

Article

Photocatalytic Degradation of Toluene, Butyl Acetate and Limonene under UV and Visible Light with Titanium Dioxide-Graphene Oxide as Photocatalyst

Birte Mull, Lennart Möhlmann and Olaf Wilke *

Bundesanstalt für Materialforschung und-prüfung (BAM), Berlin 12205, Germany; birte.mull@bam.de (B.M.); Lennart.Moehlmann@gmx.de (L.M.)

* Correspondence: olaf.wilke@bam.de; Tel.: +49-30-8104-1422

Academic Editors: Ki-Hyun Kim and Abderrahim Lakhouit

Received: 21 November 2016; Accepted: 13 January 2017; Published: 25 January 2017

Abstract: Photocatalysis is a promising technique to reduce volatile organic compounds indoors. Titanium dioxide (TiO₂) is a frequently-used UV active photocatalyst. Because of the lack of UV light indoors, TiO₂ has to be modified to get its working range shifted into the visible light spectrum. In this study, the photocatalytic degradation of toluene, butyl acetate and limonene was investigated under UV LED light and blue LED light in emission test chambers with catalysts either made of pure TiO₂ or TiO₂ modified with graphene oxide (GO). TiO₂ coated with different GO amounts (0.75%–14%) were investigated to find an optimum ratio for the photocatalytic degradation of VOC in real indoor air concentrations. Most experiments were performed at a relative humidity of 0% in 20 L emission test chambers. Experiments at 40% relative humidity were done in a 1 m³ emission test chamber to determine potential byproducts. Degradation under UV LED light could be achieved for all three compounds with almost all tested catalyst samples up to more than 95%. Limonene had the highest degradation of the three selected volatile organic compounds under blue LED light with all investigated catalyst samples.

Keywords: photocatalysis; emission test chamber; volatile organic compounds

1. Introduction

People from the Western world spend most of their time indoors, either in houses or in transportation, hence, the indoor air quality is of particular importance [1]. Though, volatile organic compounds (VOC) are ubiquitous in the indoor air, emitting, e.g., from building materials, wall and floor coverings and interior equipment. Those emissions can have a negative impact on the indoor air quality, health and wellbeing of occupants. This effect is described as sick-building-syndrome [2]. An approach to improve the indoor air quality, which has come more and more into focus during the last years, is the photocatalytic degradation of pollutants by photoredox catalysis. Photocatalytic active coatings, mostly made of the semiconductor titanium dioxide (TiO₂) [3], have been developed and tested for indoor air use. TiO₂ in its anatase modification has a band gap of 3.2 eV and can hence be activated under UV-light ($\lambda = 387$ nm). By light irradiation with a corresponding wavelength, electrons from the valence band are transferred to the conduction band and as a result electron-hole pairs are formed (Figure 1).



The excited electrons can proceed in a single electron reduction and, in the presence of O₂, form a superoxide radical anion O₂^{•-}. Simultaneously, the electron holes (h⁺) can react with H₂O to yield hydroxyl radicals OH• (single electron oxidation). These resulting radicals are highly reactive and can mineralize organic substrates to CO₂ and H₂O as generalized in equations 2 and 3 [3,4].

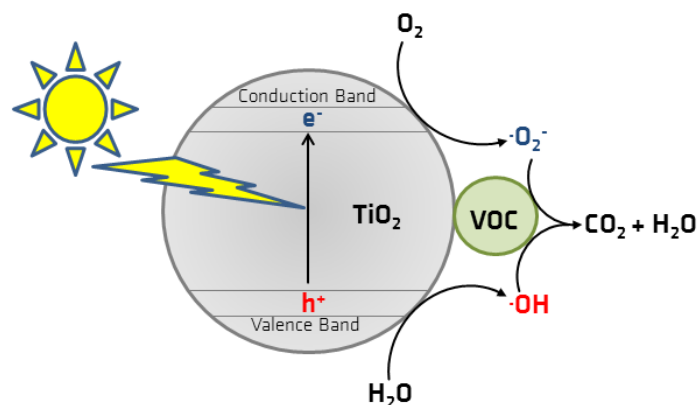
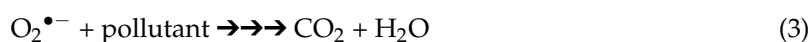
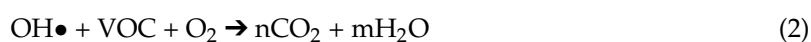


Figure 1. Photocatalytic degradation mechanism.



