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Article

# Enhanced Degradation of Ethylene in Thermo-Photocatalytic Process Using TiO<sub>2</sub>/Nickel Foam: Reaction Mechanism

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**Abstract:** Photocatalytic decomposition of ethylene was performed under UV-Led irradiation at the presence of nanocrystalline TiO<sub>2</sub> (anatase, 15 nm) supported on the porous nickel foam. Process was carried out in the high temperature chamber with regulated temperature from ambient to 125°C under flow of reacted gas (ethylene in a synthetic air, 50 ppm) with simultaneous FTIR measurements of sample surface. Ethylene was decomposed with higher efficiency in elevated temperatures with maximum of 28% at 100-125°C. The nickel foam used as support for TiO<sub>2</sub> allowed to enhance the ethylene decomposition at the temperature of 50°C. However, at 50°C the stability of ethylene decomposition was not retained within the following reaction run, but it was at 100°C. Performed photocatalytic measurements at the presence of some radicals scavengers indicated that higher efficiency of ethylene decomposition was obtained due to the improved separation of charge carriers and increased formation of superoxide anionic radicals, which were formed at the interface of thermally activated nickel foam and TiO<sub>2</sub>.

**Keywords:** thermo-photocatalysis; TiO<sub>2</sub>/nickel foam; ethylene decomposition; superoxide anionic radicals

## 1. Introduction

Ethylene, which belongs to the group of volatile organic compounds (VOCs), is a naturally occurring gas that is emitted by plants. As a phytohormone, ethylene displays both desirable and adverse impacts in storage of fresh vegetables and fruits [1]. It fulfills a crucial and beneficial role in the development of distinctive color, taste and flavors in fresh produce. On the other hand, accumulation of ethylene in plants induces premature ripening, senescence and aging which results in faster deterioration and shortening of shelf life [2,3].

Therefore, effective removal of ethylene from these areas is crucial, and a myriad of strategies have been employed to degrade it. Methods for ethylene degradation vary, spanning from biological processes that use different types of biofilters [2,4], employment of sorbents such as zeolites or activated carbon [1,5], application of air ventilation or air filtration dependent on catalytic oxidation [6,7]. However, these methods often face challenges in terms of efficiency, selectivity, and operational conditions.

Amidst the diverse strategies photocatalytic degradation is a viable substitute for mitigating ethylene-induced spoilage. This innovative approach utilizes light in the ultraviolet to visible spectrum to activate a photocatalyst, namely titanium dioxide (TiO<sub>2</sub>), which can oxidize ethylene molecules into less harmful compounds [7]. Unlike traditional methods, photocatalysis can be conducted at room temperature and atmospheric pressure, making it an environmentally friendly option that can be used in various settings. Photocatalysis also offers tailored solutions that can

optimize the degradation of ethylene according to the unique needs of different storage facilities [6–8].

While the use of titanium dioxide ( $\text{TiO}_2$ ) in photocatalytic degradation of ethylene presents a promising eco-friendly alternative, it is not without its shortcomings. Foremost among these is the recombination of electron-hole pairs within  $\text{TiO}_2$ . This significantly diminishes its photocatalytic efficiency. Furthermore,  $\text{TiO}_2$ 's ability to absorb visible light is constrained due to its large bandgap, specifically 3.2 eV in the anatase phase, which necessitates the use of ultraviolet light for efficient photocatalytic performance. This is significant since UV light comprises only about 5% of the sun's emissions [9]. Thus, utilizing UV light can be both costly and energy-intensive. Additionally, as reported in [10] the ethylene molecules display low adsorption capacity and photodegradation rate on (001) surface of titania, which was considered most reactive for the surface catalyzed reactions. Weak adsorption energy of ethylene signifies its negligible interaction with the  $\text{TiO}_2$  surface, presenting a significant challenge in the design of efficient photocatalytic materials, as strong adsorbate-surface interactions are critical for optimal performance [10,11].

Addressing these limitations a variety of methods have been investigated aiming to enhance photocatalytic performance of  $\text{TiO}_2$ . The method most commonly used to enhance the efficiency of  $\text{TiO}_2$  is through doping which can change its wide bandgap, improve visible light absorption and reduce electron-hole recombination [12]. Doping can be achieved using elements such as metals (transition [13] earth-rare [14] and noble [15]), non-metals (N [16], C [17], S [18] and others), or co-doping which involves the simultaneous introduction of multiple dopants [12,19]. Another promising approach involves the development of new composite photocatalysts. Metal organic frameworks (MOFs) are crystalline materials composed of metal clusters coordinated to organic ligands. MOFs possess unique characteristics, particularly: large specific surface area, high pore volume and alterable pore size, which contribute positively to the efficiency of photocatalysis and adsorption of gases [20]. As stated in [21] photocatalytic system made of combination of  $\text{TiO}_2$ , MIL101(Fe), and reduced carbon oxide (rGO) successfully enhanced separation efficacy of electron-hole pair as well as improved gas adsorption capacity. Recent research studies have also revealed that, photocatalysts combined with nickel foam emerged as novel composite materials in the field of photocatalytic degradation of VOCs. Nickel foam stands out for its high porosity, excellent conductivity and affordability making it particularly useful for photocatalytic systems [22]. It has been previously reported that  $\text{TiO}_2$  combined with nickel foam can be used for photocatalytic degradation of various pollutants, including toluene [23], formaldehyde [24], acetaldehyde [25–27]. As stated in our previous paper [26] the nickel foam used in combination with  $\text{TiO}_2$  considerably enhanced charge separation in  $\text{TiO}_2$ , what positively affected formation of superoxide anion radicals, which were utilized in the photocatalytic reactions.

The objective of this study was investigation of mechanism of ethylene decomposition at the presence of  $\text{TiO}_2$  supported on the nickel foam. Impact of increased temperature on the yield of photocatalytic reactions was considered.

