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Photoadsorption and photocatalytic oxidation on the metal oxides Components of tropospheric solid aerosols under the Earth's atmosphere conditions

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Abstract

An overview on quantitative characteristics (quantum yield, action spectrum, maximum amount of photoadsorbed molecules) of photoadsorption and photocatalytic processes on some metal oxides, which are main components of the tropospheric solid aerosols, is presented. For the example of MgO, it is shown that the quantitative characteristics of photoadsorption of freons obtained for the air-exposed MgO samples are significantly different from that obtained for the samples experiencing a rigid pretreatment.

It is supposed that a sensitization of insulator oxides to the solar radiation spectrum in the troposphere may be due to the formation of an adlayer on their surface under conditions of the Earth's atmosphere. © 1997 Elsevier Science B.V.

Keywords: Atmosphere; Aerosols; Photocatalysis; Photoadsorption

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1. Introduction

Recently, much attention was given to the processes on tropospheric aerosols containing semiconductor oxide photocatalysts like ZnO, TiO_2 and Fe_2O_3 (see, e.g., [1]). These oxides (except for the latter) are present in the troposphere in comparatively small amounts. The troposphere contains significantly more insulator oxides, such as SiO_2, Al_2O_3, MgO, CaO, which are the main components of continental aerosols [2]. The semiconductor oxides are mostly known as the various photocatalysts of redox reactions, being active in the presence of relatively "mild" solar radiation (near UV and VIS light) [3]. For the insulator oxides, on exposure to this radiation, photoadsorption properties are more characteristic [4].

To clarify the real role of photoadsorption and photocatalysis on tropospheric solid aerosols in the formation of the Earth's atmosphere composition, the quantitative studies of these processes are needed in conditions close to the atmospheric ones.

2. Atmospheric conditions

In contrast to "conventional" adsorption and catalytic oxidation, that typically occur very slowly at low temperature, the tropospheric conditions are rather favourable to both photoadsorption and photocatalytic oxidation due to some peculiarities of photoinduced processes. Indeed, photoadsorption and photocatalytic

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Table 1
Partial pressure of the main gas-phase components of the Earth's troposphere at the background conditions (according to [5])

Tropospheric component	Partial pressure (Torr)
N_2	590
O_2	160
H_2O	<18
CO_2	10^{-1}
CH_4	10^{-3}
H_2	4×10^{-4}
N_2O	2×10^{-4}
CF_2Cl_2 (freon 12)	10^{-4}
$CFCl_3$ (freon 11)	10^{-4}
CO	5×10^{-5}
SO_2	5×10^{-5}
NO_2	10^{-5}
NO	10^{-5}
H_2S	5×10^{-6}
O_3	2×10^{-5}–2×10^{-6}
NH_3	10^{-6}
CCl_4	10^{-7}

processes have typically a negligible or even negative activation energy [3], and for this reason they can occur both at moderate and low temperatures (ca. 300 K and below) and at small concentrations of an oxidized component (its partial pressures ca. 10^{-6} Torr). Also, in the troposphere it is easy to meet the condition to illuminate the whole surface of the solid aerosol particles.

The partial pressures of the main inorganic gas-phase components of the Earth's atmosphere near its surface, that may contribute to photoadsorption and photocatalysis on solid aerosols, are given in Table 1 (the data are taken from the handbook [5]).

