

Original Research

Photocatalytical Degradation of Toluene and Cyclohexane Using LED Illumination

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Abstract

A sol-gel process followed by hydrothermal reaction was used to prepare coupled WO_3 - TiO_2 photocatalysts with varying amounts of WO_3 in respect to TiO_2 (3 mol% and 5 mol% respectively). Additionally, photocatalysts have been subjected to different calcination temperatures of 400°C and 800°C, which allowed us to compare how these affect photodegradation efficiency. Photocatalysts were characterized under a scanning electron microscope, x-ray diffraction, and by measuring BET surface area. Photocatalytic tests have been carried out following the degradation of toluene and cyclohexane in the gas phase under LED UV light (375 nm). Elevated calcination temperature turned to enhance photocatalytical efficiency of coupled WO_3 - TiO_2 while degrading the model pollutant cyclohexane. It was demonstrated that light emitting diodes (LEDs) can be used effectively as a source of illumination in photoreactors, sufficient to obtain 90% compound elimination from the air during 15 minutes of illumination while applying a well-matched photocatalyst.

Keywords: photocatalysis, titanium dioxide, tungsten trioxide, light emitting diodes (LEDs)

Introduction

Heterogeneous photocatalysis is highly appreciated for its removal of contaminants from both water and air, since under specific conditions hydroxyl radicals are formed with the ability to mineralize various pollutants. In order to be activated, titanium dioxide requires illumination with a proper wavelength of light, resulting in the promotion of an electron from the valence to the conduction band [1]. Photons with corresponding wavelengths are absorbed by a photocatalyst, resulting in the generation of electron-hole pairs. This leads to separation of charge carriers and, consequently, to oxidation and reduction reactions on the

surface of a semiconductor [2]. Titanium dioxide exists in three polymorphs: anatase, rutile, and brookite [3]; however, only the two first have value in photocatalysis. All crystalline phases of TiO_2 are characterized with different energy band gaps, i.e., only a specific wavelength of light will activate anatase and rutile. The wavelength of radiation needed to induce excitation can be calculated from a quotient of Planck's constant ($h = 1240$) and band gap width (E_g). Anatase has a wider energy band gap of 3.2 eV, and thereby is activated under UV light. On the other hand, the rutile photoactivation energy band gap equals 2.8 eV, hence extends into the region of visible light. The disadvantage of rutile, when compared to anatase, refers to a higher recombination rate, which directly reflects on its lower photoefficiency [4].

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The principles and mechanism of photocatalysis have been widely discussed and presented in the literature [5]. However, this work considers the combined synergy of coupled semiconductors, namely titanium dioxide and tungsten trioxide. WO_3 has its valence and conduction bands correspondingly lower than those of anatase (Fig. 1). The combination of these two semiconductors results in obtaining a composite with lower energy gap, hence with the activity shifted toward the visible region. Luo et al. [6] observed easier generation of electron-hole pairs in a coupled WO_3/TiO_2 system in comparison with anatase or WO_3 . The photo-excitation mechanism of a coupled system is altered with respect to a single semiconductor. Illumination of coupled WO_3/TiO_2 results in the transfer of holes from the valence band of WO_3 toward the valence band of TiO_2 , and transfers in the opposite direction of electrons from the TiO_2 conduction band, which has more negative potential toward the WO_3 conduction band [6]. Such conditions favour photocatalytical efficiency, since the recombination rate of electron-hole pairs that slows down and the production of OH radicals is enhanced [7].

Photocatalytical reactions are mainly carried out in photoreactors equipped with an artificial illumination source. The literature clearly distinguishes between photoreactors for aqueous or gas phases. Although the illumination can be periodic or continuous, the latest report by Tokodea O. et al. [8] shows that the use of controlled periodic illumination (CPI) for photocatalysis is not necessarily advantageous. Besides solar light (possessing a broad spectrum of radiation, mainly in the range of visible light), conventional UV lamps (xenon, fluorescent, halogen, metal halide, or mercury) make the illumination source in laboratory photoreactors. Until recently, there was only a small selection of monochromatic light sources that could be applied effectively in photocatalysis. In the last few years, a new type of light source has appeared: light-emitting diodes (LEDs). LEDs that are able to continuously emit light in the UV range are of particular interest.

