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# Gas-phase photocatalytic activity of nanostructured titanium dioxide from flame aerosol synthesis

Svetlana Jõks[a], Deniss Klauson[a], Marina Krichevskaya[a,*], Sergei Preis[b], Fei Qi[c], Alfred Weber[c], Anna Moiseev[d], Joachim Deubener[d]

[a] Department of Chemical Engineering, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia
[b] LUT Chemistry, Lappeenranta University of Technology, P.O. Box 20, 53851 Lappeenranta, Finland
[c] Institute of Particle Technology, TU Clausthal, Leibnizstrasse 19, 38678, Clausthal-Zellerfeld, Germany
[d] Institute of Non-Metallic Materials, TU Clausthal, Zehntnerstrasse 2a, 38678, Clausthal-Zellerfeld, Germany

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ABSTRACT

The experimental evaluation of gas-phase photocatalytic activity of a $TiO_2$ nanopowder synthesized in a flame aerosol reactor was carried out in photocatalytic oxidation (PCO) of volatile organic compounds (VOCs). The nanopowder has an average particle size of 13 nm, anatase content 97 wt.% and the specific surface area of 102 $m^2\,g^{-1}$. The performance was compared to the benchmark photocatalyst, the commercial pyrogenic titania P25, Evonik, with the average particle size of 21 nm. The full-factorial experiments were carried out varying contact times, concentrations of pollutants and temperatures in continuous gas-flow mode degrading aliphatic acrylonitrile (AN) and aromatic toluene. Higher conversions at more stable performance were observed for the flame aerosol synthesized photocatalyst in degradation of both pollutants. While the primary particle size and specific surface area present the apparent reasons for improved PCO performance in adsorbable AN, these parameters cannot do the same in oxidation of poorly adsorbable toluene: the superior generation of hydroxyl radicals and, therefore, advanced oxidative activity are proposed as explanation. The intense dehydration of reduced size anatase crystallites at elevated temperature (130 °C) presumably resulted in decreased OH-radicals production along with the improved desorption of HCN, the PCO by-product of AN. The safe performance is thus requiring lower operational temperatures. Slower deactivation and faster restoration of catalytic activity of flame aerosol synthesized catalyst under UV-A-radiation are discussed.

## 1. Introduction

Volatile organic compounds (VOCs) are common air pollutants emitted by chemical, petrochemical, pharmaceutical, and food processing industries, pulp and paper mills, and printing and painting works [1]. VOCs catalytic control technologies could be classified dependently on the pollutants' concentration levels and contaminated air flow rates [2]. Catalytic incineration and combustion techniques require as high as hundreds of ppm concentrations of VOCs and high temperatures (250–1200 °C) for successful operation being cost-ineffective for low pollutant concentrations [3–5]. Low concentrations of VOCs are mostly treated by adsorption and biological oxidation, as well as by non-thermal plasma [2,6]. Photocatalytic oxidation (PCO) technique is of extensive interest recently as potential air-cleaning technology for lower VOCs concentrations and indoor applications [7]. PCO usually uses a near UV-irradiated $TiO_2$ semiconductor catalyst: the method has oxidation potential sufficient to oxidize the widest spectrum of pollutants at near-ambient temperature [8–10], and is also capable of microbial contamination control of indoor air [11,12]. However, the efficiency of PCO in pollution abatement seems to depend on the chemical nature of the pollutant molecule [13]: catalyst deactivation by oxidation products is the main problem in PCO of, for example, aromatic compounds, trichloroethylene, sulphur- and silicon-containing compounds and others [14–16].Commercial pyrogenic titanium dioxide P25 (Evonik) formed in oxy-hydrogen flame is routinely used as a benchmark photocatalyst in oxidation of VOCs due to its unselective fairly good photoactivity towards wide spectra of pollutants, commercial availability and low cost. However, since the PCO of many organic vapours on P25 is not sufficiently fast for commercial process implementation and the photocatalyst is often deactivated, more active catalysts should be developed. Among various methods, the flame aerosol synthesis of nanopowders is favourable technique for controlling

