of irradiation with all the UV wavelengths emitted by the mercury lamp is illustrated in Figure 2 (curve 1). In accordance with earlier work,[15] this spectrum can be taken to belong to hole V-type color centers. The kinetics of formation (growth of ΔR at wavelength $\lambda = 436$ nm) of hole color centers during sample irradiation in vacuo are illustrated in Figure 3.

Influence of Gas Photoadsorption on Photocoloration. Photoexcitation of scandia powdered particulates causes formation of surface electron and surface hole active centers which participate in surface chemical processes, e.g. in the photoadsorption of H_2, CO, and O_2. Moreover, it produces color centers at the surface and in the bulk of the particles. Free photogenerated charge carriers take part in both processes. Evidently, these processes interact with each other, owing to the existence of common steps of carrier generation and

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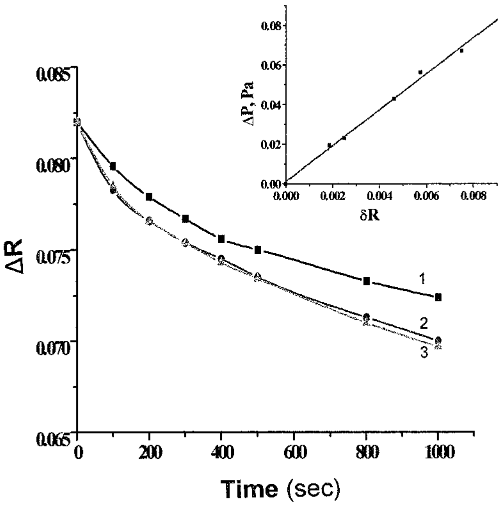

Figure 4. Kinetics of photobleaching of color centers with light at 436 nm and monitored at $\lambda = 436$ nm in vacuo (curve 1), in a hydrogen atmosphere (curve 2), and in an atmosphere of carbon monoxide (curve 3). The insert illustrates the dependence of the difference between the photobleaching in vacuo and in a hydrogen atmosphere $\{\delta R = \Delta R_{436\mathrm{nm(vac)}} - \Delta R_{436\mathrm{nm(H_2)}}\}$.

carrier migration. The difference diffuse reflectance spectra ΔR of the V-type hole centers in Sc_2O_3, obtained after irradiation of a sample for 30 min, either in an oxygen atmosphere (spectrum 2) or in a hydrogen atmosphere (spectrum 3), are also presented in Figure 2. The spectra as well as the kinetics of coloration during irradiation in the presence of either oxygen gas or hydrogen gas (see Figure 3, curves 2, 3) show that photoadsorption of oxygen induces an increase in the concentration of V-type hole color centers, whereas photoadsorption of hydrogen decreases the number of these V centers.

Photobleaching and Photostimulated Postadsorption (PhSPA). Excitation of Sc_2O_3 in the absorption band of the UV-induced formation of V-type color centers ($\lambda_{\mathrm{exc}} = 436$ nm) causes photobleaching of the band and thus a reduction in the number of such centers. The kinetics of photobleaching ($\lambda = 436$ nm) in vacuo are summarized in Figure 4. The cause of photobleaching is found in the multistep process in which the first step is photoionization of the color centers (see below). Destruction of these centers can also occur by thermal ionization. The temperature dependence on the thermoannealing of color centers ($\lambda = 436$ nm) is presented in Figure 5.

Photoionization and thermal ionization of color centers can produce free charge carriers that can lead to such surface chemical reactions as adsorption of hydrogen and carbon monoxide. The temperature dependence of the rate of hydrogen adsorption recorded in a thermoprogrammed heating regime is displayed in Figure 5. The maximum rate of thermostimulated hydrogen adsorption corresponds to the maximum rate of thermoannealing of the hole color centers. Note that control experiments showed no hydrogen adsorption (i.e. thermal oxidation) on nonirradiated scandia samples at temperatures below 737 K. In this case, the observed effect of hydrogen adsorption is one connected with the thermal destruction of the hole color centers. The apparent activation energy for this process is $E_a \approx 1.2$ eV.

