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Fast adsorptive and photocatalytic purification of air from acetone and dimethyl methylphosphonate by TiO_2 aerosol

A.S. Besov, A.V. Vorontsov *, V.N. Parmon

Boreskov Institute of Catalysis and Novosibirsk State University, Novosibirsk 630090, Russian Federation

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ABSTRACT

A high concentration (1.5×10^6 cm^{-3}) TiO_2 aerosol of the average particle size 0.5 μm was generated by a sonic method inside 0.1 m^3 Plexiglas chamber and applied for the adsorptive and adsorptive-photocatalytic purification of air from vapors of acetone and chemical agents' model dimethyl methylphosphonate (DMMP). The adsorptive capture of acetone over the TiO_2 aerosol results in establishing equilibrium adsorption state and is limited by the rate of the aerosol admission into the chamber. A model derived from the Langmuir isotherm describes well the acetone concentration vs. aerosol mass curve and allows obtaining the adsorption constant and monolayer coverage of acetone in a 10 min experiment. The UV irradiation of TiO_2 aerosol accelerates dramatically the purification from acetone at the high relative humidity (RH) of the air. Increased RH of air decreases the rate of the acetone adsorption but has a little positive effect on the rate of photocatalytic oxidation of acetone over aerosol particles. The DMMP adsorption over TiO_2 aerosol is accompanied by the immediate ($\tau < 10$ s) and irreversible hydrolysis of DMMP with the formation of gas phase methanol and adsorbed methyl methylphosphonic acid. The irreversible reactive adsorption results in the very fast air purification ($\tau = 20$–40 s) due to very small diffusion distances of substrate to the TiO_2 surface in aerosol. The increase of the air RH from 4 to 37% (296 K) decreases the rate of adsorption but accelerates significantly the rate of photocatalytic oxidation. The complete air purification from organic compounds within 10 min is possible only with the photocatalytic oxidation because the adsorption alone does not remove methanol. The time needed for the air purification over the nanosized TiO_2 aerosol is directly determined by the rate of the aerosol generation which allows a further optimization of the TiO_2 aerosol air purification. The obtained results approve experimentally a suggestion that the photocatalytic oxidation over solid atmospheric aerosols actually takes part in the Earth atmosphere and serves as an important sink for airborne organics.

1. Introduction

Since the early works by Filimonov [1], McLintock et al. [2], Lyashenko and Gorokhovatsky [3] and N. Djeghri et al. [4], heterogeneous photocatalytic oxidation over oxides is considered as a powerful method of promoting the oxidative reactions in the gas phase. Environmental concerns of the last decades initiated the fruitful application of heterogeneous photocatalytic oxidation to purification of air. Numerous studies have demonstrated the ability of photocatalytic oxidation to provide mineralization of practically any organic compounds, i.e. their complete photocatalytic oxidation into stable inorganic products under certain exposure of the system with light [5]. The technology of photocatalytic oxidation over supported TiO_2-based photocatalysts located mainly in a fixed bed is now well developed and applied in a commercial scale for the purification of air from low concentrations of both organic and inorganic compounds [6–10].

The application of the fixed bed photocatalytic reactors for the air purification requires designing both the photocatalyst-support composites as well as the geometries of their irradiation with UV light to ensure good contact between the surface of the irradiated photocatalyst and the passing air stream. As to more active unsupported photocatalysts which are free from catalytically inactive supports, these are utilized mainly in reactors of two types. First, these are small-scale reactors which are used in research and operate usually at the low airflow rates that do not cause any sufficient mass transfer limitations for the unsupported photocatalysts. The second type of reactors are those with the fluidized bed of the photocatalyst that possesses a number of advantages over the fixed bed reactors. The advantages include

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* Corresponding author. Tel.: +7 383 3269447; fax: +7 383 3331617.
E-mail address: voronts@catalysis.ru (A.V. Vorontsov).

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easy withdrawal and return of the photocatalyst for its regeneration as well as enhanced mass transfer. The fluidized bed gas phase reactors were employed for the photocatalytic oxidation of trichloroethylene [11–14], acetone [15], toluene [16], styrene [17], as well as removal of nitrogen oxides [18,9]. In such reactors, an enhancement of the photooxidation rate was observed in many cases experimentally that was explained by a decrease of effective irradiance as a consequence of the rotation of photocatalyst particles [15]. Common and well known disadvantages of the fluidized bed systems are the catalyst attrition and its carryover. The catalyst attrition makes an especially sufficient influence on photocatalytic reactions because of possibility of the light shading by the deposition of the attrition generated powders on the reactor windows or lamps used for illumination.

A particular type of the efficient and “global” fluidized bed photocatalytic reactors is known to be the Earth (and other planets) atmosphere where the photocatalyst can exist in the form of various aerosols [19–21]. However, the impact of the atmospheric heterogeneous photocatalytic reactions remains to be determined.

The possibility to provide photocatalytic oxidation at mild conditions of the environment as well as pronounced mass transfer parameters of fluidized bed or aerosol can be efficiently utilized for the emergency air purification from many airborne contaminants. Indeed, the fluidization of tiny photocatalyst particles under proper UV irradiation makes possible a quick decontamination of either indoor or outdoor air at the localized spots. In this work, we investigate the possibilities for the quick air purification from vapors of acetone and simulant chemical agent dimethyl methylphosphonate (DMMP) with the help of an aerosolized TiO_2 powder affected by UV irradiation.

