Photoinduced heterogeneous processes on phase chemical components of solid tropospheric aerosol particles

V.S. Zakharenko and A.N. Moseichuk

G.K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Novosibirsk
Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences, Tomsk

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We present some results of our investigation into the photoinduced processes in some metal oxides (In_2O_3,, Sc_2O_3, V_2O_3 and MoO_3), which can be the phase chemical components of solid tropospheric aerosols. We have determined the quantum yield and spectral behavior of the quantum yield of photoadsorption and photocatalytic oxidation in the spectral region that involves the spectrum of solar radiation in the troposphere.

Introduction

Solid tropospheric aerosols comprise a large number of compounds of certain chemical composition and in crystal form (phase chemical components). The total activity of aerosol particles can be determined by the sum of activities of separate phase components of aerosol particles. The determination of phase composition of solid aerosol particles is a complicated task, which has not yet been achieved, although in some papers the attempts have been described to solve this problem.[1,2]

The element composition of solid aerosol particles of the troposphere qualitatively[3] and for many elements quantitatively[4] corresponds to the element composition of the natural rocks of the earth's crust. This makes it possible to assume that the chemical phase composition of solid aerosol particles mainly corresponds to mineralogical composition of the earth's crust.

The comparison made between the results on the photoinduced (including photocatalytic) activity of chemical components[5] and mineralogical composition[6] of the aerosol substance showed that the minerals from the classes of “oxides and hydroxides,” “silicates,” and “carbonates” are the basic phase chemical components of solid tropospheric aerosol particles. Such particles are active in the photoinduced processes resulting in the change of gas phase composition of the earth's atmosphere.

Thus, it is known from literature that zinc oxides (mineral zincite),[7] titanium oxides (minerals rutile and anatase),[8] tin oxides (cassiterite)[9] exhibit the photocatalytic, oxidizing activity when irradiated by solar radiation in the troposphere. Reactions of photocatalytic oxidation are observed for these oxides (Table 1).[10]

We have studied the photoinduced processes (photoadsorption of oxygen and/or carbon monoxide, photocatalytic oxidation of carbon monoxide) using the oxides of indium, vanadium, and scandium. According to data of elemental analysis from Ref. 11, the atmospheric dust contains some trace quantities of these metals. Besides, the photoprocesses in the molybdenum oxide were investigated, relating to the semiconductor type of metal oxides (Mo content according to data of elemental analysis in aerosol emission after forest fires can be about 1 μg per cubic meter of air[12]).

Table 1. The width of the forbidden band E_g (Ref. 15) and red boundary λ_0 of the fundamental absorption for oxides-semiconductors, which can be the phase components of solid tropospheric aerosol

Oxide	E_g, eV	λ_0, nm
ZnO	3.2	390
TiO_2	3.0	410
SnO_2	3.7	340
In_2O_3	2.7	460
V_2O_5	2.2	560
MoO_3	2.9	430
Sc_2O_3	5.4	230

Experimental procedure

We used powdered samples of commercially available high purity In_2O_3, pure for analysis V_2O_5, and pure for analysis MoO_3. The powders of Sc_2O_3 were produced from $Sc(NO_3)_3$ at room temperature. The residue was filtered and washed by water, then it was dried in the air at a temperature about 400 K. For complete removing of the NO_3^- the residue was heated in the air at a temperature of 570 K during 1.5 hr and then at 670 K in the air during 2 hr.

Samples were deposited from water suspension in the form of thin layer on the walls of the reactor made from optical quartz. The design of the reactor is an analog of an ideally black body. Before experiments the samples underwent the oxygen-vacuum handling in a high-vacuum unit for cleaning of the surface from adsorbed organic impurities, carbon dioxide, and water.

Variations of pressure in the reaction volume were recorded with a Pirani gauge and gas composition was recorded using a mass-spectrometer designed based on the analyzer of partial pressures APDM-1.

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The quantum yield of photoadsorption or photocatalytic oxidation was determined both by the ratio between the number of photoadsorbed molecules or the number of reacting molecules of carbon monoxide and the number of absorbed quanta at the initial moment of the exposure to light.