Since TiO_2 can only be activated under UV light it has to be doped or modified to shift its working range in the visible light spectrum. Banerjee et al. published an article summarizing and describing possibilities, e.g., metal and non-metal doping, dye sensitization, combination of TiO_2 with reduced graphene oxide, to improve the visible light activity of TiO_2 [5]. Graphene is a relatively new but promising material [6] and its oxide in combination with TiO_2 is already known to successfully catalyze degradation of VOC, methyl orange and methylene blue under visible light [7–9]. With its high surface area of $2600 \text{ m}^2 \cdot \text{g}^{-1}$ [10] graphene sheets are highly reactive thus enhancing the photocatalytic activity of TiO_2 due to the fact that more π – π interactions are possible [8]. The band gap has to be below 3.0 eV to get absorption under visible light [11], the light absorption is extended by increasing the amount of GO [9]. However, if the amount of graphene in the catalyst system is too high the photocatalytic activity is reduced [12,13].

One additional substantial aspect for the reactivity is the relative humidity in the emission test chamber which can both increase or decrease the photocatalytic degradation of VOC. According to Zhao and Yang [14] and Mo et al. [15] too little water vapor results in a retard of the degradation; whereas too much water vapor is also not appropriate for the degradation process. In the second case, the water molecules and the VOC compete for adsorption positions on the TiO_2 surface. Furthermore, the effect is also depended on the inlet concentration of the VOC [16]. However, the optimum relative humidity level seems to be different depending on the investigated compound and used catalyst [17].

This work focuses on the photocatalytic degradation and investigation of potential byproducts of toluene, butyl acetate and limonene on pure TiO_2 and TiO_2 modified with different amounts of graphene oxide (GO; 0.75%, 1%, 2.5%, 5%, 10%, 14%) under UV and visible (blue) LED light. These compounds were selected because of their frequent occurrence in the indoor environment [2]. Experiments were performed in emission test chambers of various volumes under controlled climatic conditions. A reference VOC atmosphere in the range of real indoor air concentrations was created by using a gas mixing system (GMS) [18].

2. Materials and Methods

2.1. Chemicals

Toluene (108-88-3, for organic residue analysis) and methanol (67-56-1, ultra resi-analyzed) were purchased from J. T. Baker, butyl acetate (123-86-4, 99+%) and (R)-(+)-limonene (5989-27-5, 97%) from Aldrich and naphthalene d_8 in methanol ($2000 \mu\text{g} \cdot \text{mL}^{-1}$) from Restek. A graphene oxide water

dispersion was purchased from Graphenea ($4 \text{ mg}\cdot\text{mL}^{-1}$, monolayer content >95%). The TiO_2 was commercially available N-doped anatase.

2.2. Analytical Parameters and Instrumentation

Quantification was done using calibration curves (8 points) in combination with an internal standard (naphthalene d_8 in methanol). Each tube was loaded with $1 \mu\text{L}$ of internal standard and methanol was flushed off with a nitrogen stream for 10 min ($100 \text{ mL}\cdot\text{min}^{-1}$) before air samples were taken.