The troposphere is reached by the solar radiation with the wavelength >300 nm that can be absorbed only by nitric dioxide, as well as solid aerosols having semiconductor oxides in its composition. The latter oxides have the red edge of band-to-band absorption in the visible and near UV regions of solar spectrum with very high absorption coefficient $\sim10^4$ cm^{-1}; however their concentration (except of iron oxides) in composition of common continental and marine solid aerosols is low [2]. Concentration of insulator oxides in the aerosols is considerably higher (on an average there are up to 50% SiO_2 and 15% Al_2O_3 in composition of the continental tropospheric aerosols [6]), but being in a "pure" state, these oxides are able to absorb light efficiently only in the regions of wavelength shorter than 300 nm. For these insulator oxides to absorb the solar radiation with λ>300 nm, they need to be sensitized to this spectral region. Sensitization of the metal oxides in atmospheric conditions is possible as a result of both their doping with certain impurities and formation of surface compounds, e.g., after adsorption of gas-phase components of the atmosphere. So, the authors of [7] observed sensitization of tin dioxide to the visible region of the solar spectrum upon adsorption of carbon monoxide on its surface. Note that the composition of the adsorbed layer of the aerosols oxide is determined either by a relatively high concentration of the corresponding compounds in the atmospheric gas phase or by selectivity of the adsorption by components of the solid aerosol.

Indeed, in the tropospheric conditions, the oxides are affected by the gas components of the atmosphere, and primarily by the components having the higher partial pressure. According to Table 1, the latter are water, carbon dioxide and nitrogen oxides. So, according to recent studies [8] for magnesia obtained from $Mg(OH)_2$ and exposed to the atmosphere for a long time, the amount of adsorbed compounds attained are: NO and N_2 (from nitrogen oxides) ca. 1% of monolayer, CO_2 ca. 10% of monolayer, H_2O ca. one monolayer. The total amount of the adsorbed compounds in this situation equals 5 wt% (according to the data of derivatographic analysis).

Traditionally before performing experiments or using in various chemical processes, the surfaces of adsorbents and catalysts (including photoadsorbents and photocatalysts) are exposed to rigid pretreatment of various kinds. The main goal of this pretreatment (e.g., in vacuum, in an appropriate gas environment, at a certain pressure and temperature, etc.) is usually to obtain either reproducible results, which are consistent with those of other researchers, or the maximum of adsorption or catalytic (accordingly, photoadsorption or photocatalytic) activity. However, it is essential that the rigid pretreatment of a surface may result in some sufficient changes of chemical composition of the adsorption layer, stoichiometry of the surface and near-surface layers of an adsorbent or a catalyst.

In the natural atmospheric conditions, the aerosol particles are not exposed to any rigid pretreatment of the above mentioned types. So, the state of their surface corresponds approximately to the state of an

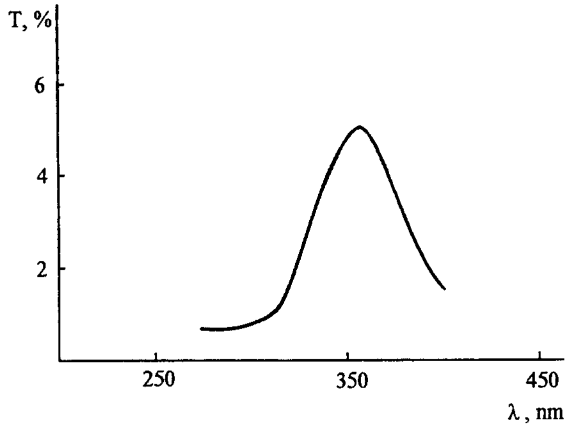

Fig. 1. A diffuse reflectance spectrum of the air-exposed MgO relative to a magnesium hydroxycarbonate reference.

insulator oxide surface obtained in rather "mild" conditions after long-duration contact with air. Thus, the (photo)catalytic and (photo)adsorption properties of the air-exposed oxide can differ sufficiently from those of pretreated oxides.

For example, the atmosphere exposed magnesia was found to absorb light with wavelengths shorter than 400 nm with maximum at 360 nm (Fig. 1) [8], while such absorption being absent on the magnesia samples exposed to a rigid oxygen-vacuum pretreatment: the red edge of band-to-band absorption by magnesia is known to be located near 178 nm. (In the above studies a magnesium hydroxycarbonate was utilized as the reference standard for diffusive reflection.)

3. Photoadsorption and photocatalytic oxidation on semiconductor oxides

A brief insight onto properties of the most known solid oxides – possible components of the atmospheric aerosols is given below.

