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Photocatalytic Treatment of Air: How to deal with the problem of TiO_2 deactivation

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In this study photocatalytic oxidation of toluene, used as model VOCs in the gas phase on different types of Ti-based catalytic materials was investigated. The objective of this work was to find out additional information regarding activity and stability of catalyst during photocatalytic treatment of the polluted air. Two designs of the photoreactor were used: classical type of an annular reactor and annular reactor with recirculation. All measurements were performed at room temperature, atmospheric pressure and at constant initial toluene concentration, relative humidity and total flow rate of the reaction mixture. Some experiments were carried out with catalysts thermally treated on different temperatures (350–450 °C). It was found out that thermal treatment of deactivated photocatalyst at higher temperature is efficient method of TiO_2 reactivation. According to results presented in this paper problem of catalyst deactivation can be partially solved by using annular reactor with recirculation of one part of reaction mixture entering the reactor.

Key words:
Annular photocatalytic reactor, deactivation, reactivation, TiO_2, toluene oxidation

Introduction

Heterogeneous photocatalysis has been intensely studied over the past decade, mostly in connection with the treatment of drinking and wastewater, air purification and its potential application in medicine and energy conversion.[1–11] Fujishima and Honda[12] were the first to describe the photocatalytic process, which related to electrolysis of water in a photoelectrochemical electrode with the use of TiO_2 as a photocatalyst. However, the examples of commercial application of photocatalysis and their application in real systems are still insignificant compared to the interest this topic arouses among the scientists. Up to date research scientists have been focused mostly on photocatalysis of water and much less of gas phase and air protection.[12] However, over past few years the interest has rapidly changed what is best shown by the fact that there are currently over 120 patents based on photocatalytic air purification.[4]

One of the greatest challenges in the design and operation of any catalytic process is the prevention of catalyst deactivation. Although catalyst deactivation is inevitable for most processes, the rate of decay can be minimized though the understanding and control of the deactivation process, i.e. through control of catalyst properties, process variables (temperature, concentration, flow rate, etc.), feedstock impurities and methods of reactants and catalyst contact.[13]

In our previous work,[14] we focused on the photocatalytic oxidation (PCO) of toluene in the

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gas phase over UV-illuminated thin layer of titanium dioxide. An attempt was made to investigate dependence of the reaction rate on various operating variables (such as water content, inlet toluene concentration and gas flow rate). Like other researchers who have dealt with similar reaction system [15–19] we noticed the existence of the catalyst deactivation. The purpose of the present work was to find out additional information regarding: (i) causes of TiO_2 deactivation, (ii) methods of catalyst reactivation or avoiding of catalyst deactivation and (iii) design considerations to prevent or minimize effect of catalyst deactivation. Several catalysts based on titanium were prepared and their photocatalytic activity was compared in particular with that of commercially purchased Degussa P-25 TiO_2.

Experimental

Photocatalyst preparation

Four samples of Ti-based materials were used to prepare photocatalytic layer. The characteristics of the catalytic samples and the code used for indicating them throughout the text are summarized in Table 1. The photocatalyst labeled TP1 was prepared using the commercial TiO_2 powder supplied by *Degussa*, now *Evonik* (Aeroxide P-25). According to manufacturer data approximately 70 % of P-25 has the anatase crystal structure and the remainder the rutile structure. TP2 was commercial Millenium PC 500 provided by *Crystal* and its crystal structure was primarily based on anatase (> 99 %).

Table 1 – *The properties of the photocatalyst employed in this work*

Photocatalyst sample	Composition	Manufacturer
TP1	TiO_2 P-25 (70 % anatase + 30 % rutile)	*Degussa* (now *Evonik*)
TP2	TiO_2 PC 500 (> 99 % anatase)	*Crystal*
TA1	TiO_2 (ca. 100 % anatase)	home made
TS1	Ti-SBA-15	home made