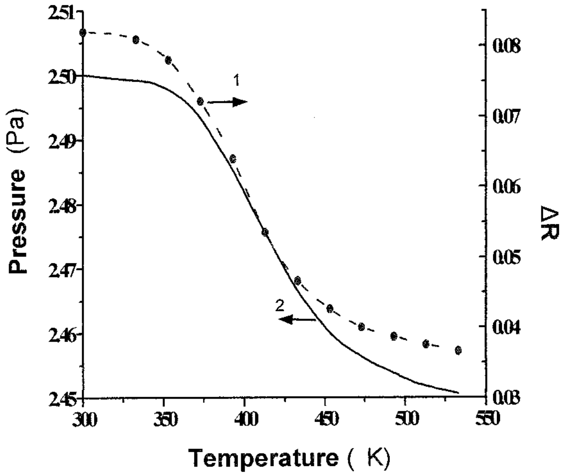

Figure 5. Plots showing the temperature dependencies of thermoannealing of color centers (curve 1) and thermostimulated adsorption of hydrogen on Sc_2O_3 particulates (curve 2).

Similar processes of adsorption of hydrogen and carbon monoxide at the scandia particle surface take place by photobleaching of the color centers. This effect was previously observed for oxygen adsorption on 10 of the 15 metal oxides surveyed.[22] The effect was examined in some detail for ZrO_2.[8,11,16] Since absorption of light by UV-induced color centers is usually shifted toward the red spectral region with respect to the spectral limit of photoactive absorption of the original state(s) of the samples, photoexcitation into these color centers leads to a red-shift of the spectral limits of surface photoreactions. This effect is designated photostimulated postadsorption (henceforth abbreviated as PhSPA), or UV-sensitization of reactions, because the UV-induced formation of color centers is a compulsory stage of the overall process. In the case of Sc_2O_3, formation of both electron and hole color centers shifts the red limits of photoadsorption of acceptor molecules (e.g. oxygen) to ~3.26 eV, i.e., to 380 nm, and of the photoadsorption of donor molecules (e.g. hydrogen and carbon monoxide) to ~2.21 eV, i.e., to ~560 nm, which correspond to the absorption regions of electron and hole color centers, respectively. The PhSPA of donor molecules increases the rate of photobleaching of hole color centers because of the appearance of an additional decay path for free holes (Figure 4, curves 2 and 3). This hypothesis is also confirmed by the existence of a linear dependence between the quantity of adsorbed gas ΔP and the extent of additional photobleaching caused by the presence of the gas relative to the extent of photobleaching witnessed in vacuo; this is given by $\delta R = \Delta R_{h\nu\mathrm{(vac)}} - \Delta R_{h\nu\mathrm{(H_2)}}$ (see the insert to Figure 4).

The kinetics of this PhSPA of molecules taking place when color centers are photoexcited can be expressed by Solonitsin's kinetic equation (eq 2) which is typical for gas photoadsorption on uniformly irradiated surfaces at sufficiently high gas pressure:[23-25]

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$$\Delta P(t) = \Delta P_{t\rightarrow\infty}\frac{t}{(t+\tau)} \tag{2}$$

from which the limiting quantity of adsorbed molecules ($\Delta P_{t\rightarrow\infty}$) at the very long times, i.e., at $t \rightarrow \infty$, can be assessed. Here t is the time of irradiation, and $\Delta P_{t\rightarrow\infty}$ and τ ($\propto E^{-1}$) are kinetic parameters (E is the light irradiance). The dependencies of $\Delta P_{t\rightarrow\infty}$ and τ for the hydrogen PhSPA process, induced by visible light at λ = 436 nm, on ΔR, which corresponds to the number (concentration) of V-type color centers, are presented in Figure 6. The linear dependence of $\Delta P_{t\rightarrow\infty}$ on ΔR supports our assumption that V-type color centers are the centers of light absorption that lead to the photochemical processes on the scandia particle surface.

