Mechanistic Studies of the Formation of Different States of Oxygen on Irradiated ZrO$_2$ and the Photocatalytic Nature of Photoprocesses from Determination of Turnover Numbers

A. V. Emeline,[†,‡] A. V. Panasuk,[§] N. Sheremetyeva,[‖] and N. Serpone*,[†,⊥]

Department of Chemistry and Biochemistry, Concordia University, Montreal, Quebec H4B 1R6, Canada,
Department of Physics, Ulyanovsk State University Branch in Dimitrovgrad, Dimitrovgrad, Russia,
Department of Photonics, Institute of Physics, State University of St. Petersburg, St. Petersburg, Russia, and
Dipartimento di Chimica Organica, Università di Pavia, Via Taramelli 10, Pavia 27100, Italia

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The photoadsorption of oxygen (photoreduction on electron surface-active centers) and the photoadsorption of hydrogen (photooxidation on hole surface-active centers) as well as the photooxidation of hydrogen in the presence of oxygen were examined over irradiated zirconia (ZrO$_2$) specimens by thermoprogrammed desorption spectroscopy (TPD) and kinetically to assess the states (forms) of oxygen species formed on the surface of zirconia. The three TPD spectral maxima observed inferred three oxygen species of varying activity in the photooxidation of hydrogen. The number of surface-active sites on the zirconia surface were quantitatively estimated (ca. 1×10^{16} centers), thereby permitting an estimate of the turnover numbers (TON) for the photooxidation of hydrogen (TON > 14.5) and for the photoreduction of oxygen (TON > 6.6). These demonstrate for the first time that a photoreaction occurring on the surface of a metal-oxide photocatalyst is *truly* photocatalytic.

Introduction

Zirconia (ZrO$_2$) demonstrates significant activity in heterogeneous photochemical processes such as in the photostimulated adsorption of oxygen, hydrogen, and methane[1−4] with quantum yields that can reach values as high as 0.04−0.05 and in the photoizomerization of 2-butene.[5−7] Photostimulated adsorption of hydrogen and methane is a dissociative process yielding H$^•$ and $^•$CH$_3$ radicals. The ultimate result of dissociative adsorption of methane is formation of higher hydrocarbons: for example, ethane, ethene, propane, and oxidation products. EPR studies by Burukina[8] have shown that the photostimulated adsorption of oxygen produces two different states (forms) of oxygen that are present on the surface of zirconia: namely, O$^{•-}$ species with $g_1 = 2.0196$, $g_2 = 2.0101$, and $g_3 = 2.0045$; O$_2^{•-}$ species with $g_1 = 2.0312$, $g_2 = 2.0099$, and $g_3 = 2.0040$. The slight difference in the anisotropy of the g-factor of the EPR signal of the O$_2^{•-}$ species recorded for the forms that desorbed below 370 °C ($g_1 = 2.0312$) and between 370 and 470 °C ($g_1 = 2.0325$) suggests that perhaps there exist at least two different O$_2^{•-}$ adsorbed species. The EPR signal of the O$^{•-}$ species was also observed after irradiation of ZrO$_2$ in vacuo, inferring that this signal is connected with hole traps on the surface and in the bulk and is not related to the adsorbed oxygen forms. The O$^{•-}$ signal does not appear during irradiation in the presence of oxygen at liquid nitrogen temperatures. Rather the O$_3^{•-}$ adsorption complex with $g_1 = 2.0124$, $g_2 = 2.0090$, and $g_3 =$

2.0010 is formed, which is unstable at the higher temperatures. This adsorption complex has been implicated in oxygen isotopic exchange processes.[8] Adsorbed superoxide radical anionic O$_2^{•-}$ species with $g_1 = 2.031$, $g_2 = 2.009$, and $g_3 = 2.000$ are also formed at the thermally activated surface as a result of oxygen adsorption on Zr^{3+} and $\textit{F}^+$-type surface centers, which are produced from the thermal reduction of the zirconia surface.[9] Zirconia has also displayed high activity in more complex surface photochemical reactions: for instance, in the photolysis of water[10] and in the photoreaction between CO$_2$ and H$_2$.[11] Although these and other processes in heterogeneous photocatalysis have been claimed to be photocatalytic, no experimental evidence in support of their photocatalytic nature has thus far been demonstrated.

The term "heterogeneous photocatalysis" has been widely used to describe photochemical events in gas−solid and liquid−solid heterogeneous systems involving in most cases metal oxides as the photocatalysts (see refs 12−18 and references therein). In many studies, however, the description of processes as being "photocatalytic" has been inferred in the best of cases since it was not based on firm experimental evidence about their catalytic nature. The problem originated because no official description of heterogeneous photocatalysis and its characteristics has yet been accepted by the photochemical community despite recent attempts.[19,20] In earlier papers,[20,21] our attention was focused on describing heterogeneous photocatalysis and photocatalysts to establish experimental procedures/protocols to help clarify the catalytic nature of a given photochemical process in heterogeneous systems. In particular, we proposed that photocatalysis be referred simply as "catalysis of a photochemical reaction".[21] Despite this concise form, this otherwise simplistic definition provides, nonetheless, a complete consideration of the phenomena of photocatalysis since it is based on well-established definitions of catalysis and photochemical reactions. In defining photocatalysis as describing a

* Corresponding author e-mail: serpone@vax2.concordia.ca or nick.serpone@unipv.it.
† Concordia University.
‡ Current address: Kanagawa Academy of Science & Technology, KSP West 614, 3-2-1 Sakado, Takatsu-ku, Kawasaki-shi, Kanagawa 213-0012, Japan.
§ Ulyanovsk State University Branch in Dimitrovgrad.
‖ State University of St. Petersburg.
⊥ Università di Pavia.

catalyzed photochemical event, we implicitly assume that all the laws of photochemistry apply equally well to photocatalysis.

