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Zinc Oxide-Based Photocatalyst on Woven Fiberglass Support for Destruction of Volatile Organic Compounds in Air

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Abstract — Method for production of photocatalysts based on zinc oxide deposited to glass fibrous woven material is discussed. The process of destruction of volatile organic compounds acetone in gaseous phase with application of the developed photocatalytic material was investigated.

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Volatile organic compounds (VOCs) are widely used by the modern industry for different applications. Those compounds are heavy toxicants and have a strong odour even at low concentrations in the ambient air. The sources of such emissions being frequently unorganized therefore influence significantly the quality of life in adjacent areas. Specifically one of the most widely used and most harmful components of the gaseous emissions from diverse anthropogenic sources is acetone. Only in USA more than 1.5 million tons of acetone are spent annually, a significant part of which evaporates and comes with gaseous emissions to the atmosphere.

Acetone is refered to the fourth class of harmfulness and can exhibit irritating and toxic effects in human organism. In the environment it generally exists in form of vapour in the air. Its maximum allowable concentration is 0.35 $mg \cdot m^{-3}$. Aceton is moderately stable in the natural environment; its photochemical destruction in atmosphere with hydroxyle radicals or under direct solar irradiation (UV irradiation) is going relatively slow with half-destruction period $\tau_{1/2} = 71 \div 80$ days [1]. Furthermore, acetone is found to be an intermediate in destruction of many other complex organic substances. Taking the above mentioned into account, solution of the problem of acetone removal from gaseous phase appears quite challenging task for protection of the environment.

Photocatalytic method is regarded as one of the most promising technologies for purification of gaseous emissions. It combines the advantages of adsorptive and destructive photochemical and catalytic methods for detoxification of emissions. The method is based on application of heterogeneous photoactive substance to absorb the contaminants. The elementary active charged particles are formed in the structure and on the surface of the material under irradiation of certain spectral region. These particles interact with complex organic substance adsorbed on the material and can promote their destruction. As a result, a transformation of toxic compounds of the emissions occurs and less harmful highest oxides of its corresponding elements appear [2, 3].

The photocatalytic systems do not require additional resources except electricity to power the source of irradiation. These systems do not normally consist of moving parts making operational wearing rather small and decreasing the need for routine service and repair [4, 5].

Photocatalytic method works at temperature of ambient environment which excludes the need for heating of the treated emissions. Photocatalysts like oxides of titanium, zinc, tin, iron, and some other transition metals are widely available and low cost, especially, in comparison with traditional palinoids-based catalysts.

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The majority of photocatalytic materials are chemically stable and irradiated surface of the materials undergoes self-cleaning, therefore, poisoning of the catalysts appears to start much more slowly than for traditional heterogeneous catalysts. All those factors underlie the rapidly growing interest for photocatalytic processes in all industrially developed countries [6].

The majority of existing technologies and, consequently, the research publications in this area are based on application of titanium dioxide. It has a very high chemical stability and low cost. However, application of TiO_2 is limited by the fact that only one of four its crystal modifications exhibits photocatalytic activity [7].

Ability of zinc oxide to initiate destruction of organic substances under irradiation is known since early 20th century with the first research on this matter published in 1926. Zinc oxide has the same advantages as TiO_2 except the high chemical stability of the latter. This has a dominant importance in selection of catalyst to be used in aqueous phase where the formation of soluble zinc compounds at pH different from 7 can be expected. However, this fact is not important for processes in gaseous phase where secondary pollution of the treated media by ions of the catalyst is excepted.

Cost of ZnO of the required grade is 20–40% lower than that of TiO_2. Moreover, ZnO is more stable in higher temperatures which are required for certain technologies for immobilization of the catalysts to carrier materials. There are also some evidences of the higher photocatalytic activity of ZnO in some applications in comparison with TiO_2, which is discussed in literature and was confirmed in our previous studies [8, 9].

Photocatalytic processes take place on the catalyst surface. Therefore their efficiency primarily depends on the size and accessibility of the surface for reagents (oxygen, water vapour, organic compounds) and for irradiation. The latter factor usually limits the efficiency of heterogeneous photocatalysis in gaseous phase. To provide enough accessibility of the surface for irradiation the catalyst should be deposited to a certain supporting material. The most efficient carriers hold a thin high-porous layer of catalyst and repeat the shape of the radiation source for maximal utilization of the light stream. The supporting material should be inert and mechanically stable enough to withstand the destructive activity of the catalyst. Proper fixation of the catalyst on the carrier is also an essential condition of the long stable operation of the system. One of the most perspective supporting material for photocatalysts is fibreglass, which is comparable to polymers, due to flexibility and to metals, due to mechanical stability. It also has the inherently high chemical resistance comparable to glass [4, 6, 10−12].