The adsorption of both compounds on the photocatalyst surface is evidently the first stage which precedes their photocatalytic oxidation. Note, however, that in contrast to acetone, DMMP is known to be able of the irreversible reactive adsorption over anatase TiO_2 [22–24]. The reactive adsorption over TiO_2 was observed also for some other compounds like diisopropyl fluorophosphonate [25], 2-chloroethyl ethylsulfide [26], etc. The ability of such irreversible adsorption over TiO_2 can accelerate sufficiently the process of the emergency air purification.

Investigation of toxic effects of nanoparticles is currently a subject of intensive research. It has been recently found that inhalation of an aerosol of nanosized TiO_2 particles can cause inflammatory response in mice lungs [27]. Therefore, TiO_2 aerosol should be used with caution for air purification in the presence of living things. This method can be, however, indispensable for very quick alleviation of lethal or severe exposures to toxic compounds since the inflammatory aftermath of a TiO_2 aerosol is much better than heavy or lethal health effects of the toxic compounds.

We applied fluidization of the UV irradiated anatase TiO_2 powder in a closed chamber to attain quick air purification. In contrast to traditional fluidized bed experiments with photocatalyst granules of sizes above tens of micrometers, the characteristic size of TiO_2 particles in our study was below 2 μm. Such small particles behave like aerosols. Since the concentration of such particles in the generated dusty cloud was large enough, the characteristic distance that substrate molecules travel before they collide with a TiO_2 particle is small. This diminishes the external diffusion time very much and accelerates largely the substrate adsorption. Also, the very small sizes of the TiO_2 particles makes the time of their precipitation long enough to allow the deep photocatalytic oxidation over aerosolized TiO_2 particles. The present study expands and details our preliminary experiments on TiO_2 aerosol [28] and provides careful discussion of the results.

2. Experimental

2.1. Materials

The photocatalyst powder applied for the reactions was TiO_2 Hombikat UV 100 (anatase 100%) with specific surface area approximately 320 m^2/g and the primary particles size 5 nm [15]. Before generating the aerosol, the TiO_2 powder was dried overnight at 120 °C; this procedure was found to be important for the efficient aerosol formation. Acetone (Reachim) and dimethyl methylphosphonate (98% Sigma–Aldrich) were used as received.

2.2. Reaction setup and methodology

The experimental setup is schematically shown in Fig. 1. The core of the setup is a 100 l cubic Plexiglas chamber. An aerosol generator is placed in the middle of the chamber floor, while a 22 W annular UV fluorescent mercury lamp TL-E/10 (Philips) is located at the center of the chamber. According to the manufacturer specifications, the radiant power emitted by this lamp in the UV region is $P = 3.9$ W. The lamp emission spectrum has an intensive maximum at wavelength 365 nm, the half-height width of the spectral line is 20 nm. This band completely falls into the TiO_2 band gap absorption region ($\lambda < 400$ nm). The photon flux of this band is $\Phi = 1.2 \times 10^{-5}$ Einstein s^{-1} as calculated with the expression

$$\Phi = P\frac{\lambda \times 10^{-9}}{N_A hc}$$

where λ is average wavelength of irradiation (nm), N_A is the Avogadro number (mol^{-1}), h is the Planck constant (J s), and c is the speed of light in vacuum ($m\ s^{-1}$).

UV irradiance ($\lambda < 400$ nm) was also determined experimentally using a radiometer and an UV cut-off filter at the center of a wall as 1.6 W/m^2 and at the center of the ceiling of the chamber as 3.4 W/m^2. Integration over the chamber surface gives an estimate of the total UV radiant power of 2.7 W that reasonably agrees with the manufacturer's specification.

Primary quantum efficiency of substrate consumption steps of photocatalytic processes was estimated using the standard formula [29]

$$\varphi = \frac{W_N}{\Phi} \tag{1}$$

where W_N is the rate of the substrate consumption on amount basis ($mol\ s^{-1}$) calculated from a concentration–time plot, Φ is the

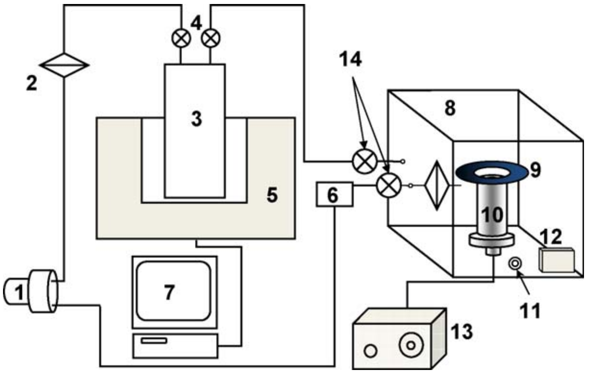

Fig. 1. Scheme of the experimental setup. (1) Membrane circulation pump, (2) 0.2 μm membrane filter, (3) long-path IR gas cell, (4) valves, (5) FT-IR spectrophotometer Vector 22 (Bruker), (6) humidity meter, (7) computer connected to FT-IR, (8) chamber, (9) UV lamp, (10) aerosol generator, (11) sampling & injection port, (12) digital thermometer, (13) signal generator, (14) spherical stopcocks.