From eq 2, the initial rate of PhSPA can be represented by:

$$\frac{\mathrm{d}P}{\mathrm{d}t}_{t\rightarrow 0} = \frac{\Delta P_{t\rightarrow\infty}}{\tau} \tag{3}$$

The dependence of the initial rate of PhSPA of hydrogen on the number of light absorbing centers, i.e., V-type color centers, which scales with the magnitude of ΔR is shown in Figure 7. The kinetic behavior can be approximated by eq 4:

$$\frac{\mathrm{d}P}{\mathrm{d}t}_{t\rightarrow 0} = \frac{A\Delta R}{B + C\Delta R} \tag{4}$$

where A, B, and C are constants. Knowledge of ΔR allows us to determine the rate of absorption of photons by scandia and takes into account only absorption of the photochemically active light by the V-type color centers. In this case,

$$E_{\mathrm{abs}} = E_{\mathrm{o}}\Delta R \tag{5}$$

where E_{o} is the irradiance of the incident actinic light. Thus, the initial quantum yield for the PhSPA process will be given by

$$\Phi = \frac{\frac{\mathrm{d}P}{\mathrm{d}t_{(t\rightarrow 0)}}\left[\frac{V_{\mathrm{reactor}}N_{\mathrm{a}}}{RT}\right]}{S_{\mathrm{reactor}}E_{\mathrm{abs}}} \tag{6}$$

The experimental dependence of the initial quantum yield $\Phi_{t\rightarrow 0}$ on $\Delta R_{436\mathrm{nm}}$ measured at λ = 436 nm is presented in Figure 7 and is expressed in eq 7:

$$\Phi_{t\rightarrow 0} = \frac{D}{B + C\Delta R} \tag{7}$$

where D is a constant. Note once again that, in this case, the quantum yield is determined by considering only absorption of the photochemically active light and is not to be regarded as the true quantum yield for the adsorber scandia. Nevertheless, this definition allows us to avoid calculations involving the absorption of the photochemically inactive light when we examine the mechanism(s) of surface photoprocesses.

Discussion

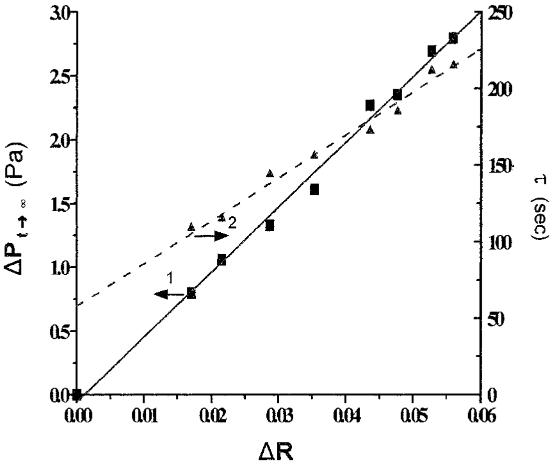
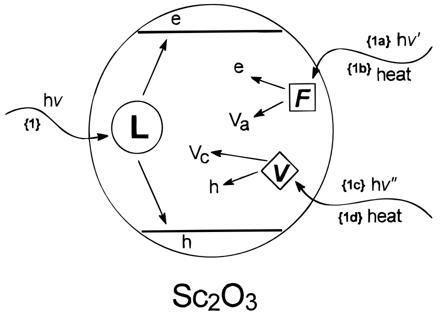


Figure 6. Dependencies of the kinetic parameters $\Delta P_{t\rightarrow\infty}$ (curve 1) and τ (curve 2) of the PhSPA process for hydrogen (λ_{exc} = 436 nm) ∞ on the extent of coloration (ΔR).

To interpret the present experimental results and observations, we consider the following sequence of simple reactions/processes leading to photoadsorption upon excitation of the scandia particulates in gas/solid systems. Stages {**1**}, {**1a**}, and {**1c**} describe the photoexcitation of the adsorber. The fundamental absorption of light by the regular lattice (L) or the extrinsic light absorption by the UV-induced defect centers, i.e., color centers of the F-type and V-type, lead to the generation of free charge carriers. Steps {**2**} and {**3**} correspond to processes of electron trapping by R and of electron/hole recombination, respectively, through preexisting defects on the scandia specimen, that is, through the recombination centers R. Formation of color centers of the F-type and V-type by trapping of electrons by anion vacancies (V_a) and holes by cation vacancies (V_c) is described by steps {**4**} and {**5**}, respectively. The latter processes are limited by the recombination of carriers trapped by the corresponding defects with free carriers of the opposite sign (stages {**6**} and {**7**}). Photoionization (steps {**1a**} and {**1c**}) and thermal ionization (stages {**1b**} and {**1d**}) of color