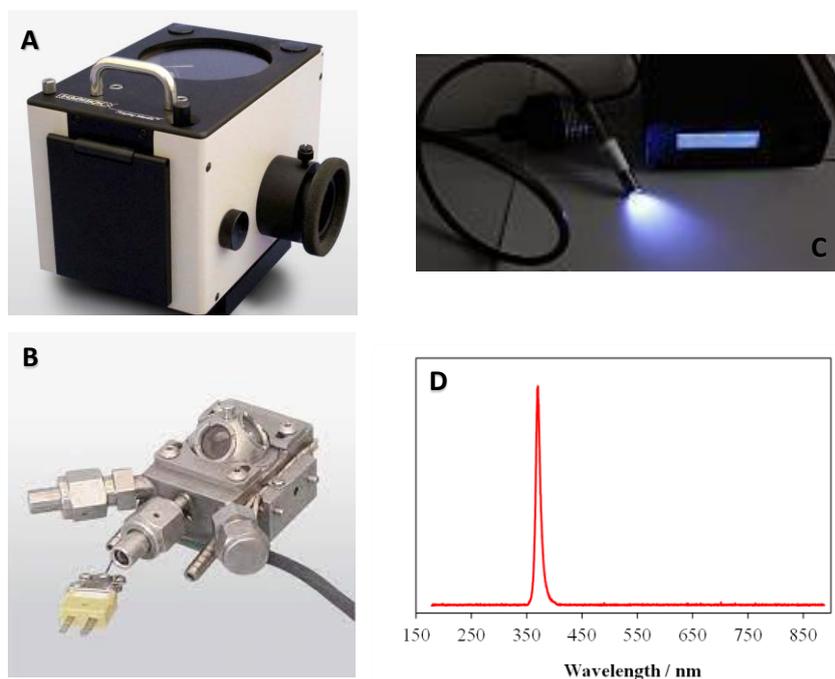
## 2. Materials and Methods

### Characteristics of materials

#### Methods

The experiments of ethylene decomposition in the thermo-photocatalytic system were carried out employing the high temperature reaction chamber (Praying Mantis, Harrick, USA), as reported in our previous paper [26]. Throughout the experimental procedure, continuous Fourier Transform Infrared (FTIR) measurements were executed using the Thermo Nicolet iS50 FTIR instrument (Thermo, USA). UV irradiation was applied through a quartz window utilizing an illuminator equipped with fiber optics and a UV-LED 365 nm diode with an optical power of 415 mW (LABIS, Poland). Gas ( $\text{C}_2\text{H}_4$  50 ppm in a synthetic dry air, Air Liquide) was supplied through the inlet regulated by a mass flow meter. Following the thermo-photocatalytic reaction, the ethylene

concentration was determined in a gas chromatograph with flame ionization detector (GC-FID, SRI, USA). The accessories used in the experimental system are shown below in Figure 1.



**Figure 1.** A) Praying Mantis™ Diffuse Reflection Accessory; B) The Praying Mantis™ High Temperature Reaction Chamber; C) The optical fibre with UV LED diode; D) the emission spectrum of UV LED diode.

TiO<sub>2</sub> sample supported on the nickel foam was placed inside the reaction chamber. The reacted gas was flowing from top to the bottom of the reactor, then was directed to the GC-FID equipped in the automatic dozen loop and was analyzed every 15 min during proceeding process. Measurements at the presence of TiO<sub>2</sub> only without nickel foam were also performed.

TiO<sub>2</sub> was analyzed through XRD measurements using a diffractometer (PANalytical, The Netherlands) equipped with a Cu X-ray source,  $\lambda = 0.154439$  nm. The measurements covered the  $2\theta$  range of  $20\text{--}90^\circ$  with a step size of 0.013. A voltage of 35 kV and a current of 30 mA were applied during the measurements.

The specific surface area of TiO<sub>2</sub> was determined from the nitrogen adsorption/desorption isotherms measured at 77 K using QUADRASORB Si analyzer (Quantachrome, USA). Before measuring sample was degassed at 105 °C for 12 h under high vacuum using MasterPrep degasser by Quantachrome.

In order to identify the dominant species participating in the photocatalytic reactions, measurements were performed at the presence of hole, hydroxyl radicals and oxygen radicals scavengers. Terephthalic acid, ethylenediaminetetraacetic acid (EDTA), and p-benzoquinone were used to trap  $\cdot\text{OH}$ ,  $\text{h}^+$ , and  $\text{O}_2^{\cdot-}$  species, respectively. The applied procedure followed the methodology reported by Q. Zeng et al. [28] and involved a mixture of 0.1 g TiO<sub>2</sub> with 0.01 g of each scavenger individually. The mixture was then loaded onto purified nickel foam and tested. An excess of scavenger was used to ensure the entire capture of demanded radicals. Decomposition of ethylene at the presence of TiO<sub>2</sub> and scavenger was carried out at 100°C under UV irradiation in a high-temperature chamber. As a control test, a mixture of 0.1 g TiO<sub>2</sub> and 0.01 g KBr was used, because KBr has been known to be chemically inert for ethylene gas.

## Materials

TiO<sub>2</sub> was synthesized through a two-step procedure: initial hydrothermal treatment of titania pulp (obtained from Police Chemical Factory, Poland) in deionized water at 150°C and 7.4 bar for 1

hour. Subsequently, the resultant mixture underwent decantation, followed by drying at 100°C, and then subjected to a tube furnace under an argon flow of 30 ml/min (heating rate: 10°C/min) until reaching 400°C, where it was maintained for 2 hours.

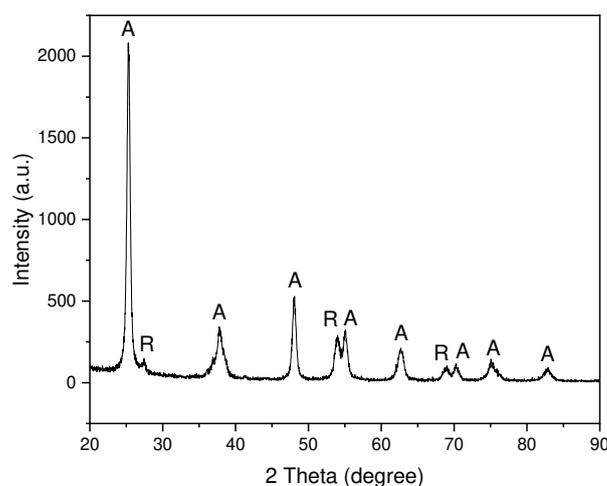
The nickel foam (sourced from China) exhibited a purity of 99.8% and possessed the following specifications: thickness of 1.5 mm, porosity ranging between 95% and 97%, and a surface density of 300 g/m<sup>2</sup>.

The chemicals utilized in the studies included: p-benzoquinone (with HPLC grade purity of over 99.5%, sourced from Fluka Analytical in Darmstadt, Germany), terephthalic acid (TA) (having a purity of 98%, obtained from Sigma-Aldrich in Saint Louis, MO, USA) and ethylenediaminetetraacetic acid (EDTA) (Pure Chemical Standards-Elemental Microanalysis).