The first reports of LED application in photoreactors appeared in 2005, when Carmignani et al. [9] received a patent on a method for purifying gaseous pollutants by means of photocatalysis that utilizing LED as a source of light. LEDs represent a relatively new source of light

used in photoreactors, since conventional illumination is still more frequently used in research. Therefore, LED applicability requires confirmation with further studies on selected pollutants. In this regard, we investigated the efficiency of toluene and cyclohexane removal in an LED TiO_2 -based photocatalyst system.

The photocatalytic degradation of hydrocarbon vapours using commercial TiO_2 photocatalyst has been extensively studied [10-11]. Toluene is very often chosen as a model pollutant in photocatalytical processes, which is very advantageous in terms of comparing obtained results. The photodegradation efficiency of toluene in the presence of titania-based photocatalysts may even reach 100% [12-13]. Toluene is one of the typical indoor volatile organic compounds, as well as a member of the BTEX group. It can be found in everyday products such as paints, lacquers, inks, adhesives, cosmetics, and gasoline, but unfortunately toluene can cause adverse health effects. Breathing its vapours can result in headache and irritation of eyes, nose, or skin, but also disorders of the central nervous system or liver and kidney damage. According to the U.S. Occupational Safety and Health Administration (OSHA), the permissible time-weighted average (TWA) exposure limit of toluene is 200 ppm.

A compound that is less frequently chosen as a model pollutant in photocatalytical reactions, but also is hazardous, is cyclohexane. Cyclohexane belongs to hydrocarbons, which are determined in the air at workplaces. According to OSHA, the permissible exposure limit for cyclohexane is 300 ppm. Poisoning may cause a range of negative symptoms, including anxiety, throat and eye irritation, dizziness and nausea, toxicity of the central nervous system, respiratory failure, and narcosis. Cyclohexane vapours form explosive mixtures with air. They are more dense than air and tend to accumulate near ground and in the lower parts of rooms. The explosive limit for cyclohexane is relatively low, in the range of 1.2-4.8%. Cyclohexane manufacturing plants use condensers to limit vapour emissions to the atmosphere. In the case of cyclohexane leakage to the air it is important to quickly degrade target pollutants. Zheng et al. [14] carried out an experiment on photodegradation efficiency of gas-phase cyclohexane in the presence of various TiO_2 nanostructures. The results demonstrate that titania-based photocatalysts can oxidize gaseous cyclohexane within 6 hours, with 96% degradation efficiency.

Our aim was to verify LED illumination for degradation of selected hydrocarbons – namely cyclohexane and toluene. LED construction allows for emitting most of its power within the desired wavelength. LEDs have an opportunity to become more popular over conventional light sources, because while having the potential for almost the same applications, they are also supposed to be more economical. LEDs can be successfully applied in photocatalysis because they have monochromatic light [15]. They may consist of III-nitride, including gallium nitride (GaN), indium gallium nitride (InGaN), aluminium gallium nitride (AlGaN), or aluminum nitride (AlN) [16]. InGaN LEDs can emit a wide spectrum of light, from UV

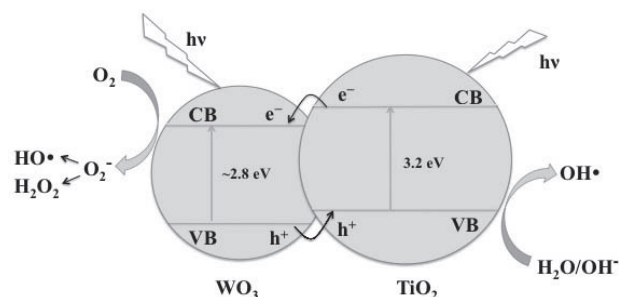


Fig. 1. Mechanism of photoexcitation of coupled WO_3/TiO_2 . CB – conduction band, VB – valence band, according to [6].

to IR. By changing the indium fraction in the active layers of InGaN, the specific wavelength spectra can be obtained [17]. It is desired that the wavelength would be optimal for the photocatalytic process, and consequently LEDs could serve as a more efficient and energy-safe source of illumination than lamps with a more flat spectrum. Another advantage of LEDs is that they are a discrete source of light and thus are easier to be built-in in photoreactors.