Air sampling was done periodically with Tenax[®] TA sorption tubes (Gerstel; 1 L with 50 or $100 \text{ mL}\cdot\text{min}^{-1}$). For the determination of lower volatile byproducts air sampling was done with Carbograph[®] 1TD (Markes International, Llantrisant, UK), a multi-bed tube containing Tenax[®] TA, Carbograph[®] 1TD and Carboxen[®] 1000, DNPH-cartridges (Supelco, Bellefonte, PA, USA; 2,4-dinitrophenylhydrazine) and silica cartridges (self-made with silica purchased from Supelco; 30 L and 60 L with $1 \text{ L}\cdot\text{min}^{-1}$).

Tenax TA[®] tubes were measured with a TD-GC-FID system (thermal desorption-gas chromatograph-flame ionization detector) for a quantitative determination. To determine the formation of byproducts measurements were done with a TD-GC-MS (mass spectrometer) system, HPLC (high performance liquid chromatography) and IC (ion chromatography) for a quantitative determination. The limit of quantification for VOC is $1 \mu\text{g}\cdot\text{m}^{-3}$, for formaldehyde $5 \mu\text{g}\cdot\text{m}^{-3}$, for acetaldehyde $7 \mu\text{g}\cdot\text{m}^{-3}$, for formic acid $4 \mu\text{g}\cdot\text{m}^{-3}$ and for acetic acid $5 \mu\text{g}\cdot\text{m}^{-3}$.

Tenax TA[®] measurements were carried out on a GC-FID system from Agilent Technologies (Santa Clara, CA, USA) (GC: 6890 N) equipped with a thermal desorption system (TDS) from Gerstel temperature program: $40 \text{ }^\circ\text{C}$ for 1 min, $40 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ to $280 \text{ }^\circ\text{C}$ for 5 min and a cooled injection system (CIS 4; temperature program: $-100 \text{ }^\circ\text{C}$ for 0.01 min, $12 \text{ }^\circ\text{C}\cdot\text{s}^{-1}$ to $280 \text{ }^\circ\text{C}$ for 3 min). Chromatographic separation of the VOC was done on a Rtx-Volatiles column (Restek; $30 \text{ m} \times 320 \mu\text{m} \times 1.5 \mu\text{m}$) with the following temperature program: splitless, $60 \text{ }^\circ\text{C}$ for 1 min, $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ to $180 \text{ }^\circ\text{C}$ for 3 min, $20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ to $260 \text{ }^\circ\text{C}$ for 5 min (run time 25 min).

Carbograph[®] 1TD and multi-bed tubes were thermally desorbed in a thermal desorption system (TD-100TM, Markes International) and trapped afterwards in a cold trap made of glass. This was connected to a gas chromatograph 6890 N (Agilent Technologies) coupled with a 5975B mass spectrometer (Agilent Technologies) for quantification and identification. The gas chromatographic separation was done on an Rxi-5MS column (Restek, $60 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$) with a constant helium flow (Alphagaz Air Liquide) of $1.5 \text{ mL}\cdot\text{min}^{-1}$. Thermal desorption was done at $300 \text{ }^\circ\text{C}$ for 10 min followed by $320 \text{ }^\circ\text{C}$ for 5 min with a flow of $50 \text{ mL}\cdot\text{min}^{-1}$. The cold trap started at $-5 \text{ }^\circ\text{C}$ and was heated up to $320 \text{ }^\circ\text{C}$ for 15 min. The transfer line was set at $180 \text{ }^\circ\text{C}$. A split (4.3:1) injection on the GC column was done and the GC oven program started at $50 \text{ }^\circ\text{C}$ (initial time 0.5 min) and heated up with $6 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ to $300 \text{ }^\circ\text{C}$ (holding time 5 min). The MS (transfer line at $300 \text{ }^\circ\text{C}$, EI-source at $230 \text{ }^\circ\text{C}$ and quadrupole at $150 \text{ }^\circ\text{C}$) operated in SCAN-mode (m/z 35–450) without solvent delay.

