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Photoinduced phenomena on the surface of wide-band-gap oxide catalysts

Alexander M. Volodin

Boreskov Institute of Catalysis, Novosibirsk 630090, Russia

Abstract

This article reviews papers devoted to the investigation of photoinduced processes on non-semiconductor oxide catalysts. The main results of our ESR in situ studies of such systems are presented. Wide-band-gap oxides are shown to constitute a new and very promising class of photocatalysts capable of functioning under illumination with visual light. It is shown that in many cases the light is initially absorbed by charge transfer complexes with the following generation of ion-radical intermediates with high reactivity.

A very important feature of photoinduced reactions in the absorption band of charge transfer complexes is a significant shift of their red edge to longer wavelengths in comparison with similar processes in homogeneous systems. In many cases, the formation of such complexes is caused by the existence of strong acceptor or donor sites typical for many oxide catalysts with pronounced acidic or basic properties.

Keywords: Surface photochemistry; Wide-band-gap oxides; Electron donor–acceptor complexes; Ion-radicals

1. Introduction

Studies in the field of heterogeneous photocatalysis are primarily initiated by the demand in the development of photochemical and photocatalytic methods for utilization of the solar energy, widening of the application of photoinduced reactions in chemical and environmental technologies, and importance of such reactions for understanding of photochemical processes taking place in the earth atmosphere. The development of physical methods for investigation of the surface made it possible to study such reactions at the molecular level and obtain information on their elementary stages starting from the absorption of light and ending by the desorption of the reaction products from the surface.

The words “heterogeneous photocatalysis” are commonly associated now with processes occurring in the intrinsic absorption bands of semiconductor oxide catalysts, primarily, titanium, zinc and tin oxides [1–5]. The width of the band gap in such oxides exceeds 3 eV, which corresponds to the near-UV light. This makes the efficiency of the application of such systems for photocatalytic transformation of the solar energy relatively low and stimulates the search of new classes of photocatalysts working under illumination with visible light.

The band gap of oxide dielectrics is significantly wider than that of semiconductor materials. Therefore, the realization of photoinduced processes in their intrinsic absorption band requires irradiation with far-UV light and is absolutely ineffective from the energetic point of view. Still, such processes can play a significant role in photochemical transformations taking place on atmospheric aerosols in the upper part of the earth atmosphere [6]. Meanwhile, photoinduced

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reactions taking place on solid–gas or solid–liquid boundaries in many cases can be accomplished with the light quantum energy significantly smaller than the band gap width of the oxides used [7–12]. In these cases, of special interest are processes, in which the light is absorbed either by intrinsic surface defects of the catalyst or by adsorption complexes. Such processes called hereafter photoprocesses in the surface absorption bands will be the main topic of discussion in this paper.

Photoprocesses on oxide dielectrics containing supported transition metal ions will not be discussed here. Such systems have been already thoroughly studied and discussed in a number of good reviews [13–15]. Typically, primary light absorption in such systems is related to the excitation of a Me=O bond with the formation of long-living charge transfer complex (CTC) in the triplet state. This state has high reactivity and is responsible for chemical transformations of adsorbed molecules. It is important that known systems of this class exhibit photocatalytic activity only in the UV region. This is related to the high energy necessary for the excitation of Me=O bonds.

A significant progress in the investigation of possible applications of dispersed oxide dielectrics as photocatalysts has been achieved in the latest decade. An analysis of the recent data indicates that such systems can be considered as a new promising class of photocatalysts capable of initiating photochemical and photocatalytic transformations of adsorbed molecules under illumination not only with the UV light but also with visible light. In this case the red edge of the photoinduced reactions taking place on such systems can be below 2 eV, which corresponds to the red and even near IR light.

Naturally, the existence of surface sites capable of absorbing light in this spectral region is the key factor for accomplishing the photoinduced reactions. In our opinion, it is convenient to divide photoprocesses in the surface absorption bands of oxide catalysts into two large groups:

1. Photoprocesses induced by absorption of light in the “intrinsic” surface absorption bands, which are initiated by the primary light absorption by various surface defects and coordinatively unsaturated structures: In this case, adsorbed and gas-phase molecules can participate in the charge separation and various chemical reactions. However, their presence does not affect the spectral characteristics of the primary photoprocesses.
2. Photoprocesses induced by absorption of light in the absorption bands of adsorption complexes: In this case, light is absorbed by an adsorption complex, and spectral parameters of such processes are determined both by the structure of the surface and properties of its active sites, and by the properties of adsorbed molecules.

The first group of the processes is represented, first of all, by photoprocesses at illumination in the absorption bands of surface coordinatively unsaturated ions, which have been studied in more detail for alkaline-earth metal oxides [16–20]. It is notable that the narrowing of the band gap in the row of alkaline-earth metal oxides MgO–CaO–SrO–BaO is accompanied by a decrease of the energy required for the excitation of such surface structures. Still, for all oxides it corresponds to the UV light ($\lambda < 380$ nm) [18].

Relatively recently it has been shown that it is possible to initiate the photosorption and photocatalytic processes by the light absorption by defects created on oxide dielectrics by the preliminary UV irradiation. It has been reliably established that such preliminary irradiation results in the formation of relatively stable defects (color centers) on the surface of oxides, which are able to absorb visible light and initiate photochemical transformations of adsorbed molecules [21–25]. Most probably, such color centers can initiate photocatalytic reactions under illumination with the visible light without a need in regeneration of the sites by the UV irradiation.