Considering photocatalysis as a branch of catalysis allows us, therefore, to expand the rules that normally apply in general catalysis to photocatalysis. In particular, the photocatalyst must be restored to its original chemical and thermodynamic state at the termination of the photoreaction. Moreover, the photocatalyst alters the reaction pathway so as to yield a profit on the energy profile of the photoreaction. For example, the photocatalyst typically causes the spectral sensitization of the photochemical reaction toward photons of lower energy than is required by the corresponding homogeneous photochemistry. Consequently, to characterize photochemical events in heterogeneous systems, we need to invoke and implicate parameters from both photochemistry and catalysis. Thus, quantum yield and photonic efficiency are borrowed from photochemistry. These two parameters can be used to estimate the relative activity of photocatalysts; that is, the ability of a photosystem to transform the photon energy into one or more chemical sequences. However, both these photochemical parameters remain silent as to whether a photoprocess in a heterogeneous system is truly photocatalytic. Only for an ideal stationary photocatalytic process does the quantum yield (and thus photonic efficiency) remain constant in time. In practice, however, any chemical or physical secondary process can alter the value of this parameter, thus making it kinetically variable. Accordingly, only parameters borrowed from the field of catalysis can answer the question as to whether a given photon-induced process is photocatalytic. One such parameter is the turnover number (TON),[21] which causes no difficulty in homogeneous (photo)catalysis. When this parameter exceeds unity for a given time interval, the photoreaction is said to be photocatalytic, regardless of secondary events/reactions that may accompany the process. Otherwise, the photoprocess represents simply a stoichiometric heterogeneous photoreaction.

In the present paper, we report the results of a mechanistic study into the formation of various states (forms) of oxygen produced over irradiated zirconia (ZrO_2) under various conditions. We also examine the photooxidation of hydrogen in the presence of molecular oxygen over irradiated powdered ZrO_2 as a model reaction. In particular, we present experimental evidence that this photooxidation reaction and the related photoadsorption (i.e., photoreduction) of oxygen belong to the class of truly photocatalytic processes.

Experimental Section

The high purity grade powdered ZrO_2 (IREA, Russia) was produced from zirconium oxychloride. The specific surface area of the sample determined by the BET method with nitrogen gas was ca. 7 m^2 g^{-1}. X-ray diffraction structural methods confirmed that the sample contained only the monoclinic crystal form.

Ubiquitous organic impurities and adsorbed molecules on the metal oxide specimen surface were removed by thermal pretreatment ($T = 900$ K) in an oxygen atmosphere ($P = 100$ Pa) and then in vacuo for a few days. Reproduction of the original state of the specimens between experiments was achieved by heating in oxygen for ca. 1 h. Experimental errors in kinetic measurements that may have been caused by the nonreproducibility of the original state of the ZrO_2 specimen do not exceed ~10%.

Powdered samples were contained in a quartz cell (path length, 5 mm; illuminated area, 6 cm^2) connected to a high-vacuum setup that was equipped with an oil-free pump system.
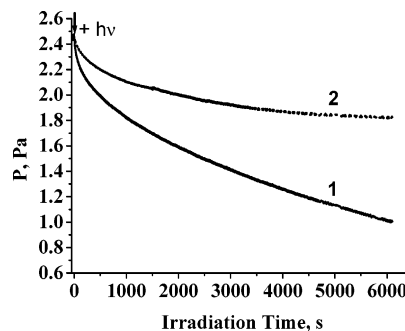

Figure 1. Kinetics of photostimulated adsorption of (1) oxygen and (2) hydrogen on zirconia.

The ultimate gas pressure in the reaction cell was ca. 10^{-7} Pa. The volume of the reactor was 50 cm^3. Hydrogen gas was obtained by the thermal decomposition of TiH_4, and oxygen was obtained by the thermal decomposition of $KMnO_4$. A Pirani-type manometer (sensitivity, 20 mV Pa^{-1} for O_2 and 24 mV Pa^{-1} for H_2) was used to measure gas pressures in kinetic studies. Monitoring of the gas composition and identification of thermodesorption products were conducted using a mass spectrometer (MX-7301; Russia). Thermodesorption was carried out in the linear heating regime at a rate of 0.25 K min^{-1}. Irradiation of the solid specimens was carried out with a 120-W high-pressure mercury lamp (DRK-120, MELZ, Russia); the light irradiance at wavelengths below 400 nm (6 mW cm^{-2}) was measured through a water filter using a thermoelement (IOFI, Russia; sensitivity, 1.5 V W^{-1}). The photon flow at wavelengths below 250 nm was about 10^{15} photons cm^{-2} s^{-1}.

Diffuse reflectance spectra (DRS; $BaSO_4$ was the reference) were recorded with a Karl Zeiss Spekord M-40 spectrophotometer (Jena, Germany) equipped with an integrating sphere assembly and interfaced to a computer. In our experiments, the movable high vacuum setup/quartz cell system was moved as a unit between the position of irradiation and the thermal treatment of the specimen to the position for recording spectra; both were fixed with high precision in appropriate positions.