### 3. Results

#### 3.1. Physicochemical properties of TiO<sub>2</sub>

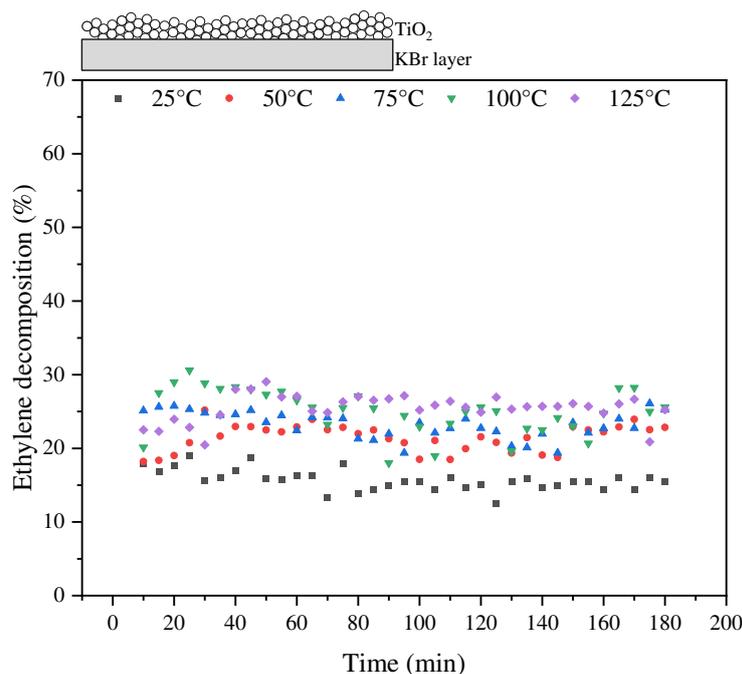
The XRD pattern of the prepared TiO<sub>2</sub> sample was shown in Figure 2. The primary crystalline phase observed in the TiO<sub>2</sub> sample was anatase. Low intensity signals assigned to rutile phase were also observed. Calculation of an average crystallites size of anatase was performed based on the Scherrer equation. The calculated size of anatase crystallites was equaled approximately 15 nanometers. Performed calculations of phase composition indicated that share of rutile in this TiO<sub>2</sub> was around 4 wt%. Measured BET surface area of TiO<sub>2</sub> was equaled 167 m<sup>2</sup>/g.



**Figure 2.** XRD pattern of TiO<sub>2</sub>.

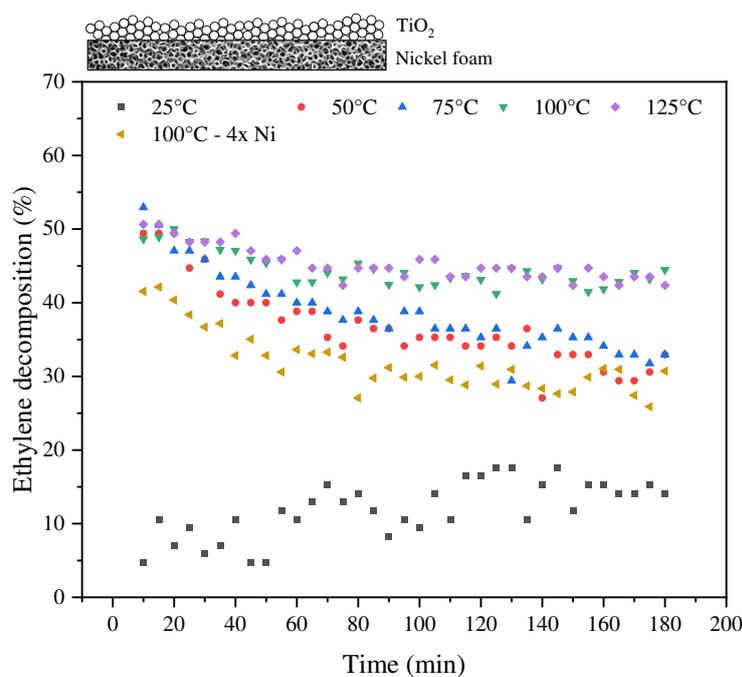
#### 3.2. Thermo-photocatalytic decomposition of ethylene at the presence of TiO<sub>2</sub> and TiO<sub>2</sub>/nickel foam under UV light

The results of thermo-photocatalytic decomposition of ethylene under UV-LED illumination at the presence of TiO<sub>2</sub> supported on KBr are shown in Figure 3. The percentage of ethylene decomposition ranged from about 18% at 25°C to about 28% at 100-125°C. Higher temperature of the photocatalytic process resulted in somewhat higher ethylene decomposition. Some fluctuations of ethylene removal were noted within a time of UV irradiation.



**Figure 3.** Photocatalytic decomposition of ethylene under UV irradiation at various reaction temperatures at the presence of TiO<sub>2</sub>/KBr.

In the next step TiO<sub>2</sub> was supported on the nickel foam and the photocatalytic process of ethylene decomposition was repeated. The results from the performed experiments are shown in Figure 4. High increase in ethylene decomposition was observed when process was carried out at elevated temperature, the maximum yield (50%) was achieved at the temperatures of 100-125°C. The yields of the photocatalytic reactions were decreasing in time of the going process, however at 100-125°C reached a certain stability after 60 min with a drop of efficacy around 5% only.

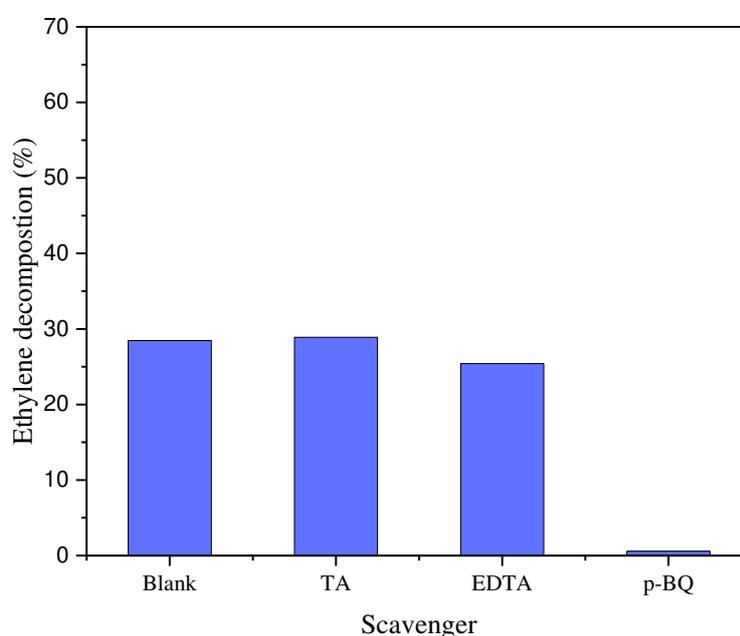


**Figure 4.** Photocatalytic decomposition of ethylene under UV irradiation at various reaction temperatures at the presence of TiO<sub>2</sub>/nickel foam.

### 3.3. Thermo-photocatalytic decomposition of ethylene at the presence of radicals scavengers

Some radicals scavengers were added to TiO<sub>2</sub> in order to examine the share of the formed reactive radicals in the photocatalytic reactions related to the decomposition of ethylene. Process was carried out at 100°C at the presence of TiO<sub>2</sub> mixed with a scavenger and supported on nickel foam. The obtained results are presented in Figure 5. Photocatalytic decomposition of ethylene at the presence of TiO<sub>2</sub>/nickel foam at 100°C with addition of some radicals scavengers.

After adding terephthalic acid (TA) to TiO<sub>2</sub>, (the scavenger of hydroxyl radicals), the decomposition of ethylene was unchanged compared to the blank test with TiO<sub>2</sub> only. On the other hand, when EDTA was added to TiO<sub>2</sub> as a hole scavenger the degradation of ethylene slightly decreased. The introduction of p-benzoquinone (p-BQ), acting as a scavenger for superoxide anion radicals caused almost completely inhibition of the photocatalytic process. These experiments revealed that superoxide anion radicals played the leading role in the process of ethylene degradation.



