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Photocatalytic Degradation of Organic Pollutants in Air by Application of Titanium Dioxide Nanoparticles

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In this study we report of the synthesis and application of photocatalytic properties of titanium dioxide nanoparticles for cleaning of organic pollutants in the air on the example of organic pollutant –ethylene. Photocatalytic process, realized by application of titanium dioxide nanoparticles, has been carried in various time and temperature regimes in UV-reactor. By deep coating method the glass beads were coated by titan dioxide nanoparticles, which have been preliminarily obtained by sol-gel method.By gas chromatography method was determined 70%degradation of gaseous ethylene by the application of photocatalytic properties of TiO_2 nanoparticles.

1. Introduction

Titanium is spread in earth crust in the amount nearly 0.63% that means titanium is one of the most abundant elements. According to the crystal form of titanium,it occurs mostly as anatase, rutile and brookite (Dorian et al. 2011). All these crystalline forms can be obtained artificially in laboratory conditions (Primet et al. 1971, Beck et al. 1986, Lu et al. 1995). Because of metastable forms of brookite and anatase, their structures may change at room temperature. Rutile is considered to be the most stable crystalline form (Ulrike et al. 2002).
Titanium dioxide reflects nearly 96% of the visible light spectrum, that's why it is colourlessfor the human eye (Manuel et al. 2014, Vyacheslav et al. 2006, Miguel et al. 2012). There are numerous papers reporting of application of titanium compounds in various fields: paintings, plastic, floor coverings, rubber, paper and in pharmaceutical industry (Harloff et al. 2010, Onoda et al. 2012). The chemical stability and non-toxicity of titanium oxide make it useful material for food packaging industry, biomedical applications and cosmetics (Yoon et al. 2011). Due to such properties of titanium dioxide as prevalence, profitability, high stability and harmlessness to the environment, it also found its application in terms of solving of the concerns of environmental remediation in particular wastewater treatment, disinfection and air purification.
Titanium dioxide nanoparticles are very sensitive to the visible spectrum of light and, especially, towards ultraviolet radiations (Jin et al. 2013, Nishizawa et al. 2014, Kaneko et al. 2014). This property makes them unique photocatalytic material. Based on this, they are used for the surface treatment, splitting of complex organic radical and as catalyst in the degradation of contaminants (Kansal et al. 2012, Dibble et al. 1990, Canterino et al. 2009, Andreozzi et al. 2011).
The purpose of this study is the synthesis of TiO_2 nanoparticles by sol-gel methods from alkoxide precursors and application of photocatalytic properties of titanium dioxide nanoparticles for decomposition of organic pollutants in the air on the example of organic pollutant – ethylene. It should be noted that the size of titanium dioxide nanoparticles ranges at 15 - 30 nm . (Muhammad et al. 2011)

2. Experimental

2.1 Materials and equipment

All chemicals, used in the synthesis, were of analytical grade and used as received. Ethylene, isopropanol, Titanium IV İsopropoxide TTİP were purchased from Sigma-Aldrich .

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Equipment

Synthesis of TiO2 nanoparticles were carried out by sol-gel methods from TTIP precursor using T-mixer and glove box. The dried TiO_2 NPs were prepared by vacuum drying of the sols at $25^0$with further sintering of the dried gels at 650℃ for 1 hour. The morphology and distribution of the TiO_2nanoparticles was studied by scanning electron microscope,energy dispersive spectrum (EDS) analysis, and X-Ray Diffraction (XRD). Photocatalytic degradation of ethylene was carried out in the UV reactor (the source of UV radiation was the UV lamp (250 W ultra-high pressure mercury lamp)). The grade of photocatalytic degradation of ethylene was monitored by gas chromatograph GC-2010 Plus.

Scanning electron microscope (SEM) analysis and energy dispersive spectrum (EDS) analysis of prepared samples of TiO_2 nanoparticles were taken on Field Emission Scanning Electron Microscope JEOL JSM-7600F at an accelerating voltage of 15.0 kV, SEI regime.

XRD X-ray diffraction analysis was performed on Rigaku Mini Flex 600 XRD diffractometer at ambient. In all the cases, Cu K a radiation from a Cu X-ray tube (run at 15 mA and 30 kV) was used. The samples were scanned in the Bragg angle 2 h range of $20–90^0$.