Results

Irradiation of the heterogeneous system containing either oxygen or hydrogen in the gas phase over a bed of ZrO_2 causes the photostimulated adsorption of the corresponding gases,[1,2] that is the photoreduction of molecular oxygen and the photooxidation of molecular hydrogen (Figure 1). A priori, one may assume that the temporal decay of gas pressure observed during irradiation of a mixture of hydrogen and oxygen (ratio of 5:2, respectively) in the gas phase over ZrO_2 (Figure 2) should be an additive process of the two photochemical processes. However, the magnitude of the change in pressure during irradiation of the gas mixture over zirconia was much greater than the sum of the changes in pressure of the two corresponding photostimulated adsorption processes. This infers the existence of two possibilities: either (1) there exists a synergistic effect that leads to an intensification of the photostimulated coadsorption of the two gases or (2) there exists an additional photostimulated reaction between one or more of the states (forms) of oxygen with hydrogen, which causes a greater loss of pressure than was otherwise expected. An additional feature of the photostimulated process in the gas mixture, which points to the alteration of the mechanism of the photoreaction, is the different kinetic behavior from the kinetics of the photostimulated adsorption of the pure gases. Although the kinetics of the photostimulated adsorption events display saturation with time,
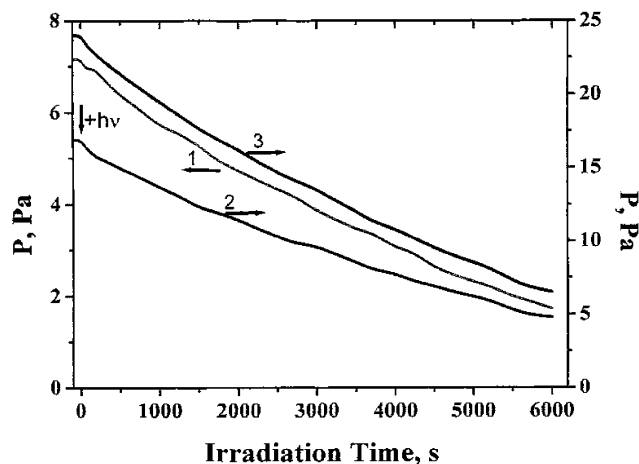
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Figure 2. Kinetics of the changes of partial pressure of (1) oxygen, (2) hydrogen, and (3) total pressure of the gas mixture during the photooxidation of hydrogen over zirconia.
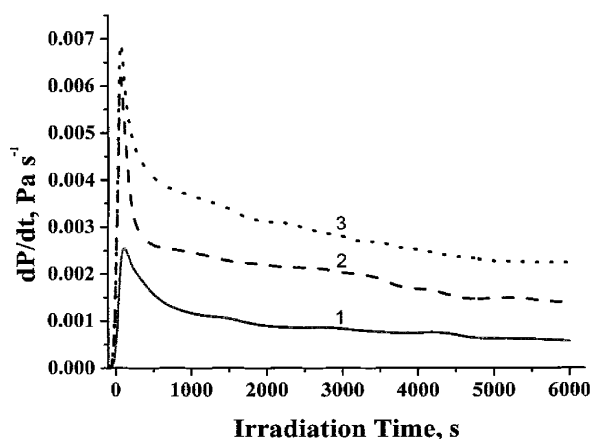

Figure 3. Time evolution of the rates of changes of partial pressure of (1) oxygen, (2) hydrogen, and (3) total pressure of gas mixture during the photooxidation of hydrogen over zirconia.

Figure 4. (a) TPD spectra of photoadsorbed oxygen at different times of irradiation. (b) TPD spectra of photoadsorbed oxygen accumulated at the surface of zirconia during the photooxidation of hydrogen at different times of irradiation.

after a short period of irradiation the kinetics of the photo-process(es) in the gas mixture follow near zero-order kinetics; that is, the rate of the photoreaction becomes nearly constant. This is also true for the behavior of the rate of loss of oxygen and hydrogen in the gas phase as evidenced in Figure 3. Therefore, the mechanism for the loss of oxygen pressure in the gas phase during the photoreaction must differ from that of the photostimulated adsorption of the pure gases.

To understand the difference(s) in behavior, the irradiation was interrupted during the photostimulated adsorption of pure oxygen as was the photoreaction between the mixture components at several different time periods so that we could monitor the accumulation of oxygen species on the surface of zirconia by thermoprogrammed desorption techniques (TPD). The relevant TPD spectra for the photoadsorption of pure oxygen are illustrated in Figure 4a and for the photoadsorption of oxygen in the presence of hydrogen at various irradiation times in Figure 4b.

The TPD spectra for the accumulation of oxygen at the surface of zirconia during the photoadsorption process and during the photooxidation of hydrogen for a short (30 s) and long period (6000 s) of irradiation are depicted, respectively, in Figure 5, panels a and b. It is evident that the TPD spectra of photoadsorbed oxygen represent complex, poorly resolved spectral curves for which a detailed analysis is rendered difficult because of (1) the unknown nature of surface adsorption sites,
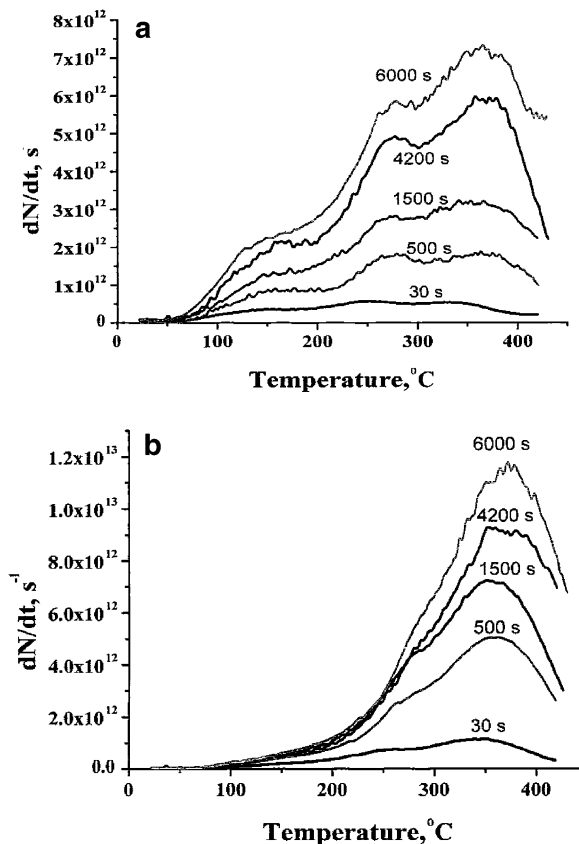
(2) the unknown energy distribution of these sites, and (3) the lack of mechanistic details of the desorption process(es). Although a detailed analysis of the TPD spectra of preadsorbed oxygen species was beyond the scope of the present studies, we nonetheless discerned three resolved maxima at 150, 270, and 370 °C, respectively, in the TPD spectra of photoadsorbed oxygen. The maxima correspond to three possible states of oxygen. It is evident from the TPD spectra that these oxygen species accumulate on the surface in a similar manner during irradiation, although the high-temperature maximum increases somewhat more at the longer irradiation times. Concomitantly, one oxygen species accumulates at the surface during the photoreaction involving the H_2-O_2 gas mixture. The species corresponds to the high-temperature maximum (compare Figure 5, panels a and b) and appears to predominate at longer times of irradiation. The oxygen species that desorb at the lower temperatures do not accumulate to any significant extent.

