TiO$_2$ PHOTOCATALYTIC SYSTEMS FOR AIR CLEANING

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ABSTRACT

Emission of volatile organic compounds (VOCs) in indoor and outdoor air has become a serious problem causing different degrees of hazard to public health. Among various techniques proposed for their abatement, we used TiO$_2$ photocatalysis as one of the advanced oxidation processes (AOPs) becoming increasingly popular for chemical treatment of contaminated water and air. To this aim we developed several photocatalytic systems for water and air cleaning that employ photocatalyst material either in powder or in thin-film form. In this contribution we focus on air-cleaning systems with TiO$_2$-based catalyst powders and coatings that are active towards elimination of model VOC (toluene) in the air flow under near-UV irradiation. The design of both, photoreactor and photocatalyst, is of a key importance to achieve high efficiency of a photocatalytic system. Our synthesis is based on the low-temperature sol-gel processing of anatase-titania nanocrystalline colloids, which were also combined with commercial highly active powders (Degussa P25 and Millennium PC500) and with a silica binder component in case of coatings to attain their mechanical integrity. To increase the photocatalytic activity of sol-gel titania by means of preventing aggregation of the nanocrystallites, the as-prepared aqueous titania sol was loaded into mesoporous silica support with a high specific surface area. A beneficial influence of the mesoporous silica host on the low-temperature prepared titania powder for the removal of an organic contaminant from the gaseous phase was clearly shown. It contributed to the better adsorption capacity in the dark phase and also higher photocatalytic activity, which was determined in a tailor-made gaseous reactor system.

Keywords: TiO$_2$ photocatalysis, composite TiO$_2$/SiO$_2$, toluene, solid-gas photoreactor

INTRODUCTION

AOPs are defined broadly as oxidation processes which are primarily based on the intermediacy of the hydroxyl radicals in the mechanism resulting in the destruction of the contaminant compound. Some of the processes to obtain these radicals are: O$_3$ treatment, H$_2$O$_2$ treatment, UV treatment and their combination, Fenton's treatment and photocatalysis. Heterogeneous photocatalysis process uses semiconductor as a catalyst in combination with UV radiation and oxygen. It can be carried out in both gaseous and liquid media. The overall photocatalytic process can be divided into five independent steps: mass transfer of reactants (contaminants) to the catalyst surface, adsorption of the reactants on the catalyst surface, photochemical reaction on the surface, desorption of the products from the surface and mass transfer of the products from the surface into the bulk of the fluid [1].

Titanium dioxide is the most extensively used photocatalyst because of its high photocatalytic efficiency, stability towards photocorrosion, no toxicity and low cost. On the other hand, its activation by UV light, poor adsorption and relatively low surface area lead to limitations in exploiting the photocatalyst to the best of its photoefficiency. When combined with a mesoporous/nanoporous support, such a composite material may offer some advantages: (i) formation of separated titania nanoparticles in the final composition, (ii)

increase of adsorption capacity especially for non-polar compounds, (iii) lower scattering of UV irradiation [2].

VOCs are common air pollutants and can be found in both outdoor and indoor environments [3]. The treatment techniques based on adsorption only transfer the contaminant from air to another phase. Therefore, an activation of adsorbent material such as meso-ordered silica with photocatalytic titania shall lead to chemical destruction of VOC pollutant adsorbed. Toluene was taken as a model VOC in our photodegradation studies, for which we constructed the gaseous reactor system that accommodates either powder or thin-film catalyst. The photocatalytic degradation of toluene was followed by on-line coupling of gas chromatography-mass spectrometry (GC-MS) [4].

EXPERIMENTAL
Photocatalyst synthesis

TiO_2/SiO_2 composites in a powder form were synthesized according to the procedure described in detail in [5]. Ordered mesoporous SBA-15 silicate material was used as a high-surface-area support for photocatalytically active TiO_2. The aqueous crystalline anatase-TiO_2 sol obtained from $TiCl_4$ precursor was deposited to the appropriate amount of SBA-15 via the sol-gel impregnation method. After drying at 60 °C for 24 h the resulting powder samples were designated as Ti/SBA-15(x), where x denotes the Ti/Si nominal molar ratio that was adjusted to 1/2, 1/1 and 2/1. For comparison, unsupported TiO_2 was prepared from the same titania sol and resulting powder sample designated as Ti1. The commercial photocatalyst, a Millennium PC500 was used as a reference photocatalyst.