Materials and Methods

All applied reagents were of analytical grade and used without further purification. Titanium-based photocatalysts were prepared by the sol-gel method using titanium tertbutyl oxide as a precursor (TBT \geq 97%, supplied by Fluka). While the solution was thoroughly mixed, we added ammonium para-tungstate (ApT, 99.99%) – a precursor of tungsten trioxide – or pure tungsten trioxide (99.99%) from Sigma-Aldrich to the solution. The amount of ammonium paratungstate or pure WO₃ used in the preparation step was calculated on the assumption that the content of WO₃ in the photocatalysts after synthesis should be equal to 3 or 5 mol% of the photocatalyst dry mass. After thorough stirring the solution was transferred to a hydrothermal reactor. Next, it was centrifuged, dried, and calcined at 400°C or 800°C. A more detailed account of this procedure can be found elsewhere [18]. The samples were chosen based on earlier data regarding process parameters and characterization of photocatalysts done by Mioduska et al. [18]. In the cited paper, although pertaining to the aqueous phase, photocatalysts calcined at 800°C were characterized with enhanced photodegradation efficiency compared with those calcined at lower temperatures. An increase in calcination temperature above 400°C resulted in favorable reduction of the amorphous phase in the coupled WO₃-TiO₂ photocatalyst. Photocatalysts calcined at 400°C were also chosen, since it is a very common temperature described in the relevant literature and may be a reference.

The specific surface area was determined by the multi-point Brunauer-Emmett-Teller (BET) method by liquid nitrogen adsorption at 77 K on a Micromeritics Gemini V. Emission scanning electron microscope (FEI Quanta FEG 250) with ET secondary electron detector that we used to study surface morphology of coupled WO₃-TiO₂

photocatalysts. Beam accelerating voltage was maintained at 10 kV. The structure of catalysts was also characterized by X-ray diffraction technique (XRD) using a Rigaku MiniFlex with Cu-K α 2 radiation.

The photocatalytic activity of prepared photocatalysts was evaluated with respect to the degradation of toluene and cyclohexane vapours, with initial concentration at 200 and 150 ppm, respectively. The samples were irradiated with an array of 25 UV LEDs characterized with λ_{max} equal to 375 nm (Liteon Optoelectronics through-hole lamp, LTL2V3TU75K). The photocatalyst was coated onto a glass plate and mounted in a 30 cm³ reaction cell (stainless steel flat, circular reactor). Illumination was external through a quartz wall. After closing the reactor, either toluene or cyclohexane were passed through the reactor for 1 minute, a blind sample was taken, and the illumination was switched on for 15 minutes. During that time probes were taken every 5 minutes and analysed for cyclohexane or toluene in a gas chromatograph (PerkinElmer, model Clarus 500, fused silica capillary column Elite-5 with 5% diphenyl and 95% dimethyl polysiloxane stationary phase). Gas samples were analyzed for primary contaminants (i.e. cyclohexane or toluene). The results are provided in terms of cyclohexane/toluene conversion, defined as:

$$\begin{aligned} &\% \text{ cyclohexane/toluene conversion} \\ &= (C_0 - C) / C_0 \times 100 \end{aligned}$$

...where C_0 is influent hydrocarbon concentration and C is effluent hydrocarbon concentration at any given time.

Results and Discussion

Four experiments on two different model pollutants were carried out to determine whether the LED-photocatalyst system has the potential to degrade organic compounds. The results are presented in Table 1. Fig. 2 graphically presents the photodegradation of cyclohexane and toluene under UV LED light ($\lambda_{\text{max}} = 375\text{nm}$) in the presence of 3 mol% WO₃-TiO₂ and 5 mol% WO₃-TiO₂ photocatalysts, respectively, calcined at 400°C and 800°C. Results presented in Table 1 show that the heat treatment of a photocatalyst had less influence on the photodegradation efficiency in the case of toluene.

Table 1. Degradation efficiency of coupled WO₃-TiO₂ photocatalysts after 15-minute illumination with 375 nm LEDs and 62 W/m² average power flux.

Photocatalyst	Target pollutant	Photocatalyst calcination temperature (°C)	Elimination (%)	Specific surface area BET (m ² /g)
3 mol% WO ₃ -TiO ₂	cyclohexane	400	70	134
3 mol% WO ₃ -TiO ₂	cyclohexane	800	90	6
5 mol% WO ₃ -TiO ₂	toluene	400	88	183
5 mol% WO ₃ -TiO ₂	toluene	800	78	5