Significantly different photoprocesses not related to the light absorption by a catalyst have been discovered by Frei and coworkers [26–28]. They have shown the possibility of selective photooxidation of various hydrocarbons with molecular oxygen on Y zeolites under illumination with visible light. It is interesting that the red edge of such processes appears in many cases in the region of red and near IR light. The authors believe that in such systems the light is absorbed by electron donor–acceptor (EDA) complexes located in the zeolite channels, with the following electron transfer to the oxygen molecule:

$$[\mathrm{RH} \cdot \mathrm{O_2}] \overset{h\nu}{\rightleftarrows} [\mathrm{RH}^+ \cdot \mathrm{O_2}^-]^*$$

A subsequent proton abstraction from the hydrocarbon radical cations in the above CTC seems to be the first stage of chemical transformation resulting in the formation of selective oxidation products [28]:

$$[\mathrm{RH}^+ \cdot \mathrm{O_2}^-]^* \rightarrow [\mathrm{R}^\bullet + \mathrm{HO_2}^\bullet] \rightarrow \text{Products}$$

The experimentally observed decrease of the light energy required for the excitation of the $[\mathrm{RH}\cdot\mathrm{O_2}]$ complexes in the cavities of zeolites exchanged with alkaline or alkaline-earth metal ions is very significant in comparison with similar complexes in solutions and can exceed 2–3 eV [26–28]. The authors believe that it is caused by strong electrostatic fields present in the zeolite channels, which favor stabilization of very polar charge transfer states in such complexes. Selective oxidation products formed in the photochemical reactions stay inside the zeolite channels and are reliably identified by IR spectroscopy.

Similar photoprocesses initiated by the visible light have been recently observed on Ba-exchanged zeolites of different structure (BaX, BaY, BaZSM-5) [29]. In the same paper the possibility of desorption of the photooxidation products (benzaldehyde for the photooxidation of toluene and acrolein for the photooxidation of propylene) has been demonstrated for the BaZSM-5 zeolites.

Thus, obtained experimental results indicate that photochemical and even photocatalytic selective oxidation of organic molecules by molecular oxygen can be provided on wide-band-gap oxides under their illumination with visible and even near IR light.

A significantly different type of photoinduced processes in the absorption bands of ad-complexes has been discovered and studied in our group for oxide catalysts with distinct Lewis acidity [30–33]. Such systems often possess strong surface acceptor sites ($\mathrm{A_s}$) capable of forming EDA complexes with adsorbed donor molecules (D)

$$\mathrm{D} + \mathrm{A_s} \rightleftarrows [\mathrm{D} \cdot \mathrm{A_s}]$$

Illumination of such complexes into the intermolecular electron transfer band can result in the spatial separation of charges and stabilization of radical cations on the surface, which are reliably identified by ESR. It has been shown that similar processes can also take place under thermal excitation of such complexes

$$[\mathrm{D} \cdot \mathrm{A_s}] \overset{kT,h\nu}{\rightleftarrows} [\mathrm{D}^+ \cdot \mathrm{A_s}^-]^* \rightarrow \mathrm{D}^+ + \mathrm{A_s}^-$$

Counter ions ($\mathrm{A_s}^-$) formed in this reactions are usually not observed by ESR.

Special attention has been paid to zeolites and sulfated zirconia. These are two of very few systems, for which it is possible to observe primary radical cations of adsorbed compounds and to study their reactions. It is also important that photoinduced processes in such systems can be initiated with visible light. For instance, the red edge for ZSM-5 zeolite with adsorbed benzene is close to λ=436 nm (blue light) [30–32]. Meanwhile, on sulfated zirconia, which has significantly stronger acceptor sites, benzene radical cations can be formed under illumination with green light (λ=546 nm) [33]. The possibility of the photocatalytic cracking of pentane in the presence of molecular oxygen has been demonstrated in the same paper. This reaction can also be initiated by illumination with the visible light, and, most likely, involves EDA complexes as key intermediates.

Another interesting reaction taking place under illumination in the absorption band of adsorption complexes is the reduction of aromatic nitrocompounds adsorbed on donor sites of basic oxides [32,34]. EDA complexes are key intermediates in this reaction. Their excitation into the CTC band results in the formation of radical intermediates registered by ESR.

One more interesting example of photoinduced reactions by the illumination in the absorption band of adsorption complexes is the recently discovered photoadsorption of freons on MgO under conditions similar to atmospheric ones [35,36]. In these papers it has been shown that prolonged contact of magnesium oxide with the atmosphere results in the formation of surface structures capable of initiating the photosorption processes after absorbing near-UV light ($\lambda \leq 365$ nm).

Many of the above reactions involve the formation of charge transfer states after the absorption of light. In many cases, such processes initiate spatial separation of charges followed by the stabilization of radical ions. The investigation of the structure of radical ions formed and spectral characteristics of photoinduced processes yields valuable information on the nature and properties of initial (ESR silent) surface structures responsible for the light absorption. In most cases, the concentration of such structures on the surface is low. This makes ESR with its high sensitivity the most informative method for investigation of photoinduced processes taking place on the surface of oxide catalysts.

In the present paper the results of in situ ESR studies of different classes of photoinduced processes taking place on the surface of dispersed wide-band-gap oxides are reviewed.

Experimental techniques, details on the preparation of catalysts and their pretreatment are reported in earlier papers [12,31,32]. Unless otherwise stated, the samples were subjected to a prolonged oxygen-vacuum treatment at 773 K performed to remove adsorbed water, CO_2 and "biographic" organic pollutions from the surface.

2. Photoinduced processes at illumination into intrinsic surface absorption bands

In many cases the illumination into the absorption band of intrinsic surface defects of oxides result in the charge separation and stabilization of electron and hole centers on their surface. Such centers are highly reactive and, usually, paramagnetic. Our data on the mechanism of formation of such centers on the MgO and CaO surface are presented below.