2.2 The synthesis of TiO_2 nanoparticles by the sol-gel method.

The sol-gel process is considered to be the hydrolysis-condensation reactions. The TiO_2 nanoparticles were obtained with using of the T-mixer (Zdrakov et al. 2015). T-mixer consists of three main parts: two thermostatic cameras; T-shaped and butterfly-shaped and actually mixer (Figure 1).Preliminarily were prepared the solution A (4.458 mL of TTIP and 45.542 mL isopropanol) and solution B (0.526 mL of H_2O and 49.47 mL isopropanol). The solutions A and B simultaneously were injected into cameras.

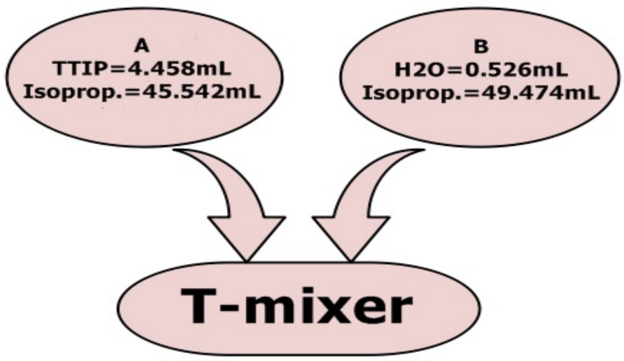
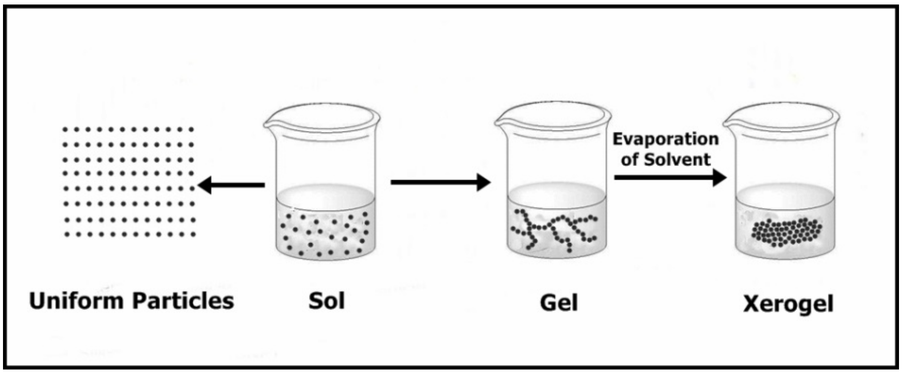


Figure 1. Schematic representation of mixing of two solutions in the T-mixer

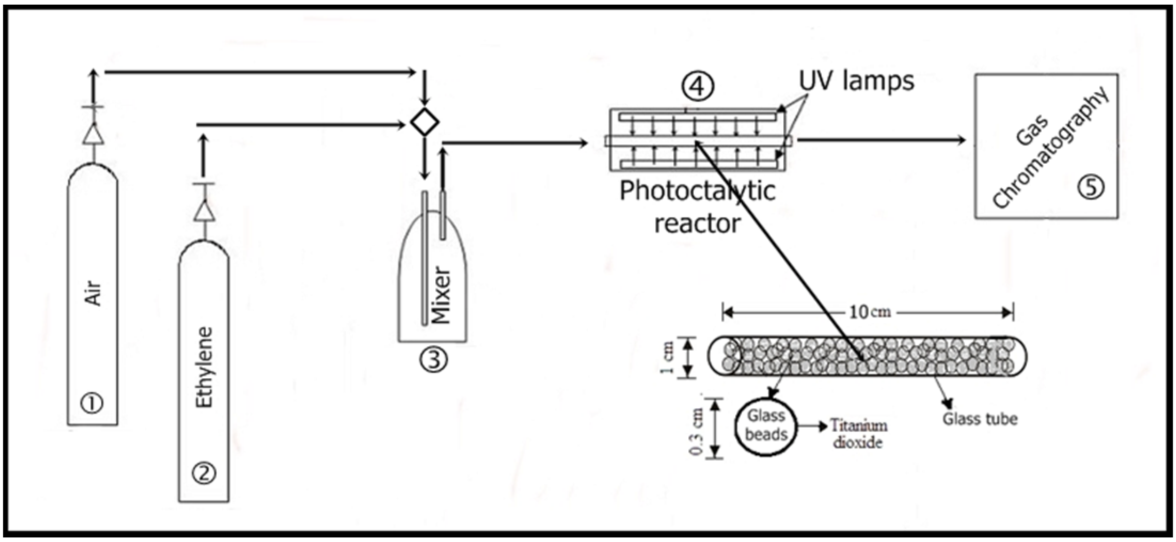
The procedure was carried out under the nitrogen atmosphere, in order to prevent the contact with atmospheric oxygen, as well as for cooling the reaction mixture. The stirring process in the T-mixer takes approximately 0.5-1.7 seconds. Two injections of solutions A and B were mixed under high pressure. The high pressure affected to the process of hydrolysis and oxidation and this provides the rapid nucleation without agglomeration (Scheme 1).



