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GAS-PHASE PHOTOCATALYTIC OXIDATION OF VOLATILE ORGANIC COMPOUNDS

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ABSTRACT

Substances emitted into the atmosphere by human activities in urban and industrial areas cause environmental problems such as air quality degradation, respiratory diseases, climate change, global warming, and stratospheric ozone depletion. Volatile organic compounds (VOCs) are major air pollutants, emitted largely by industry, transportation and households. Many VOCs are toxic, and some are considered to be carcinogenic, mutagenic, or teratogenic. A wide spectrum of VOCs is readily oxidized photocatalytically. Photocatalytic oxidation (PCO) over titanium dioxide may present a potential alternative to air treatment strategies currently in use, such as adsorption and thermal treatment, due to its advantageous activity under ambient conditions, although higher but still mild temperatures may also be applied.

The objective of the present research was to disclose routes of chemical reactions, estimate the kinetics and the sensitivity of gas-phase PCO to reaction conditions in respect of air pollutants containing heteroatoms in their molecules. Deactivation of the photocatalyst and restoration of its activity was also taken under consideration to assess the practical possibility of the application of PCO to the treatment of air polluted with VOCs. UV-irradiated titanium dioxide was selected as a photocatalyst for its chemical inertness, non-toxic character and low cost. In the present work Degussa P25 TiO_2 photocatalyst was mostly used. In transient studies platinized TiO_2 was also studied.

The experimental research into PCO of following VOCs was undertaken:
- methyl *tert*-butyl ether (MTBE) as the basic oxygenated motor fuel additive and, thus, a major non-biodegradable pollutant of groundwater;
- *tert*-butyl alcohol (TBA) as the primary product of MTBE hydrolysis and PCO;
- ethyl mercaptan (ethanethiol) as one of the reduced sulphur pungent air pollutants in the pulp-and-paper industry;
- methylamine (MA) and dimethylamine (DMA) as the amino compounds often emitted by various industries.

The PCO of VOCs was studied using a continuous-flow mode. The PCO of MTBE and TBA was also studied by transient mode, in which carbon dioxide, water, and acetone were identified as the main gas-phase products. The volatile products of thermal catalytic oxidation (TCO) of MTBE included 2-methyl-1-propene (2-MP), carbon monoxide, carbon dioxide and water; TBA decomposed to 2-MP and water. Continuous PCO of

TBA proceeded faster in humid air than dry air. MTBE oxidation, however, was less sensitive to humidity. The TiO_2 catalyst was stable during continuous PCO of MTBE and TBA above 373 K, but gradually lost activity below 373 K; the catalyst could be regenerated by UV irradiation in the absence of gas-phase VOCs.

Sulphur dioxide, carbon monoxide, carbon dioxide and water were identified as ultimate products of PCO of ethanethiol. Acetic acid was identified as a photocatalytic oxidation by-product. The limits of ethanethiol concentration and temperature, at which the reactor performance was stable for indefinite time, were established. The apparent reaction kinetics appeared to be independent of the reaction temperature within the studied limits, 373 to 453 K. The catalyst was completely and irreversibly deactivated with ethanethiol TCO.

Volatile PCO products of MA included ammonia, nitrogen dioxide, nitrous oxide, carbon dioxide and water. Formamide was observed among DMA PCO products together with others similar to the ones of MA. TCO for both substances resulted in the formation of ammonia, hydrogen cyanide, carbon monoxide, carbon dioxide and water. No deactivation of the photocatalyst during the multiple long-run experiments was observed at the concentrations and temperatures used in the study.

PCO of MA was also studied in the aqueous phase. Maximum efficiency was achieved in an alkaline media, where MA exhibited high fugitivity. Two mechanisms of aqueous PCO – decomposition to formate and ammonia, and oxidation of organic nitrogen directly to nitrite - lead ultimately to carbon dioxide, water, ammonia and nitrate: formate and nitrite were observed as intermediates. A part of the ammonia formed in the reaction was oxidized to nitrite and nitrate. This finding helped in better understanding of the gas-phase PCO pathways.

The PCO kinetic data for VOCs fitted well to the monomolecular Langmuir-Hinshelwood (L-H) model, whereas TCO kinetic behaviour matched the first order process for volatile amines and the L-H model for others. It should be noted that both L-H and the first order equations were only the data fit, not the real description of the reaction kinetics. The dependence of the kinetic constants on temperature was established in the form of an Arrhenius equation.

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LIST OF PUBLICATIONS

The present thesis includes the following scientific publications, referred to in the text as Appendices 1-5.

1. Preis, S., Falconer, J. L., del Prado Asensio, R., Capdet Santiago, N., Kachina, A., Kallas, J. (2006) Photocatalytic oxidation of gas-phase methyl *tert*-butyl ether and *tert*-butyl alcohol. *Applied Catalysis B: Environmental*, 64 (1-2): 79-87

2. Preis, S., Kachina, A., Capdet Santiago, N., Kallas, J. (2005) The dependence on temperature of gas-phase photocatalytic oxidation of methyl tert-butyl ether and tert-butyl alcohol. *Catalysis Today*, 101(3-4): 353-358

3. Kachina, A., Preis, S., Kallas J. (2006). Catalytic TiO_2 oxidation of ethanethiol for environmentally benign air pollution control of sulphur compounds. *Environmental Chemistry Letters*, 4: 107-110

4. Kachina, A., Pres, S., Lluellas, G.C., Kallas, J. (2007). Gas-phase and aqueous photocatalytic oxidation of methylamine: the reaction pathways. *International Journal of Photoenergy*, article ID 32524, 6 p., DOI:10.1155/2007/32524

5. Kachina, A., Preis, S., Kallas J. (2007). Gas-phase photocatalytic oxidation of dimethylamine: the reaction pathways and kinetics. *International Journal of Photoenergy,* article ID 79847, 4 p., DOI: 10.1155/2007/79847

The author's contribution to the content of the publications is as follows:

1. The author carried out the experimental and calculation work in the parts entitled "Continuous-flow PCO", "Reaction rates" and "Photocatalyst lifetime".

2. The author carried out and described the experiments with photocatalytic oxidation of MTBE.

3. All the experiments and calculations were done by the author. The author interpreted the results and wrote the paper with co-authors.