2.1. Magnesium oxide

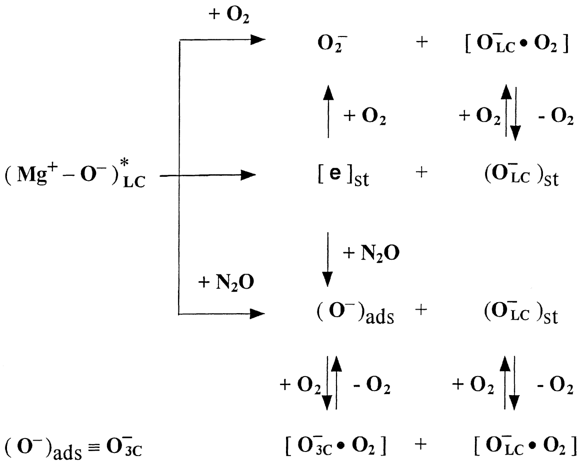
Magnesium oxide is one of the most widely studied systems with respect to the identification of the radical forms of oxygen stabilized on its surface [18,32,37]. The absorption bands associated with the excitation of surface low-coordinated structures $(Me^{2+}–O^{2-})_{LC}$ including 3- and 4-coordinated oxygen anions are readily distinguished in the luminescence excitation and diffuse reflectance spectra [16–18]. The role of such structures in photocatalytic processes has been studied in detail. As in the case of catalysts containing transition metal ions, the photoexcitation of such structures results in the formation of a charge transfer state, which initiates photocatalytic reactions [19,20]:

$$(Mg^{2+}–O^{2-})_{LC} \overset{h\nu}{\rightleftarrows} (Mg^{+}–O^{-})_{LC}{}^{*} \rightarrow \text{photocatalysed reaction}$$

Absorption bands of surface low-coordinated structures $(Me^{2+}–O^{2-})_{LC}$ including 3-coordinated (λ=274 nm) and 4-coordinated (λ=230 nm) oxygen anions are readily distinguished for MgO [16–18]. The photocatalytic activity of magnesium oxide is observed in the same spectral region [19,20]. Note that the excitation of bulk and subsurface F-type defects (anion vacancies with one or two electrons, F^{+} and F sites, respectively) is possible on MgO in the similar spectral region. This excitation is accompanied by the generation of charge carriers and can result in the photoadsorption of molecules from the gas phase with their further chemical transformations [21].

A detailed investigation of the formation of different types of oxygen radical anions under MgO illumination has shown that in all cases they are related to the primary light absorption by coordinatively unsaturated surface structures and can be described by the following scheme [32,38,39]:

$$(Mg^{2+}–O^{2-})_{LC} \overset{h\nu}{\rightleftarrows} (Mg^{+}–O^{-})_{LC}{}^{*}$$



In the same papers it has been shown that the efficiency of the charge separation and stabilization of electron and hole defects during the illumination of the MgO surface under vacuum is not high. The memory effect to the prior illumination does not exceed 3–5% for magnesium oxide. The introduction of acceptor molecules, such as O_2 or N_2O, results in a 20–30-fold increase of the charge separation efficiency and corresponding growth of the concentration of different oxygen radical anions stabilized on the MgO surface.

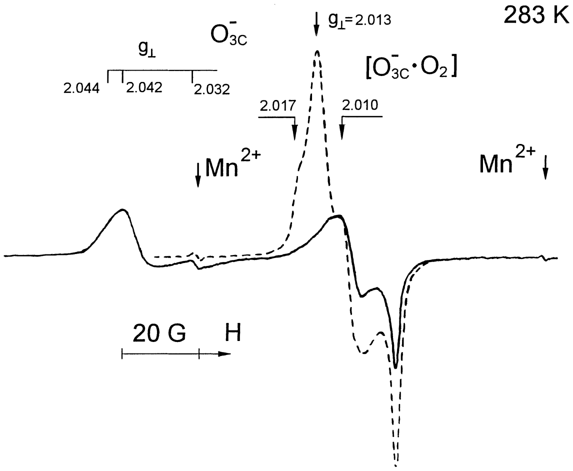


Fig. 1. ESR spectra of MgO observed after illumination (λ=280 nm) at 298 K and O_2 pressure 13 Pa (dashed line) and after following 30 min evacuation at 298 K (solid line). The spectra are registered at 283 K.

Fig. 1 presents typical ESR spectra of radical forms of adsorbed oxygen formed during photoadsorption at 283 K. The formation of O_{3C}^- radical anions ($g_\perp$=2.042, $g_{||} \cong g_e$), which are transformed into $[O_{3C}^- \cdot O_2]$ complexes ($g_\perp$=2.013, $g_{||} \cong g_e$) in the presence of oxygen in the gas phase, is reliably registered under these conditions [40,41]. The heat of the formation of such complexes measured under equilibrium conditions is 77±5 kJ/mol [41].

Photoinduced processes on the MgO surface result in the stabilization of (O^-) radical anions in different coordination: O_{3C}^- and O_{4C}^- with significantly different spectral manifestations (Table 1) and chemical properties. Their appearance is due to the differences in the coordination of oxygen anions in the initial complexes $(Me^{2+}–O^{2-})_{LC}$ responsible for the primary light absorption. It is interesting that O_{ads}^- radical anions resulting from the decomposition of N_2O molecules on the electron sites are always identical to O_{3C}^- radical anions [32].

Note that on MgO, all discussed photoprocesses require irradiation with UV light ($\lambda \leq 300$ nm).