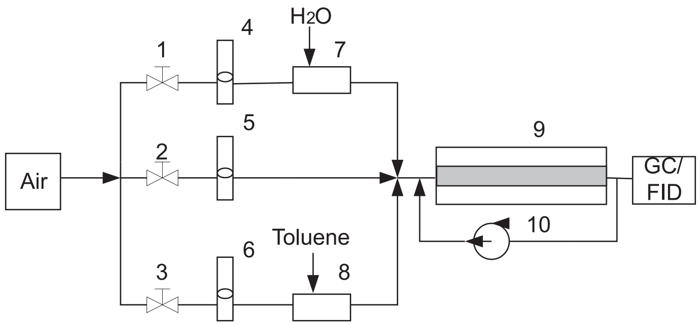
TA1 sample was home-made TiO_2 (100 % of anatase) prepared by the sol–gel method: an appropriate amount of tetrabutyl titanate was slowly dissolved into ethanol, then a mixture of dilute aqueous solution of nitric acid and ethanol was added to the above solution under stirring conditions. The reaction mixture had the following molar composition: $Ti^{4+} : H_2O : H^+(HNO_3) : C_2H_5OH = 1 : 4 : 0.015 : 12$. The solution was strongly stirred until the gels were formed and then placed at room temperature for 10–15 h, followed by being washed with deionized water, then filtered and dried at 80 °C. Thus obtained samples were calcined in air at 300 °C for 2h.

The parent SBA15 support was prepared by the method of Zhao et al.[20] by means of neutral triblock copolymer surfactants. Titanium was grafted by post-synthesis.[21] The titanium amount was 10 wt %. The photocatalyst was labeled TS1.

The Ti-based catalytic layer was coated on the inner wall of the outer tube of the annular reactor using homogeneous suspensions (1g Ti-based material/100 ml isopropanol) of certain powder materials. Modified spin coating process was used for preparation of very thin layers of the photocatalyst. In a short line, the suspension was poured into a rotating tube and simultaneously dried in the hot air. The TiO_2-coated tube was heated at 110 °C for 2 hours. TiO_2 loading density was 22.3 μg cm^{-2}.

Annular photocatalytic reactor system setup

The photocatalytic oxidation of toluene was performed in an annular photoreactor equipped with an 8 W fluorescent black light blue lamp (*Sylvania*, UVA light at 315–400 nm). High purity synthetic air (20.5 % O_2 in N_2, *Messer*) was used as oxidant. The photoreactor feed stream resulted from mixing a dry air in a saturation flask containing distilled water at 20 °C and a dry air stream with toluene (*Aldrich)* at the specified flow rates of the gas carrier through the saturators. Flow rates were regulated using the flow meters (*Cole Palmer*). The secondary air flow was introduced into the mainstream in order to dilute the reaction mixture and to obtain the desired concentration of the reactant at the reactor inlet. The reaction gas mixture flowed between the reactor's inner and outer tube. The inner tube was made of quartz glass because of its transparency for UV light. Two configurations of photoreactor were used: classical type of an annular photocatalytic reactor (designed to be run in a single-pass) and annular reactor with partial recirculation. All measurements were carried out at the initial concentration of toluene of $2.68 \cdot 10^{-3}$ g dm^{-3}, relative humidity (RH) of 50 %, and at total flow rate of reaction mixture of $40 \cdot 10^{-3}$ dm^3 min^{-1}. The membrane peristaltic pump was applied to circulate a particular amount of the fluid containing a reactant to the reactor entrance. Experiments were performed in the range of the recirculation flow rate, v_R from 0.5 to 2.5 dm^3 min^{-1}, corresponding to recirculation ratios from 12 to 61. Shematic representation of the experimental setup is presented in Fig. 1. The rates of the photocatalytic oxidation of toluene were based on the difference in toluene concentration before and after UV illumination at the steady-state conditions.



F i g . 1 – *The shematic diagram of the experimental setup. 1,2,3 – Needle valves, 4,5,6 – Flow meters, 7,8 – Saturators with bidistilled water or toluene, 9 – Annular photocatalytic reactor, 10 – Recirculation pump*

TiO_2 reactivation

Reactivation of TiO_2 (P25) photocatalyst was achieved by thermal treatment in the air atmosphere. Thermal treatment of the Ti-based catalytic layer coated on the inner wall of the outer tube of the annular reactor was carried out in a furnace *Nabertherm* L5/11/B180 at different temperatures (350, 400 and 450 C). The temperature was increased slowly up to desired temperature and then keeping the catalyst at this temperature for 2 hours.