The relevant kinetics of accumulation of oxygen on the surface of irradiated zirconia, as determined from the TPD spectra, are portrayed in Figure 6a as the number of oxygen molecules (N_{O2}) against irradiation time. They demonstrate that although only the high temperature form(s) of oxygen accumulates on the surface, the total amount of oxygen adsorbed during the photooxidation of hydrogen is significantly greater (curve 2) than during the photostimulated adsorption of oxygen alone (curve 1), especially at the shorter times of irradiation. At the same time, when ZrO_2 particles were exposed to irradiation for longer periods this difference tended to diminish as evident from the ratio between the number of photoadsorbed oxygen molecules during the photooxidation of hydrogen (N_{O2}^{ox}) and in the absence of hydrogen (N_{O2}^{ads}). This N_{O2}^{ox}/N_{O2}^{ads} ratio
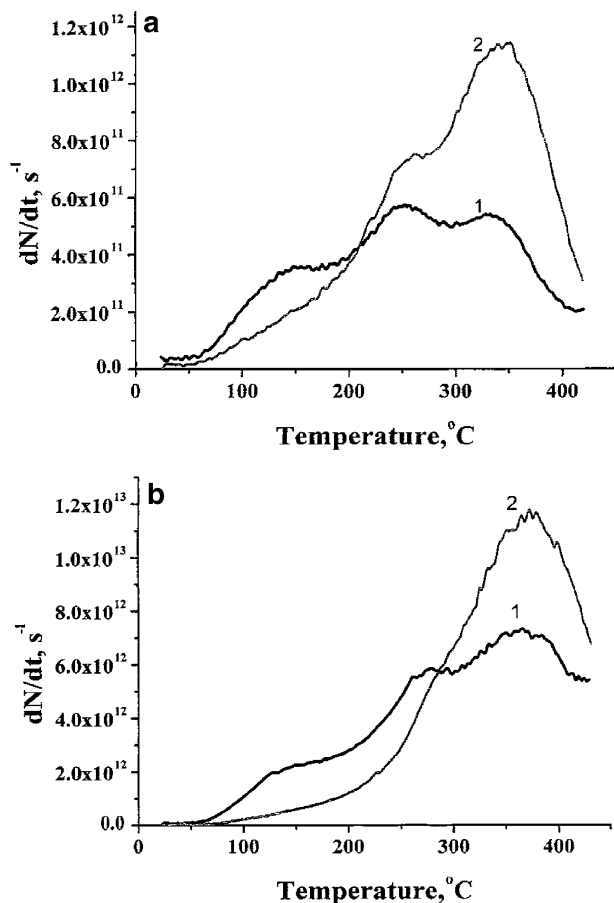
Figure 5. (a) TPD spectra of oxygen accumulated at the surface of zirconia during (1) the photostimulated adsorption of oxygen and (2) the photooxidation of hydrogen after 30 s of irradiation. (b) TPD spectra of oxygen accumulated at the surface of zirconia during (1) the photostimulated adsorption of oxygen and (2) the photooxidation of hydrogen after 6000 s of irradiation.

Figure 6. (a) Kinetics of oxygen accumulated at the surface of zirconia during the (1) photostimulated adsorption of oxygen and (2) the photooxidation of hydrogen. (b) Time evolution of the ratio between the amount of oxygen accumulated at the surface of zirconia during the photooxidation of hydrogen and the photostimulated adsorption of oxygen.

Figure 7. Difference diffuse reflectance spectra (DRS) corresponding (1) to the absorption of Zr^{3+} defect sites formed during the reduction of zirconia and (2) to surface Zr^{3+} active centers for oxygen adsorption.

approaches unity at longer irradiation times (Figure 6b). We should point out that all the forms of photoadsorbed oxygen, including those that desorb at high temperature, are actively involved in the photooxidation of hydrogen and that all disappear completely after a certain time of irradiation in the presence of hydrogen.