3.1. ZnO

Zinc oxide is known to be the most active photoadsorbent and photocatalyst among all metal oxides. Oxygen and methane photoadsorption was observed on illumination at the surface absorption band of ZnO [9], while photocatalytic oxidation of different organics and carbon monoxide on illumination at the band of fundamental absorption (see, e.g., [3,10]). The results of the cited studies were obtained after a rigid oxygen-vacuum pretreatment of the oxide. Without such a pretreatment, a prolonged consumption of oxygen from the gas phase was registered upon illuminating the oxide surface; this consumption is supposedly connected to the oxidation of adsorbed organic compounds [11]. In this state a significant amount of carbon dioxide and water is also present on the oxide surface [13].

According to the data of Solonitsyn et al. [13], the maximum amount of oxygen and methane photoadsorbed on the zinc oxide surface, 0.01% of the monolayer, can be obtained upon mixing the powdered ZnO.

CO and CO_2 photoadsorption on ZnO was also observed but has a small value [14,15].

3.2. TiO_2

Dispersed TiO_2 is the most studied photocatalyst for both liquid and gas-phase photocatalysis (see, e.g., the articles in this issue of the journal). Note that for titanium dioxide photoadsorption and photocatalytic processes are observed mostly at the band of its fundamental absorption, and quantum efficiency of these processes can be near 1% or even higher [16–18]. The maximum amount of photoadsorbed molecules attains ~0.01% of monolayer of the oxide surface [13]. In the initial state (before the oxygen-vacuum pretreatment) the adsorbed layer contains both carbon dioxide and considerable amount of water [19,20]. Without the surface pretreatment and upon illuminating in the oxygen atmosphere, an oxygen consumption is observed from the gas phase for oxidation of adsorbed organic compounds (see, e.g., [21]). The presence of such compounds on the TiO_2 surface together with the impregnated platinum can result in some cases in hydrogen evolution (observed, e.g., in titanium dioxide suspension in pure 1 N H_2SO_4 [22]).

In water-organic suspensions of TiO_2, well known is the sensitization of titanium dioxide to the visible spectral region upon adsorption of organic or metallocomplex dyes on the TiO_2 surface. For example, in the presence of surface platinum, such sensitization can reveal in the reaction of photocatalytic dehydrogenation of organic compounds under VIS light [23–25].

3.3. *SnO_2*

This semiconductor oxide seems to be not very common for atmospheric aerosols. However, it also appears to be a subject for numerous experimental studies. In the initial state the surface of SnO_2 contains the adsorbed water, that can be totally removed upon heating at 473 K, hydroxyl groups and carbonates [26]. After a rigid oxygen-vacuum pretreatment, a photoadsorption of O_2 as well as H_2 and CH_4 was recorded on tin dioxide [16]. A photoadsorption activity was observed at the fundamental absorption band, along with photocatalytic oxidation of carbon monoxide [21,27] and ammonia [28]. The quantum yields of these processes on SnO_2 attain 4% for the O_2 photoadsorption and 10% for photocatalytic oxidation of CO [7,16,21].

As indicated above, a possibility for the insulator oxides to participate in photoadsorption and photocatalytic processes in the troposphere may be connected only with the possibility of their sensitization to the solar radiation reaching the Earth's troposphere, most probably as a result of formation of some adsorbed or surface layers of oxides in the tropospheric conditions. Such a sensitization by the adsorbed or surface compounds was observed for tin dioxide in oxygen and nitric oxide photoadsorption after carbon monoxide adsorption on its surface [7]. The authors of this study suggested SnO_2 to be sensitized by the surface carbonates formed after the carbon monoxide adsorption.

3.4. *Fe_2O_3*

Among the oxides considered in this work, iron oxide is the only substance possessing a catalytic activity even at room temperatures, e.g., in the reaction of carbon monoxide oxidation [29]. Unfortunately, iron oxides have no pronounced properties of a photocatalyst, at least for photocatalytic oxidation of CO, hydrocarbons and ammonia [21,28].