2.2. Calcium oxide

In general, the mechanism of the photoinduced formation of radical forms of adsorbed oxygen on CaO is similar to that presented above for MgO. However, there are a number of differences between the two systems [32,42,43]:

1. Illumination with longer wavelength ($\lambda \leq 365$ nm) is required for initiation of photoprocesses on CaO.
2. The memory effect to prior irradiation exceeds 30% on CaO (in comparison with 3–5% on MgO).
3. O^- radical anions in different coordination O_{3C}^- and O_{4C}^- similar to those observed on MgO can be formed on CaO as well. However, neither of them can be observed by ESR directly. Their identification and investigation require different test reactions. The formation of complexes with molecular oxygen $[O_{LC}^- \cdot O_2]$ with typical ESR spectra is the most convenient among them (Table 1).

Fig. 2 presents typical ESR spectra observed after the illumination of an oxidized CaO sample in the presence of molecular oxygen. Note that the spectral regions of the photoinduced formation of complexes $[O_{3C}^- \cdot O_2]$ and $[O_{4C}^- \cdot O_2]$ are significantly different. The illumination near the red edge of the absorption (λ=365 nm) results in the preferential formation of $[O_{3C}^- \cdot O_2]$ complexes. An increase of the light energy (λ=303 nm) increases significantly the efficiency of the formation of $[O_{4C}^- \cdot O_2]$ complexes.

Table 1
Parameters of the EPR spectra of different types of O^- and $[O^- \cdot O_2]$ complexes observed on the MgO and CaO surfaces [32,40–43]

	O_{3C}^-		$O_{3C}^- \cdot O_2$			O_{4C}^-	$O_{4C}^- \cdot O_2$		
	$g_\perp$	$g_{||}$	g_1	g_2	g_3		g_1	g_2	g_3
MgO	2.033÷2.044	2.002	2.017	2.010	2.002	[a]n.o.	2.015	2.010	2.002
For T>250 K			$g_\perp$=2.013, $g_{||}$=2.002						
CaO	n.o.		2.015	2.009	2.002	n.o.	$g_\perp$=2.012, $g_{||}$=2.004		
			2.016	2.009	2.002				

[a] Anion-radicals not observed in EPR.

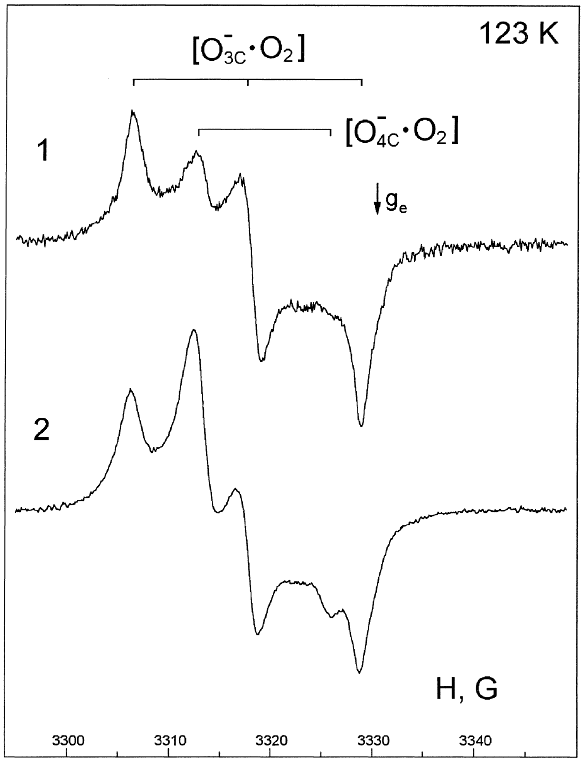


Fig. 2. ESR spectra of CaO observed at 123 K and O_2 pressure 4 Pa after illumination (λ=365 nm) for 70 min (1) and after additional illumination (λ=303 nm) for 10 min (2). The spectra are registered at 123 K.

Thus, it is possible to affirm that the formation of radical forms of adsorbed oxygen on the CaO surface during its illumination in the surface absorption band involves different types of low-coordinated surface oxygen anions. In all cases this process can be described by the scheme shown earlier for MgO.

The electron and hole centers are formed under illumination and stabilized on the surface due to the existence of definite defects on the initial oxide surface. Therefore, the ratio between different types of radical forms of adsorbed oxygen formed under illumination and their concentrations give information on the nature and concentration of surface defects on which the light absorption with the following stabilization of the radical particles takes place. From this point of view, it was interesting to study the effect of the CaO activation temperature on the photoinduced reactions. Naturally, similar conditions were used for the generation of the radical particles on different samples.

Fig. 3 presents the results of such experiments. One can see that an increase of the CaO dehydroxylation temperature results in a significant redistribution between the concentrations of O_{4C}^- radical anions (registered as $[O_{4C}^- \cdot O_2]$ complexes) and O_{3C}^- radical anions (registered as $[O_{3C}^- \cdot O_2]$ complexes) with an increase of the latter. It is important that such a change of the state of the surface is not related to the removal of surface oxygen, as the treatment in oxygen at any temperature does not regenerate the initial state of the catalyst. Meanwhile, even a short treatment of such sample with H_2 leads to a complete regeneration of the surface with respect to the reactions under study.