In this study we investigated a range of technological approaches to prepare the photocatalytic materials based on zinc oxide deposited to fiberglass. In the process of thermal treatment in air media of the woven fibreglass impregnated with zinc salt solution,zinc oxide is formed. It is attached to the carrier by adhesion and partly by sintering with the glass surface.

OBJECTS AND METHODS

As a precursor for formation of ZnO without any additives negatively affected the photocatalysis (like halogens or sulphur compounds which are formed if zinc chloride or zinc sulphate are used) zinc nitrate was used as the most widely available zinc salt. Alternatively, zinc acetate was used as more environmentally friendly reagent, since it does not give toxic nitrogen oxides in thermal processing.

To prepare the fibreglass photocatalytic material the samples of fibreglass cloth were impregnated with saturated solutions of the aforementioned salts for 30 min, after which they were dried and burned in muffle chamber. The burnt samples were then washed with distilled water for 2 min to evaluate the fastness of fixation of zinc oxide to the surface.

It was shown that the optimal temperature for burning the samples was 350°C for zinc acetate and 300°C for zinc nitrate. At those temperatures the yield of oxide determined with X-ray fluorescent spectroscopic measurement of zinc concentration in samples reached 95−99% of the theoretically possible stoichiometric values. It was also determined after quick washing of samples in distilled water that oxide layer resulting using zinc acetate is 25–30% weaker attached to the fibres than that resulting from zinc nitrate. According to those results, zinc nitrate as a precursor as chosen, since it required less energy for thermal treatment and produced the oxide layer more strongly attached to the support.

It was also demonstrated that organic compounds used in preparation of fibreglass woven materials to protect fibres decreased the fastness of fixation of the oxide layer to the supporting material in textile treatment and increased duration of thermal treatment and consumption of energy, as a consequence. In the samples where the coupling organic agents were previously re-

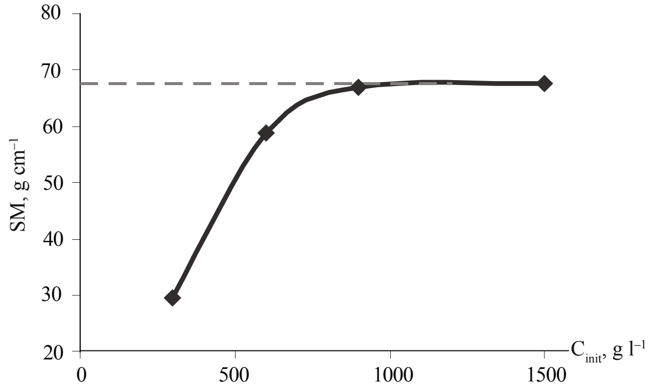


Fig. 1. Dependence of the specific mass of ZnO (*SM*) in the fiberglass samples on the initial concentration of $Zn(NO_3)_2$ (C_{init}) in the impregnating solution.

moved by burning at 500°C oxide layer was distributed more evenly on the surface (evaluated with microscope observation) and was 35–40% more strongly attached to the material compared to the samples without preliminary treatment.

Using the impregnating solutions of a range of concentrations (from 300 to 1500 g l^{-1}) the yield of zinc oxide (measured as zinc) with rather high fastness of fixation changed according to the dependence shown at Fig. 1.

Those data suggest the logarithmic character of the dependence. Maximal amount of zinc oxide on the supporting material is achieved at the initial concentration of zinc nitrate in the solution of 1000 g l^{-1}.

RESULTS AND DISCUSSION

Samples of the fibreglass photocatalytic material prepared with the above described method were studied to determine their ability to destruct VOCs in air media. For the study an experimental assembly was used which exterior and construction are presented on Figs. 2 and 3.

Experimental assembly consisted of the annular tube reactor with outer body of stainless steel (1) and inner coaxial quartz sleeve where the source of UV radiation (2) was placed. The UV radiation source was the standard mercury low-pressure 8 W lamp Phillips G8T5 TUV. This type of lamps produces almost monochromatic irradiation in the far UV range (γ-UV) with maximum (over 95%) of emission at the wavelength 253.7 nm.

Photocatalytic material (3) was placed between the steel body and the quartz sleeve. At the opposite ends of the reactor body the inlet and outlet pipes (4) for gaseous media circulation were located.

Changes of composition of the gaseous media were monitored with IR-Fourier spectrometer (7) equipped with pass-through gas cuvette (6) with the optical pathway 100 mm and KBr windows 40 mm in diameter. The cuvette was attached with polyethylene pipes to the reactor. For circulation of the gaseous phase within the assembly a microventilator (5) with the output about 5 cm^3 sec^{-1} was used. A chromatographic injection port (8) was connected to the reactor inlet to allow precise injection of the studied compounds into the assembly. Gas cuvette was added to the reactor outlet. Inner volume of the assembly was completely isolated from the outer air.