$$\begin{array}{llll} \{\mathbf{2}\} & e + R \rightarrow R^- & \{\mathbf{3}\} & h + R^- \rightarrow R \\ \{\mathbf{4}\} & e + V_a \rightarrow F & \{\mathbf{5}\} & h + V_c \rightarrow V \\ \{\mathbf{6}\} & e + V \rightarrow V_c & \{\mathbf{7}\} & h + F \rightarrow V_a \\ \{\mathbf{8}\} & e + S \rightarrow S^- & \{\mathbf{9}\} & h + S^- \rightarrow S \\ \{\mathbf{10}\} & S^- + M \rightarrow M^-_{\mathrm{ads}} & \{\mathbf{11}\} & h + Z \rightarrow Z^+ \\ \{\mathbf{12}\} & e + Z^+ \rightarrow Z & \{\mathbf{13}\} & Z^+ + M \rightarrow M^+_{\mathrm{ads}} \end{array} \tag{8}$$

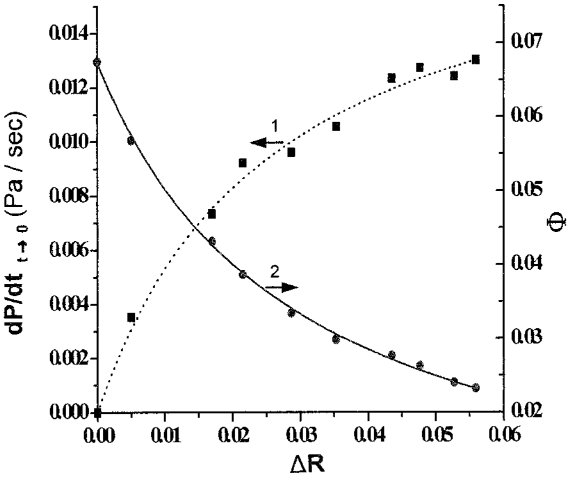


Figure 7. Dependencies of the initial rate (curve 1) and quantum yield (curve 2) of the PhSPA process for hydrogen ($\lambda_{exc} = 436$ nm) on the extent of coloration (ΔR).

centers also restrict their accumulation by producing free carriers. Carrier trapping by the surface defects S and Z (stages {**8**} and {**11**}) yields the corresponding surface active centers S^- (electron centers) and Z^+ (hole centers). The lifetime of these active centers is governed by different deactivation modes. One of the more likely modes that deactivates surface active centers is recombination of trapped carriers with free carriers of the opposite sign (steps {**9**} and {**12**}). Another possible path for the annihilation of surface active centers is thermal ionization, namely $S + \text{heat} \rightarrow S^- + h$, and $Z + \text{heat} \rightarrow Z^+ + e$. Under our experimental conditions of moderate light irradiance and usage of microcrystals, the probability of recombination of trapped carriers through tunneling must be very low. Steps {**10**} and {**13**} describe the interaction of acceptor and donor molecules (M) of the gases with electron and hole surface active centers, respectively, that leads to adsorption of molecules on the surface of the adsorber. Band-to-band recombination of free electrons and holes has not been considered in the proposed mechanism (see eqs 8) because of the low probability for this process inherent in wide band gap solids owing to the restrictions imposed by energy and momentum conservation rules. There is also no step(s) presented here that describes the photodesorption of adsorbed molecules; in control experiments we observed no photodesorption of either H_2 or CO, and the fraction of photodesorbed oxygen molecules during a 30-min UV light exposure did not exceed 10%.

The rate of photoadsorption of donor molecules (e.g. H_2 and CO) in the proposed mechanism can be designated by

$$\frac{dP}{dt} = -k_{13}[Z^+]P \tag{9}$$

where

$$[Z^+] = \frac{k_{11}[h][Z_o]}{k_{12}[e] + k_{13}P} \tag{10}$$

under quasi-steady-state conditions for both Z^+ and for the charge carriers (e and h), and for $([Z^+] + [M^+_{ads}]) \ll [Z_o]$, which is true initially at time $t \rightarrow 0$. The initial rate of photoadsorption will then be given by

$$\frac{dP}{dt}_{t\to 0} = \frac{-k_{11}[h][Z_o]k_{13}P}{k_{12}[e] + k_{13}P} \tag{11}$$