Low temperature adsorption forms (states) of oxygen can also be produced from "dark" adsorption on the partially reduced zirconia surface. This state of the surface was formed by heating the zirconia specimen at 600 °C under a dynamic vacuum. Following such a treatment, a new absorption band was observed in the diffuse reflectance spectra (Figure 7, curve 1), which corresponds to the absorption by Zr^{3+} states, that is by low-coordinated Zr^{4+} cations with trapped electrons.[1,22,23] Adsorption of oxygen causes the partial decrease of the absorption in this band (curve 2) as a result of electron transfer from a Zr^{3+} surface center to the oxygen molecule to form $O_2^{\bullet-}$ adsorbate species. These data are in accord with the inferences reported earlier by Liu et al.[22] that on the surface of zirconia with particles size larger than 50 nm (as is presumably the case in our experiments, taking into consideration the low surface area—see above) the thermal reduction of the surface in vacuo causes the formation of Zr^{3+} centers as a major type of defects rather than oxygen vacancies. Partial decrease of the absorption by Zr^{3+} defects suggests that these defects migrate, albeit partially, from the surface to the bulk because of the greater mobility of oxygen anions at high temperatures.[24]
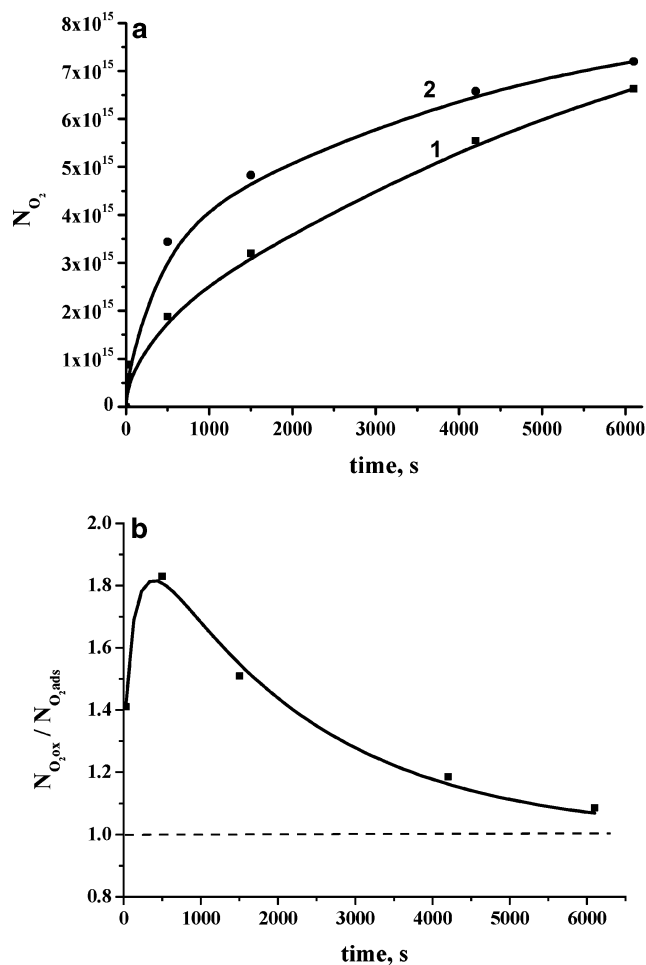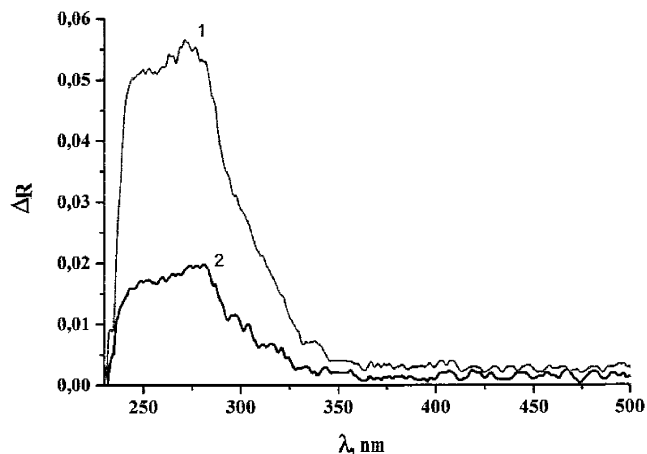
The corresponding TPD spectrum of the oxygen species adsorbed on Zr^{3+} centers formed during the surface reduction is presented in Figure 8 (curve 1); it corresponds to the first maximum in the TPD spectra of photoadsorbed oxygen and is the most reactive form in the photooxidation of hydrogen. However, the results of our experiments show that this form is
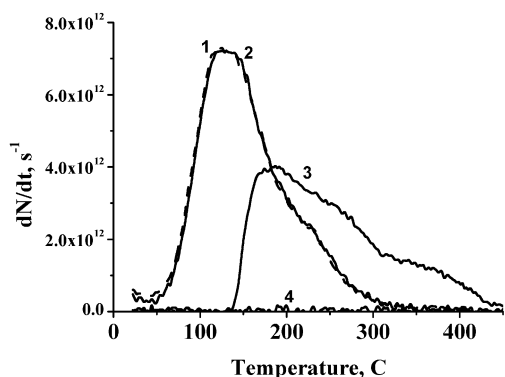
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Figure 8. TPD spectra of oxygen adsorbed on the surface of reduced zirconia before (1) and after (2) addition of hydrogen, after irradiation for 1000 s in vacuo (3), and in the presence of hydrogen (4). Note that the sample had been kept in the dark for 1000 s in the presence of hydrogen (curve 2) prior to irradiation.
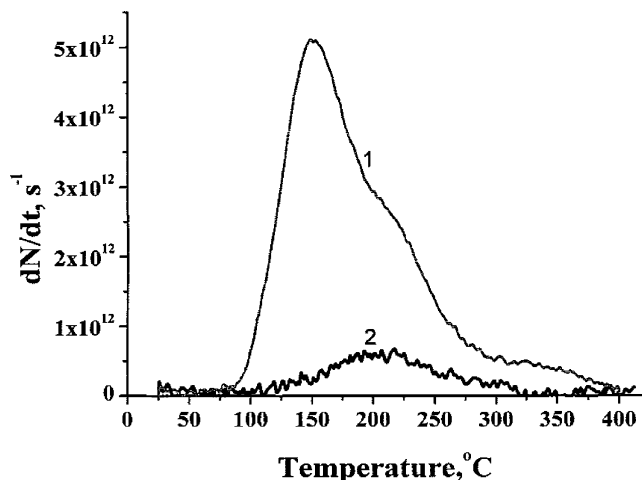

Figure 9. TPD spectra of oxygen adsorbed on the surface of reduced zirconia after irradiation for 1000 s in vacuo (1) and in hydrogen (2) of one-third of the cell area.

Figure 10. PhICL emission from (1) the irradiated area of the cell and from (2) the nonirradiated part of the cell induced by the post-adsorption of hydrogen on the irradiated surface of zirconia (amplified by a factor of 5).

absolutely inactive in the oxidation of hydrogen under dark conditions (see curve 2 in Figure 8). At the same time, this state of oxygen becomes active in the reaction with hydrogen under irradiation; its absorption feature disappeared completely under such conditions (see curve 4, Figure 8). The control experiment demonstrates that irradiation in vacuo causes the transformation of the oxygen TPD spectrum to produce only the higher temperature form(s) of oxygen but not the disappearance of oxygen on the surface (curve 3, Figure 8). Accordingly, we conclude that the low temperature oxygen forms react with hydrogen only under irradiation, and that light is the necessary factor not only for the photoadsorption of oxygen but also for the photooxidation of hydrogen.

To gain an understanding of what the activation mechanism of the photooxidation of hydrogen is, either photoactivation of preadsorbed oxygen or photoactivation of hydrogen, the following experiments were carried out. Oxygen was preadsorbed on the reduced surface of zirconia. Subsequently, the upper two-thirds of the cell were screened (masked) from irradiation, thereby precluding any photoreaction in this part of the cell. Irradiation of the system in vacuo resulted in the TPD spectrum illustrated in Figure 9 (curve 1) represented as an expected combination of curves 1 and 2 in Figure 8. However, if irradiation was carried out in the presence of hydrogen, which also led to photoadsorption of hydrogen on the irradiated part of the cell, no low temperature forms of oxygen were detected
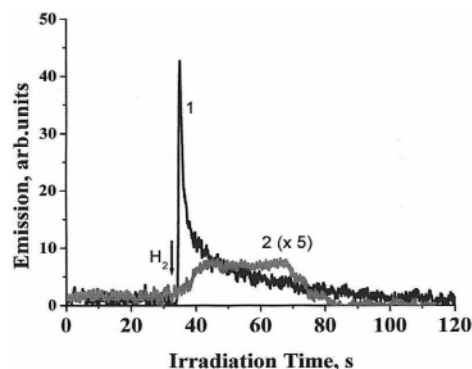
in the TPD products (curve 2, Figure 9). Therefore, we conclude that activation of hydrogen during its photoadsorption on the surface of zirconia is responsible for the photoreaction of hydrogen with preadsorbed oxygen.