HPLC measurements were done on 1100 Series (Agilent Technologies) equipped with an ULTRASEP ES ALD column ($125 \text{ mm} \times 2 \text{ mm}$) with a pre-column ($10 \text{ mm} \times 2 \text{ mm}$). The column temperature is set to $25 \text{ }^\circ\text{C}$. Acetonitrile (solvent A) and a mixture of water and tetrahydrofuran (1:16.7; solvent B) were the used solvents. The pump program was the following: 30% solvent A, 70% solvent B with a flow of $0.5 \text{ mL}\cdot\text{min}^{-1}$; 30% solvent A, 70% solvent B with a flow of $0.5 \text{ mL}\cdot\text{min}^{-1}$ for 5 min; 32% solvent A, 68% solvent B with a flow of $0.5 \text{ mL}\cdot\text{min}^{-1}$ for 10 min; 32% solvent A, 68% solvent B with a flow of $0.6 \text{ mL}\cdot\text{min}^{-1}$ for 30 min; 83% solvent A, 17% solvent B with a flow of $0.6 \text{ mL}\cdot\text{min}^{-1}$ for 55 min; 30% solvent A, 70% solvent B with a flow of $0.6 \text{ mL}\cdot\text{min}^{-1}$ for 60 min; 30% solvent A, 70% solvent B with a flow of $0.5 \text{ mL}\cdot\text{min}^{-1}$ for 70 min. The detector wavelength was set at 365 nm and 380 nm.

IC measurements were carried out on a Thermo Scientific ICS 2100 instrument equipped with a Dionex IONPAC[®] AS18 ($2 \times 250 \text{ mm}$) column. The oven was set to $30 \text{ }^\circ\text{C}$. A KOH-solution was

used as eluent generator with water as solvent. The chromatographic separation was done as follows: 0 min: eluent concentration: 1 mmol; 23 min: eluent concentration: from 1 mmol to 50 mmol; 33 min: eluent concentration: from 50 mmol to 1 mmol; 43 min: end run.

2.3. Chamber Parameters

VOC degradation was investigated in 20 L and 1 m³ emission test chambers. The 20 L emission test chambers operated under the following conditions. A translucent plate of borosilicate glass was used as chamber cover and the light sources were placed on top of it. The chambers were equipped with a stirrer to guarantee a homogenous air distribution. A GMS was used to generate stable toluene, butyl acetate and limonene concentrations. The GMS consists of a mixing chamber ($V = 24$ L), into which the gaseous VOC are transferred by a nitrogen stream. This mixing chamber is supplied with an air flow ($114 \text{ L}\cdot\text{h}^{-1}$) of purified and dry air to get a concentration reduction of the generated VOC. Two 20 L emission test chambers were connected to the mixing chamber (Figure 2). An air flow of $200 \text{ mL}\cdot\text{min}^{-1}$ was transferred into these chambers where the degradation experiments were carried out. The photocatalytic degradation was investigated at $T = 23 \text{ }^\circ\text{C}$, relative humidity (r.h.) = 0%, air change rate $n = 0.6 \text{ h}^{-1}$ and a loading factor of $0.5 \text{ m}^2\cdot\text{m}^{-3}$, which describes the ratio of catalyst surface (m^2) to emission test chamber volume (m^3). These parameters were not changed during all experiments.



Figure 2. Experimental setup of the gas mixing chamber with two connected 20 L emission test chambers. Both chambers are equipped with ceramic tiles and one is irradiated with UV light.

The 1 m³ emission test chamber was directly connected to the GMS without interposing of a mixing chamber. Hence, the VOC concentration was adjusted by the chambers air change rate, which was set at 1 h^{-1} . Degradation experiments were performed at a relative humidity of 40% with a loading factor of $0.03 \text{ m}^2\cdot\text{m}^{-3}$.