which is analogous to the experimental dependence expressed by eq 1. A similar expression can easily be obtained for the initial rate of photoadsorption of acceptor molecules (oxygen). Note that in eq 10, the lifetime of the surface active center Z^+ depends on the efficiency of recombination and on the concentration of surface electrons, i.e., $\tau_{Z^+} = (k_{12}[e])^{-1}$. Obviously, if sample irradiation is terminated, free electrons are no longer produced and the lifetime of the remaining surface active centers becomes unlimited (i.e. $\tau_{Z^+} \rightarrow \infty$), provided there are no other deactivation pathways for the surface centers. Hence, these same centers can be long-lived centers for the postadsorption of molecules ($\tau_{Z^+} > 10^2$ s) once irradiation is terminated, and during irradiation centers for the photoadsorption of gas molecules are short-lived ($\tau_{Z^+} = 0.7 \pm 0.2 \times 10^{-3}$ s). Experimental results (see Figure 2, curve 4) infer that photoadsorption of the donor molecules CO and H_2 takes place on surface active centers of the hole V-type.

If $k_{13}P \gg k_{12}[e]$ in eq 11, i.e., at sufficiently high gas pressures, the rate of photoadsorption is then given by

$$\frac{dP}{dt} = -k_{11}[h][Z] \tag{12}$$

equal to the rate of generation of surface active centers (stage {**11**}). In this case, there is only one path for the decay of surface active centers: interaction of the center with gas molecules, and hence the probability of annihilation of such centers (stage {**12**}) through recombination becomes negligible. Monte Carlo computer simulations[16,17,26] show that the difference in recombination decay probability in vacuo and in the presence of gases may be the principal cause for the the influence of gas photoadsorption on the photocoloration of the scandia adsorber.

A simple interpretation of this influence can be achieved on the basis of the charge conservation rule. Taking into account the concentration of free and trapped carriers on the particles during irradiation of the solids in vacuo, the charge conservation rule requires that

$$[e] + [F_{vac}] = [h] + [V_{vac}] \tag{13}$$

where $[F_{vac}]$ and $[V_{vac}]$ describe the total concentration of trapped electrons and trapped holes, respectively. When wide band gap solids are irradiated under moderate light irradiances, the concentration of trapped carriers becomes far greater than the concentration of free carriers for short times after the beginning of irradiation, i.e., $[F, V] \gg [e, h]$; this simplifies eq 13 to

$$[F_{vac}] = [V_{vac}] \tag{14}$$

Equation 14 is also valid for deeply trapped carrier after irradiation of Sc_2O_3, typical of this metal oxide. Irradiation of solids in the presence of gases causes carrier

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(26) Emeline, A. V.; Ryabchuk, V. K.; Serpone, N. *J. Am. Chem. Soc.* Submitted for publication.

trapping by adsorbed or photoadsorbed molecules. The charge conservation condition for photoadsorption of O_2 is then

$$[F] + [O_2^-] = [V] \tag{15}$$

and for hydrogen photoadsorption it is

$$[F] = [V] + [H_2^+] \tag{16}$$

To simplify the discussion, we have not considered dissociative adsorption of the gaseous diatomic molecules.

Combination of eqs 15 and 16 with eq 14 yields

$$\Delta[F] + [O_2^-] = \Delta[V] \tag{17}$$

and

$$\Delta[F] = \Delta[V] + [H_2^+] \tag{18}$$

where additional F-like centers $\Delta[F] = [F] - [F_{vac}]$ and $\Delta[V] = [V] - [V_{vac}]$ are given by the difference between the concentration of F and V color centers after preirradiation of Sc_2O_3 in the presence of H_2 or O_2 gases relative to those in vacuo. These considerations explain the absorption growth of hole centers in the presence of O_2 , as well as the decrease in the absorption of hole centers in a H_2 atmosphere.

The photoionization of V-type color centers leads to the appearance of free holes (step {**1c**} of eqs 8). Their recombination with trapped electrons (F-centers; stage {**7**}) prevents retrapping of holes by the cation vacancies (stage {**5**}) and causes the photobleaching of the absorption of V-type centers. Nevertheless, the process of retrapping of holes also takes place to restore some of the V-type centers. Both processes are in competition. During sample excitation with light at 436 nm, there is no light absorption by the electron centers (stage {**1a**}) and thus no free electrons are produced to recombine with trapped holes (stage {**6**}). The origin(s) of the influence of gas adsorption on the rate of photobleaching of the color centers depends on the type of surface active centers available. If the surface active centers are the V-type centers (deep hole traps), their lifetime during photoexcitation with light at 436 nm will be limited only by the photoionization process, since there is no recombination with free electrons. Assuming that the light absorption cross section of such centers is $\sigma = 1 \times 10^{-16}$ cm^2 and the experimental light photon fluence is $10^{15} - 10^{16}$ photons s^{-1} cm^{-2}, the estimated lifetime of the centers is then ~1−10 s, which is much longer than the recombination lifetime (see above). In this case, the surface V-type active centers behave as long-lived centers of postadsorption and their bleaching is caused by reaction with gas molecules.