This phenomenon can be most naturally related to the reversible dehydroxylation of the CaO surface dur-

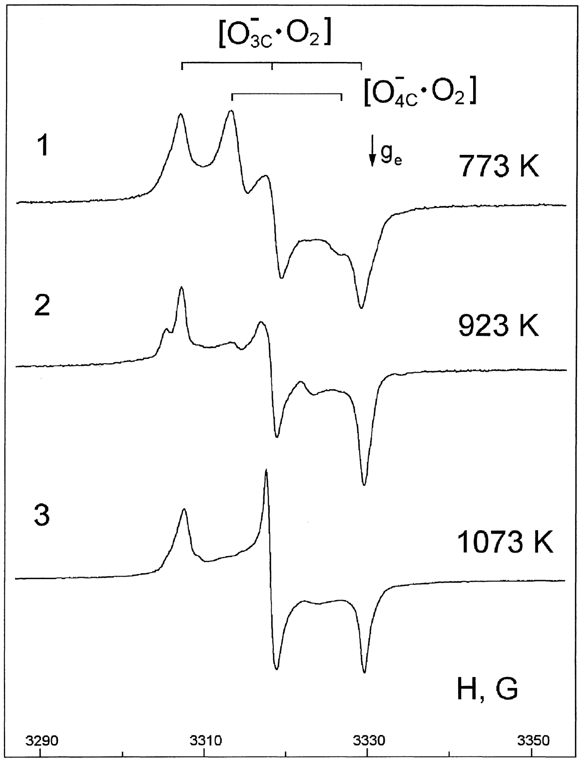


Fig. 3. Effect of CaO evacuation temperature on the formation of different forms of adsorbed oxygen during illumination under similar conditions (T=143 K, λ=313 nm, t=40 min, $P(O_2)$=4 Pa). The spectra are registered at 143 K.

ing the high-temperature treatment. This indicates that $O_{3C}{}^-$ and $O_{4C}{}^-$ radical anions described in the present review and their non-paramagnetic precursors are distinguished by the presence of an additional hydroxyl group in the coordination sphere of the 4-coordinated anions. This fact makes it possible to understand why $O_{ads}{}^-$ radical anions formed during the N_2O decomposition as a result of the interaction of oxygen atoms with the surface electron sites are always identical to $O_{3C}{}^-$ radical anions. This appears to be connected with the need in the appearance of additional ligands formed during the surface hydroxylation in the coordination sphere of the $O_{3C}{}^-$ radical anions for the formation of $O_{4C}{}^-$ particles.

The available literature data indicate that the oxygen adsorption on CaO activated under vacuum at high temperature (T>1173 K) results in the formation of radical anions stabilized on the surface [44,45]. The ESR spectra presented in these papers seem to evidence the formation of $O_2{}^-$ radical anions and $[O_{3C}{}^- \cdot O_2]$ complexes. This brings also natural questions: what processes result in the formation of radical anions without illumination and why do they result in the formation of electron ($O_2{}^-$) and hole ($O_{3C}{}^-$) centers? It is very likely that the formation of the radical forms of adsorbed oxygen in such processes follows the same mechanism as in the case of light-induced processes involving the excitation of surface complexes:

$$(\mathrm{Me}^{n+}\text{–}\mathrm{O}^{2-})_{\mathrm{LC}} \overset{\Delta E}{\rightleftarrows} (\mathrm{Me}^{(n-1)+}\text{–}\mathrm{O}^{-})_{\mathrm{LC}}{}^{*}$$

The energy needed for the formation of the excited state can result from the reoxidation of the reduced oxide or its structural rearrangement. The possibility of the formation of oxygen radical anions via such a mechanism was earlier shown for the reoxidation of partly reduced vanadium oxide with molecular oxygen [46].

The data reported in this section indicate that in all cases the formation of charge transfer complexes with the following charge separation is a necessary stage for the generation of various oxygen radical anions on the surface of wide-band-gap oxides. Such radical anions have high reactivity. Therefore, their formation in the photoinduced processes discussed above can be considered to be the first stage of photochemical and photocatalytic transformations of various molecules on the surface of oxide dielectrics.

3. Light-induced processes of ion-radical formation at illumination in the absorption band of adsorption complexes

The adsorption of various molecules on the surface of oxide catalysts with wide-band-gap possessing pronounced acidic or basic properties is often accompanied by the appearance of noticeable coloring. This indicates the formation of surface ad-complexes capable of absorbing visible light. The investigation of the nature of such complexes as well as the possibility of the initiation of photochemical and photocatalytic reactions by illumination into this absorption band are of considerable importance. The simplest situation takes place in the case of the formation of EDA complexes between adsorbed molecules and donor or acceptor surface sites of the catalysts. The existence and strength of such sites are usually connected with the acidic or basic properties of oxide catalytic systems. The illumination of EDA complexes into the charge transfer band can often result in the initiation of ion-radical reactions. The observed shift of the spectral region of such photoprocesses is a function of the electron affinity of the acceptors and ionization potential of donors forming the EDA complexes. Therefore, their red edge can be used for comparison of the strength of donor and acceptor sites on the surface of different oxide systems.

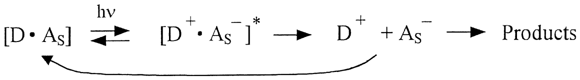
The investigation of photoinduced processes in the absorption bands of adsorption complexes was performed by in situ ESR. This method has high sensitivity and often makes it possible to identify primary ion-radical products formed under illumination as well as to follow their subsequent chemical transformations.

3.1. Photoinduced processes with participation of radical cations on ZSM-5 zeolites and sulfated zirconia

The possibility of the formation of aromatic radical cations stabilized on the surface of oxide materials during their illumination with UV light or γ-irradiation is known for a long time [47–49]. However, only recently it was shown that it is possible to perform similar photoprocesses on the surface of acid catalysts with very strong acceptor sites under illumination with visible light [30–33]. The formation of benzene radical cations on ZSM-5 zeolites and sulfated zirconia has been studied in detail.