Analytical methods

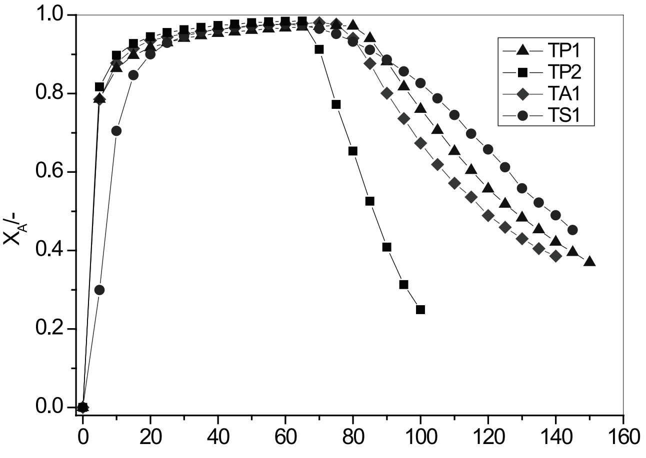
Toluene concentrations were measured on-line by gas chromatograph (*Shimadzu* GC-2014) equipped with a flame ionization detector. The measurement system included highly purified nitrogen as carrier gas and *Carbowax 20M* column (length 3m, i.d. 2 mm). Analysis was performed using a program package *Shimadzu GCSolution*®. The operating conditions of the GC were as follows: column temperature of 120 C, detector temperature of 250 C. Additionally, high performance liquid chromatograph (*Shimadzu Prominence*) equipped with UV/Vis detector (λ = 210 nm) was used to analyze the intermediate products over deactivated TiO_2 catalyst. Small amount of deactivated catalyst (0.02 g) was suspended in methanol for several hours to extract adsorbed organic compounds and the resulting solution was examined with HPLC using *Waters Spherisorb ODS2* column (length 15 m, i.d. 0.46 mm). Instrument calibration was performed using standard solutions of benzaldehyde and benzoic acid (5 mM) or their equimolar solution (0.1 mM).

Results and discussion

Deactivation of the photocatalyst is among the most severe practical problems, and its importance is reflected by the large number of papers claiming to solve it.[4,15,16,19,22] Different approaches are reported in the literature, but usually they are related to various post treatment of undesired by-products formed under reaction conditions, of which the following are important to mention: thermal treatment at elevated temperatures (> 400 °C),[23] photocatalytic treatment using simultaneous UV illumination and exposure to humidified air,[15,24] ozone purging in the presence of water vapour,[25] washing with alkaline solutions.[26] Another approach to eliminate or moderate deactivation is through modifications of catalyst composition and/or process or process conditions.

In this work different catalysts are used with purpose to investigate their photocatalytic activity and stability during photocatalytic oxidation of toluene, used as model volatile organic compound (VOC). The laboratory photoreactor used in the first set of experiments was an annular reactor designed to run in a single-pass mode. Dependence of toluene conversion on time of UV illumination for all catalyst is presented in Fig. 2.

The results indicate that the shape of curves is very similar regardless of photocatalyst applied. Surprisingly, the Ti-SBA-15 showed even better results than the TiO_2 P-25, especially at longer exposure time of photocatalyst to UV illumination. Generally, three characteristic periods can be observed on the curves. The first period can be considered as a period of initiation. During this period toluene conversion rapidly increases and reaches a maximum value, which indicated that the process is non-stationary. The most likely explanation of such behaviour is a time-dependent increase in photocatalyst activity, which can be attributed to the formation of hydroxyl radicals. As can be seen this period is very short and lasts for about 10 min, depending



F i g . 2 – *Conversion vs. exposure time to UV lamp for different PCO catalysts (annular reactor without recirculation)* on the reaction conditions. This is followed by a period of constant toluene conversion or constant activity of photocatalyst (maximum conversion was ca. 0.98), after which conversion starts to decrease with illumination time, indicating deactivation of the photocatalyst. It may be noted that the home-made photocatalyst, designed as TA1 shows greater stability (slower decrease of activity) compared to commercial TP2, regardless of the almost identical chemical composition (both were in almost anatase form). Obviously, the stability of the photocatalyst is affected by the method of its preparation. In addition, the physical properties and loading of the catalysts are also very critical for the stability of the photocatalysts. Reason for more stable TS1 photocatalyst is not clear, however its higher stability probably can be correlated with the possibility of competitive adsorption of water and toluene molecules and subsequent desorption of photooxidation products from the surface of the catalyst.