The same result demonstrating that adsorption of hydrogen on photoinduced adsorption centers is responsible for the reaction with preadsorbed oxygen was obtained from the post-adsorption of hydrogen. In this experiment, the upper two-thirds section of the cell was screened from irradiation in the same manner as in the previous experiment. Irradiation of the cell was carried out in vacuo to produce long-lived photoinduced surface centers for the post-adsorption of hydrogen.[4,25,26] On termination of irradiation, hydrogen was then introduced into the cell. It must be emphasized that no reaction occurred between oxygen preadsorbed in the dark and gaseous hydrogen in the absence of irradiation. No forms of preadsorbed oxygen were detected in the TPD spectrum after introduction of hydrogen into the cell. Moreover, a photoinduced chesor-luminescence (PhICL) emission[4,25] was detected from the nonirradiated section of the cell (curve 2, Figure 10); the emission decay kinetics were completely different from the corresponding kinetics of the PhICL phenomenon seen from the irradiated part of the cell (curve 1, Figure 10). This points to a sufficient mobility and lifetime of the activated hydrogen that can reach the nonirradiated section of the cell and react with the preadsorbed oxygen whose form(s) desorbs at low temperature in the TPD spectra.

Discussion

The experimental results indicate that, after irradiation of the ZrO_2 specimen, the first stage in the photoreaction is the photostimulated adsorption of gases, which is typical of many reactions in heterogeneous (photo)catalysis. Hence, after irradiation of the metal oxide specimen, the first step of photoadsorption is generation of photoinduced surface-active centers (eqs 1 and 2) that originate from the trapping of photogenerated electrons and photogenerated holes by surface defects:

$$e^- + S(V_a; Zr^{4+}) \rightarrow S^-(\boldsymbol{F^+}; \boldsymbol{F}; Zr^{3+}) \qquad (1)$$

$$h^+ + V_c \rightarrow \boldsymbol{V}(O_s^{\bullet-}) \qquad (2)$$
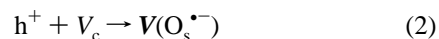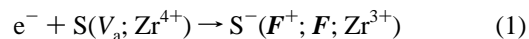
namely, anion vacancies (V_a) and Zr^{4+} cations for the electrons (eq 1) and cation vacancies (V_c) for the holes (eq 2).[1,4,25] Photoadsorption of oxygen takes place on the surface-active electron centers S^- (eq 3), which denote the active centers Zr^{3+},

F^+, and F-type surface defects:[1, 2]

$$S^- + O_2 \rightarrow (S-O_2^{\bullet-}{}_{ads}) \quad (3)$$
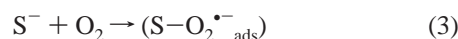
Photoadsorption of hydrogen occurs through interaction of hydrogen molecules with surface-active hole centers[1,4,25] as illustrated by

$$H_2 + O_S^{\bullet-} \rightarrow OH_S^- + H^\bullet \quad (4)$$
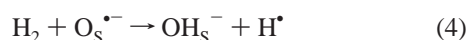
During photoirradiation of the photocatalyst in vacuo, the decay of surface-active centers arises from the recombination of trapped carriers with free charge carriers of the opposite sign (electrons or holes, respectively)[2] (eqs 5 and 6).

$$S^- + h^+ \rightarrow S \quad (5)$$

$$V + e^- \rightarrow V_c \quad (6)$$
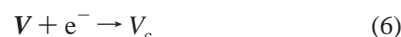
As shown in previous studies,[1,25] the photostimulated adsorption of oxygen causes the formation of photoinduced (mostly surface) hole defects of the V-type to increase by decreasing the efficiency of hole trapping by surface-active electron centers (S^-). Indeed, at sufficiently high gas pressures (the case in our experiments) the rate of photoadsorption of hydrogen is equal to the rate of generation of the corresponding surface-active centers. That is, from reaction 2 we obtain

$$\frac{dV}{dt} = k_2[h^+][V_c] \quad (7)$$

and the rate of change in the surface hole concentration is given by

$$\frac{d[h^+]}{dt} = g - \frac{[h^+]}{\tau_h} \quad (8)$$

where g is a function describing the generation of holes on the surface and τ_h is the lifetime of the holes (in vacuo) given by eq 9 and by eq 10 in the presence of oxygen.

$$\frac{1}{\tau_h} = k_2[V_c] + k_5[S^-] \quad (9)$$

$$\frac{1}{\tau_h} = k_2[V_c] \quad (10)$$

Hence, photoadsorption of oxygen leads to an increase of the lifetime of the holes and, consequently, to an increase of the hole concentration on the metal-oxide surface. This results in an increase of the rate of photostimulated adsorption of hydrogen in the presence of oxygen in the gas phase as compared to the photostimulated adsorption of hydrogen when there is no photoadsoprtion of oxygen.

The same is true for the influence of the photostimulated adsorption of hydrogen on increasing the efficiency of the photoadsorption of oxygen. In this case, adsorption of hydrogen on surface hole centers, $O_S^{\bullet-}$, destroys these defects thereby preventing electron recombination with surface trapped holes with the consequence that the surface concentration of electrons increases as does the efficiency of formation of surface-active electron centers, S^-. At the same time, as shown by the experimental results, all the oxygen forms participate in the reaction with hydrogen (curve 4, Figure 8). Those forms that desorb at low temperature and correspond to oxygen adsorption

on Zr^{3+} surface-active centers possess the highest activity in the photoreaction and essentially do not accumulate on the surface.