Benzene has relatively high ionization potential (I_P=9.24 eV). Therefore, its EDA complexes even with the strongest organic acceptors (trinitrobenzene, tetracyanoethylene, etc.) in homogeneous systems, and absorb in the near-UV spectral region [50]. The absorption of the EDA complexes formed after adsorption of the benzene molecules on acceptor sites of chlorinated alumina is observed in the same spectral region [51]. However, for ZSM-5 zeolites and sulfated zirconia with very strong acceptor sites a significant red shift of the absorption of such complexes is observed. So, the formation of benzene radical cations is possible even under illumination with visible light (Fig. 4).

The radical cations formed are stable up to 180–220 K. A further temperature increase leads to their destruction resulting from the recombination processes and secondary transformations. In general, the processes under discussion can be described by the following scheme:



$$[\mathrm{D}\cdot\mathrm{A_S}] \overset{h\nu}{\rightleftarrows} [\mathrm{D}^{+}\cdot\mathrm{A_S}^{-}]^{*} \longrightarrow \mathrm{D}^{+} + \mathrm{A_S}^{-} \longrightarrow \text{Products}$$

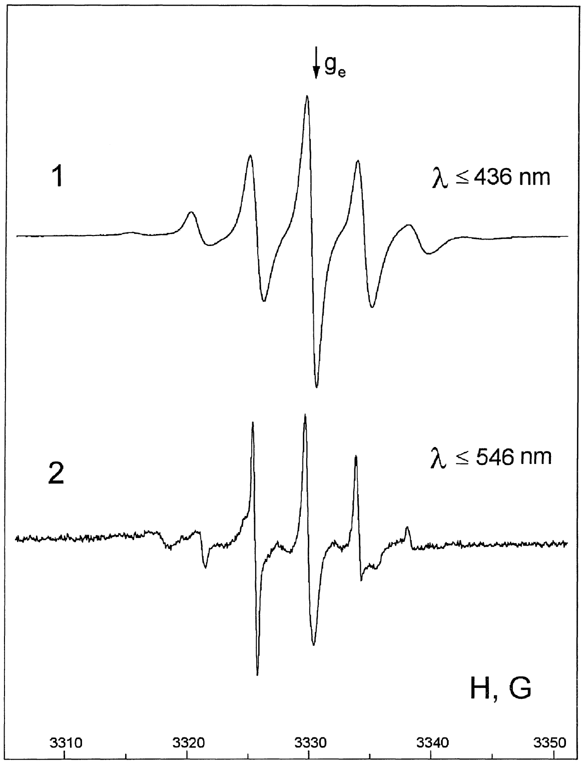


Fig. 4. ESR spectra of photoinduced benzene radical cations on ZSM-5 zeolite (1) and on sulfated zirconia (2).

No information on the chemical nature of products resulting from such secondary transformations are available to date. However, there is no doubt that some products are formed. These processes account for considerable irreversible changes of the initial state of the system with respect to the following illumination (Fig. 5).

Reversible broadening of the ESR spectra of photoinduced benzene radical cations is observed in the presence of paramagnetic oxygen molecules in the gas phase. This indicates that they are stabilized on the surface and are accessible to vapor-phase molecules. So, it is possible to investigate their interaction with various gaseous molecules in a wide temperature range.

The photocatalytic cracking of pentane on the surface of sulfated zirconia is one of the few known examples of photocatalytic reactions on the surface of wide-band-gap oxides. The isomerization of pen-

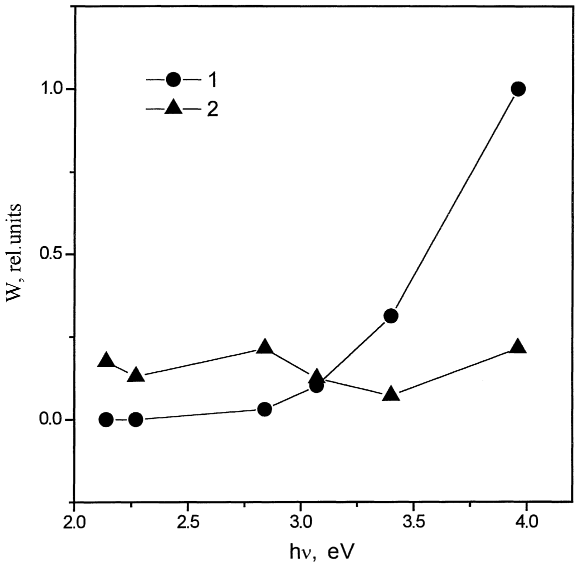


Fig. 5. Effect of light wavelength on the initial rate, *W*, of formation of the benzene radical cations on ZSM-5 zeolite at 123 K. 1 — initial sample, 2 — sample after prolonged illumination (λ=365 nm) followed by relaxation at 295 K.

tane to *iso*-pentane with 98% selectivity takes place on this catalyst at room temperature. *iso*-Butane and branched hexanes are formed as side products in small amounts. The illumination of the reaction mixture in the oxygen atmosphere results in a significant increase of the *iso*-butane yield (Fig. 6). The reported data indicate that the cracking process can be initiated even by the illumination with yellow light (λ=578 nm). In all cases, *iso*-butane and branched hexanes are formed in close molar amounts. This indicates that the photoinitiated process involves the formation of C_{10} intermediates.