In our previous work[14] deactivation of the photocatalyst was observed. FTIR experiments performed over deactivated catalyst have confirmed the presence of benzaldehyde and benzoic acid adsorbed on the surface of the TiO_2, which led to the blocking of the active sites. In this study additional experiment are conducted to confirm these results. Results of HPLC analysis, as shown in Fig. 3, once more confirmed adsorption of benzoic acid on deactivated TiO_2 catalyst.

Next task was to find an appropriate way of catalyst's reactivation.[27] The influence of thermal treatment on toluene conversion at different time of illumination is shown on Fig. 4. As can be seen, thermal treatment was found to be very efficient method, especially at temperature of 450 °C. It was also observed colour change of the catalyst during the reactivation, i.e. the catalyst has changed colour from light-yellow to white. It may be noted that heat pre-treatment leads to a slower decline of catalyst activity regardless of treatment temperature. Complete reactivation of the catalyst treated at 450 °C was in accordance with the thermal stability of the oxidation intermediates that block the active sites on the surface of catalyst. The temperature required for complete oxidation of benzaldehyde and benzoic acid is 360 and 420 °C, respectively.[22] Thus, reactivation of the catalyst required a temperature of 420 °C or slightly higher, as was the case in this work.

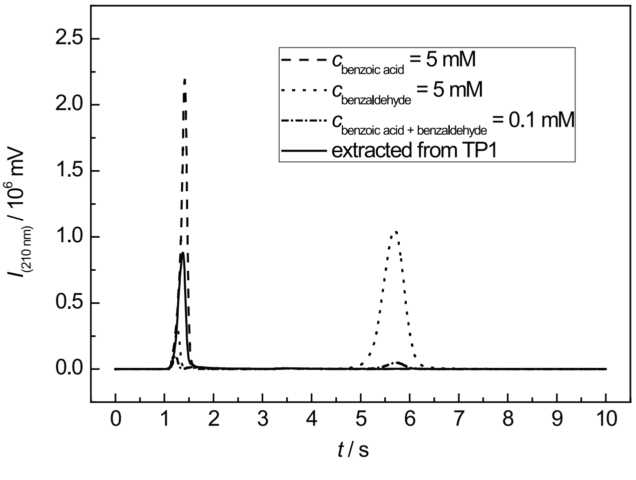


Fig. 3 – *Identification of the adsorbed surface species responsible for the deactivation of the photocatalyst*

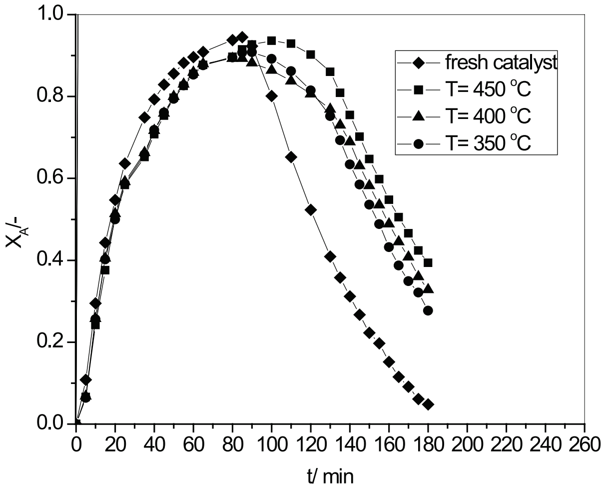


Fig. 4 – *Influence of the thermal treatment on the photocatalyst activity and stability (TP1 catalyst)*

Another approach to fight deactivation is by changing the flow mode inside the reactor. One way to achieve this is to use the annular reactor with mixing of reaction mixture accomplished by recirculation. Comparison of results obtained using commercial TP1 photocatalyst located in classic type of annular reactor (without recirculation) and in an annular reactor at different recirculation flow rates is given in Fig. 5. Similar results were observed with the use of other photocatalysts (Fig. 6). Decreased conversion ascribed to catalyst deactivation was intense in reactor without recirculation (see Fig. 5) because of much lower linear velocity of the reaction feed over catalyst surface. On the other hand, in reactor with recirculation (Figs. 5 and 6) the linear velocities were considerably higher so that accumulation of reaction intermediates was difficult. Obviously, photocatalytic properties were also affected by the recirculation flow rate.