4. The author performed the experimental work and supervised the work of the undergraduate student who contributed the part of data of aqueous PCO of methylamine. The paper was written by the author together with co-authors.

5. All the experiments and calculations were done by the author. The author interpreted the results and wrote the paper with co-authors.

LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

VOCs	Volatile Organic Compounds
PCO	Photocatalytic Oxidation
MTBE	Methyl *Tert*-Butyl Ether
TBA	*Tert*-Butyl Alcohol
TCO	Thermal Catalytic Oxidation
MA	Metylamine
DMA	Dimethylamine
2-MP	2-Methyl-1-Propene
L-H	Langmuir-Hinshelwood

Symbols

C	concentration of reactant [mol m^{-3}]
e^-	electron
h^+	positively charged hole
k	reaction rate constant [mol m^{-3} s^{-1}]
K	Langmuir adsorption coefficient of reactant [m^3 mol^{-1}]
r	PCO reaction rate [mol m^{-3} s^{-1}]
A_r	pre-exponential factor for the reaction rate constant [mol m^{-3} s^{-1}]
A_{ads}	adsorption coefficient [m^3 mol^{-1}]
E	activation energy of the reaction [kJ mol^{-1}]
ΔH	adsorption enthalpy [kJ mol^{-1}]
R	universal gas constant [kJ mol^{-1} K^{-1}]
T	temperature [K]

1 INTRODUCTION

Substances emitted into the atmosphere by human activities in urban and industrial areas cause environmental problems such as air quality degradation, respiratory diseases, climate change, global warming, and stratospheric ozone depletion. Volatile organic compounds (VOCs) are major air pollutants, emitted largely by industry, transportation and households. Many VOCs are toxic, and some are considered to be carcinogenic, mutagenic, or teratogenic. Consequently, effective air cleaning procedures are necessary. Methods for air cleaning can be divided into two categories - combustible and non–combustible processes (Carp et al., 2004).

In non-combustible processes, VOCs released with the waste gas are collected. Contemporary techniques in this area include adsorption, condensation, and biological filtration. In combustible processes, VOCs in the gas phase are destroyed by thermal and catalytic incineration. Both of these technologies have disadvantages and limitations in practical applications. For example, the efficiency of activated carbon adsorption significantly decreases at temperatures higher than 311 K. Moreover, safe handling, transportation and utilization of the used carbon may be problematic. Although thermal incineration is quite effective, it consumes significant amounts of auxiliary fuel. While catalytic incineration may be operated at a lower temperature than thermal incineration, catalytic incineration is relatively costly and causes waste problems such as: ash, deactivated catalysts, greenhouse gases. Photocatalytic oxidation (PCO) presents an alternative to the above-mentioned methods, exhibiting considerable potential in oxidation of organic compounds under ambient conditions. It has been reported that the use of UV-illuminated TiO_2 can result in the degradation of VOCs and even nitrogen and sulphur oxides in air (Peral and Ollis, 1992; Lawryk and Weisel, 1996). Titanium dioxide in its anatase form is widely used as a photocatalyst. Although TiO_2 photocatalysts were initially applied to water treatment, in recent years it has been shown that the photocatalytic detoxification of VOCs is generally more efficient in the gas phase than the aqueous phase. Thus, interest in PCO in air treatment has increased, including

applications of air stripping in water treatment with following cleaning of air. This method of water treatment has been used to separate halogenated and non-halogenated VOCs from water (Carp et al., 2004). Photocatalytic oxidation over titanium dioxide may present a potential alternative for air treatment strategies due to its advantages such as the fact that the photocatalytic oxidation reaction proceeds effectively under ambient conditions, although higher temperatures may also be applied.

1.1 Objectives

The objective of the present research was to disclose routes of chemical reactions, and estimate the kinetics and the sensitivity of gas-phase PCO towards reaction conditions in respect of air pollutants containing heteroatoms in their molecules. Deactivation of the photocatalyst and restoration of its activity was also taken under consideration to assess the practical possibility of the application of PCO to the treatment of air polluted with certain VOCs. UV-irradiated titanium dioxide, most often Degussa P25, was selected as a photocatalyst for its chemical inertness, non-toxic character and low cost.

Experimental research into PCO of the following VOCs was undertaken:
- methyl *tert*-butyl ether (MTBE) as the basic oxygenated motor fuel additive and, thus, a major non-biodegradable pollutant of groundwater;
- *tert*-butyl alcohol (TBA) as the primary product of MTBE hydrolysis and PCO;
- ethyl mercaptan (ethanethiol) as one of the reduced sulphur pungent air pollutants in the pulp-and-paper industry;
- metylamine (MA) and dimethylamine (DMA) as the amino compounds often emitted by various industries.

The present research had the objective of studying the gas-phase PCO of the VOCs mentioned above with a transient and a continuous flow method in simple thin-film tubular reactors. The intermediate objectives included the identification of volatile PCO products and, thus, the establishment of possible reaction pathwas, the characteristics of the reaction kinetics and examination of the catalyst life time. Thermal catalytic

oxidation (TCO) experiments were carried out to verify the reliability of the findings in comparison with published data available for TCO.

1.2 Air pollutants under consideration: an overview

Volatile organic compounds are organic air pollutants, emitted into the atmosphere from a variety of sources, including vehicles, fossil fuel combustion, steel-making, petroleum refining, fuel refilling, industrial and residential solvent use, paint application, manufacturing of synthetic materials (plastics, carpets), food processing, agricultural activities and wood processing and burning. The most significant problem related to the emission of VOCs is the possible production of photochemical oxidants (ozone, peroxyacetyl nitrate). Tropospheric ozone, formed in the presence of sunlight from NO_x and VOC emissions, creates a potential risk to public health, is damaging to crops and is involved in the formation of acid rain. Emissions of VOCs also contribute to localized pollution problems of toxicity and odor. Many VOCs take part in the depletion of the stratospheric ozone layer and may play a significant role in global warming (Manahan, 1994). The present work was focused on the air pollutant VOCs characterized below.

1.2.1 Methyl *tert*-butyl ether

Methyl *tert*-butyl ether (MTBE) was the most widely used motor fuel additive in the USA until 1998 and is still the basic oxygenated additive used nowadays in the rest of the world. As a result of massive production of MTBE, significant amounts are found in groundwater because of storage tank and pipeline leaks and fuel spills (Johnson et al., 2000).