The effect of light on the pentane cracking appears to indicate that the reaction is initiated on strong surface acceptor sites by the electron transfer in surface EDA complexes with the formation of very unstable radical cation intermediates. An obvious induction period indicates that the adsorption complexes that absorb the light are formed in the course of the reaction. Most probably, such complexes contain *iso*-pentane, which is the major product of the reaction. In this case, the photocatalytic process can be described by the following scheme:

$$\text{Pentane} \rightarrow \textit{iso}\text{-pentane} \rightarrow \textit{iso}\text{-butane} + \sum \textit{iso}\text{-hexane}$$

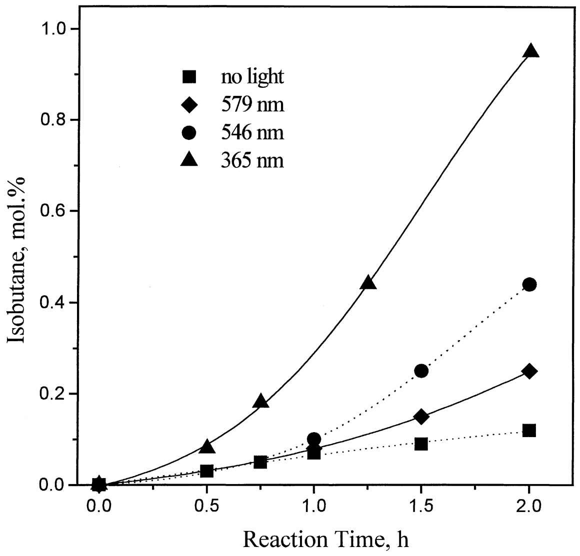


Fig. 6. Effect of illumination on *iso*-butane yield during the pentane conversion on sulfated zirconia at 300 K.

The concentration of strong acceptor sites on the sulfated zirconia samples studied does not exceed 5×10^{16} sites/g. For the *iso*-butane formation process, the estimation of the turnover number based on this amount of active sites under study gives the value of about 10^4 for the experiment with the use of green light [33]. This means that the observed cracking reaction is indeed photocatalytic. Most likely, similar photoreactions can be realized on other types of acid catalysts with sufficiently strong acceptor sites.

3.2. Photoinduced reduction of aromatic nitrocompounds on surface donor sites of oxides and in donor solvents

The formation of Ph–N(O)$^\bullet$–OR nitroxyl radicals in homogeneous systems during the photolysis of aromatic nitrocompounds (NB) in the presence of molecules acting as donors of hydrogen atoms (D) is known in the literature [52,53]. Usually it is considered that the first stage of such processes involves the light absorption by the nitrocompound with the subsequent reaction of its triplet excited state with a donor molecule. However, the studies of the spectral characteristics of these reactions have shown that the position of their red edge depends on the ionization potential of the donor molecules used (Table 2). This brought us to the conclusion that the formation of radicals in such systems results from the primary light absorption by EDA complexes and can be described by the following scheme [54]:

$$\mathrm{NB} + \mathrm{D} \rightleftarrows [\mathrm{NB}\cdot\mathrm{D}] \overset{h\nu}{\rightleftarrows} [\mathrm{NB}^- \cdot \mathrm{D}^+]^* \rightarrow \mathrm{R}^\bullet$$

It was shown that similar transformations could take place for nitrobenzene molecules adsorbed on the surface donor sites (D_S) of alumina. In this case,

Table 2
Dependence of the position of the red edge of the light-induced formation of radicals on the ionization potential, I_P, of solvent for sym-trinitrobenzene and sym-trichlorotrinitrobenzene in a homogeneous solution and for nitrobenzene on the surface of γ-Al_2O_3

Acceptor	Toluene, I_P=8.78 eV	*o*-Xylene, I_P=8.56 eV	Mesitylene, I_P=8.40 eV
TNB	3.4	3.04	2.85
TCTNB	3.04	2.85	–
Nb_{ads}/Al_2O_3	2.85	2.3	–

the photochemical reaction requires the formation of three-component complexes including a donor surface site, a nitrobenzene molecule adsorbed on it and a donor solvent molecule [32,55]:

$$\mathrm{NB} + \mathrm{D_s} \rightleftarrows [\mathrm{NB}\cdot\mathrm{D_s}] \overset{+\mathrm{D}}{\rightleftarrows} [\mathrm{D}\cdot\mathrm{NB}\cdot\mathrm{D_s}]$$

$$[\mathrm{D}\cdot\mathrm{NB}\cdot\mathrm{D_s}] \overset{kT,h\nu}{\rightleftarrows} [\mathrm{D}\cdot\mathrm{NB}\cdot\mathrm{D_s}]^* \rightarrow {}^{\bullet}\mathrm{R_{st}}$$

The donor solvent molecules (D) appear to be an integral part of such complexes and their properties determine the spectral characteristics of the photoprocesses.

Comparing the results obtained for the photolysis of sym-trinitrobenezne (TNB) and a stronger acceptor sym-trichlorotrinitrobenzene (TCTNB) in solution with similar data on nitrobenzene (NB) adsorbed on surface donor sites of alumina (Table 2), it is natural to conclude that the surface photoprocesses require significantly lower energies of light than the analogous homogeneous ones. This means that the NB molecule adsorbed on the surface active sites has substantially stronger acceptor properties with respect to the donor molecules than TNB and TCTNB molecules. This makes it possible to carry out photochemical reactions with the participation of aromatic nitrocompounds in the adsorption layer even under illumination with visible light.