Measurements of photoadsorption activity were conducted at the oxygen pressure of 1 Pa and photocatalytic activity at the pressure of stoichiometric mixture ($2CO + O_2$) 10 Pa at a temperature of 300 K.

Spectra of diffuse reflection were recorded using a KCVU-12 spectrophotometer with an attachment for diffuse reflection measurements from a SPECORD M-40 spectrophotometer.

The other details of the measurement procedure can be found in the literature.[13,14]

Results and discussion

Figure 1 shows the spectral behavior of the quantum yield of photoinduced processes in the indium oxide.

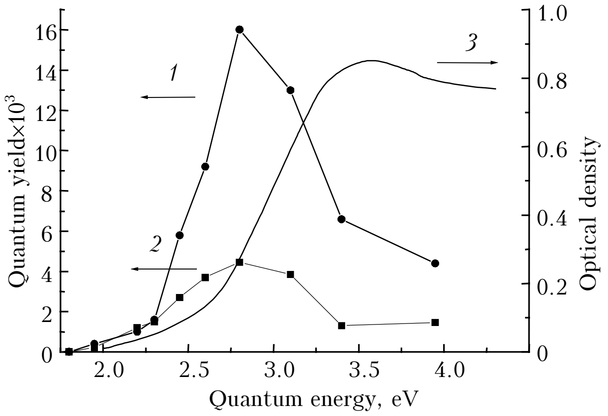

Fig. 1. The spectra of the quantum yields of oxygen photoadsorption (*1*), oxygen photoadsorption from stoichiometric mixture $2CO + O_2$ (*2*), and of the optical density of diffuse reflection relative to lithium fluorine (*3*) obtained for In_2O_3.

Photocatalytic oxidation of carbon monoxide is observed at quantum energy higher than 2.7 eV, i.e., in the fundamental absorption band of indium oxide (see Table 1 and spectrum of diffuse reflection of indium oxide in Fig. 1, curve *3*). Photocatalytic oxidation of carbon monoxide in this absorption band is characterized by low negative energy of activation (about 1 kcal/mol) that agrees well with the mechanism of photocatalytic oxidation proposed in Ref. 15. According to this mechanism the interaction of carbon monoxide occurs with activated surface oxygen at the moment of its discharge by a mobile free hole of a valence band of metal oxide. The first order of reaction of photocatalytic oxidation of carbon monoxide at illumination by a monochromatic light with the quantum energy of 2.84 eV also corresponds to this mechanism.

The illumination of In_2O_3 surface by quanta with the energy below 2.7 eV results in the removal of oxygen only from the stoichiometric mixture but reactions of photocatalytic oxidation of carbon monoxide are not observed.

Photoadsorption of oxygen on the indium oxide has a reproducible character in case if before the photoadsorption the oxide is heated in vacuum of $\sim 10^{-3}$ Pa during 1 hour at a temperature of 680 K. The spectral behavior of the quantum yield of photoadsorption of oxygen for the indium oxide after such treatment is presented in Fig. 1, curve *2*. The oxygen photoadsorption from stoichiometric mixture $2CO + O_2$ for the indium oxide after high-temperature oxygen treatment has lower quantum yield (Fig. 1, curve *1* for quantum energies below 2.7 eV). The lower values of the quantum yield of oxygen photoadsorption from $2CO + O_2$ mixture are most likely connected with the difference in the treatment of indium oxide before the measurements of the photoadsorption rates because the oxygen photoadsorption from “pure” oxygen was preceded by high-temperature treatment in vacuum while before the photoadsorption from the mixture $2CO + O_2$ the indium oxide was treated in oxygen at high temperature. If the same indium oxide treatment is made before the photoadsorption measurements using pure oxygen, this would result in a decrease of the photoadsorption rate.