**Figure 5.** Photocatalytic decomposition of ethylene at the presence of TiO<sub>2</sub>/nickel foam at 100°C with addition of some radicals scavengers.

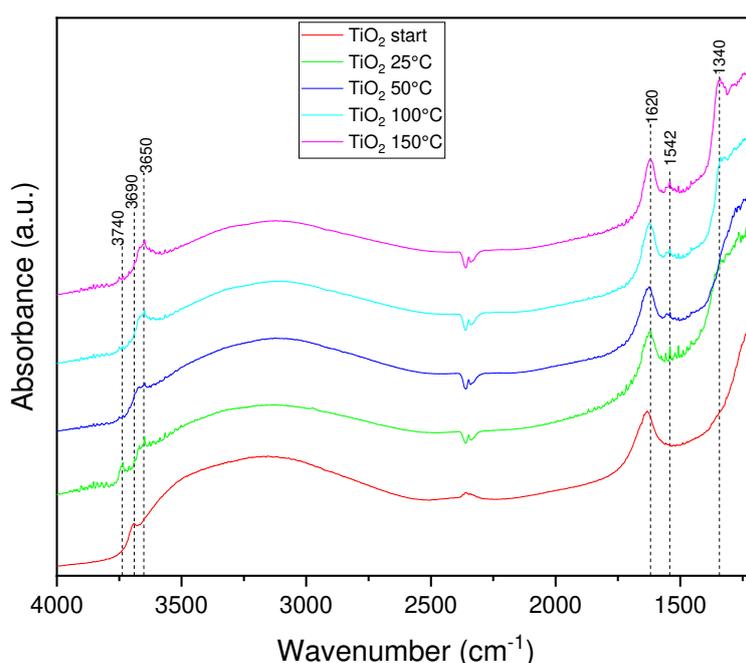
### 3.4. FTIR spectra of the photocatalyst surface measured at the condition of the photocatalytic process of ethylene decomposition

Figures 6–8 contain FTIR spectra illustrating the interaction of ethylene with titania surface during thermo-photocatalytic processes. In situ, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was applied. FTIR spectra presented in Figure 6 are illustrating the changes in the chemical structure of TiO<sub>2</sub> surface exhibited to ethylene gas (50 ppm in air), UV irradiation and thermal heating. The starting TiO<sub>2</sub> material contained hydroxyl groups only, as indicated FTIR bands at 3690 and 1620 cm<sup>-1</sup> assigned to OH groups and that at 3700-2500 m<sup>-1</sup> assigned to molecular adsorbed water. During photocatalytic process of ethylene decomposition conducted at increased temperature, some new bands appeared. At 25°C strong band at 3740 cm<sup>-1</sup> was observed together with another broad and weak at 3650 cm<sup>-1</sup>. At the same time the intensity of a broad band at 3700-2500 cm<sup>-1</sup> declined. According to Park et al. [29] the band at 3740 cm<sup>-1</sup> is attributed to OH groups adsorbed on TiO<sub>2</sub> surface and is formed after desorption of physically adsorbed water molecules, which can be observed through the diminish the intensity of the band at 3700-2500 cm<sup>-1</sup>. The band at

3650  $\text{cm}^{-1}$  is also attributed to OH groups adsorbed on  $\text{TiO}_2$  surface, but on the other site. According to Bhattacharyya et al. [13], such bonded OH groups are very labile for dihydroxylation and can participate in formation of  $\text{CH}_3\text{-CH}_2\text{-O}$  species. Whereas the band at 3740  $\text{cm}^{-1}$  is clearly observed at 25°C only, the other at 3650  $\text{cm}^{-1}$  has been increasing with increase reaction temperature. The kinetic studies of ethylene decomposition showed, that the bands assigned to hydroxyl groups at 3650 and 3740  $\text{cm}^{-1}$  appeared and disappeared in FTIR spectra within a reaction time. Therefore it is speculated, that formation of  $\text{CH}_3\text{-CH}_2\text{-O}$  species as well as hydroxyl radicals with share of these OH groups is highly realistic. New appeared bands at 1542 and 1340  $\text{cm}^{-1}$  are observed at higher temperatures, such as 50-150°C and can be attributed to the C=C stretching vibrations and  $-\text{CH}_2$  symmetric scissoring vibrations of adsorbed ethylene, respectively [13]. These studies indicated, that adsorption of ethylene could be increased at higher reaction temperatures, whereas high adsorption of hydroxyl groups on titania surface (the band at 3740  $\text{cm}^{-1}$ ), which took place at 25°C disrupted interaction of ethylene molecules with titania surface. It was already reported in the literature [30], that ethylene is less strongly adsorbed onto the  $\text{TiO}_2$  surface than water. Negative impact of high adsorption of water molecules onto  $\text{TiO}_2$  surface during ethylene decomposition was also observed by the other researchers [13]. Therefore ethylene decomposition under UV at 25°C was much lower than at elevated temperatures. Lower adsorption of ethylene on titania surface resulted in lower degree of its decomposition. In Table 1 there is a list of some identified functional groups present on  $\text{TiO}_2$  surface during photocatalytic process of ethylene decomposition.