Because it has a high solubility in water (about 50 g L^{-1} at 20 ˚C (Squillace et al., 1996)) and is resistant to biodegradation (Bradley et al., 1999) in ground water systems, MTBE can be present miles from the original spill (Landmeyer et al., 1998) and is expected to persist in groundwater for many years (Barker, 1998). Based on current MTBE toxicological data, a maximum drinking water level of 100 μg MTBE L^{-1} is suggested (Hartley et al., 1999), although this recommended advisory level does not take into

consideration evidence of the carcinogenic character of MTBE in humans (Clary, 1997). *Tert*-Butyl alcohol has been reported as a primary product of photocatalytic degradation and hydrolysis of MTBE in aqueous media (Baretto et al., 1995; Bertelli and Selli, 2004; Aguera et al., 2004).

Air stripping is a reliable technology to remove VOCs from groundwater, but needs additional pervaporation equipment for MTBE (Keller and Bierwagen, 2001) due to its low Henry's constant value. The MTBE-laden air has to be treated before release to the atmosphere. A few studies have reported PCO of vapour-phase MTBE (Raupp and Junio, 1993; Idriss et al., 1997; Alberici and Jardim, 1997; Park et al., 2003), although little information is available on the kinetics and the composition of PCO products.

1.2.2 Ethanethiol

Volatile organic compounds containing reduced sulphur, such as thiols and thioethers, also known as mercaptans, are released mostly from biological activities and a number of manufacturing processes, such as papermaking and petroleum refining. Mercaptans are highly toxic and corrosive, have obnoxious odours and an extremely low odour threshold (Sax, 1984). The natural atmospheric oxidation of VOCs containing reduced sulphur leads to the formation of tropospheric SO_2, which eventually becomes sulphuric acid, the compound responsible for acid rain (Butler, 1979).

Incineration, regenerative thermal oxidation and wet scrubbers are the air pollution control technologies used to treat reduced sulphur compounds (Rafson 1998; Kastner and Das, 2002). Thermal elimination methods, however, have high operating costs, produce a greenhouse gas (CO_2) and require SO_2 scrubbing. Wet scrubbers require costly oxidizing chemicals, such as ClO_2 or NaOCl, need large amounts of water, and can produce chlorinated hydrocarbons if not properly controlled (Kastner and Das, 2002). Environmentally benign and cost-effective air pollution control technology for reduced sulphur compounds is far from perfect and still a topic of research, for example, in the pulp-and-paper industry.

1.2.3 Amino compounds

The chemical, pharmaceutical, and petrochemical industries are among sources producing waste streams containing organic nitrogen-containing compounds. Dimethylamine (DMA) is used as a dehairing agent in tanning, in synthesis of dyes, rubber accelerators, pharmaceuticals, soaps and cleaning compounds, and as a fungicide and is a toxic air pollutant, thus it presents an object for study in this work (Lewis, 1997).

Methylamine (MA) decomposition under oxidative conditions has been reported by different researchers; an exhaustive review was published by Kantak et al., (1997). It has been reported that at 623 K, a greater part of MA is initially converted to NH_3, with a small fraction forming NOx increasing with the increased O_2 concentration. At low temperatures, around 523 K, hydrogen cyanide (HCN) is not formed in appreciable quantities, due to early C−N bond scission. At higher temperatures (1160–1600 K), however, HCN has been observed as a product of MA thermal decomposition (Hwang et al., 1990). Higashihara et al. (1987) suggested that the MA thermal decomposition may be a combination of two pressure- and temperature-dependent processes: the unimolecular scission of the C−N bond and the stripping of four H atoms from the parent molecule to form HCN and H_2.

In the gas phase, a common industrial practice is incineration, which for nitrogen-containing compounds may result in the formation of nitrogen oxides such as NO, NO_2, and possibly N_2O, contributing to the formation of photochemical smog, the greenhouse effect, and stratospheric ozone depletion. To mitigate these unwanted environmental effects equipment modifications, selective non-catalytic and catalytic reduction processes have been required in order to reduce NO_x emissions (Kantak et al., 1997). Photocatalytic oxidation may present an alternative to thermal oxidation of amino compounds without formation of prohibitively high yields of nitrogen oxides or cyanides.

2 GAS-PHASE PHOTOCATALYTIC OXIDATION

The basis of photocatalysis is the photoexcitation of a semiconductor solid as a result of absorption of electromagnetic radiation, often, but not exclusively, in the near ultraviolet spectrum. Under near-UV irradiation a suitable semiconductor material may be excited by photons possessing energies of sufficient magnitude to produce conduction band electrons and valence band holes. These charge carriers are able to induce reduction or oxidation respectively. At the surface of the TiO_2 particle these may react with adsorbed species (Matthews, 1986).

2.1 TiO₂ applications in gas-phase photocatalysis

Titanium dioxide is widely used in industry; its high refractive index in visible light permits its use as a pigment material. Its use as a catalyst and catalyst support where it interacts with the supported phase as a promoter and photocatalyst is well known (Martin et al., 1995; Bayarri et al., 2005).

Titanium dioxide can have three different crystalline phases - brookite, anatase and rutile, where Ti atoms are included into deformed oxygen octahedra. The number of shared edges of the octahedra distinguishes the different crystalline phases. Three octahedra edges are shared in brookite, four in anatase, and two in rutile, making different densities and photocatalytic activity for each phase (Lopez et al., 1995).

Anatase has an energy band gap of 3.2 eV and can be activated by UV radiation with a wavelength up to 387.5 nm. Thus, only 4-5% of the solar energy reaching the ground level could be utilised in PCO when TiO_2 is used as photocatalyst (Zhang et al., 1994). The oxidative potential of a positively charged hole exceeds the one of any known oxidant at ambient conditions (Carey, 1992), which makes practically every organic compound possible to be oxidised photocatalytically.

The commercialization of TiO$_2$-based photocatalytic products commenced in the mid-1990s. However, this industry has grown very quickly. The products of the industry can be divided into five categories (Table 2.1.1). The market share of purification facilities grew at the highest rate, from 9% in 2002 to 33% in 2003, which was mainly due to the contribution of air purification products, including air cleaners and air conditioners (Fujishima and Zhang, 2006).