Red boundary of the fundamental absorption band of scandium oxide is located at the quantum energy of 5.4 eV (see Table 1) and therefore reactions of photocatalytic oxidation under the action of quanta of solar tropospheric radiation ($h\nu \le 4.1$ eV), based on our and literature data, are not observed. Oxygen photoadsorption on Sc_2O_3 has been recorded and the spectral behavior of the quantum yield of photoadsorption is shown in Fig. 2 (curve *1*). As in the case of indium oxide, the quantum efficiency of oxygen photoadsorption on scandium oxide after high-temperature treatment of adsorbent surface in oxygen is less than the oxygen photoadsorption from stoichiometric mixture $2CO + O_2$ (Fig. 2, curve *2*). In the case of scandium oxide we also observe the hydrogen photoadsorption and photoadsorption of methane and carbon monoxide in the spectral range of solar radiation[16] in the troposphere.

For vanadium and molybdenum oxides the spectra of action of these processes were only estimated because of their low activity in photoinduced processes (see Table 2).

From that estimation it follows that the photocatalytic oxidation of carbon monoxide by oxygen also takes place under the action of solar radiation in the troposphere.

Thus, from the data obtained it follows that the photocatalytic activity is observed in the range of fundamental absorption of oxides of indium, vanadium, and molybdenum at quantum energies being larger than the width of forbidden zone of the corresponding oxide. Conditions of treatment of the surface of the oxides studied and conditions of their production differ from conditions of the origin and surface formation of such oxides in the troposphere. Evidently, those are not optimal for observation of high quantum efficiency in the reaction of photocatalytic oxidation of carbon monoxide. However, the data obtained point to a possibility, in principle, of removing the atmospheric pollutions due to their photocatalytic oxidation by oxygen on the surface of oxides of indium, vanadium, and molybdenum.

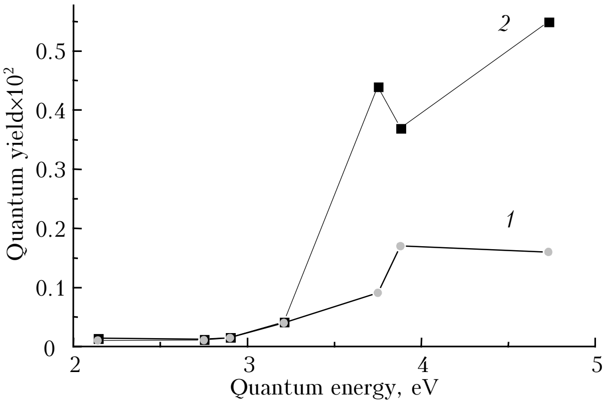

Fig. 2. Spectral dependences for Sc_2O_3: quantum yields of oxygen photoadsorption (*1*) and oxygen photoadsorption from stoichiometric mixture $2CO + O_2$ (*2*).

Table 2. Initial photocatalytic activity of the oxides of titanium, vanadium, and molybdenum under the illumination with light from a mercury-vapor lamp DRSh-250 and the ($2CO+O_2$) mixture pressure 10 Pa at a temperature of 300 K

Oxide	Intensity	Photooxidation rate of CO, molecule · s^{-1}
TiO_2	0.1 J_0	$4.8 \cdot 10^{13}$
V_2O_5	J_0	$8.1 \cdot 10^{12}$
MoO_3	J_0	$9.8 \cdot 10^{10}$

Note. J_0 is the mercury-vapor lamp radiation flux density (an OSL-1 illuminator with a thermal filter) when the radiation flux density through the interference filter 400 nm is equal to $4.7 \cdot 10^{15}$ photons · s^{-1} · cm^{-2}.

Conclusions

Thus, metal oxides of semiconductor type, which may present as phase components in the particles of solid tropospheric aerosol, are active (except for scandium oxide) in the transformations of carbon monoxide to carbon dioxide under the action of solar radiation ($h\nu < 4.1$ eV) in the troposphere. At the known concentration of these oxides as phases, which are part of particles of solid tropospheric aerosol, we can determine the contribution of the reaction of photocatalytic oxidation on these metal oxides to the removal of atmospheric gas-phase carbon monoxide.

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