3.3. Photoinduced formation of O_2^- *radical anions on* ZrO_2 *surface in the presence of adsorbed organic molecules*

The formation of molecular oxygen radical anions O_2^- during the oxygen adsorption on oxide materials containing adsorbed organic molecules is well known (see, e.g. [56–58]). It is usually supposed that a heterolytic dissociation of a hydrocarbon molecule on an acid–base pair is the first stage of such processes:

$$\mathrm{R{-}H} + (\mathrm{O}^{2-})_{\mathrm{surf}} \rightarrow (\mathrm{OH}^-)_{\mathrm{surf}} + \mathrm{R_{ads}}^-$$

The carbanion formed donates easily an electron to an oxygen molecule to form both molecular oxygen radical anion O_2^- stabilized on the surface and very unstable radical intermediates

$$\mathrm{R_{ads}}^- + \mathrm{O_2} \rightarrow \mathrm{O_2}^- + \mathrm{R}^{\bullet}$$

Such reactions have been studied in more detail for alkaline-earth metal oxides. They are related to the presence of low-coordinated ions on their surface. Interestingly, even methane can be involved in such reactions over MgO samples activated at temperatures above 973 K [59].

Earlier we have shown that similar processes can be accomplished on the surface of zirconium dioxide [60]. Prior to the experiments, the samples were subjected to the activation in air or under vacuum in the temperature range of 573–973 K. It was found that the photoinduced formation of O_2^- radical anions on such catalysts is possible even under irradiation with visible light (Fig. 7).

In all cases it was possible to initiate this process both thermally and by illumination. An increase of the activation temperature resulted in a decrease of the

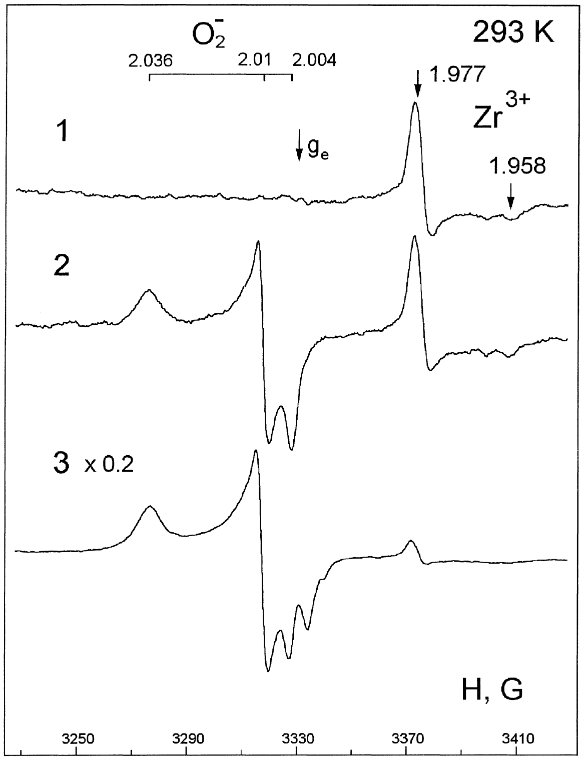


Fig. 7. ESR spectra of the oxygen radical anions formed at room temperature in 24 h after O_2 adsorption on ZrO_2 with preadsorbed toluene (1); after additional illumination (λ=436 nm) for 30 min (2); and after illumination with unfiltered mercury lamp light for 5 min (3).

activation energy of thermal reactions and a shift of the red edge of the light-induced reactions to longer wavelengths.

The maximum achievable concentration of O_2^- radical anions is determined by the concentration of the sites where the radical anions can be stabilized. This concentration depends only on the preparation procedure of the zirconia sample, being not affected by the temperature of its activation and the method used for the generation of the radicals. The sites are formed during the preparation of the catalysts. Then, their concentration is not changed during the following thermal treatments at temperatures below that of the initial calcination step [60].

There is no doubt that the adsorption complexes accounting for the primary light absorption in such systems must contain a surface site (S), an adsorbed donor hydrocarbon molecule (or a product of its dissociative chemisorption) (D), and an acceptor O_2 molecule. Most likely, the general scheme of such reaction is similar to that presented above for the description of the reduction of aromatic nitrocompounds. It is very likely that the first step is the formation of adsorption EDA complexes responsible for the absorption of light. The thermal or light-induced excitation of such complexes results in the charge separation and stabilization of O_2^- radical anions on the surface:

$$\mathrm{D} + \mathrm{S} \rightleftarrows [\mathrm{D}\cdot\mathrm{S}] \overset{+\mathrm{O}_2}{\rightleftarrows} [\mathrm{O}_2\cdot\mathrm{D}\cdot\mathrm{S}]$$

$$[\mathrm{O}_2\cdot\mathrm{D}\cdot\mathrm{S}] \overset{kT,h\nu}{\rightleftarrows} [\mathrm{O}_2\cdot\mathrm{D}\cdot\mathrm{S}]^* \rightarrow \mathrm{O}_2^-$$

The available experimental data are not sufficient to make a final answer on the composition of the complexes responsible for the absorption of light in such systems. No information on the structure of oxidation products formed in these processes is available to date. Still, the fact of the initiation of such photochemical reactions by visible light is important as it is.

4. Conclusion

The analysis of the available literature data and experimental results presented in this review makes it possible to claim that the wide-band-gap oxides form a new promising class of photocatalytic systems capable of working under illumination with visible light. In most cases, charge transfer complexes are responsible for the primary light absorption in such systems, which can result in the formation of highly reactive ion-radical intermediates.

Another important feature of photoinduced reactions at illumination in the absorption band of the ad-complexes consists in a significant shift of the red edge of such processes to longer wavelengths in comparison with similar processes in the respective homogeneous systems. The value of this shift is determined by the properties of the surface active sites. The formation of such complexes are related to the presence of strong surface acceptor or donor sites typical for many oxides with pronounced acidic or basic properties.

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