Table 2.1.1. TiO$_2$-based photocatalytic products that have appeared on the market (Fujishima and Zhang, 2006)

Categories	Products	Properties
Exterior construction materials	Tiles, glass, tents, plastic films, aluminum panels, coatings,	Self-cleaning
Interior furnishing materials	Tiles, wallpaper, window blinds,	Self-cleaning, antibacterial
Road-construction materials	Soundproof walls, tunnel walls, road-blocks, coatings, traffic signs and reflectors, lamp covers	Self-cleaning, air-cleaning
Purification facilities	Air cleaners, air conditioners, purification system for wastewater and sewage, purification system for pools	Air-cleaning, water-cleaning, antibacterial
Household goods	Fibers, clothes, leathers, lightings, sprays	Self-cleaning, antibacterial
Others	Facilities for agricultural uses	Air-cleaning, antibacterial

A very important application of TiO_2 photocatalysts is the purification of indoor air. Malodorous substances such as ammonia, hydrogen sulphide, acetaldehyde, toluene, methyl mercaptan etc., involve serious risks to health or comfort. Their concentrations in indoor air are low, making it suitable for TiO_2-based PCO. A photocatalyst-type air cleaner is typically composed of TiO_2-based filters, UV lamps, and a fan for air circulation. TiO_2 nanoparticles are coated on or dispersed in the body of filters with active carbon or zeolite as co-adsorbents. In contrast to the single function of adsorption for active carbon filters in conventional air cleaners, the TiO_2-based photocatalyst filter can decompose the adsorbed pollutants instead of accumulating them, and thus it exhibits better air cleaning performance. In addition, the photocatalyst-type air cleaner can also kill the bacteria floating in indoor air, which is very important for applications in hospitals, institutions for the elderly and schools (Fujishima and Zhang 2006).

2.2 Parameters and conditions influencing PCO

Photocatalytic oxidation is a typical heterogeneous reaction process thus making several factors important for the process rate, dependent on the rate limiting stage: chemical reaction, adsorption of the pollutant or desorption of reaction products. In this chapter some factors characteristic for gas-phase reactions are introduced.

2.2.1 Catalyst supports and loading

Photocatalytic gas-phase reactions are rarely organised in a fluidised bed or in the stream of the catalyst, being mostly carried out in reactors with photocatalysts attached to surfaces. Various supports and immobilization methods for TiO_2 photocatalysis have been reported by different researchers; an exhaustive review has been published by Carp et al., (2004). Strategies focussed on supported TiO_2 have been developed in order to immobilize the TiO_2 photocatalyst, to increase the illuminated specific catalyst area, to increase the adsorption capacity and surface area of the photocatalyst, and to influence the selectivity of the photocatalytic reaction (Carp et al., 2004). It has been reported that the attachment procedure consists of the fixation of preliminarily prepared titania powder using various methods such as silane coupling (Jackson et al., 1991), immobilization in a

polymer matrix (Brezová et al., 1994), electrophoretic deposition on conducting glass (Byrne et al., 1998), stainless steel (Byrne et al., 1998; Fernández et al., 1995), titanium foil, or tin coated glass (Fernández et al., 1995), and spray coating (Fernández et al., 1995; Tennakone et al., 1995). Another route is the coating of the support by in situ catalyst generation as a result of a combined physical and chemical transformation like sol–gel synthesis (Sabate et al., 1991; Aguado and Anderson, 1993; Kim and Anderson, 1994) and chemical vaporization from $TiCl_4$ (Jackson et al., 1991; Sato et al., 1989). The following support materials are used: glass beads (Jackson et al., 1991), fibre glass (Robert et al., 1999; Lee et al., 2001), glass pellets (Yamazaki et al., 2001; Bouazza et al., 2007), glass sheets (Anderson et al., 1988), silica (Sato, 1988; Xu et al., 1999; Aguado et al., 2002; Alemany et al., 1997; Chun et al., 2001; Hu et al., 2003), organo-clays (Ilisz et al., 2002), stainless steel (Zhu et al., 2001), rutile TiO_2 (Loddo et al., 1999), fibre textile (Ku et al., 2001), Al_2O_3 (Lee et al., 2001; Pirkanniemi and Sillanpää, 2002) quartz beads (Benoit-Marquie et al., 2000; Hermann et al., 1997), honeycomb (Fernandez et al., 1995), polyethene and polypropylene films (Tennakone and Kottegoda, 1996), fabrics (cotton and polyester) (Park and Kim, 2004), paper (Iguchi et al., 2003), activated carbon (Herrmann et al., 1999; Nozawa et al., 2001; Takeda et al., 1998), and zeolites (Sampath et al., 1994). In spite of so many efforts, it is still unclear which methods and supports are most convenient in terms of mechanical stability and photochemical reactivity (Carp at al., 2004).

A common disadvantage of attached photocatalysts on solid supports is their reduced photocatalytic efficiency (Mathews, 1990; Sabate et al., 1992). This decrease in activity has been correlated with a reduction of active surface (Alemany et al., 1997; Galan-Fereres et al., 1995), mass-transfer limitations (Ollis et al., 1991; Ray and Beenackers, 1997; Dijkstra et al., 2001), and the presence of foreign cationic impurities (Si^{4+}, Na^+, Cr^{3+}, Fe^{3+}) in the deposit layer (as a consequence of the thermal treatment necessary to improve TiO_2-support adhesion), which increases the e^-/h^+ recombination rate (Robert et al., 1999). This disadvantage contradicts the purpose of the catalyst attachment, although there seems to be little choice: a powdered photocatalyst even in a fluidized bed has to be attached to a support (Lim and Kim, 2004; Zhang et al., 2006).

To improve the contact surface, the catalyst loading could be increased. Normally, the PCO rate increases with increasing photocatalyst amount due to an increase in the surface area of the porous catalyst available for adsorption and degradation. However, for immobilized TiO_2 there is an optimum thickness of the catalyst film, since not only the contact surface, but also the internal mass transfer resistance for both organic species and photogenerated electrons/holes will increase with increasing thickness. This improves the electron-hole recombination possibility and, as a consequence, the degradation performance is reduced (Carp at al., 2004).