However, in water suspension of a partially reduced iron oxide, water was reported to be reduced to hydrogen, under the action of light [30]. Also, in a colloidal state, Fe_2O_3 reveals some activity under the action of light in the formation of H_2O_2 and decomposition of chlorinated hydrocarbons [31].

4. Photoadsorption on insulator oxides

Pure insulator oxides (SiO_2, Al_2O_3, MgO, CaO) do not exhibit a photocatalytic activity in the most spectral region of solar radiation, especially in the region of solar radiation in the troposphere [27,28,32]. Indeed, the fundamental absorption band of these oxides reveals at the wavelengths less than 200 nm [1], while the photocatalytic activity is connected usually with the formation of electron–hole pairs upon absorption of radiation quanta by a solid. For this reason one can assume that in the case when a remarkable photocatalytic activity in the visible spectral region was observed on the natural oxide materials like sand, chalk, volcanic ash, etc. [33–37], this activity evidently was attributed to the presence of traces of metals, whose oxides have a high photocatalytic activity in the visible region of solar spectrum (e.g., TiO_2, ZnO, SnO_2) [38].

A remarkable photoadsorption of various gases on the pure insulator oxides is observed at wavelengths less than 300 nm, as follows from the spectral dependencies of the O_2, H_2 and CH_4 photoadsorption and N_2O photodecomposition on SiO_2, Al_2O_3, MgO and CaO [4,39]. However, the amount of photoadsorbed molecules in these cases attained only the level of 0.1% of monolayer [4].

Note that except the influence on concentration of the main components of the Earth's gas phase, the processes of photoadsorption on the solid tropospheric aerosols, like the photocatalytic oxidation, may also result in cleaning the atmosphere from some dangerous pollutants such as ozone depleting halogen-containing hydrocarbon compounds as well as freons.

It should be noted that the above-mentioned photoadsorption activity of the insulator oxides was determined after a rigid oxygen-vacuum pretreatment of their surface at high temperature.

In [40] photoadsorption of a set of freons on the MgO surface which had not experienced an oxygen-vacuum pretreatment was studied. In this situation the oxide surface contained initially the adsorbed water, carbon dioxide and nitrogen oxides [41]. The studies were provided over freons of the methane set (CF_2Cl_2 – freon 12, CHF_2Cl – freon 22) and of the ethane set (CH_2FCF_3 – freon 134^a) at conditions close to atmospheric conditions.

For providing these experiments magnesia with the "pure" grade qualification of industrial production obtained by decomposition of magnesium hydroxide was sedimented from the water suspension on the inner walls of a cylindrical reactor made of molybdenum glass. Then the reactor was dried in air for a long time at room temperature. The soldering of the reactor to a high-vacuum set-up was followed by its evacuation at room temperature to the pressure of 10^{-7} Torr for some hours. Therewith the water vapours were frozen in the reaction volume trap.

In these conditions the already mentioned adsorbed water, carbon dioxide and nitrogen oxides (surface state "I") were indeed left over the magnesium oxide surface. Note that for the other above-mentioned metal oxides, except for CaO, the presence of the adsorbed nitrogen oxides on the surface is not typical.

After filling the reactor with freon 134^a at a pressure of 10^{-2} Torr, the illumination of the MgO surface in such a state results in the complete freon photoadsorption to partial pressure less than 10^{-6} Torr. Upon photoadsorption of the freon in small portions (initial pressure 10^{-2} Torr), the total quantity of the irreversibly photoadsorbed freon attained 10% of monolayer calculated in respect to the whole surface area of magnesium oxide. This distinguishes remarkable photoadsorption of the freon on magnesium oxide from that of oxygen, hydrogen and methane after the oxygen-vacuum pretreatment of MgO where the final coatings of the photoadsorbent comprise only 0.1% of monolayer for the illuminated area [4], as well as from the photoadsorption of the same gases on ZnO and TiO_2 pretreated at high temperature (the attained coating is near 0.01% of monolayer, also for the illuminated area) [13].