TiO_2/SiO_2 composites in a coating form were synthesized and immobilized on Al-sheets using two commercial titania powders (Degussa P25 and Millennium PC500, mass ratio 1:1) with a silica/titania binder and without a binder, thoroughly described in [6]. Silica/titania binder was prepared from the following main constituents: refluxed titania aqueous sol derived from titanium isopropoxide precursor, tetraethyl orthosilicate and commercial colloidal silica Levasil 200/30%. The source of highly photocatalytically active TiO_2 was mixture of Degussa P25 and Millennium PC500 suspended in the binder solution and ultrasonically treated. Before applying this hybrid sol on the Al-sheets (34 cm × 1 cm), they were protected by the silica thin film derived from trimethoxy silane, tetraethyl orthosilicate and Levasil 200/30% (sample Al-p). After each application of the sol, the resulting TiO_2/SiO_2 coatings were heat-treated at 150 °C for 1 h. The procedure was repeated until the amount of catalyst reached 1 mg/cm^2 (sample titania/binder/Al-p). As a reference photocatalyst, suspension of the two commercial titania powders without a binder component was applied on the Al-sheets (sample titania/Al).

Instrumental

The X-ray powder diffraction (XRD) patterns were obtained on a PANalytical X'Pert PRO high-resolution diffractometer. The average crystallite sizes were determined from the Scherrer's equation using the broadening of the (1 0 1) anatase peak reflection. The specific surface area was evaluated from nitrogen sorption isotherms obtained at 77 K by a Micromeritics Tristar 3000 instrument. For the calculation of energy band gaps, diffuse reflectance spectra were measured on a Perkin-Elmer Lambda 19 UV–vis–NIR spectrophotometer equipped with an integrating sphere.

Photocatalytic experiments

The photoreactor system was constructed for the gaseous photocatalytic experiments and connected on-line to GC-MS (Fig. 1). Its description and optimized operational parameters are given in [4]. The reactor chamber consists of six low-pressure mercury

fluorescent lamps which were used as a UVA radiation source (15 W, broad maximum at 355 nm, Philips CLEO) and the reflective surface of polished aluminum placed behind the lamps. The reaction cell with powder catalyst was made from a Duran glass tube (10 mm inner diameter, 27 cm height) and positioned vertically in the center of the photoreactor. A porous frit at the bottom allowed distributing finely the inlet gaseous mixture through the catalyst powder. The reaction cell with immobilized catalyst on Al-sheets, fastened around the axis in a special teflon holder (Fig. 1), was made from a Duran glass tube (42 mm inner diameter, 42 cm height) and positioned horizontally in the center of the photoreactor. Three Al-sheets with immobilized catalyst were used in the experiments.

The regulated feed gas consisted of dry air, humidified air and toluene. The flow rates of both dry and humidified air were adjusted to 0.2 L/min to obtain the total air flow 0.4 L/min containing 45-50% humidity. Toluene was injected using a syringe pump and its flow was 0.25 μL/min, final volume of injected toluene in the system was 0.140 mL. In case of powder samples, 0.1 g of photocatalyst was loaded into the reactor cell for each run. An internal gas flow rate was usually between 1000 and 1400 mL/min allowing fluidization of the catalyst particles. The concentration of toluene was measured in constant time intervals during the dark phase and during photochemical reaction by GC (Varian 3900) coupled with the mass spectrometer (Varian Saturn 2100 T).
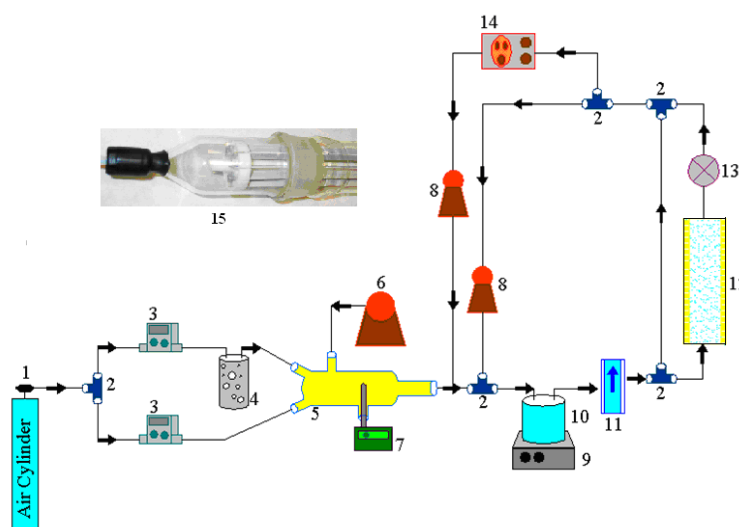

Figure 1. Scheme of the in-situ gaseous photoreactor system: (1) gas regulator, (2) 3−way valve, (3) mass flow meter/controller, (4) humidifier, (5) mixing chamber, (6) syringe pump, (7) thermometer and humidity meter, (8) diaphragm pump, (9) water bath, (10) reservoir vessel, (11) flow meter, (12) reactor cell with surrounding UVA lamps, (13) sampling port, (14) GC–MS, (15) photo of the part of reactor cell with the catalyst on Al-sheets.