On the basis of the mechanism proposed herein, the expression for the rate of photobleaching in vacuo is given by

$$\frac{d[V_{(vac)}]}{dt} = -k_{1c}E[V] + k_5[h][V_c] \tag{19a}$$

$$\frac{d[V_{(vac)}]}{dt} = -k_{1c}E[V] + k_5[h]\{[V_{c(bulk)}] + [V_{c(surf)}]\} \tag{19b}$$

where the total concentration of cation vacancies $[V_c]$ is given by the sum of bulk and surface vacancies, i.e., $[V_c] = [V_{c(bulk)}] + [V_{c(surf)}]$. To simplify our consideration of the proposed mechanism, we have assumed that the cross sections of hole trapping by bulk cation vacancies and by surface cation vacancies are equal. Also, taking that $[V_{c(surf)}] = Z$ so that $k_5 = k_{11}$, the rate of photobleaching in the presence of gases at sufficiently high pressures can then be described by eq 20a:

$$\frac{d[V_{(gas)}]}{dt} = -k_{1c}E[V] + k_5[h][V_{c(bulk)}] + k_5[h][V_{c(surf)}] + \frac{dP}{dt} \tag{20a}$$

where dP/dt is the rate of PhSPA of gas molecules and is equal to the rate of formation of surface hole centers, i.e., $dP/dt = -k_5[h][V_{c(surf)}]$. Thus eq 20a becomes:

$$\frac{d[V_{(gas)}]}{dt} = -k_{1c}E[V] + k_5[h][V_{c(bulk)}] \tag{20b}$$

Subtraction of eq 20b from eq 19b yields

$$\frac{d[V_{(vac)}]}{dt} - \frac{d[V_{(gas)}]}{dt} = k_5[h][V_{c(surf)}] = -\frac{dP}{dt} \tag{21}$$

Note that since

$$\frac{d(\Delta R)}{dt} = (\mathrm{const})\frac{d[V]}{dt} \tag{22}$$

eq 21 can then be represented as

$$\frac{d(\delta R)}{dt} = \frac{d(\Delta R_{(vac)})}{dt} - \frac{d(\Delta R_{(gas)})}{dt} = \mathrm{const}\left(\frac{d[V_{(vac)}]}{dt} - \frac{d[V_{(gas)}]}{dt}\right) = -(\mathrm{const})\frac{dP}{dt} \tag{23a}$$

or after integration

$$\delta R = \Delta R_{h\nu(vac)} - \Delta R_{h\nu(gas)} = (\mathrm{const})\Delta P \tag{23b}$$

where $\Delta P = P(0) - P(t)$, consistent and in agreement with the experimental results depicted in Figure 4.

The initial rate of PhSPA on excitation of V-type color centers under steady-state conditions for the free holes may be expressed as

$$\left.\frac{dP}{dt}\right|_{t\to 0} = \frac{k_{1c}k_{11}[V]E[Z_o]}{k_3[R^-] + k_5([V_{c,o}] - [V]) + k_7[F] + k_{11}[Z_o]} \tag{24}$$

where E is the light irradiance and $[V_{c,o}]$ is the initial concentration of cation vacancies. Considering the accordance between the modeling eq 24 and the experimental kinetics that follow eq 3, we can infer that

$$\Delta P_{t\to\infty} = (\mathrm{const})[Z_o][V] \tag{25}$$

and thus,

$$\tau = \frac{k_3[\mathrm{R}^-] + k_5([\mathrm{V}_{\mathrm{c,o}}] - [\mathrm{V}]) + k_7[\mathrm{F}] + k_{11}[\mathrm{Z}_\mathrm{o}]}{(\mathrm{const})E} \qquad (26)$$