In contrast to freon 134^a, freon 22 (CHF_2Cl) is able to adsorb on the MgO surface in the state "I" even in darkness up to the coating equal to 2% of monolayer at the freon pressure of 10^{-2} Torr. On the magnesium oxide, a remarkable photoadsorption of freon 22 is observed too. However, neither dark- nor photoadsorption of freon 12 has been observed for the studied MgO. Photoadsorption of $CHCl_3$ and CH_2ClCH_2Cl also was not recorded on the magnesium oxide in contrast to a noticeable dark adsorption of these compounds.

Photoadsorption of freons 22 and 134^a on the air-exposed magnesium oxide appeared to be completely irreversible: the photoadsorbed freons do not desorb on heating the oxide up to the temperature of 370 K. Therewith in the gas phase the fluorine–chlorine-containing products of the freons decomposition are not observed as well.

For a quantitative evaluation of the photoadsorption efficiency in cleaning the atmosphere from halogen-containing organic compounds under the action of solar light, it is necessary to know the spectral dependencies of the photoadsorption quantum yield. In [40] such measurements have been conducted for photoadsorption of freon 134^a on magnesium oxide in the state "I". According to these data, the irreversible freon photoadsorption is observed at wavelengths shorter than 400 nm and quantum yield attains 6% for wavelengths close to 313 nm (Fig. 2). As mentioned above, in this wavelength region, the sample of magnesium oxide with the surface state obtained upon long-air exposure has the light absorption of 0.04 at ca. 400 nm.

The light absorption in the mentioned spectral region retains even after long-duration evacuation of MgO at 620 K, resulting in removal of nitrogen oxides and considerable amount of water from its surface due to magnesium hydroxide decomposition occurring at temperature 550 K [42].

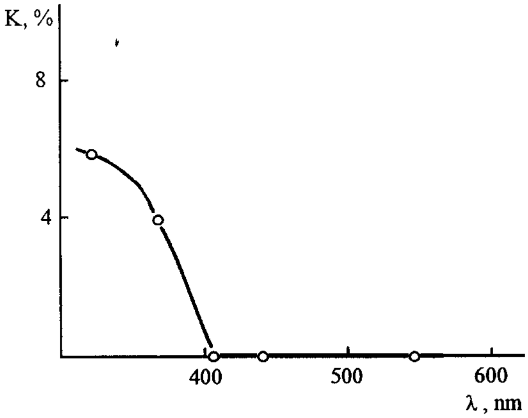

Fig. 2. Spectral dependence of the quantum yield of freon 134^a photoadsorption on the air-exposed MgO (according to [40]).

After a rigid oxygen-vacuum pretreatment of magnesium oxide, the long-wave absorption in the wavelength region close to 360 nm is not observed at all [41].

5. Conclusions

There is a rather definite possibility for photoadsorption and photocatalytic processes on the solid tropospheric aerosols to affect the formation of the Earth's atmosphere composition. The problem now is to find the extent to which this possibility is realized in nature. To answer this question, quantitative data are needed for characterizing the processes of photoadsorption and photocatalytic oxidation for all the main components of the atmospheric gas phase, as well as for the components of the atmospheric gas phase present in low and trace concentrations but polluting the atmosphere or affecting the state of the "ozone" layer of the atmosphere. Such data must be obtained for the conditions of the real atmosphere, both for semiconductor oxides which are quite photoactive but present in low concentrations, and for insulator oxides which seem to be less active but being the main components of the solid tropospheric aerosols. Of importance is that a sufficient increase in photoactivity of the insulator oxides in the spoken photoprocesses may be expected upon formation of the adsorbed layer on their surface. As a result, a sensitization of these oxides to the spectrum of solar radiation in the troposphere can occur, as it was observed for the air-exposed magnesium oxide in the irreversible freon photoadsorption.

For further reading

Ref. [12]

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