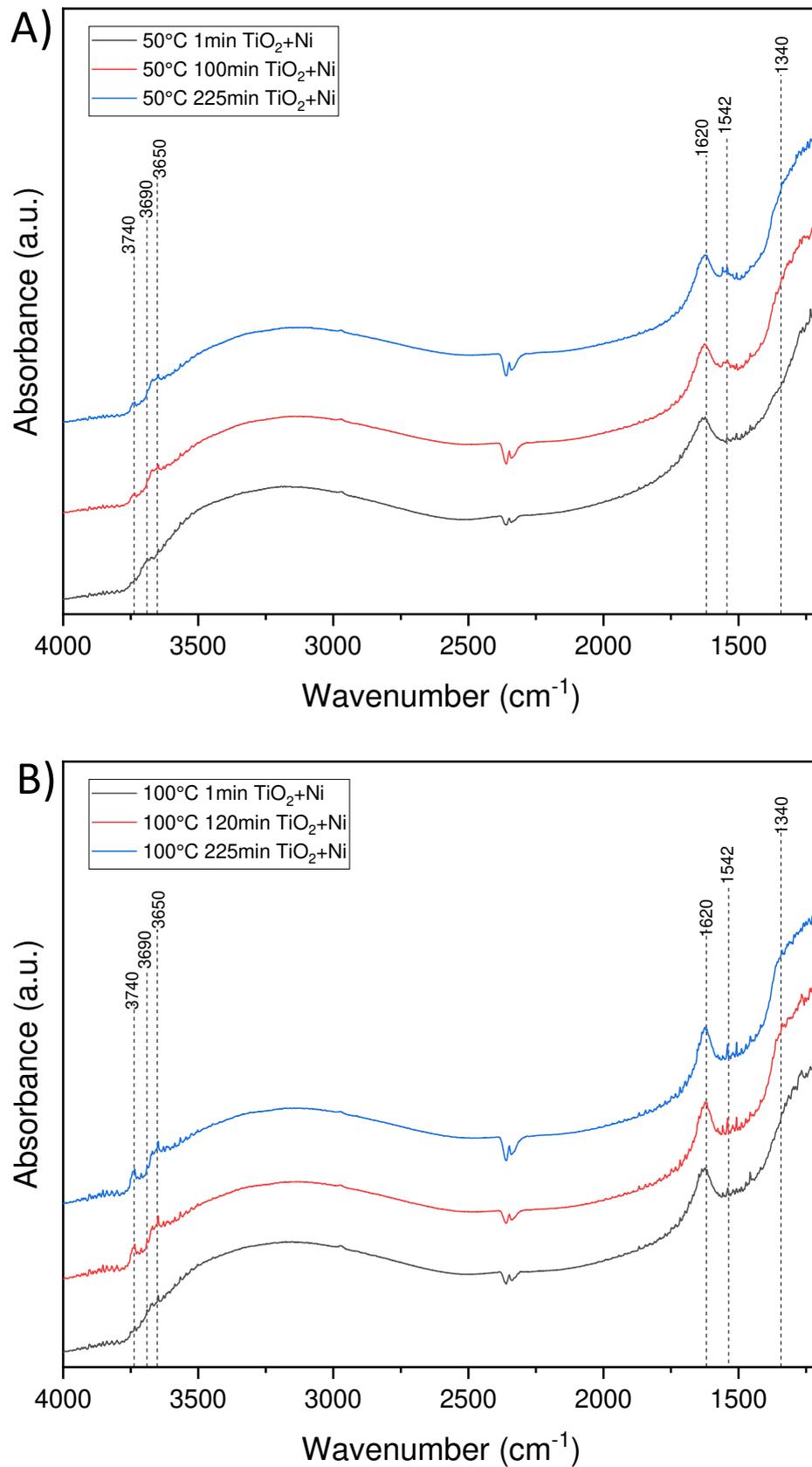
**Table 1.** Characteristics of FTIR bands.

Functional group	Wavenumber [ $\text{cm}^{-1}$ ]	Reference
C=C	1542	[13]
C=O		
$-\text{CH}_2$	1340	[13]
$\text{H}_2\text{O}$	2500-3600	[13]
$-\text{OH}$	3740, 3690, 3650	[11,13]
$-\text{OH}$	1620	[11]



**Figure 6.** In situ FTIR spectra of titania surface during the photocatalytic decomposition of ethylene using  $\text{TiO}_2$ .

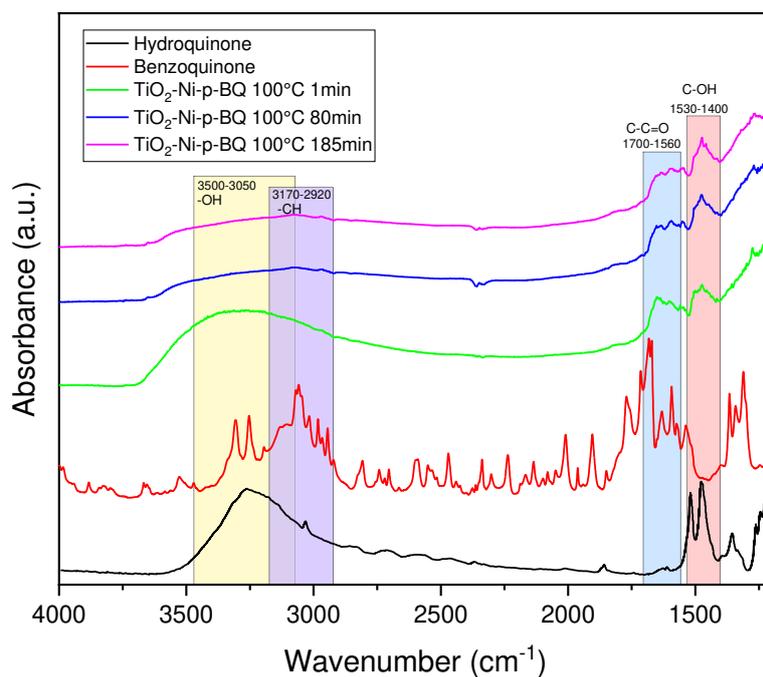
Figure 7 shows FTIR spectra, which are illustrating the changes in titania chemical surface, when it was supported on nickel foam and submitted to the photocatalytic ethylene decomposition at temperatures of 50 and 100°C. These FTIR spectra were recorded at different times of the photocatalytic process (1 min, 120 and 225 min). At 50°C new bands clearly appeared at 1542 and 1360  $\text{cm}^{-1}$  within the progress of the photocatalytic process and the other bands at 1340  $\text{cm}^{-1}$  and 3650  $\text{cm}^{-1}$  were subtly visible also. At 100°C, the most intensive band was observed at 3740  $\text{cm}^{-1}$ , but this at 1542  $\text{cm}^{-1}$  was poorly visible due to the high noise of the spectral signals. The band recorded at 1542  $\text{cm}^{-1}$  can be assigned to C=C vibrations in the adsorbed ethylene, as it was described earlier or can be a result of  $\nu(\text{C}=\text{O})$  vibrations in the acetate ions ( $\text{COO}^-$ ) formed as the product of ethylene transformation [11,29]. Taking into account, that at 50°C the percentage of ethylene decomposition is decreasing with proceeding time of UV irradiation, it is stated, that band at 1542  $\text{cm}^{-1}$  is related to some acetate species, which are byproducts of ethylene decomposition. According to some researchers [29], these species can be strongly held on  $\text{TiO}_2$  surface. In our previous studies [11], some acetate species were also identified on  $\text{TiO}_2$  surface upon ethylene decomposition with higher dose, 200 ppm. Therefore it can be concluded, that at 50°C there is an deactivation of  $\text{TiO}_2$  surface with time, due to the incomplete decomposition of ethylene, whereas at 100°C this process is insignificant and there is observed high adsorption of OH groups on the titania surface (band at 3740  $\text{cm}^{-1}$ ), which most likely come from the ethylene mineralization. These adsorbed OH ions on  $\text{TiO}_2$  surface can take part in hydroxyl radicals formation, enhancing mineralization of ethylene species. Similar effect was observed by Park et al. [29].