As shown by the EPR studies of Liu et al.,[22] oxygen adsorption on Zr^{3+} and F^+ surface-active centers results in the formation of $O_2^{\bullet-}$ adsorbed species. The same adsorption form of oxygen was detected by EPR techniques as a product of the photostimulated adsorption of oxygen[8] on photoinduced surface-active centers (see above). Therefore, we can assume that the low temperature form of oxygen in the TPD spectra is a superoxide radical anionic species $O_2^{\bullet-}$ adsorbed on Zr^{3+}. Note that this form of adsorbed oxygen possesses low activity in the dark.[22] Typically, high activity on metal oxides in processes occurring in the dark is demonstrated by the oxygen adsorbed species $O^{\bullet-}$ that are formed through dissociative adsorption of oxygen. However, since all the forms of adsorbed oxygen show no activity in the dark, we conclude that this form of adsorbed oxygen is not produced during the photostimulated adsorption of oxygen. The same conclusion can be reached with respect to the possible formation of $O_3^{\bullet-}$ species that result from the interaction of molecular dioxygen with surface-active hole centers $O_S^{\bullet-}$ since these centers remain active in the post-adsorption of hydrogen. Note that this form of adsorbed oxygen was detected on irradiated ZrO_2 only at liquid nitrogen temperatures[8] (see also Introduction). By contrast, oxygen species that desorb at the higher temperatures are much less active. It should also be pointed out that in addition to Zr^{3+} and F^+ surface-active centers, surface-active F centers can also participate in the adsorption of oxygen. However, in this case such a defect represents an anion vacancy with two trapped electrons. As a result, one can expect that oxygen adsorption on these F-type defects might result in the formation of O_2^{2-} species,[27] which possess the least activity both in the dark and under irradiation. To our knowledge there exists as yet no confirmatory evidence of the formation of such O_2^{2-} species on the zirconia surface.

A possible mechanism for the transformation of the low-temperature oxygen species to a high-temperature species might involve cleavage of the bond between the active site and adsorbed oxygen molecules to form a pre-desorbed oxygen state (eq 11)

$$\{Zr^{4+}-O_2^{\bullet-}\} \text{ or } \{Zr^{3+}-O_2\} + h^+ \rightarrow Zr^{4+} + O_{2\,ads} \quad (11)$$
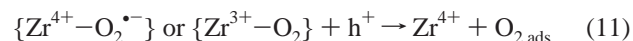
which can then interact with electron active sites, such as F-type centers, before its (photo)desorption to form new adsorbed oxygen species (eq 12).

$$F^+ + O_{2\,ads} \rightarrow \{V_a - O_2^{\bullet-}\} \quad (12)$$
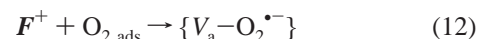
Photodesorption of oxygen from reduced zirconia was not observed under our conditions. However, the amount of oxygen remaining on the surface after UV irradiation is ca. 20−25% less than the amount of preadsorbed oxygen initially present. Note that photodesorption of pre-photoadsorbed oxygen from the oxidized zirconia surface does occur. Although this simple proposed mechanism is consistent with the experimental data, it may not be the sole pathway for the transformation on the basis of presently available data alone.

Thus, on the basis of experimental results we conclude that in addition to the photostimulated adsorption of H_2 and O_2 gases there is also the photooxidation of hydrogen. However, even the most active forms of adsorbed oxygen do not react with molecular hydrogen in the gas phase. Interaction of hydrogen with photoinduced surface-active hole centers ($O_S^{\bullet-}$) is required

to promote the reaction with photoadsorbed oxygen. Note that hydrogen adsorption is a homolytic dissociative adsorption process that produces hydrogen atoms (eq 4).
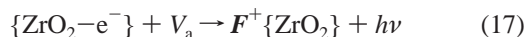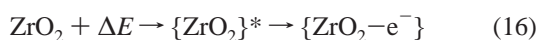
The experiments carried out with a partially irradiated cell demonstrate that these hydrogen atoms possess sufficient mobility to spillover on the nonirradiated portion of the zirconia specimen and to react with preadsorbed oxygen (eq 13) as a first step in the reaction.

$$H^\bullet + O_2^{\bullet-} \rightarrow HO_2^- \qquad (13)$$
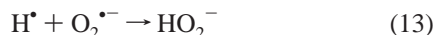
The same hydrogen atoms are responsible for the photoinduced chesorluminescence (PhICL) emission from the nonirradiated portion of zirconia through interaction either with low-coordinated surface lattice oxygen anions[4,25,27] (eq 14)

$$H^\bullet + O_S^{2-} \rightarrow OH_S^- + e^- \qquad (14)$$
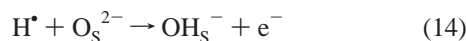
or through excitation of zirconia by the energy released from the recombination of hydrogen atoms (eqs 15 and 16),[4,25] followed by radiative electron trapping by anion vacancies (eq 17).

$$H^\bullet + H^\bullet \rightarrow H_2 + \Delta E \qquad (15)$$

$$ZrO_2 + \Delta E \rightarrow \{ZrO_2\}^* \rightarrow \{ZrO_2 - e^-\} \qquad (16)$$

$$\{ZrO_2 - e^-\} + V_a \rightarrow F^+\{ZrO_2\} + h\nu \qquad (17)$$

The same reaction sequence occurs during the photoreaction between the components in the gas mixture over zirconia. However, there is no reason to believe that the reaction of a spillovered hydrogen atom with preadsorbed oxygen is the only process that can lead to the photooxidation of hydrogen on the zirconia particle surface. It is also possible that there exists a direct interaction between hydrogen molecules and preadsorbed oxygen species, which are turned into their reactive state through photoexcitation in a way similar to the manner in which hydrogen is photooxidized on alkali halide surfaces.[28] The above mechanism remains silent on the question as to whether the photoreaction between the components of the gas mixture is a photocatalytic event, since it is not clear whether the reaction products block the active centers or whether those centers are capable of participating in the next reaction cycle.