2.2.2 Photocatalyst deactivation

Photocatalyst deactivation is a crucial issue in practical applications. The analysis of published material reveals that photocatalyst deactivation is generally found in continuous-flow photocatalytic reactors with a surface attached catalyst (Sauer and Ollis, 1996). Depending on the character of the organic compounds, either reversible or irreversible deactivation was evidenced (Piera et al., 2002; Peral and Ollis, 1997). The catalyst may be deactivated either by formation of surface intermediates with higher adsorption ability than the target pollutant (reversible deactivation) or by sticky "heavy" products that are difficult to decompose or desorb (irreversible deactivation).

An extensive review of the reactivation of the photocatalyst has been published by Carp et al., (2004). They propose the following regeneration schemes:

- thermal regeneration at high temperatures. Lower temperatures result in the conversion of reaction intermediates to lesser volatile ones, accelerating the formation of carbonaceous deposits (Piera et al., 2002);
- photocatalytic regeneration using simultaneous UV illumination and exposure to humidified air. Photocatalytic regeneration may be more practical than thermal regeneration, particularly in indoor air treatment systems because it can be carried out at

ambient temperatures. However, since the surface intermediates leading to activity loss are presumably recalcitrant to photocatalytic regeneration, it requires longer regeneration times than thermal regeneration (Ameen and Raupp, 1999; Cao et al., 2000);

- O_3 purging in the presence of water vapour (Wang et al., 2003);

- rinsing with alkaline solutions (Sun, 2003);

- rinsing with hydrogen peroxide or potassium persulphate solutions (Albirici and Jardim, 1997; Wang et al., 2007).

2.2.3 Effect of humidity

The influence of water vapour on the gas-phase PCO rate depends on its content, the concentration of the pollutant species, and the process exterior parameters. The continuous consumption of hydroxyl radicals in PCO requires replenishment to maintain catalytic activity, i.e. provide OH·-radicals formed from their precursors, OH⁻-ions. A suitable equilibrium between increased formation of OH·-radicals and competition for the adsorption sites between the pollutant and the water molecules exists at low water vapour contents. Upon increase of the vapour content, this equilibrium may be upset and more water vapour molecules may adsorb on the catalyst surface. A competition for the adsorption sites between water and the target organic and/or oxygen molecules occurs and a considerable decrease in the amount of organic molecules adsorbed on the TiO_2 surface is observed (Obee and Brown, 1995; Lichtin and Avudaithai, 1996). Additionally, water adsorption favours electron–hole recombination (Park et al., 1999). Nevertheless, numerous studies indicate that a certain degree of humidity, usually exceeding the amount produced by the oxidation of the organics, is necessary to maintain hydroxylation and to avoid the blockage of the TiO_2 surface by partially oxidized products (Ameen and Raupp, 1999; Maira et al., 2001.)

2.2.4 Concentration of the pollutant

The PCO rate of organic substrates usually exhibits saturation behaviour: the apparent rate increases disproportionally with the increased concentration of a VOC, i.e. the increase in the pollutant concentration results in a decreased relative conversion degree of the pollutant. This phenomenon is often inaccurately interpreted as a decrease in the reaction rate, even getting to review papers (Carp et al., 2004), although a decrease in the conversion degree does not mean a decrease in the reaction rate. The reaction may decrease in its rate on the condition of the catalyst deactivation, as was discussed earlier (see 2.2.2).

Heterogeneous reactions are often sufficiently well described as a data fit, although rarely follow the described mechanism, with the Langmuir – Hinshelwood (L-H) equation (see 2.3), which indicates adsorption as a prerequisite of reaction. At a high concentration of pollutant all catalytic sites become occupied so that a further increase in the pollutant concentration does not affect the actual catalyst surface concentration, and therefore, this results in even constant reaction rate and, thus, in a decreased pollutant conversion degree.

Another possible explanation of the saturation behaviour of PCO is the relation between, on the one hand, generation and migration of photogenerated electron–hole pairs and, on the other, their reaction with organic compounds. At low concentrations, the reaction dominates the process and, therefore, the degradation rate increases linearly with the pollutant concentration. However, at high concentrations of pollutant, the generation of electron-hole pairs will become the governing step, and the degradation rate increases slowly with concentration, and for a given illumination intensity, even a constant degradation rate may be observed as a function of concentration.

Intermediates generated during the PCO also affect the adsorption and oxidation rate of their parent compounds. A higher initial concentration will yield a higher concentration of adsorbed intermediates, which will affect the overall rate (Carp et al., 2004).

2.3 Reaction kinetics

The L-H model of monomolecular reaction kinetics has been widely used for the description of gas-phase photocatalytic reactions (Kim and Hong, 2002; Alberici and Jardim, 1997). The equation for the simplest monomolecular reaction can be presented as follows:

$$r = \frac{kKC}{1+KC},$$
(1)

where r is the reaction rate (mol m^{-3} s^{-1}), C is the concentration of the reactant (mol m^{-3}), k is the reaction rate constant (mol m^{-3} s^{-1}), and K is the Langmuir adsorption coefficient (m^3 mol^{-1}).

The complex mechanisms of photocatalytic reactions are difficult to describe in a simple model for an extended reaction time. Therefore, the kinetic modelling is usually restricted to the analysis of the initial rate of photocatalytic degradation. This can be obtained from a minimum detectable conversion of the reactant at a minimum contact time. A standard means of using the equation (1) is to demonstrate linearity of data when plotted as the inverse rate vs. inverse concentration (Kim and Hong, 2002).

$$\frac{1}{r} = \frac{1}{k} + \frac{1}{kK}\frac{1}{C},$$
(2)

According to Vannice et al. (1979), mechanisms other than the Langmuir - Hinshelwood mechanism can have the same mathematical form. They note that the values of the standard entropy of adsorption ΔS_a^o must conform to certain rules in order to support the proposed reaction model: ΔS_a^o must be negative and must have an absolute value smaller than the standard entropy in the gas phase S_g^o. A less stringent rule is offered as a guideline for dissociative adsorption: $10 \leq - \Delta S_a^o \leq 12.2 - 0.00014\,\Delta H$.