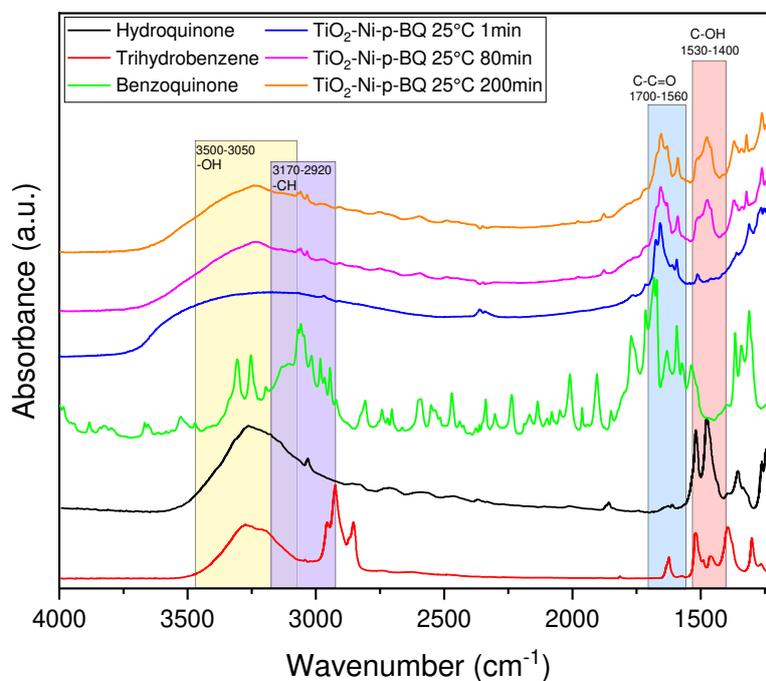
**Figure 7.** In situ FTIR spectra of titania surface recorded during the photocatalytic decomposition of ethylene using TiO<sub>2</sub>/nickel foam, A) at 50°C and B) at 100°C.

In next step mechanism of p-BQ reaction with superoxide anionic radicals, which were formed on TiO<sub>2</sub>/nickel foam was studied at the presence of ethylene gas (50 ppm in air) and UV-LED irradiation. The measurements were performed at 25 and 100°C. The obtained FTIR spectra recorded during photocatalytic processes at the beginning, after 80 and 185-200 min, are presented in Figures 8-9. It is clearly observed, that within proceeding time of reaction, p-benzoquinone reacts to hydroquinone. This was evidenced by a decrease in the intensity of the bands at 1560-1700 cm<sup>-1</sup> assigned to the -C-C=O groups in p-BQ with simultaneous increase in the intensity of the bands at 1530-1400 cm<sup>-1</sup> corresponding to the -OH groups in hydroquinone (HQ). In addition, the hydroxyl groups originally present on TiO<sub>2</sub> surface are consumed in time of proceeding reactions (band at 2700-3600 cm<sup>-1</sup> region). Furthermore, at 25°C (Figure 9) there is much higher increase in the intensity of the -OH groups assigned to HQ located in the ranges 3500-3050 and 1530-1400 cm<sup>-1</sup> [31,32]. There is a high probability, that p-BQ undergoes photolysis under UV irradiation and water and then 1,2,4-trihydroxybenzene (1,2,4-THB) is formed, which is further oxidized to HQ. Such mechanism was already reported in the literature [33]. High increase in the intensity of band at 3500-3050 cm<sup>-1</sup> can be a results of overlapping both spectra, 1,2,4-THB and HQ. Such phenomenon was not observed at 100°C. It is stated, that at 25°C under UV irradiation there is desorption of water molecules physically bounded with the titania surface, which take part in the reaction of p-BQ photolysis. At 100°C titania surface is less hydroxylated than at ambient temperature and then mechanism of p-BQ conversion to HQ can proceed by the other pathway. In the absence of water p-BQ can be transformed to HQ through the photocatalytic reaction with TiO<sub>2</sub> by scavenging electrons or superoxide anionic radicals [33]. These reactions are determined by the presence of oxygen and pH solution. In our studies application of p-BQ as a scavenger resulted in high suppressing of ethylene decomposition. It is concluded, that superoxide anionic radicals play an important role in the photocatalytic process of ethylene decomposition.

Measured FTIR spectra of titania surface during ethylene decomposition at the presence of EDTA (the hole scavenger) indicated, that adsorption of hydroxyl groups on TiO<sub>2</sub> (the band at 3740 cm<sup>-1</sup>) was lower than in case of using TiO<sub>2</sub> only. Scavenging of holes by EDTA caused, that OH groups were less attracted to the titania surface and as a consequence less quantities of hydroxyl radicals were formed. These studied revealed, that hydroxyl radicals generated by the reaction of holes with hydroxyl anions take part in ethylene decomposition as well. Scavenging of holes by EDTA decreased yield of ethylene removal from the gas stream. Contrary to that, addition of terephthalic acid (TA) to TiO<sub>2</sub> did not caused any changes in the yield of the photocatalytic system. Recorded FTIR spectra of TiO<sub>2</sub> surface during photocatalytic process did not indicate any changes in TA structure. It is stated, that reaction of TA with OH radicals formed upon TiO<sub>2</sub> excitation was hindered due to the low mobility of these radicals and possible lack of contact. The other situation takes place in an aqueous medium, where hydroxyl radicals can easily desorb from titania surface and participate in the photocatalytic reactions.



**Figure 8.** In situ FTIR spectra of titania surface during the photocatalytic decomposition of ethylene using  $\text{TiO}_2$ -p-BQ/nickel foam at  $100^\circ\text{C}$ .



**Figure 9.** In situ FTIR spectra of titania surface during the photocatalytic decomposition of ethylene using  $\text{TiO}_2$ -p-BQ/nickel foam at  $25^\circ\text{C}$ .

#### 4. Discussion

TiO<sub>2</sub> supported on the nickel foam can be the sufficient photocatalyst for ethylene decomposition when reaction is conducted under UV and elevated temperatures, such as 100°C. At ambient temperature, TiO<sub>2</sub>, either supported on Ni foam or not, appeared to have the lowest activity. Most likely at this temperature mobility of electrons was lower than in the case of thermal conditions, moreover physically adsorbed water molecules on titania surface could participate in the speeding up recombination process. The certain amount of hydroxyl groups adsorbed on the titania surface is beneficial, because they can take part in reaction with photogenerated holes to form hydroxyl radicals. However high hydroxylation of TiO<sub>2</sub> surface conducts to suppress of oxygen uptake by photogenerated electrons and limits formation of oxygen radicals [29]. It was also observed lower adsorption of ethylene on TiO<sub>2</sub> surface at ambient temperature due to the high hydroxylation of surface. Increased adsorption of ethylene on TiO<sub>2</sub> was noted at higher temperatures and was crucial to achieve higher yield of ethylene decomposition. However adsorbed ethylene was following decomposition to other species before reaching the total mineralization to CO<sub>2</sub> and H<sub>2</sub>O. Therefore oxidation of formed reaction products with reactive radicals was necessary. Performed measurements of ethylene decomposition at the presence or radicals scavengers revealed, that superoxide anionic radicals played the main role in the photocatalytic decomposition of ethylene. The highest yield of ethylene decomposition was achieved for process conducted at 100°C at the presence of TiO<sub>2</sub> supported on nickel foam, almost no deactivation occurred, process was stable in time. Such promising results were obtained, because activation of nickel foam occurred at 100°C, most likely mobility of electrons was increased and some superoxide anionic radicals were formed on the border of Ni foam and TiO<sub>2</sub>. Nickel foam improved separation of free charges and enhanced formation of reactive radicals. Therefore no any byproducts were observed on TiO<sub>2</sub> surface during photocatalytic decomposition of ethylene at the presence of TiO<sub>2</sub>/nickel foam at 100°C, the exceptions are hydroxyl anions, which were a source for hydroxyl radicals production. L. Chen et al. postulated, that superoxide anionic radicals played a key role in the photocatalytic decomposition of ethylene [21]. The other researchers investigated formation of oxygen radicals upon ethylene decomposition in air and UV irradiation by EPR technique [29]. Firstly, they observed formation of hydroxyl radicals and Ti<sup>3+</sup> centers, whereas later on O<sub>2</sub><sup>-</sup> radicals appeared together with O<sub>3</sub><sup>-</sup>. The authors explained that O<sub>3</sub><sup>-</sup> radicals were formed through the reaction of hole trapping (O<sub>1</sub><sup>-</sup>) with oxygen, and O<sub>2</sub><sup>-</sup> radicals by oxygen adsorption on Ti<sup>3+</sup> centers [29]. Our studies showed certain activity of photogenerated holes in ethylene decomposition. There is a probability, that both, O<sub>2</sub><sup>-</sup> and O<sub>3</sub><sup>-</sup> radicals are formed upon photocatalytic process.