The increase of the recirculation flow rate lead to decrease of the photoactivity in the series: TP1 > TA1 > TP2 > TS1 (Fig. 6). Apparently, the stability of catalysts, i.e. resistance to deactivation was improved using the annular reactor under recirculation mode.

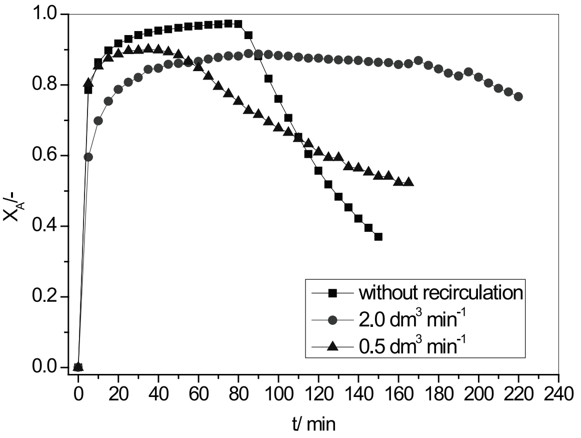


Fig. 5 – *Conversion vs. exposure time to UV lamp for different recirculation flows (TP1 photocatalyst)*

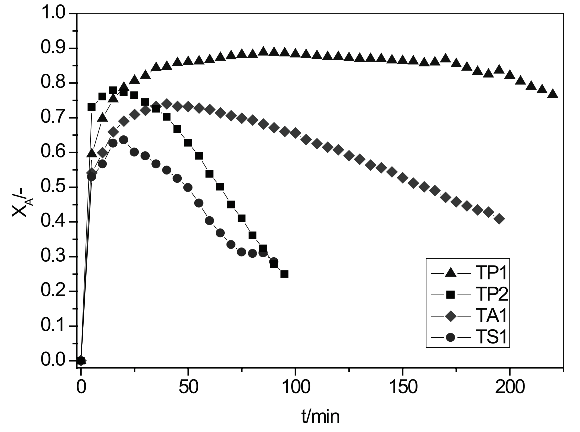


Fig. 6.– *Conversion vs. exposure time to UV lamp for different catalysts (recirculation flow rate of 2 dm^3 min^{-1})*

Conclusions

The photocatalytic oxidation of toluene over different type of Ti-based catalytic materials was carried out in the photocatalytic annular reactor operated in two different flow modes: classic type of annular reactor and annular reactor with recirculation. The analysis of the conversion *vs* illumination time curves showed that all catalysts have very high activity depending on the reaction conditions and catalysts used. Three characteristic periods were observed on time-conversion curves: i) the period of the initiation, ii) the period of constant activity and iii) the period of decreasing activity (catalyst deactivation). Decreasing activity of the catalyst was explained by the adsorption of benzoic acid as reaction intermediates on the active sites, which was confirmed by FT-IR and HPLC analysis of used (deactivated) catalyst. Thermal treatment of deactivated photocatalyst on the higher temperature was found to be an efficient method of catalyst reactivation. The catalytic activities of the Ti-based materials located in the classic type of annular reactor (without recirculation) were quite similar. The increase of the recirculation flow rate lead to slower decrease of the catalyst activity. Finally, the stability of photocatalysts, i.e. their resistance to deactivation can be improved using the annular reactor under recirculation mode.

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Symbols

$I_{(210\ nm)}$ – peak intensity at wavelength of 210 nm, mV
RH – relative humidity, –
t – time, min
X_A – conversion, –
v_R – recirculation flow rate, dm^3 min^{-1}

Greek letters

λ – wavelength, nm

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