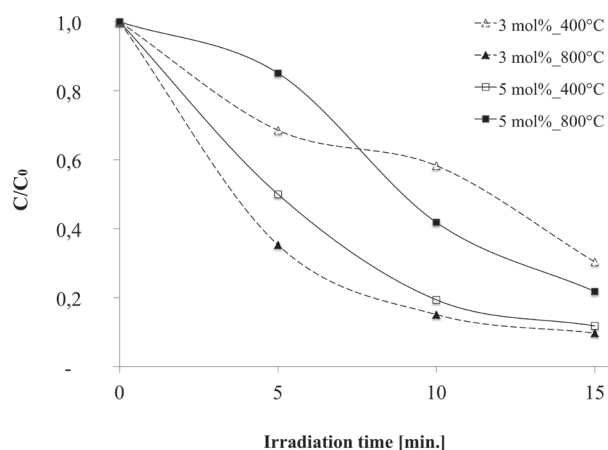


Fig. 2. Photodegradation of cyclohexane and toluene under UV LED light ($\lambda_{\text{max}} = 375\text{nm}$) in the presence of 3 mol% $\text{WO}_3\text{-TiO}_2$ and 5 mol% $\text{WO}_3\text{-TiO}_2$ photocatalysts, respectively, calcined at 400°C and 800°C.

The amount of cyclohexane was easier decreased in the presence of 3 mol% $\text{WO}_3\text{-TiO}_2$ calcined at 800°C than at 400°C. In order to find the cause for that result, we additionally determined the BET surface area for coupled $\text{WO}_3\text{-TiO}_2$ photocatalysts. We observed a significant decrease in the value for photocatalysts calcined at 800°C, which was around 23 to 36 times smaller than the surface area of the photocatalyst for 3 mol% $\text{WO}_3\text{-TiO}_2$ and for 5 mol% $\text{WO}_3\text{-TiO}_2$, respectively, calcined at 400°C. Sintering of grains might have caused such a reduction.

Although photocatalysts with smaller BET surface area are expected to be less effective in degradation of target pollutants, the experiments showed the opposite. The increase in calcination temperature resulted in the formation of active crystal phase of anatase as well as the

rutile phase. According to Długosz et al. [19], the mixture of anatase and rutile exhibited higher photocatalytic efficiency because of one-way electron transfer from the anatase conduction band to the rutile conduction band, allowing for more efficient electron hole charge separation. Both our photocatalysts had very high activity when calcined at elevated temperatures, which is typical for the coexistence of anatase and rutile phases. This explains that the high surface area cannot by itself determine degradation efficiency. Too much developed surface area may also promote the adsorption of impurities at the surface, thus reducing photocatalytic activity.

SEM images were also created in order to determine the difference in morphology that might have influenced the photoactivity of the samples. Coupled $\text{WO}_3\text{-TiO}_2$ photocatalysts were selected for microscopic analysis, having the same composition (5 mol% WO_3 in respect to TiO_2), but calcined at 400°C and 800°C (Fig. 3). Both samples are characterized with spherical particles. The inverse relationship between particle size and BET surface area was observed. Comparing Fig. 3a) with 3b) we can see that the size of particles is influenced by the heat treatment process. Photocatalysts calcined at 800°C have bigger nanoparticles compared to those calcined at 400°C.

The XRD patterns of coupled 5 mol% $\text{WO}_3\text{-TiO}_2$ composite confirmed that the photocatalyst calcined at 400°C consisted solely of anatase, while an increase in temperature to 800°C resulted in partial phase transformation from anatase to rutile (80% to 20%, respectively). In both samples only the monoclinic phase of tungsten trioxide was observed. Prepared powders were nanocrystalline regardless of the value of calcination temperature.

Experiments presented in the relevant literature usually applied monochromatic lamps with 254 nm for toluene removal [12, 20-21]. The power flux varies depending on the construction of a photoreactor, and is