These studies showed beneficial effect of using TiO<sub>2</sub> supported on nickel foam, when process was carried out at 100°C. Separation of charge carriers in TiO<sub>2</sub>, dehydroxylation of surface and formation of superoxide anionic radicals are the most important issues for effective decomposition of ethylene in air.

#### 5. Conclusions

Application of TiO<sub>2</sub> supported on the nickel foam can enhance the photocatalytic decomposition of ethylene under UV-LED irradiation and increased temperature up to 100°C. It was confirmed, that increase temperature of the photocatalytic process conducted to activation of nickel foam and TiO<sub>2</sub> and caused enhanced generation of superoxide anionic radicals, which took place in ethylene decomposition. Nickel foam appeared to be an effective catalyst accelerating the photocatalytic process.

**Author Contributions:** M.T.: investigation, data curation, formal analysis, writing-original draft preparation, visualization; P.M. investigation, data curation, formal analysis, writing-original draft preparation, visualization; B.T.: conceptualization, methodology, writing-review and editing, project administration

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**Data Availability Statement:** Data will be available in repository ZUT.

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

## References

1. N. Pathak, O.J. Caleb, M. Geyer, W.B. Herppich, C. Rauh, P. V. Mahajan, Photocatalytic and Photochemical Oxidation of Ethylene: Potential for Storage of Fresh Produce—a Review, *Food Bioproc Tech.* 10 (2017) 982–1001. <https://doi.org/10.1007/s11947-017-1889-0>.
2. L. Elsgaard, Ethylene Removal by a Biofilter with Immobilized Bacteria, 1998. <https://journals.asm.org/journal/aem>.
3. N. Keller, M.N. Ducamp, D. Robert, V. Keller, Ethylene removal and fresh product storage: A challenge at the frontiers of chemistry. Toward an approach by photocatalytic oxidation, *Chem Rev.* 113 (2013) 5029–5070. <https://doi.org/10.1021/cr900398v>.
4. H.Z. Moghadam, B. Kheirkhah, A. Kariminik, Ethylene Removal by Bio-filters in order to Increase Storage Life of Bananas, *International Journal of Life Sciences.* 9 (2015) 62–65. <https://doi.org/10.3126/ijls.v9i5.12696>.
5. A.W.J. Smith, S. Poulston, L. Rowsell, L.A. Terry, J.A. Anderson, A new palladium-based ethylene scavenger to control ethylene-induced ripening of climacteric fruit, *Platin Met Rev.* 53 (2009) 112–122. <https://doi.org/10.1595/147106709X462742>.
6. D. Martínez-Romero, G. Bailén, M. Serrano, F. Guillén, J.M. Valverde, P. Zapata, S. Castillo, D. Valero, Tools to maintain postharvest fruit and vegetable quality through the inhibition of ethylene action: A review, *Crit Rev Food Sci Nutr.* 47 (2007) 543–560. <https://doi.org/10.1080/10408390600846390>.
7. N. Pathak, O.J. Caleb, C. Rauh, P. V. Mahajan, Efficacy of photocatalysis and photolysis systems for the removal of ethylene under different storage conditions, *Postharvest Biol Technol.* 147 (2019) 68–77. <https://doi.org/10.1016/j.postharvbio.2018.09.006>.
8. M. Hussain, N. Russo, G. Saracco, Photocatalytic abatement of VOCs by novel optimized TiO<sub>2</sub> nanoparticles, *Chemical Engineering Journal.* 166 (2011) 138–149. <https://doi.org/10.1016/j.cej.2010.10.040>.
9. S. Kumar, A.G. Fedorov, J.L. Gole, Photodegradation of ethylene using visible light responsive surfaces prepared from titania nanoparticle slurries, *Appl Catal B.* 57 (2005) 93–107. <https://doi.org/10.1016/j.apcatb.2004.10.012>.
10. G. Shi, A. Mahmood, G. Lu, X. Wang, S. Tong, M. Ge, X. Xie, J. Sun, Adsorption and Photodegradation of Acetaldehyde and Ethylene on TiO<sub>2</sub> (001) Surface: Experimental and First Principle Studies, *Catal Letters.* 149 (2019) 2728–2738. <https://doi.org/10.1007/s10562-019-02813-8>.
11. P. Rychtowski, B. Tryba, A. Skrzypaska, P. Felczak, J. Sreńscek-Nazzal, R.J. Wróbel, H. Nishiguchi, M. Toyoda, Role of the Hydroxyl Groups Coordinated to TiO<sub>2</sub> Surface on the Photocatalytic Decomposition of Ethylene at Different Ambient Conditions, *Catalysts.* 12 (2022). <https://doi.org/10.3390/catal12040386>.
12. J. Xia, L. Dong, H. Song, J. Yang, X. Zhu, Preparation of doped TiO<sub>2</sub> nanomaterials and their applications in photocatalysis, *Bulletin of Materials Science.* 46 (2023) 13. <https://doi.org/10.1007/s12034-022-02847-6>.
13. K. Bhattacharyya, S. Varma, A.K. Tripathi, S.R. Bharadwaj, A.K. Tyagi, Mechanistic insight by in situ FTIR for the gas phase photo-oxidation of ethylene by V-doped titania and nano titania, *Journal of Physical Chemistry B.* 113 (2009) 5917–5928. <https://doi.org/10.1021/jp8103529>.
14. Z. Rao, X. Xie, X. Wang, A. Mahmood, S. Tong, M. Ge, J. Sun, Defect Chemistry of Er<sup>3+</sup>-Doped TiO<sub>2</sub> and Its Photocatalytic Activity for the Degradation of Flowing Gas-Phase VOCs, *Journal of Physical Chemistry C.* 123 (2019) 12321–12334. <https://doi.org/10.1021/acs.jpcc.9b02093>.
15. Q. Zhang, S. Ye, X. Chen, X. Song, L. Li, X. Huang, Photocatalytic degradation of ethylene using titanium dioxide nanotube arrays with Ag and reduced graphene oxide irradiated by  $\gamma$ -ray radiolysis, *Appl Catal B.* 203 (2017) 673–683. <https://doi.org/10.1016/j.apcatb.2016.10.034>.
16. Y.H. Lin, C.H. Weng, A.L. Srivastav, Y.T. Lin, J.H. Tzeng, Facile Synthesis and Characterization of N-Doped TiO<sub>2</sub> Photocatalyst and Its Visible-Light Activity for Photo-Oxidation of Ethylene, *J Nanomater.* 2015 (2015). <https://doi.org/10.1155/2015/807394>.
17. Y.T. Lin, C.H. Weng, F.Y. Chen, Key operating parameters affecting photocatalytic activity of visible-light-induced C-doped TiO<sub>2</sub> catalyst for ethylene oxidation, *Chemical Engineering Journal.* 248 (2014) 175–183. <https://doi.org/10.1016/j.cej.2014.02.085>.