2.4. Light Sources

As light sources a UV LED lamp ($\lambda = 365 \text{ nm}$; irradiance of $1.9 \text{ mW}\cdot\text{cm}^{-2}$ in a distance of 25 cm) and a blue LED lamp ($\lambda = 455 \text{ nm}$; irradiance of $1.9 \text{ mW}\cdot\text{cm}^{-2}$ in a distance of 25 cm) were used for the experiments in the 20 L emission test chambers. Degradation experiments in a 1 m³ emission test chamber used an UV lamp ($\lambda_{\text{min}} = 297 \text{ nm}$; irradiance of $5.6 \text{ W}\cdot\text{m}^{-2}$ in a distance of 25 cm) and blue LED lights ($\lambda = 444 \text{ nm}$; irradiance of $5.9 \text{ W}\cdot\text{m}^{-2}$ in a distance of 25 cm).

2.5. Degradation Experiments under UV and Visible Light

2.5.1. General Information

Customary ceramic tiles ($10 \text{ cm} \times 10 \text{ cm}$) were coated with the catalyst (GO-modified and pure TiO_2). Seven different GO- TiO_2 amounts (A–G, Table 1) were tested, each with two diverse catalyst

loadings (39 and 78 mg, samples A–F). The catalysts were applied by spraying and either cured for 60 min at 100 °C (samples A–F) or for 360 min at 470 °C (sample G). For sample G, only one loading amount was tested, which differs from the others. For sample D a third loading applied by doctor blade technique was tested as well. All irradiation experiments lasted up to 7 days and air sampling was done periodically. Before each experiment the chambers were tested for blank values. Furthermore, it was tested beforehand if the VOC are degraded by photolysis under UV LED and blue LED light, which they did not. Hence, degradation was achieved photocatalytically.

2.5.2. Degradation Experiments in 20 L Emission Test Chambers

The chambers were loaded with the respective catalyst samples under exposure of the reference VOC atmosphere. Unexpectedly, after the installation of samples A to E the limonene and butyl acetate concentrations dropped significantly (down to 0 $\mu\text{g}\cdot\text{m}^{-3}$). The reason for that was a strong adsorption of these compounds onto the catalyst surface. Over time, the concentration increased again due to saturation; however, it took between 1 and 5 weeks until equilibrium and thereby a constant VOC atmosphere was reached. In contrast to that the adsorption of toluene was negligible. Since it could take up to 5 weeks until an adsorption-desorption equilibrium was achieved, sample B-1 and B-2 were pre-stored in a toluene, butyl acetate and limonene atmosphere in a desiccator for up to 24 days. After this time saturation of the catalyst samples was achieved and the degradation experiments could be started within one day after loading the catalyst samples in the emission test chambers. After the concentrations had stabilized, the degradation experiments were started by irradiation of the catalyst samples with either UV LED or blue LED light. For an overview of the starting concentrations see Table 1.

Table 1. Maximum initial concentrations.

Sample	GO (%)	Catalyst Loading (mg)	Toluene ($\mu\text{g}\cdot\text{m}^{-3}$)	Butyl Acetate ($\mu\text{g}\cdot\text{m}^{-3}$)	Limonene ($\mu\text{g}\cdot\text{m}^{-3}$)
A-1	0	39	230	130	110
B-1	0.75	39	100	140	170
B-2	0.75	78	100	220	390
C-1	1	39	190	120	60
C-2	1	78	230	140	40
D-1	2.5	39	140	130	100
D-2	2.5	78	150	110	90
D-3 *	2.5	5	90	140	80
E-1	5	39	80	120	100
E-2	5	78	90	140	40
F-1	10	39	220	190	420
F-2 #	10	78	230	170	330
G-1	14	10	80	120	140

* Applied by doctor blade technique; # investigated only under UV light.

2.5.3. Degradation Experiments in a 1 m³ Emission Test Chamber

The main focus of the experiments in a 1 m³ emission test chamber was the determination of potential byproducts. For that reason, concentrations higher than usual indoor air concentrations were generated (Table 2). The experiments were done with two samples, A-1 (pure TiO₂) and D-1 (2.5% GO), under UV LED light at 40% relative humidity. Three catalyst samples were loaded into the emission test chamber simultaneously. For the determination of potential byproducts air sampling was done additionally with CarboGraph[®] 1TD tubes, multi-bed tubes, DNPH-cartridges and silica cartridges.