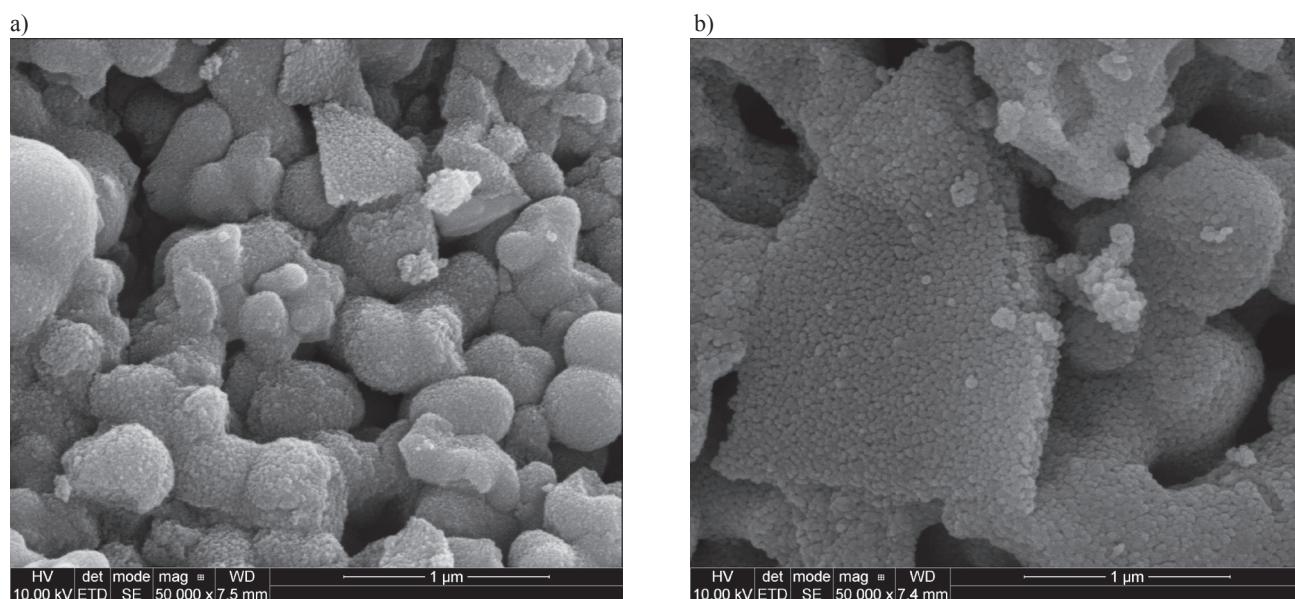


Fig. 3. SEM images for samples 5 mol% $\text{WO}_3\text{-TiO}_2$ calcined at a) 400°C and b) 800°C.

not always specified. Keshmiri et al. [20] examined the photocatalytical oxidation of toluene. They carried out experiments with two UV lamps with higher intensity of 254 nm and 365 nm, having different power flux equal to 30 W/m² and 21 W/m², respectively, and observed that illumination with 254 nm provided a better photocatalytic oxidation rate of toluene (up to 3.9 g/m²/h). Lamp intensity was indicated as the primary reason for better photodegradation. Similar conclusions were drawn by Kim et al. [22], who investigated the effect of total irradiation on the photo-oxidation process of cyanide and stated that the removal efficiency is clearly linked with applied light intensity. Although the LEDs used in our experiments were of quite low energy ($\lambda_{\text{max}} = 375 \text{ nm}$), they secured an average light intensity of 62 W/m². Ten minutes of irradiation resulted in clear concentration drop of analysed model pollutants in the presence of coupled WO₃-TiO₂ photocatalysts (Fig. 2). The degradation rate of cyclohexane was faster in the presence of photocatalysts calcined at 800°C (3 mol% WO₃-TiO₂), and a similar degradation rate was observed for 5 mol% WO₃-TiO₂ calcined at 400°C in toluene removal. Total removal was not observed, although in both cases 15 minutes of irradiation resulted in degradation of around 90% of target pollutants. We should also emphasize that despite the calcination temperature and the type of model pollutant, in the presence of coupled WO₃-TiO₂ photocatalysts and relatively short illumination time with UV LEDs we obtained a high degradation level. Kim et al. [22] not only emphasized the importance of irradiation, but also drew attention to the high removal efficiency of LEDs as a source of light, with respect to consumption of electrical energy. Our experiments effectively used LEDs as a source of illumination and confirmed that LED illumination can be successfully used in photocatalytical degradation of toluene or cyclohexane.

Conclusions

The correlation of obtained results of BET surface area, particle size, and shape determined under a scanning electron microscope, as well as XRD diffractograms indicating crystalline phase, does not directly translate into photocatalytical efficiency in degradation of different model pollutants, namely cyclohexane and toluene. However, a comparison of the results shows that the calcination temperature of the prepared photocatalysts significantly affected the efficiency of degradation. Photocatalysts calcined at 800°C were more effective than those calcined at 400°C regarding the removal of cyclohexane. Much less data is specified with respect to the gas phase, and thus it is more difficult to compare obtained results with those presented in relevant literature. Research incorporating varying process conditions, wavelength, power flux, and illumination time is on its way in order to verify if LEDs, especially UV-LEDs, can serve as a better light source in gas photoreactors, and also

to confirm that while having lower power consumption one can obtain at least similar degradation rates.

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