Turnover Numbers

To answer the above query it is necessary to determine the TON of the photoprocess. If the surface-active centers were blocked by the reaction products, or if the photostimulated adsorption of gases were the only photoprocess that took place in the heterogeneous system, then the TON would likely not exceed unity. For a reaction to be described as photocatalytic, the TON must be greater than unity.[20,21]

Determination of the TON of a photoprocess necessitates an estimate of the number of surface-active centers that participate in the reaction. This has represented a most challenging problem in heterogeneous photocatalysis because there has been no quantitative description of the nature of what is typically referred to as an active center in heterogeneous photocatalysis. Typically, the concentration of the active centers on the surface of a metal oxide photocatalyst remains elusive. To complicate matters, there is also some uncertainty with the value of the area of the irradiated surface of the photocatalyst. Therefore, even if the concentration of active centers were known, it would be difficult
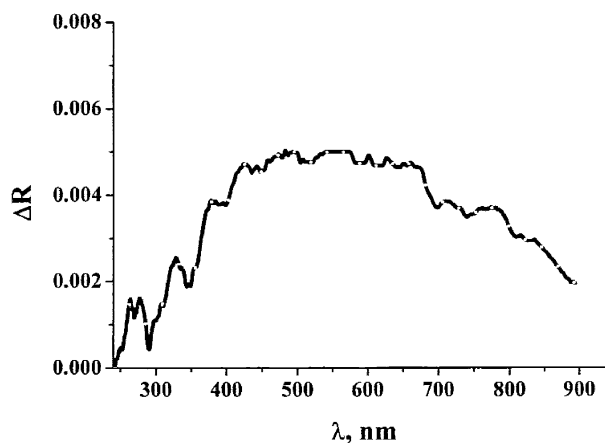

Figure 11. Difference diffuse reflectance (DRS) spectra corresponding to the absorption of long-lived active centers in the post-adsorption of oxygen.

to estimate the number of active centers actually involved in the photochemical events.

In the present study, we used the description of active centers proposed earlier[20,21] to determine the TON of a photoreaction between hydrogen and oxygen over irradiated zirconia. Three experimental approaches were considered.

The first approach is based on the known value of the post-adsorption coefficient[26] and on the application of diffuse reflectance spectroscopy (DRS) to determine the number of long-lived surface-active centers of the post-adsorption of oxygen. The difference DRS spectrum corresponding to the absorption by the surface centers for the post-adsorption of oxygen is illustrated in Figure 11. Using the coefficient reported earlier by Burukina et al.[29,30] to calculate the number of color centers from ΔR at $\lambda = 650$ nm, we obtain the number of such centers to be 1×10^{15} (eq 18).

$$N = \frac{\Delta R_{650nm}}{4.7 \times 10^{-18}} = 1 \times 10^{15} \text{ centers} \qquad (18)$$

In our recent paper,[26] we estimated the coefficient of post-adsorption of oxygen at $t \rightarrow \infty$ as $\eta = 0.1$ (eq 19):

$$\eta = \frac{N_{post-ads}}{N_{photo-ads}} = 0.1 \qquad (19)$$

where $N_{post-ads}$ is the number of long-lived centers for the post-adsorption of oxygen and $N_{photo-ads}$ denotes the total number of surface-active electron centers (both long-lived and short-lived). Therefore, the total number of surface-active centers is $1 \times 10^{15}/\eta = 1 \times 10^{16}$.

The second approach is based on the determination of the number of post-adsorbed oxygen molecules from the TPD spectrum, which we estimate as 9.4×10^{14} at sufficiently long irradiation times. Assuming that one adsorbed molecule occupies one surface-active center and taking into account the coefficient of post-adsorption $\eta = 0.1$, the total number of surface-active centers is 9.4×10^{15}, in fairly good agreement with the earlier approach that gave 1×10^{16} centers.

In the third approach, the total number of surface-active centers can also be obtained by extrapolation of the kinetic curve that represents the accumulation of photoadsorbed oxygen species obtained from the TPD spectra (see Figure 6a). This yields 8.8×10^{15} such centers as the limit of $t \rightarrow \infty$, which corresponds to the maximal number of surface-active centers, again in fair accord with the above estimates.

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The change in oxygen pressure during the photoreaction of the components in the gas mixture over zirconia (pressure, 5 Pa) corresponds to $M_{O2} = 6.2 \times 10^{16}$ oxygen molecules involved in all the photoprocesses that take place at the surface of zirconia. Consequently, TON is given by eq 20 after 6000 s of irradiation.

$$\text{TON} = \frac{M_{O2}}{N} = \frac{6.2 \times 10^{16}}{9.4 \times 10^{15}} = 6.6 \qquad (20)$$

The result suggests that on average about 6.6 molecules of oxygen react with the same surface-active center during the time course of the photoreaction. Note that the TON for the photoadsorption of oxygen is greater than unity, as required for the process to be photocatalytic.

Assuming that the total number of surface-active centers for hydrogen is about the same as for oxygen and taking into consideration that 1.4×10^{17} hydrogen molecules are involved in the reaction, the estimated TON for hydrogen is then 14.5 after 6000 s of reaction time. This means that on average about 14.5 molecules of hydrogen react with the same surface-active center during the experimental time of the photoreaction. Again the TON is greater than unity. Therefore, the nominal photoreaction between the components of the gas mixture over powdered zirconia is truly a photocatalytic process.

As evident from the TPD spectra and the kinetics of oxygen accumulation on the surface, the photostimulated adsorption of oxygen is a significant side reaction, which is the most likely factor responsible for the rather low value of TON. The same is true with respect to the photoadsorption of hydrogen. Another factor that diminishes the TON value is the strong nonuniformity of irradiation of the zirconia specimens. In this regard, because of strong light absorption, the accumulation of oxygen on the surface may already be saturated so that its photocatalytic reaction with hydrogen may have reached a stationary rate. By contrast, the photoadsorption of gases in the inner layers of the powdered specimen may still be in the initial stages of accumulation. Thus, our estimates of turnover numbers for the two photoprocesses represent but lower limits only and do not correspond to the actual TON values. This notwithstanding, however, even these lower limits confirm that the photoprocesses examined in the present study are indeed photocatalytic.

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