Table 2. Initial concentrations.

Sample	GO (%)	Catalyst Loading (mg)	Toluene ($\mu\text{g}\cdot\text{m}^{-3}$)	Butyl Acetate ($\mu\text{g}\cdot\text{m}^{-3}$)	Limonene ($\mu\text{g}\cdot\text{m}^{-3}$)
A-1	0	39	290	380	360
D-1	2.5	39	290	390	330

3. Results

3.1. Results of the Experiments in 20 L Emission Test Chambers

A degradation of toluene, butyl acetate and limonene was achieved with pure TiO_2 and TiO_2 -GO catalyst samples under UV LED light (Table 3). Within 24 h the degradation maxima were achieved and stayed constant until the light was switched off. By using GO amounts of 10% and 14% the VOC degradation was inhibited under UV and blue LED light. This phenomenon is already described in the literature by Aleksandrzak et al. [13] for the photocatalytic degradation of phenol. The photocatalytic degradation was highest when using single layered graphene, while by increasing the amount of layers, the photocatalytic degradation decreased. It is assumed that this effect is a result of surface and electronic properties of graphene oxide with TiO_2 , e.g., the transport of electron-hole pairs between TiO_2 and GO is reduced. Under blue LED light limonene was degraded in most cases but butyl acetate could only be degraded by six samples, whereas toluene could not be degraded at all (see Table 3). Limonene has the highest degradation rate of the three VOC, which becomes most obvious by comparing the results obtained under blue LED light (Table 3). When using pure TiO_2 only limonene could be degraded under blue LED light, but when GO was introduced into the catalytic system butyl acetate was also degraded at least in some cases. This might be a result of the fact that graphene oxide enhances the reactivity of the catalytic system due to the formation of more π - π interactions between catalyst and VOC.

Table 3. Degradation (%) of toluene, butyl acetate and limonene under UV and blue LED light.

Sample	GO (%)	Catalyst Loading (mg)	UV LED Light			Blue LED Light		
			Toluene (%)	Butyl Acetate (%)	Limonene (%)	Toluene (%)	Butyl Acetate (%)	Limonene (%)
A-1	0	39	>95	>95	>95	0	0	92
B-1	0.75	39	>95	>95	>95	0	12	>95
B-2	0.75	78	>95	>95	>95	0	10	>95
C-1	1	39	>95	>95	>95	0	0	>95
C-2	1	78	>95	>95	>95	0	39	>95
D-1	2.5	39	>95	>95	>95	0	14	>95
D-2	2.5	78	>95	>95	>95	0	34	>95
D-3 *	2.5	5	>95	>95	>95	0	0	92
E-1	5	39	93	>95	>95	0	11	>95
E-2	5	78	94	>95	>95	0	0	>95
F-1	10	39	23	92	94	0	0	14
F-2	10	78	18	81	84	n.m.	n.m.	n.m.
G-1	14	10	0	26	>95	0	0	10

* Applied by doctor blade technique; n.m.: not measured.

3.2. Results of the Experiments in a 1 m³ Emission Test Chamber

Degradation experiments were performed with samples A-1 and D-1. Both catalyst samples showed a slight degradation of all VOC after 24 h (Table 4). The degradation obtained in the 1 m³ emission test chamber was lower than in the 20 L emission test chambers (Table 3), which might be caused by the lower loading factor (20 L emission test chamber: $L = 0.5 \text{ m}^2\cdot\text{m}^{-3}$; 1 m³ emission test chamber: $L = 0.03 \text{ m}^2\cdot\text{m}^{-3}$) and the higher air change rate (20 L emission test chamber: $n = 0.6 \text{ h}^{-1}$;

1 m³ emission test chamber: $n = 1 \text{ h}^{-1}$) resulting in a shorter reaction time of the VOC molecules with the catalyst.