18. W.K. Jo, H.J. Kang, Aluminum sheet-based S-doped TiO<sub>2</sub> for photocatalytic decomposition of toxic organic vapors, *Cuihua Xuebao/Chinese Journal of Catalysis*. 35 (2014) 1189–1195. [https://doi.org/https://doi.org/10.1016/S1872-2067\(14\)60076-0](https://doi.org/https://doi.org/10.1016/S1872-2067(14)60076-0).
19. H. Yang, B. Yang, W. Chen, J. Yang, Preparation and Photocatalytic Activities of TiO<sub>2</sub>-Based Composite Catalysts, *Catalysts*. 12 (2022). <https://doi.org/10.3390/catal12101263>.
20. X. Mei, H. Yuan, C. Li, Study on the MOF Frame Pt-TiO<sub>2</sub> Hybrid Photocatalyst and Its Photocatalytic Performance, *Sustainability*. 15 (2023) 1403. <https://doi.org/10.3390/su15021403>.
21. L. Chen, X. Xie, X. Song, S. Luo, S. Ye, W. Situ, Photocatalytic degradation of ethylene in cold storage using the nanocomposite photocatalyst MIL101(Fe)-TiO<sub>2</sub>-rGO, *Chemical Engineering Journal*. 424 (2021). <https://doi.org/10.1016/j.cej.2021.130407>.
22. B. Ji, W. Zhao, J. Duan, L. Fu, L. Ma, Z. Yang, Immobilized Ag<sub>3</sub>PO<sub>4</sub>/GO on 3D nickel foam and its photocatalytic degradation of norfloxacin antibiotic under visible light, *RSC Adv*. 10 (2020) 4427–4435. <https://doi.org/10.1039/c9ra08678a>.
23. Q. Zhang, F. Li, X. Chang, D. He, Comparison of nickel foam/Ag-supported ZnO, TiO<sub>2</sub>, and WO<sub>3</sub> for toluene photodegradation, *Materials and Manufacturing Processes*. 29 (2014) 789–794. <https://doi.org/10.1080/10426914.2014.892616>.
24. L. Yang, Z. Liu, J. Shi, H. Hu, W. Shangguan, Design consideration of photocatalytic oxidation reactors using TiO<sub>2</sub>-coated foam nickels for degrading indoor gaseous formaldehyde, *Catal Today*. 126 (2007) 359–368. <https://doi.org/10.1016/j.cattod.2007.06.017>.
25. W. Shangguan, H. Hu, W. Xiao, J. Yuan, J. Shi, TiO<sub>2</sub> / SiO<sub>2</sub> composite films immobilized on foam nickel substrate for the photocatalytic degradation of gaseous acetaldehyde, *International Journal of Photoenergy*. 2008 (2008). <https://doi.org/10.1155/2008/679421>.
26. B. Tryba, P. Miądlicki, P. Rychtowski, M. Trzeciak, R.J. Wróbel, The Superiority of TiO<sub>2</sub> Supported on Nickel Foam over Ni-Doped TiO<sub>2</sub> in the Photothermal Decomposition of Acetaldehyde, *Materials*. 16 (2023). <https://doi.org/10.3390/ma16155241>.
27. H. Hu, W. Xiao, J. Yuan, J. Shi, D. He, W. Shangguan, High photocatalytic activity and stability for decomposition of gaseous acetaldehyde on TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> composite films coated on foam nickel substrates by sol-gel processes, *J Solgel Sci Technol*. 45 (2008) 1–8. <https://doi.org/10.1007/s10971-007-1650-7>.
28. Q. Zeng, X. Xie, X. Wang, Y. Wang, G. Lu, D.Y.H. Pui, J. Sun, Enhanced photocatalytic performance of Ag@TiO<sub>2</sub> for the gaseous acetaldehyde photodegradation under fluorescent lamp, *Chemical Engineering Journal*. 341 (2018) 83–92. <https://doi.org/10.1016/j.cej.2018.02.015>.
29. D.-R. Park, J. Zhang, K. Ikeue, H. Yamashita, M. Anpo, Photocatalytic Oxidation of Ethylene to CO<sub>2</sub> and H<sub>2</sub>O on Ultrafine Powdered TiO<sub>2</sub> Photocatalysts in the Presence of O<sub>2</sub> and H<sub>2</sub>O, *J Catal*. 185 (1999) 114–119. <https://doi.org/10.1006/jcat.1999.2472>.
30. X. Fu, L.A. Clark, W.A. Zeltner, M.A. Anderson, Effects of reaction temperature and water vapor content on the heterogeneous photocatalytic oxidation of ethylene, *J Photochem Photobiol A Chem*. 97 (1996) 181–186. [https://doi.org/10.1016/1010-6030\(95\)04269-5](https://doi.org/10.1016/1010-6030(95)04269-5).
31. L.E. Mphuthi, M.R. Maseme, E.H.G. Langner, Ti(IV)-Exchanged Nano-ZIF-8 and Nano-ZIF-67 for Enhanced Photocatalytic Oxidation of Hydroquinone, *J Inorg Organomet Polym Mater*. 32 (2022) 2664–2678. <https://doi.org/10.1007/s10904-022-02327-8>.
32. W. Ammawath, Y.B.C. Man, B.S. Baharin, R.B.A. Rahman, A new method for determination of tert-butylhydroquinone (TBHQ) in RBD palm olein with FTIR spectroscopy, *Journal of Food Lipids*. 11 (2004) 266–277. <https://doi.org/10.1111/j.1745-4522.2004.01142.x>.
33. O. Fónagy, E. Szabó-Bárdos, O. Horváth, 1,4-Benzoquinone and 1,4-hydroquinone based determination of electron and superoxide radical formed in heterogeneous photocatalytic systems, *J Photochem Photobiol A Chem*. 407 (2021). <https://doi.org/10.1016/j.jphotochem.2020.113057>.

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