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* Corresponding author. Tel.: +372 6202850; fax: +372 6202856.
*E-mail addresses:* lanka@starline.ee (S. Jõks), deniss.klauson@ttu.ee (D. Klauson), marina.kritsevskaja@ttu.ee (M. Krichevskaya), sergei.preis@lut.fi (S. Preis), fei.qi@mvt.tu-clausthal.de (F. Qi), weber@mvt.tu-clausthal.de (A. Weber), anna.moiseev@tu-clausthal.de (A. Moiseev), joachim.deubener@tu-clausthal.de (J. Deubener).

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crystal structure, particle size and its distribution, thus resulting in generation of open-structure agglomerates [17–21] with catalytic performance exceeding commercial photocatalyst P25 in degradation of aliphatic dichloroacetic acid (DCA) and aromatic 4-chlorophenol (4-CP) in aqueous solutions [22]. The size and crystal phase composition of $TiO_2$ nanoparticles have been shown crucial for their activity in aqueous phase [23]. However, the lower hydration of catalyst surface in gas-phase PCO brings forward the process sensitivity to the pollutants adsorption–desorption and surface characteristics inducing the difference in photocatalytic activity with aqueous phase. The data on the efficiency of flame synthesized $TiO_2$ catalysts in air treatment, however, are scarce, only the degradation of acetaldehyde and methanol in batch reactor was described by Balázs et al. [24] using relatively coarse (over 50 nm) anatase nanoparticles from flame synthesis. The improved PCO efficiency in aqueous phenol removal was attributed to the increase in the polyhedral-to-spherical particles ratio, although no improvement was seen in VOCs oxidation in air. To assure the photocatalytic activity of the newly synthesized material exceeding the one of commercially available materials, the gas-phase tests are necessary.

The continuous gas-flow mode used in present research allows following the adsorption/desorption equilibrium of initial pollutants and PCO products, as well as higher concentrations of pollutants could ascertain the deactivation limits of tested photocatalytic materials. Hazardous air pollutants aromatic hydrophobic toluene and aliphatic heteroatomic acrylonitrile (AN) were chosen for gas-phase performance studies of one of the photocatalyst samples F3 synthesized by Moiseev et al. [22] in comparison with commercial P25. AN is detected as an in-door air component emitted by commercial fibrous polymeric materials, resins and smoking tobacco [25,26]; it can induce gene mutations, chromosome aberrations, unscheduled DNA synthesis and cell transformation [27]. Toluene is used as admixture to motor fuel improving octane ratings and also in the synthesis of various organic chemicals and pharmaceuticals, in the production of polymers and as a solvent in paints, coatings, synthetic fragrances, adhesives, inks and cleaning agents [28]. The central nervous system, kidneys, liver and heart are the primary targets for toluene toxicity [29].

The PCO of toluene using commercial $TiO_2$ catalysts has been extensively studied [30–32]. Regardless of some discrepancies in the PCO products composition, benzoic acid and benzaldehyde intermediates were found to be the products deactivating the photocatalyst [33–35]. Thus, the rate-limiting stage for toluene complete oxidation is PCO of adsorbed intermediates, the degradation rates of which are slower than the one of the parent compound [14,36]. Toluene presents serious problem in the long-term photocatalyst activity exhibiting pronounced deactivation properties [7,37]. The abundance in published data allows toluene being a reference pollutant in characterization of the catalysts and the abatement methods in general. PCO of AN vapours was less studied, the results of P25 and sulphated $TiO_2$ application were described in recent publications [38,39].

The objective of present paper was to evaluate the gas-phase photocatalytic activity of the new flame synthesized F3 nanopowder photocatalyst compared to commercial P25: the experiments were carried out varying the pollutant concentration, residence time and temperature following the deactivation issues.

## 2. Experimental

### 2.1. Materials and analyses

Acrylonitrile (purity ≥ 99.5%, Sigma–Aldrich) and toluene (purity ≥ 99.5%, Lach-Ner) were used as the test air pollutants.