Scheme 1. Sol-gel synthesis process of TiO_2nanoparticles

2.3 The process of photocatalysis.

The transparent glass beads (d=0.3 mm) have been chosen as photocatalyst carrier. The glass beads were coated by deep coating method with obtained TiO_2 NPs. For this purpose the glass beads were cleaned with isopropanol and acetone, and placed into dry box for 2 hours at temperature 80-100^{0}C and then they were covered by deep coating method with TiO_2 nanoparticles. Then the coated beads was drying at 45 ^{0}C during 4 hours in the dry box.



Scheme 2. The schema of photocatalytic process wit application of TiO_2 nanoparticles

The mixture of air, gaseous nitrogen and ethylene was blow through UV reactor (Scheme 2) under the UV radiation at 450 nm. The UV reactor is the glass tube filled with glass beads, coated with nanoparticles of titanium oxide. The length of tube was 10sm with d=1sm.

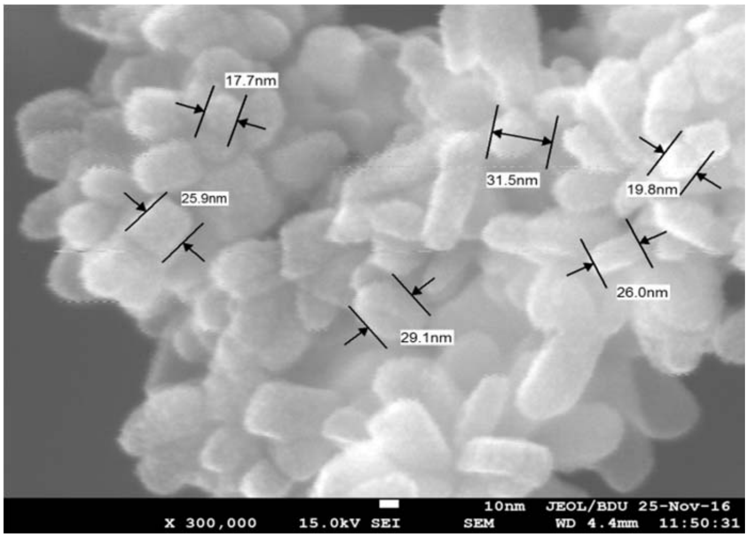
3. Results and Discussion

In accordance of modern concepts, the electrons in the semiconductor titanium dioxide exist in free and bound states. In the free state, the electrons move through the crystal lattice, in the bound state –they mostly associated with ion of crystal lattice and take part in the chemical bonding. For transfer of an electron from a bound state to the free state must be expended not less than 3.2 e V of energy. This energy can be supplied by the quant of light with a wavelength longer than 390 nm (Akira et al. 1972). When photon of light is absorbed in TiO_2it induces forming a free electron (e-) and electron vacancy - hole (h +), which recombine or migrate in the semiconductor, partially localized at structural defects of its crystal lattice. Then, excited electron of TiO_2, can participate in the course of photocatalytic reaction.