The dependence of the L–H kinetic parameters, the reaction rate constant and the Langmuir adsorption coefficient on temperature is analyzed in the form of Arrhenius equations:

$$k = A_r e^{-E/RT}, \qquad (3)$$

$$K = A_{ads} e^{-\Delta H/RT}, \qquad (4)$$

where A_r and A_{ads} are pre-exponential factors for the reaction rate constant and the adsorption coefficient, mol m^{-3} s^{-1} and m^3 mol^{-1}, respectively; E and ΔH are the activation energy of the reaction and the adsorption enthalpy, kJ mol^{-1}; R is the universal gas constant, kJ mol^{-1} K^{-1} and T is temperature, K.

The plots $ln\ k$ and $ln\ K$ versus 1/T are constructed. The slopes of the straight lines, the intercepts and the regression coefficients are calculated using the trend lines of the plots. The values of E and ΔH are calculated respectively as the slope of the plots $ln\ k$ and $ln\ K$ versus 1/T multiplied by the universal gas constant; and A_r and A_{ads} are the exponential of the intercepts.

3 RESULTS AND DISCUSSION

3.1 Experimental methods and conditions

The experimental device (Fig 3.2.1) used for continuous-flow PCO made use of an annular reactor (Fig. 3.2.2). The inner diameter of the photocatalytic reactor was 33 mm, total volume of the reactor 0.105 L, and if not otherwise specified, the annular gap (between the lamp and inner wall of the reactor) was 3.5 mm. The volume of the reactor was reduced to 0.055 L when amino compounds were photocatalytically oxidized due to their high PCO rate: the reaction had to proceed slowly enough to permit determination of the difference between the inlet and outlet concentrations of the VOC. A 365-nm 15-W low-pressure mercury UV-lamp (Sylvania, UK), was positioned coaxially in the reactor. In PCO of ethanethiol, a 254-nm lamp was used as a more powerful source of radiation energy. The reactor assembled with the lamp was coated inside with TiO_2 (Degussa P25) by sequential rinsing with a TiO_2 aqueous suspension fifty times, each rinse followed by drying at 105 ºC. Both the UV-lamp and the inner surface of the outer wall of the reactor were thus coated in most cases (double-side reactor); for studies of amino compounds oxidation only the inner wall of reactor was coated due to their fast oxidation (mono-side). Approximately, 0.9 g of TiO_2 coated about 640 cm^2 (1.4 mg cm^{-2}) of the double-side reactor, and 0.3 g of TiO_2 coated about 197 cm^2 (1.5 mg cm^{-2}) of the mono-side reactor. The irradiance of the TiO_2-coated UV-lamp was measured with a UVX Radiometer at the surface next to the lamp and averaged about 0.6 mW cm^{-2} in the double-side reactor with the 365-nm lamp for PCO of MTBE and TBA, and 1.4 mW cm^{-2} in the double-side reactor with the 254-nm lamp for PCO of ethanethiol, and 3.8mW cm^{-2} for PCO of MA and DMA in the mono-side reactor with 365-nm lamp.

In the experiments with PCO of MA and DMA only the inner wall of the reactor was coated with TiO_2 (Degussa P25) by a smaller number of rinsings with a TiO_2 aqueous suspension; the suspension was applied only 25 times to reduce the amount of the catalyst. The reactor was assembled with the lamp after the catalyst had been attached to the reactor's wall.

An evacuated gas cylinder was first filled with the desired amount of gaseous VOC through an injection port, and then filled with synthetic air (20% O_2, 80% N_2). The air stream containing VOC was blended with diluent gas to deliver the desired VOC concentration to the reactor. The temperature in the reactor during the PCO reactions was varied from 333 to 453 K. The temperature was adjusted with heating tape wrapped around the reactor. The tape was controlled with a temperature regulator Omega CN 9000A with a K-type thermocouple. The temperature deviations did not exceed ±1K.

The gas flow rate was 3.5 Lmin^{-1} (3.03 Lmin^{-1} for PCO of MA and DMA), which made the contact time equal to 1.8 second (1.1 s for PCO of MA and DMA). This contact time was sufficient to reliably register the difference between VOC concentrations in the inlet and outlet streams, keeping that difference within a limit of a few ppmv. The reaction products were analyzed by a Perkin Elmer 2000 FT-IR spectrometer equipped with a Sirocco 10.6 m gas cell. Inlet concentrations of VOC varied from 10 to 560 ppmv ($6.7 \cdot 10^{-4}$ to $2.5 \cdot 10^{-2}$ mol L^{-1}). TCO of VOC was conducted in the same reactor, without UV-radiation in the dark, at temperatures from 388 to 573 K.

Table 3.1.1 presents the temperature range of PCO and TCO reactions for the substances under consideration.

Table 3.1.1 Temperature ranges for the photocatalytic and thermocatalytic reactions

Substance	PCO Temperature range, K	TCO Temperature range, K
MTBE	333 - 403	388 - 433
TBA	333 - 393	393 - 453
Ethanethiol	373 - 453	373 - 453
MA	353 - 373	573
DMA	353 - 413	573

3.2 Catalyst life-time and reaction products

The deactivation of the photocatalyst (TiO_2) in the PCO experiments and the identified reaction products are summarised in Table 3.2.1.

Titanium dioxide partially lost its activity at temperatures below 373 K in PCO of MTBE and TBA; TBA induced smaller deactivation of TiO_2 than MTBE (see Appendices 1 and 2). The study was carried out in two different modes: transient and continuous-flow PCO. Transient PCO consisted of oxidation of the volatile compound, preliminary adsorbed onto the photocatalyst surface, with analysis of the oxidation products. The analysis of the products was carried out towards both desorbed volatile compounds on the course of PCO and the adsorbed products by means of temperature-programmed desorption and temperature programmed oxidation. Continuous PCO study presents by itself the analysis of inlet and outlet spectra of VOCs and their volatile oxidation by-products in the gas flow passing through the PCO reactor.