Pyrogenic photocatalyst Aeroxide $TiO_2$ P25 from Aerosil® process was kindly donated by Evonik Industries (Hanau, Germany) [40–42]. The photocatalyst material labelled F3 used in this study was synthesized as described in [22]: the vapour of the catalyst precursor titanium tetrachloride was formed by passing dry argon gas through a bubbler submerged to the $TiCl_4$-liquid at room temperature. Methane, oxygen and nitrogen were premixed with Ar/$TiCl_4$ and the mixture was introduced into the burner. The flame temperature during synthesis was about 900 °C. The $TiO_2$ particles were collected on a glass fibre filter placed about 50 cm above the flame. The overall synthesis reaction is given in Eq. (1):

$$TiCl_4(g) + 4O_2(g) + 2CH_4(g) \rightarrow TiO_2(s) + 4HCl(g) + 2CO_2(g) + 2H_2O(g) \quad (1)$$

The feed flow rate of Ar/$TiCl_4$ was varied between 5 and 60 L $h^{-1}$ with the synthesized $TiO_2$ samples labelled from F1 to F6 in ascendant row of manufacturing rate. The PCO activity of the photocatalyst materials was studied with the aqueous solutions of DCA and 4-CP (see Section 1) ranking the materials in the ascendant order: P25 < F6 < F5 < F4 < **F3** ≅ F1 ≅ F2 [22]. F3 produced at 12 L $h^{-1}$ of Ar/$TiCl_4$ feed rate was selected for gas-phase PCO study as the one with high photocatalytic activity.

The specific surface area of titania powders was determined from the five-point nitrogen adsorption isotherm obtained from Brunauer–Emmett–Teller (BET) measurements using the Gemini 2360 Surface Area Analyzer (Micromeritics, USA). Transmission electron microscopy (TEM) micrographs were obtained with the JEM-2100 microscope (JEOL) operating at 120 kV. The average primary particle size $d_{TEM}$ was estimated as of more than 300 particles. The crystalline phase composition was analysed by X-ray diffraction (XRD) using a Siemens D5000 Kristalloflex instrument and scanning the $2\theta$ range from 15 to 70° at the increment of 0.04°. The relative weight fraction of rutile was determined using Rietveld full-profile refinement with Topas R Software.

Diffuse reflection spectra of P25 and F3 were obtained on a UV-Vis-NIR spectrophotometer Perkin-Elmer Lambda 950, equipped with 150 mm integrating sphere, using Spectralon® as white reference. Simultaneous thermal gravimetric (TG) and differential thermal gravimetric (DTG) analyses were performed on Netsch STA 409 PC Luxx thermal analyzer (TG resolution 2 μg) coupled with mass spectrometer (MS) gas analysis system QMS 403C Aeolos; 100 mg of photocatalyst material was heated in $Al_2O_3$ crucible with a heating rate of 10 K $min^{-1}$ under nitrogen gas conditions (flow rate of 1 mL $min^{-1}$).

### 2.2. Preparation of $TiO_2$ coating

For photocatalytic experiments the photocatalyst material was fixed to the inner walls of the reactor; the surface of the lamp was free from the catalyst. The coating was formed by the 10-wt.% $TiO_2$ slurry in distilled water mechanically stirred overnight. The reactor vessel was repeatedly rinsed with $TiO_2$ slurry with each rinse followed by drying at 120 °C for 2 h. The weighted $TiO_2$ coating mass of 0.9 g corresponded to the catalyst loading of 1.2 mg $TiO_2$ per $cm^2$ of irradiated reactor surface. The roughness of both suspension coatings measured by means of surface profiler TENCOR P-10 was in the range of 1 μm.

Field emission scanning electron microscopy (FE SEM, Dual-Beam Helios Nanolab 600, FEI) was performed to visualize the catalyst coating.

### 2.3. Photocatalytic tests

Gas-phase photocatalytic experimental equipment was described in detail by Krichevskaya and Preis [36]. The