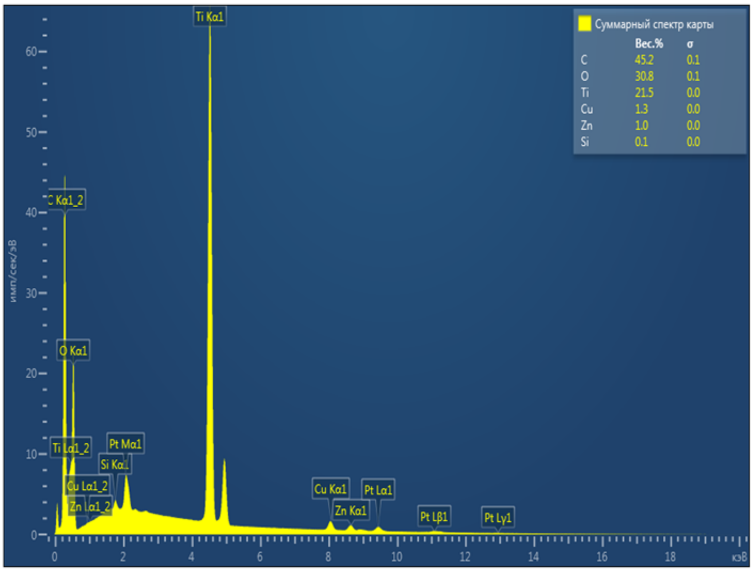
Increased activity of nanosized photocatalysts can be explained by a high degree of dispersion of the material, i.e., the number of atoms on the surface or crystal is comparable to the number of atoms located inside. Also, at nano scaled semiconductor photocatalysts, the electron wavelength becomes comparable with the size of the crystal.

Due to high sensitivity of titanium dioxide nanoparticles to the visible spectrum of light and, especially, towards ultraviolet radiations we synthesized TiO_2 nanoparticles by sol-gel method and tested its photocatalytic properties in degradation of ethylene. The morphology and size distribution of TiO_2 nanoparticles were studied by SEM, EDS and XRD methods. The results of analysis revealed that synthesized nanoparticles mostly consist of rutile structure forms.

The prepared nanoparticles were analysed by SEM and EDS methods, and the results are presented on Figure 2 (a,b). As it seen from Figure 2 (a) the obtained nanoparticles are homogenous and the size of nanoparticles varies in the range from 15 to 30 nm. The points, identified in the EDS spectra in Figure 2(b),demonstrate the presence of Ti and O as the main elements of the sample and support the data of TiO_2 nanoparticles formation (the other peaks are corresponding to Cu and C, being characteristic of the carbon-coated grid).This very well correlates with the results, obtained from XRD analysis.



a)



b)

Figure 2. a) SEM image of the TiO_2 NPs; b) EDS spectra of TiO_2NPs

The purity and crystalline properties of the TiO_2 nanoparticles were investigated by powder X-ray diffraction (XRD) method. The XRD patterns are shown in Figure 3. All the XRD peaks were well defined and corresponded to TiO_2at rutile phase. In the pattern all lines can be indexed, using the ICDD (PDF-2/ Release 2011 RDB) DB card number 00-001-1292. The pattern of TiO_2 NPs has characteristic peaks at 27.50° (110), 36.04° (101), 41.18° (111), 54.23° (211). The average crystal size, estimated from (110) peak, using the Scherrer formula, is 18 nm for TiO_2 pattern nanoparticles.
For the evaluation of the photocatalytic activities of the prepared TiO2 nanoparticles toward UV irradiation, the concentration change of ethylene at 450 nm was monitored as a function of visible light irradiation time by gas chromatography method. Figure 4 shows plots of ethylene concentration change with visible irradiation time. The process of photocatalitic degradation of ethylene has been carried under the UV radiation of 450-550nm wavelengths, during 300-500 min at 35-45^{0}C.
As it can be seen from Figure 4 the photocatalytic process starts from the moment of UV irradiation. Calibration time takes 10-30 min. The initial content of organic pollutant (ethylene) in air was 120 PPM. The control of photocatalytic degradation of ethylene was conducted by chromatographic methods. It was found that maximum value of ethylene degradation is70%. Photocatalytic process allows us to purify air by means of

photocatalysis that takes place in the presence of titanium dioxide nanoparticles by oxidation of ethylene up to CO_2 and H_2O.