Byproducts detected for sample A-1 were formaldehyde, acetic acid, formic acid and traces of crotonaldehyde, octenal, nonenal and undecenal. Degradation of sample D-1 resulted in similar byproducts namely formaldehyde, acetaldehyde, acetic acid, formic acid and traces of octenal (Table 4). Formaldehyde, acetaldehyde, formic acid and acetic acid are already literature known byproducts of photocatalytic toluene degradation [19]. The same applies to the formed byproducts of limonene [20].

Table 4. Degradation of volatile organic compounds (VOC) in a 1 m³ emission test chamber at 40% relative humidity under UV light.

Sample	Toluene (%)	Butyl Acetate (%)	Limonene (%)	Formaldehyde ($\mu\text{g}\cdot\text{m}^{-3}$)	Acetaldehyde ($\mu\text{g}\cdot\text{m}^{-3}$)	Formic Acid ($\mu\text{g}\cdot\text{m}^{-3}$)	Acetic Acid ($\mu\text{g}\cdot\text{m}^{-3}$)
A-1	5	10	12	9	n.d.	14	32
D-1	9	21	15	18	10	55	43

n.d.: Not detected.

3.3. Influence of Relative Humidity

According to the literature [14,15] a certain amount of relative humidity is necessary to obtain photocatalytic degradation by using TiO₂ as catalytic material (see Section 1). The experiments presented in this article were either performed at 0% relative humidity (20 L emission test chamber) or 40% relative humidity (1 m³ emission test chamber). A better VOC degradation was obtained at 0% relative humidity for catalyst samples made of pure TiO₂ and combinations of TiO₂ and GO as can be seen by comparing the results in Tables 3 and 4. This outcome disproves the theory that a certain level of relative humidity is inevitable to obtain photocatalytic degradation. Consequently, in the presented experiments the superoxide radical anion might lead to photocatalytic VOC degradation. This radical is formed of the atmospheric oxygen in the air and is also strong enough to degrade VOC. This is supported by an article from Sun et al. [21] where the superoxide anion radical is described as the active species which degrades toluene photocatalytically.

4. Conclusions

Various TiO₂-GO composite photocatalysts have been tested for the degradation of reference VOC toluene, butyl acetate and limonene at typical indoor air concentration levels at 0% relative humidity. During irradiation experiments it has been revealed, that a modification of TiO₂ with trace amounts of GO (0.75%–5%) is beneficial for its photocatalytic performance under blue light. Increasing the amount of GO (10% or higher) however significantly reduces its activity both under UV as well as blue light irradiation.

Adsorption on the catalyst surface strongly affected the time for the degradation experiment. Toluene showed no adsorption onto the catalyst but butyl acetate and limonene adsorbed on its surface. It took up to 5 weeks until an adsorption-desorption equilibrium was achieved. For the investigation of photocatalytic degradation, it is very important to distinguish between adsorption and degradation. When measuring the decrease of VOC concentrations, it is necessary to ensure that the decrease is induced only by degradation.

In an experiment with VOC air concentrations of approximately 300 $\mu\text{g}\cdot\text{m}^{-3}$ at 40% relative humidity it was investigated if byproducts are formed during the degradation process. Byproducts already known from literature, e.g., formaldehyde, acetaldehyde, formic acid and acetic acid, could be detected. Unfortunately, those byproducts might be more harmful than the original VOC. For that reason, it would be helpful to develop catalysts which do not form byproducts but only water and carbon dioxide. The described test method is a useful tool for such development.

Acknowledgments: The research project was supported by the Federal Ministry of Economics and Technology under grant number KF2201064ZG3.

Author Contributions: Birte Mull and Olaf Wilke conceived and designed the experiments. Lennart Möhlmann performed the experiments and analyzed the data. Birte Mull wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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