Acetone ((CH_3)$_2$CO)), water, and carbon dioxide (CO_2) were the main gas-phase oxidation products. Formic acid (HCOOH) was an intermediate that remained adsorbed on the TiO_2 until it was further oxidized. Some products appeared in the gas-phase because they were displaced from the surface by the reactants or other products. For this reason, the product distributions were different in transient and continuous-flow PCO. TBA oxidized faster than MTBE and acetone. Water increased the transient PCO rate of adsorbed TBA, acetone, and formic acid. Continuous-flow PCO of TBA was enhanced in the presence of water, whereas PCO of MTBE was less sensitive to water vapour. The TiO_2 was not a good oxidation catalyst in the dark, but it decomposed both MTBE and TBA to form 2-methyl-1-propene ((CH_3)$_2C_2H_2$), and this decomposition was orders of magnitude faster for MTBE. Above 373 K, MTBE and TBA decomposed in the absence of UV light, and this decomposition dominated above 403 K. Water increased the transient PCO rate of adsorbed TBA, acetone, and formic acid. Continuous PCO of TBA was faster in humid air than in dry air, but MTBE oxidation was less sensitive to humidity.
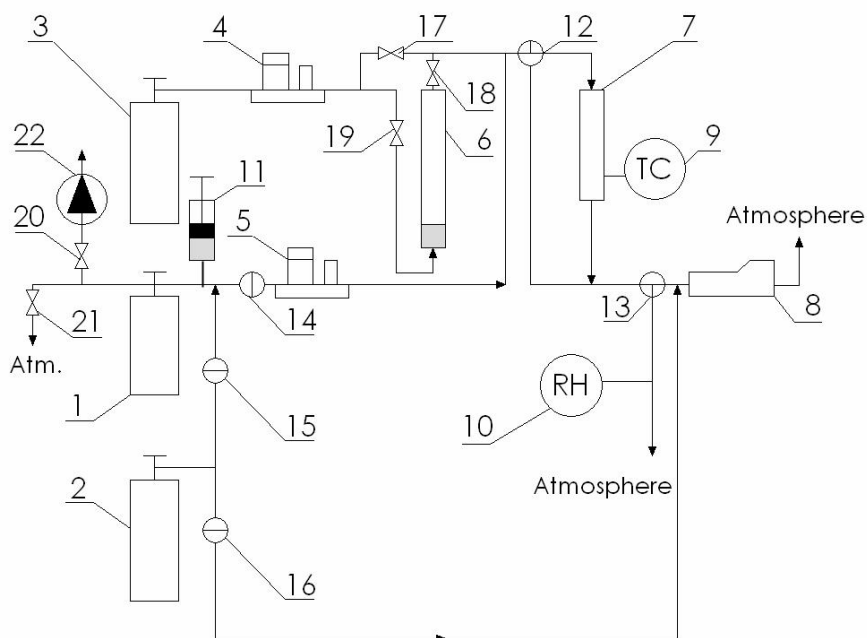
Figure 3.2.1 Scheme of experimental device: 1 – contaminated air tank; 2 – recharge and cell purge tank; 3 – diluent tank; 4, 5 – gas mass flow controllers; 6 – humidifier; 7 – reactor; 8 – FTIR gas analyzer; 9 – temperature controller; 10 – thermohygrometer; 11 – injection port; 12-13 – T-valves; 14-16 – stop-cock valves; 17-21 – regulatory valves; 22 – vacuum pump

Figure 3.2.2 Scheme of simple tubular reactor: 1 – UV-lamp; 2 – reactor; 3 – heating tape; 4 – thermocouple

Table 3.2.1 Catalyst deactivation temperature ranges and reaction products

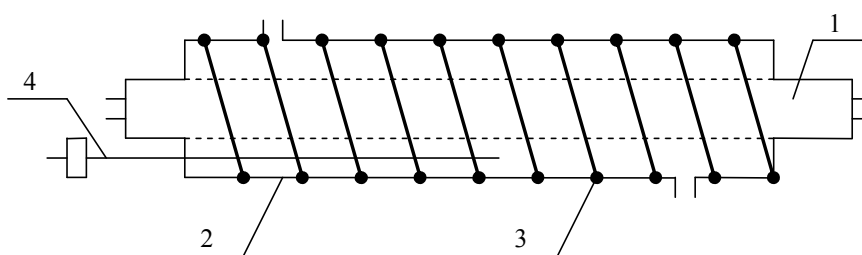|	Deactivation in PCO, temperature range, K	Reaction products	
		PCO	TCO
MTBE	<373	$(CH_3)_2CO$, CO_2, H_2O, HCOOH	$(CH_3)_2C_2H_2$, CO, CO_2, H_2O
TBA	<373	$(CH_3)_2CO$, CO_2, H_2O, HCOOH	$(CH_3)_2C_2H_2$, H_2O
Ethanethiol	373 - 453	SO_2, CO, CH_3COOH, CO_2, H_2O	-
MA	-	NH_3, N_2O, NO/NO_2, CO_2, H_2O	NH_3, HCN, CO_2, H_2O
DMA	-	NH_3, NO/NO_2, N_2O, $HCONH_2$, CO_2, H_2O	NH_3, HCN, CO_2, H_2O

In PCO of ethanethiol (Appendix 3) the deactivation of TiO_2 followed the accumulation of adsorbed oxidation by-products, such as acetic acid (CH_3COOH), which were easily removed from the surface by UV-radiation in the absence of ethanethiol in the air flow. Titanium sulphate accumulated on the TiO_2 surface. Sulphur dioxide (SO_2) was produced by the reaction of photocatalytic oxidation of ethanethiol partially adsorbed by TiO_2 and subsequently oxidised to sulphuric acid on the surface of the catalyst. The partial dissolving of TiO_2 presumably reduced the number of active sites of the photocatalyst (Vorontsov et al., 2003). The last consequence was observed as a gradual decrease in photocatalyst activity. Long-term photocatalytic operation of the reactor resulted in partial deactivation of the catalyst. The colour of the photocatalyst turned from white to yellowish. For example, at an initial concentration of ethanethiol of 20 ppmv the conversion rate decreased from 50 to 20% at all temperatures within 4 to 5 h. A similar picture was observed with other ethanethiol concentrations: a stable conversion degree of about 15 to 20% achieved in 4 to 5 h in the first experiment run remained for subsequent

runs when the catalyst was not recovered. The thermal catalytic oxidation of ethanethiol in the dark proceeded with low intensity at the beginning of oxidation. The catalyst soon lost its activity entirely. For example, at 100 ppmv the outlet concentration of ethanethiol became equal to the inlet one in a few minutes; at 10 ppmv complete inactivation of the catalyst was observed in three hours. The thermal decomposition of ethanethiol was, therefore, not studied in the present research.