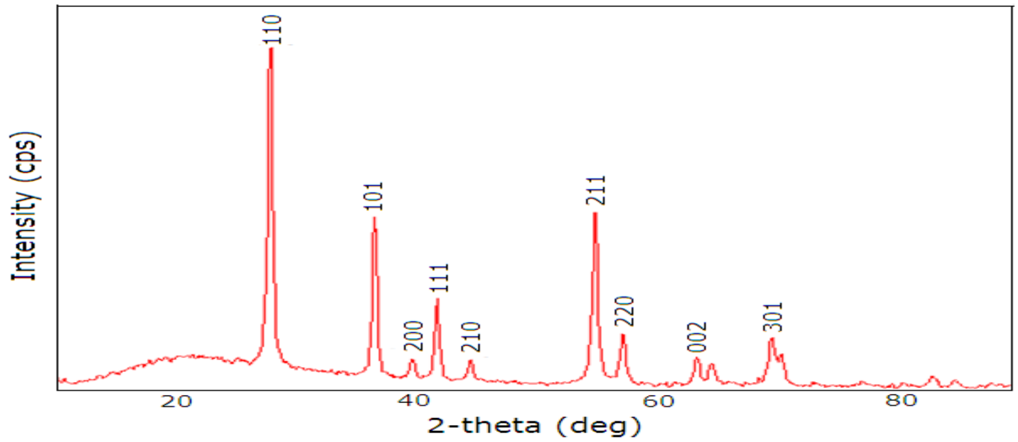


Figure 3 . XRD pattern for the TiO_2 NPs

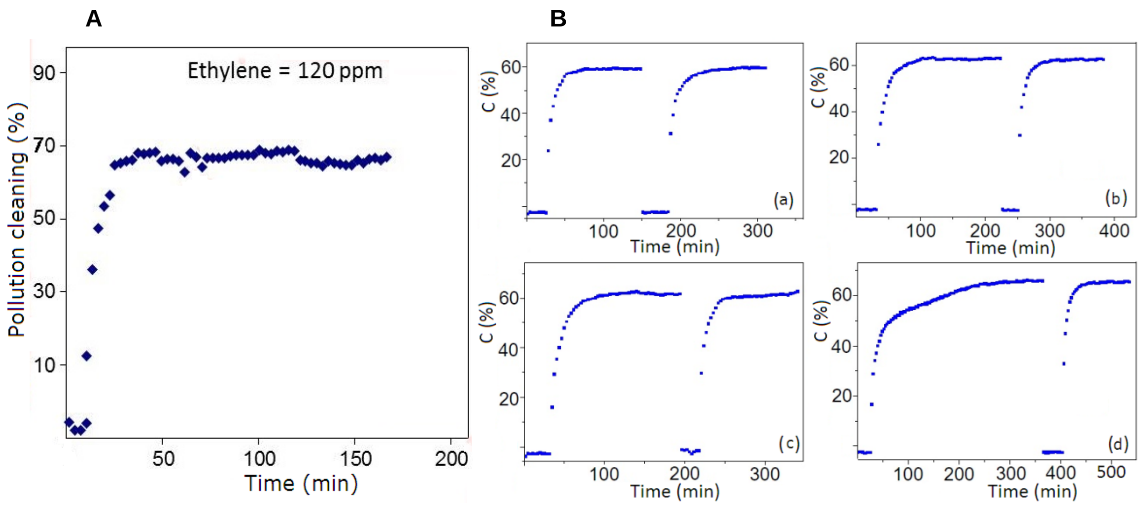


Figure 4. Photocatalitic degradation of ethylene under the UV radiation of 450-550 nm wavelengths, at various temperature-time regimes: A) τ=170 min; T=45^0 ,B) (a) τ= 300 min, T =35^0; (b) τ= 400 min, T =35^0; (c) τ= 350 min, T =35^0; (d) τ= 500 min, T =35^0

4. Conclusion

In this paper we reported about successful synthesis and characterization of TiO_2 nanoparticles at rutile phase, where titanium dioxide revealed a promising semiconductor photocatalyst properties towards photocatalytic decomposition of ethylene under visible light. The effectiveness of TiO_2 under absorbing of visible light (450 nm) irradiation was monitored by evaluation of the photocatalytic process of degradation of gaseous organic pollutant molecules.
The process was repeated 10 times and there was not observed the inactivation of catalyst. Therefore, this process is considered very profitable, expedient and economically efficient. Given the above, it can be concluded that this process is sustainable, environmentally friendly and economical.

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