RESULTS AND DISCUSSION

Some physico-chemical characteristics, dark adsorption capacity and photocatalytic activity of the representative samples are summarized in Table 1. The upper four rows represent results for powder samples and the lower three rows belong to coating samples. The course of adsorption and the photocatalytic degradation of toluene on the two types of synthesized samples are shown in Fig. 2. Due to different geometry of the two reactor cells and catalyst amount, the photocatalytic data between powder and coating samples cannot be compared, while the data obtained inside one or another group of samples are directly comparable.

The rapid fall of toluene concentration in the dark period corresponded to its adsorption on the surface of particular sample and to its dilution in the reactor cell. The highest observed capacity of SBA-15 correlates with the highest surface area of SBA-15. The deposition of titania on SBA-15 silica lowers surface area of the resulting material (Table 1) and at the same time specifically affects adsorption of toluene on the surface. After switching on UVA irradiation (time 0 in Fig. 2) the concentrations of toluene were decreasing according to first-order reaction. As expected, the samples of bare silica (powder or immobilized on Al support as protection layer) did not show any photocatalytic activities. In presence of titania the photodegradation of toluene proceeded more slowly on pure titania compared to titania supported on silica. This effect was especially pronounced in case of powder samples where mesoporous silica support was used (compare Ti1 with Ti/SBA-15(*x*) curves). The observed lower photocatalytic activity of unsupported titania could be caused by the aggregation of titania nanoparticles in the absence of the silica support that might reduce the direct contact of gaseous toluene molecules on the surface of TiO_2 nanoparticles. Fig. 2 shows that even low-temperature titania (Ti1), when loaded in appropriate host, can become as highly photoactive as Millennium PC500. Fig. 2 also shows that very good photocatalytic activities with fast degradation kinetics (order not determined due to few number of points) can be achieved with the immobilized catalyst on Al-sheets. Silica binder in this case contributes to better mechanical stability of the coatings (good adherence to the substrate) and even improves significantly their dark adsorption capacity.

Table 1. Some physico-chemical characteristics, dark adsorption capacity (% of adsorbed toluene) and photocatalytic activity (reaction rate constant) of the analyzed samples.

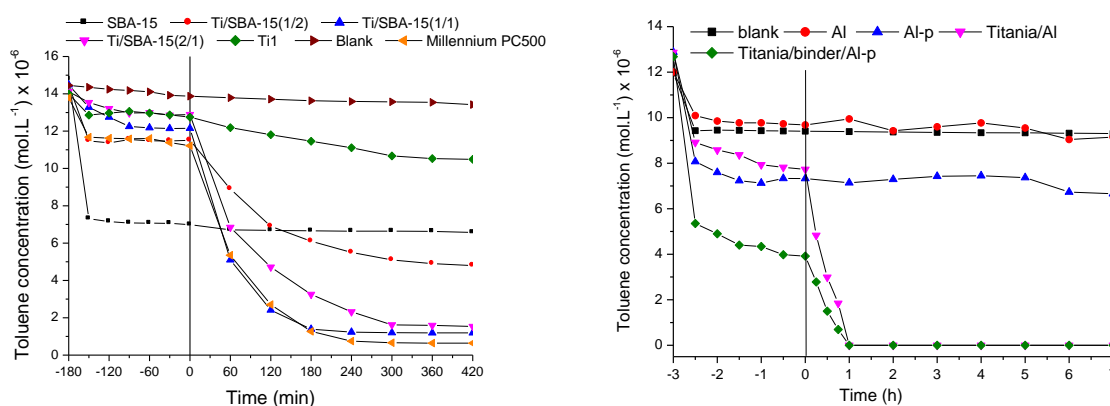| Sample	TiO_2 share in powder or coating (wt%)	Crystallite size (nm)	S_{BET} (m^2/g)	Band gap (eV)	Dark ads. capacity (%)	Rate constant k (min^{-1})
SBA-15	0	-	589	-	53	0
Ti/SBA-15(1/1)	58	-	498	3.20	16	0.0121
Ti1	73	8	80	3.11	9	0.0006
Millennium PC500	100	5-10	300	-	19	0.0114
Al-p	0	-	-	-	22	0
Titania/binder/Al-p	74	14	133	3.34	47	-
Titania/Al	100	14	132	3.39	13	-

Figure 2. Dark adsorption and photodegradation curves of toluene (left: powder samples, right: coatings on Al).

CONCLUSION

Titania/silica photocatalysts in powder and coating form were synthesized and their functional properties evaluated in the gaseous photoreactor system constructed in the laboratory. The composite catalyst showed improved properties compared to pure photoactive TiO_2 in both catalyst forms. The very good photocatalytic activity obtained with the immobilized catalyst on Al-sheets is particularly promising because this configuration implies simplified operation with regard to fluidized-bed reactor and represents a step forward towards target application in an air-cleaning device.

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