In the experiments with photocatalysts the degree of removal of a substance from gaseous phase was determined as a % ratio of difference between its initial and current concentrations to the initial concentration of the substance. Also the concentration of carbon dioxide was controlled in the media, as the basic indicator of destruction of the organic compounds. The experiments were repeated 3 times without changing of the photocatalyst, whereas no significant diminution of the acetone removal rate was observed. The results (the average means) are presented in Fig. 4. Time keeping was started from the moment of switch on the UV lamp. Before this recirculation of the gaseous media in the assembly was conducted for 3 minutes to align the concentration of acetone in the apparatus.

It can be seen from the data that the destruction of acetone and formation of CO_2 occur with gradual deceleration of reaction at a dynamic dependence typical for such processes

Measured concentrations of carbon dioxide suggest that the amount of CO_2 formed at destruction of acetone is lower than expected from stoichiometry of the reaction of complete mineralization calculated from the decay of acetone during the process. This can be explained with several arguments:

- binding of carbon in form of non-volatile inorganic compounds on the catalyst surface;
- predominance of adsorption processes over destruction in removal of organic matter from gaseous phase;

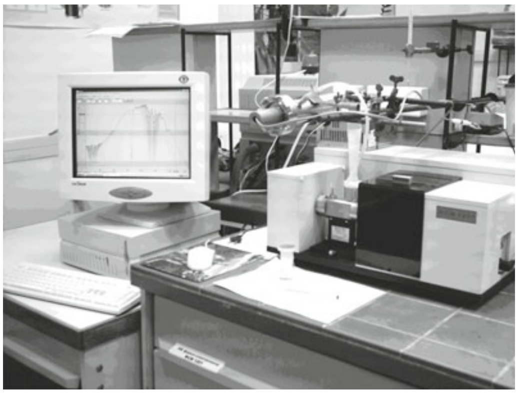


Fig. 2. Experimental assembly exterior.

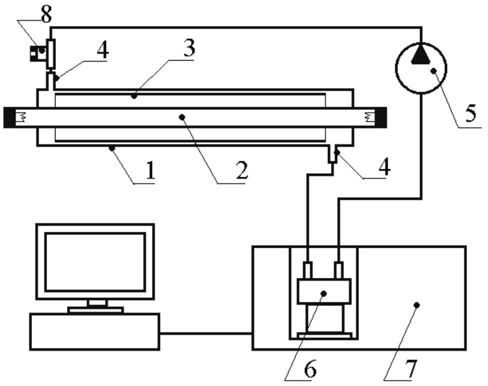


Fig. 3. Experimental assembly conceptual scheme.

- multistage reactions of destruction of organic compounds.

According to the obtained results, it can be definitely concluded that photocatalytic process of destruction is taking place in the studied system. To confirm the photocatalytic nature of reaction the results were compared to dark experiments (without UV irradiation). The comparison proves that destruction process (detected by carbon dioxide build up) does not go without irradiation of the catalytic material.

Theoretically, the amount of CO_2 formed in photocatalytic destruction of organic compounds should correspond to the amount of carbon atoms in the destructed organic molecules However, in practice such a correspondence did not always take place. Firstly, destruction of organic compounds in the system was not complete, as some part of those could be adsorbed on the inner surfaces of the experimental assembly. Secondly, some part of the organic matter, particularly, due to the deficiency of oxygen, could undergo changes yielding in low-volatile compounds, which did not easily desorbed from the catalyst in experimental conditions. Thirdly, part of the resulting inorganic carbon could be trapped in form of surface carbonate ions according to mechanism presented at scheme of destruction of ethanol:

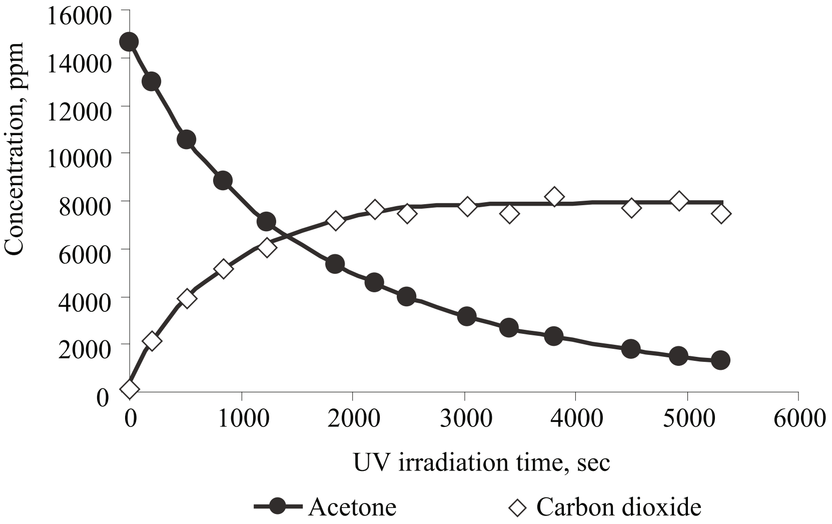
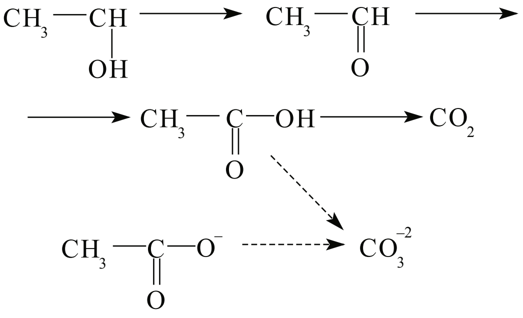
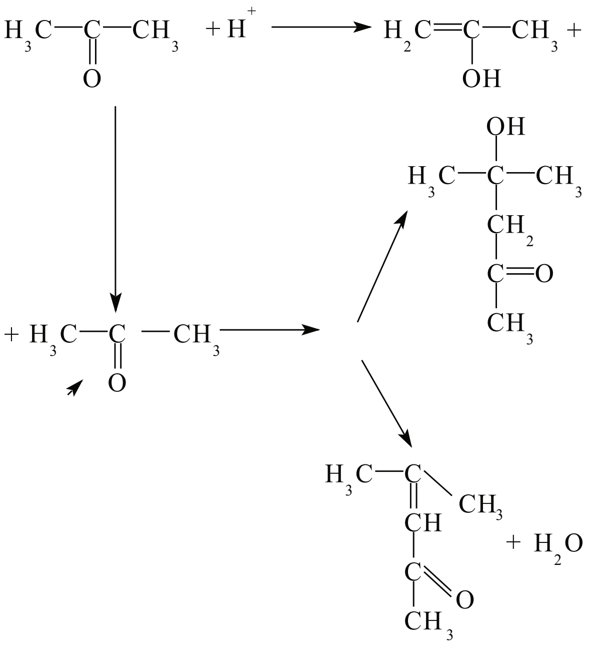


Fig. 4. Changes of concentrations of acetone and carbon dioxide in photocatalytic process.



Possibility of formation of less volatile compounds in photochemical reactions was discussed by many authors. The following scheme of condensation of organic compounds under oxygen deficiency can be given as an example of this reaction [13]:



Every reaction similar to those can lead to deactivation of the catalyst. However, in the process discussed in this study these reactions are hardly probable since there always is a multifold stoichiometric excess of oxygen in the inner gaseous media, even at relatively high concentrations of organic compounds. Moreover, even if such low-volatile products would accumulate on the surface of the catalyst, it is highly probable that they would be destroyed and mineralized further when the amount of oxygen in the system increased.

For comparative evaluation of the efficiency of the developed photocatalytic material an experiment was carried out with zinc oxide layered on the inner surface of the steel reactor body. Zinc oxide has certain adhesion to various surfaces. ZnO coating was formed with 3 g l^{-1} dispersion of the oxide in water and then dried at 105°C and cooled to the room temperature. After the experiments the oxide layer was removed by washing the surface with 0.1 M HCl solution.

When the oxide layer on the inner surface of the reactor was used as photocatalyst the observed degree of removal of acetone from the gaseous media in 1 h was in average 83±4%. Using the previously developed fibreglass photocatalytic material degree of removal in 1 h achieved 93±3%. These results showed a statistically sound prevalence in efficiency of the developed material. This prevalence could be attributed to the more highly developed surface of the woven fibreglass material. This fact does again confirm the prospectives of using the woven supports for the catalysts.

The photocatalytic materials based on woven glass are very promising due to their ease of use and low cost. The important feature is a possibility to use these materials in filtering devices, for which the overall efficiency is expected to be higher compared to the reactors similar to the one used in the present study. In the same time the membrane (filtering) reactors are mostly required for air disinfection rather than for removal of VOCs. For the latter task the non-filtering materials would have longer service life and lower aerodynamic resistance [14].

CONCLUSIONS

Results of the study show the potential efficiency of photocatalyst based on zinc oxide and of the photocatalytic materials on the fibreglass woven support for removal of volatile organic compounds from the gaseous media (air). Infrared spectrometry method used for control of gaseous phase speciation proved to be enough efficient, though it required deep integration of experimental assembly and the measuring system. Further studies are also required for determination pathways of the photocatalytic destruction of VOCs in gaseous phase and its products and intermediates.

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