When considering gas-phase PCO of MA and DMA (Appendices 4 and 5) the photocatalyst demonstrated stable activity at the temperature and concentration ranges tested in the experiments (Table 3.2.1). The minor deactivation of the photocatalyst may be explained by referring to the phenomena reported by Kolinko et al. (2007): nitric acid composed of negligible amounts of transformed nitrogen enhances the alkaline MA adsorption on an acidic TiO_2 surface having organic nitrates, and ammonium nitrate also photocatalytically oxidized with no additional HNO_3 formation. Slow, or zero after the first formation of nitric acid, the accumulation of nitrates makes the catalyst deactivation rate also slow or zero.

3.3 Reaction kinetics

The numbers of the reaction rate constants k and the Langmuir adsorption coefficients K at different temperatures are presented for the PCO reactions in Table 3.3.1. One can see the reaction rate constants increasing and the adsorption coefficient decreasing with increasing temperature.

Table 3.3.1 Reaction rate constants and Langmuir adsorption coefficient for PCO of VOCs on TiO_2

Temperature (K)	MTBE		TBA		Ethanethiol		MA		DMA	
	K (m^3 mol^{-1})	k (mmol m^{-3} s^{-1})	K (m^3 mol^{-1})	k (mmol m^{-3} s^{-1})	K (m^3 mol^{-1})	k (mmol m^{-3} s^{-1})	K (m^3 mol^{-1})	k (mmol m^{-3} s^{-1})	K (m^3 mol^{-1})	k (mmol m^{-3} s^{-1})
333	3500 ± 700	0.20 ± 0.05	730 ± 140	1.20 ± 0.2	-	-	-	-	-	-
353	1600 ± 200	0.30 ± 0.04	650 ± 15	1.30 ± 0.03	-	-	148 ± 1	6.6 ± 0.1	193 ± 1	2.2 ± 0.1
373	580 ± 10	0.55 ± 0.01	400 ± 15	1.90 ± 0.06	371 ± 1	0.40 ± 0.1	125 ± 1	8.7 ± 0.1	147 ± 1	3.1 ± 0.1
388	490 ± 30	0.60 ± 0.01	-	-	-	-	-	-	-	-
393	-	-	370 ± 50	2.10 ± 0.07	258 ± 1	0.60 ± 0.1	93 ± 1	10.5 ± 0.1	26 ± 1	15.0 ± 0.1
403	400 ± 50	0.60 ± 0.01	-	-	-	-	-	-	-	-
413	-	-	-	-	-	-	77 ± 1	12.5 ± 0.1	25 ± 1	16.0 ± 0.1
423	-	-	-	-	144 ± 1	0.90 ± 0.1	-	-	-	-
453	-	-	-	-	24 ± 1	5.0 ± 0.1	-	-	-	-

The TCO kinetic constants for MTBA and TBA were found and are described in detail in Appendix 2.

In contrast to PCO, TCO kinetic behaviour for MA and DMA indicated the first order process: the conversion degree varied proportionally with the inlet concentration of MA and DMA at 573 K. A minor influence of temperature on the apparent ethanethiol PCO rate was observed. For example, at an inlet concentration of 100 ppmv, ethanethiol degradation increased from 13 to 19 % when the temperature was raised from 373 to 453 K (Appendix 3), which was explained by the decreased adsorption of ethanethiol on TiO_2 with increasing temperature compensating the growth of the chemical transformation rate.

The numbers of the pre-exponential factors, the activation energy of the reaction and the adsorption enthalpy determined in the present research are given in Table 3.4.1. The reaction activation energy E is close to the adsorption energy ΔH for all substances under consideration, i.e. both the adsorption and the reaction rate have approximately equal sensitivity to temperature. The PCO rate constant for MTBE and DMA appears to be more sensitive to temperature change than for TBA and MA respectively, since it has larger Arrhenius equation parameters.

Table 3.4.1 Arrhenius equation parameters for the PCO of VOCs on TiO_2

Parameter	MTBE	TBA	Ethanethiol	MA	DMA
	Temperature range (333 to 373 K)	Temperature range (333 to 373 K)	Temperature range (373 to 453 K)	Temperature range (353 to 413 K)	Temperature range (353 to 413 K)
ΔH, kJ mol^{-1}	-38 ± 1	-15 ± 2	-45 ± 1	-14 ± 1	-42 ± 1
A_{ads}, m^3 mol^{-1}	0.003 ± 0.002	4.0 ± 0.5	2.2×10^{-4}	1.5 ± 0.5	$1.25 \cdot 10^{-4}$
E, kJ mol^{-1}	27 ± 1	11 ± 2	42 ± 1	13 ± 1	42.1 ± 1
A_r, mol m^{-3} s^{-1}	3.0 ± 0.1	0.07 ± 0.01	272 ± 1	0.5 ± 0.5	$0.35 \cdot 10^4$

Conclusions

The results reported in the present research brought new knowledge in the field of gas-phase PCO. The low-molecular VOCs of environmental concern containing hetero-atoms in their molecules were studied in detail considering reaction products and pathways, and reaction kinetics and its dependence on the experimental parameters. PCO is a promising method for the elimination of different VOCs due to its advantageous activity under ambient conditions, although higher but still mild temperatures may also be applied.

Gas-phase PCO studies resulted in improved understanding of the MTBE and TBA oxidation mechanism on TiO_2 and platinised TiO_2: PCO, TCO and oxidation products were determined; the L-H model parameters of the reaction kinetics were obtained; and the role of air humidity was clarified.

The limits of ethanethiol concentration and the reaction conditions at which the performance of the reactor's work was stable for indefinite time were established. Photocatalytic oxidation products for ethanethiol were identified. The kinetics of photocatalytic oxidation of ethanethiol was well described with the monomolecular L-H model, although it did not exhibit full conformity to all rules supporting the physical meaning of the reaction model.

Methyl amine and DMA were easily oxidized photocatalytically on UV-irradiated TiO_2. The volatile PCO products of MA and DMA were determined. The PCO reaction kinetics fitted the L-H description. The photocatalyst demonstrated stable activity at the temperature and concentration ranges tested in the experiments.

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APPENDICES