in accordance with the experimental dependence of the kinetics parameter τ on the light irradiance E in eq 2.[23−25] Now, if $[\mathrm{V}_{\mathrm{c,o}}] \gg [\mathrm{V}]$ and if the number of electron color centers is proportional to the number of hole color centers (see eq 14), i.e., if $[\mathrm{F}] = (\mathrm{const})[\mathrm{V}]$, the dependence expressed by eq 26 then corresponds to the experimentally observed dependence: i.e., $\tau = a + b[\mathrm{V}]$ (see Figure 6). Under otherwise identical conditions, eq 24 can then be written as

$$\left.\frac{\mathrm{d}P}{\mathrm{d}t}\right|_{t\to 0} = \frac{k_{1c}k_{11}[\mathrm{V}]E[\mathrm{Z}_\mathrm{o}]}{(k_3[\mathrm{R}^-] + k_5[\mathrm{V}_{\mathrm{c,o}}] + k_{11}[\mathrm{Z}_\mathrm{o}]) + k_7(\mathrm{const})[\mathrm{V}]} \qquad (27a)$$

or more simply as

$$\left.\frac{\mathrm{d}P}{\mathrm{d}t}\right|_{t\to 0} = \frac{a[\mathrm{V}]}{b + c[\mathrm{V}]} \qquad (27b)$$

again in good accord with the experimental dependence of the initial rate of PhSPA of hydrogen (eq 4). In the proposed mechanism, the rate of absorption of photons at t→0 is given by: $E_{\mathrm{abs}} = k_{1\mathrm{c}}[\mathrm{V}]E_\mathrm{o}$. Consequently, the quantum yield can be described as

$$\Phi = \frac{k_{11}[\mathrm{Z}_\mathrm{o}]}{k_3[\mathrm{R}^-] + k_5[\mathrm{V}_{\mathrm{c,o}}] + k_7[\mathrm{F}] + k_{11}[\mathrm{Z}_\mathrm{o}]} \qquad (28a)$$

or as

$$\Phi = \frac{k_{11}[\mathrm{Z}_\mathrm{o}]}{(k_3[\mathrm{R}^-] + k_5[\mathrm{V}_{\mathrm{c,o}}] + k_{11}[\mathrm{Z}_\mathrm{o}]) + k_7(\mathrm{const})[\mathrm{V}]} \qquad (28b)$$

That is, Φ has the same functionality as

$$\Phi = \frac{d}{b + c[\mathrm{V}]} \qquad (28c)$$

which concurs well with the experimental dependence seen in eq 7. Note that since we have assumed that $[\mathrm{V}_\mathrm{c}] \gg [\mathrm{V}]$ and $[\mathrm{F}] = (\mathrm{const})[\mathrm{V}]$ (see the conditions for eq 27a), this apparent inverse dependence of Φ on the concentration of V-type color centers is caused by changes in the concentration of electron F-type centers because of the recombination of free holes with trapped electrons (see stage {**7**} in eqs 8). It does not depend directly on the concentration of light absorption centers of the V-type.

Conclusions

The principal conclusions from this study are manyfold: (1) Formation of color centers causes an uncertainty in the determination of the spectral limits of surface photoreactions because these centers appear immediately on irradiation and cause the spectral limit to red-shift toward lower energies. (2) The interaction of surface chemical processes and formation of color centers should be taken into consideration in the development of the kinetics and of the corresponding mechanisms, since there is a strong connection between these two processes as a consequence of the charge conservation rule. (3) The experimental results concerning the influence of photoadsorption of gases on photocoloration and photobleaching can be used to determine the type of color centers. Indeed, as evident from the results obtained, on one hand the concentration (absorption) of hole color centers increases in oxygen and decreases in hydrogen during sample excitation in the fundamental absorption band. On the other hand, the rate of photobleaching of hole color centers is faster in a hydrogen atmosphere and is practically the same (if the wavelength at which the kinetics is measured corresponds only to absorption by hole centers) or less (if both F and V centers absorb at the same wavelength at which kinetics is measured) in an oxygen atmosphere. The opposite situation is true for electron color centers. (4) Formation of color centers decreases the quantum yield of surface photochemical processes because of the recombination of carriers through color centers, but increases the total efficiency of these processes because of the photobleaching of color centers when the sample is irradiated at all UV wavelengths emitted by the light source employed.

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