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Solar photocatalysis for gas-phase air cleaning: from lab to pilot plant studies

ABSTRACT

Heterogeneous photocatalysis or photocatalytic oxidation (PCO) has been recognized over the recent decades as one of the most promising technologies for air treatment.

The present thesis aims to evaluate the efficiency of solar gas-phase PCO as well as to provide fundamental understanding of different titanium dioxide (TiO₂)-based photocatalysts toward the elimination of air pollutants such as volatile organic compounds (VOCs). The following objectives were addressed: (i) synthesis and characterization of TiO₂ nanotubes as well as nitrogen modified TiO₂ nanotubes and nanoparticles; (ii) preparation of TiO₂-based materials and their immobilization as thin films on different supports using the dip-coating technique; (iii) evaluation of photocatalytic activity of the prepared photocatalysts and its dependence on different operational conditions (flow rate – Q_{feed} ; pollutant concentration – C_{voc} , feed; relative humidity – RH, irradiance – I ; presence/absence adsorbed molecular oxygen) using a lab-scale single-pass continuous-flow annular photoreactor; (iv) description of PCO mechanisms; (v) evaluation of photocatalytic activity of selected materials in a pilot-scale photoreactor for continuous removal of VOCs.

Gas-phase PCO of perchloroethylene (PCE) (574 – 2442 ppm) was carried out in a lab-scale annular photoreactor ($r = 23.2$ mm) under catalytic (UV TiO₂) conditions. The photoreactor was assembled with a catalytic bed made of glass spheres packed with the benchmark TiO₂ P25 catalyst (Evonik®) filling the voids between the spheres. A UVC lamp ($\lambda = 253.7$ nm) was located inside an inner tube (quartz or glass) of the photoreactor. The PCO of PCE was evaluated upon three parameters and employing the photoreactor with the glass inner tube (mimicking UV fraction of solar radiation); briefly: (1) for a 4.25 fold increase in CPCE, feed (from 574 ppm to 2442 ppm), a reduction of ~76 % (from 63 % to 35 %) on the PCE conversion was observed; (2) increasing the Q_{feed} (from 59 cm³ min⁻¹ to 300 cm³ min⁻¹) led to lower PCE conversions (from 81 % to 33 %); (3) for a 3.33 fold reduction in RH (from 40 % to 12 %), the PCO efficiency merely decreased ~1.2 times. Although 97 % of initial PCE was converted into CO₂ and water through pure photolysis using the quartz inner tube, only 51 % of mineralization was attained through PCO when the glass inner tube was used. A mathematical model was developed taking into consideration the following main assumptions: (a) steady-state operation; (b) isothermal and isobaric conditions; (c) ideal gas behaviour; (d) axial symmetry; (e) constant porosity of the bed (uniform packing shape and distribution); (f) axially dispersed plug flow; (g) no heat transfer resistance and no thermal and UV radiation gradients; (h) no mass, velocity, and UV radiation gradients in the radial direction. Assuming that only PCE and H₂O are the major species as well as that intermediates and/or reaction products do not influence PCE degradation kinetics, it was shown that PCE and H₂O molecules may have to be considered in association with different specific active sites of the TiO₂ surface since Langmuir-Hinshelwood bimolecular non-competitive two types of sites model described better the experimental data.

PCO of gas-phase PCE and n-decane was also assessed employing the lab-scale annular photoreactor under simulated solar radiation. Cellulose acetate monolithic structures coated with two different TiO₂ photocatalytic films (prepared from aqueous suspensions of P25 from Evonik® and PC500 from Cristal®) were employed as catalytic bed (L_{catalytic bed} = 160 mm). The reactor was equipped with a compound parabolic collector (CPC) allowing the whole reactor and bed illumination. PC500 film provided higher conversion and mineralization of PCE and n-decane than those obtained with P25 film, most likely due to the higher specific surface area of TiO₂ PC500. Conversions of both pollutants (C_{dec}, feed = 71 ppm and CPCE, feed = 1095 ppm) were close to 100 % using PC500 film when Q_{feed} = 150 cm³ min⁻¹, I = 38.4 WUV m⁻² and RH = 20 %. Competitive adsorption between the pollutants and water molecules on the PC500 film surface was found above 20 % of RH. Results showed that gas-phase molecular oxygen has a fundamental role in the PCO reaction, as the conversion of pollutants is drastically impaired in its absence, suggesting that photocatalytic mechanism consists of: (i) oxidation reactions promoted by reactive species formed from the adsorbed molecular oxygen (O₂•⁻, HOO•); (ii) contribution of the oxygen from the lattice of TiO₂; (iii) hydroxyl radical (HO•) formation on the TiO₂ surface. PCO mechanism of chlorinated compounds such as PCE, may also include a series of reactions involving Cl• radicals.

The best performing photocatalyst (TiO₂ PC500) was then incorporated into an exterior (water based) vinyl paint, supported on the cellulose acetate monolithic structure and tested under simulated solar radiation. 60 % of the PCE (CPCE, feed = 1100 ppm) and 98 % of the n-decane (C_{dec}, feed = 41 ppm) feed concentrations were converted when using Q_{feed} = 75 cm³ min⁻¹, RH = 40 % and I = 38.4 WUV m⁻². In addition, the results revealed an optimum surface density (~0.87 mg cm⁻²) to achieve the highest performance; also, increasing the exposed area to radiation by removing the outer wall of the monolithic structure, the PCO of PCE was enhanced by, approximately, 58 % (from 38 % to 60 %) under the same experimental conditions.

Considering that TiO₂ is a wide bandgap semiconductor, only active under UV radiation, TiO₂ modification with nitrogen was studied to enhance its performance for solar applications. TiO₂ nanotubes were synthesized by hydrothermal treatment of TiO₂ P25 and chemical modification was performed by grinding urea (nitrogen source) with the TiO₂ nanotubes, followed by thermal treatment. The same procedure was applied to bare TiO₂ P25 nanoparticles. The results revealed that nitrogen-modification of TiO₂ P25 decreased the photocatalytic activity towards PCO of gas-phase PCE under simulated solar radiation: bare TiO₂ P25 presented the highest activity (67 % of PCE conversion) whereas only 35 % of conversion was attained over N0.50P25-380 (material with a urea:TiO₂ weight ratio of 1:2 and calcined at 380 °C). However, when these particular materials were tested in aqueous-phase, N0.50P25-380 showed the highest photocatalytic activity for PCO of diphenhydramine (emerging water pollutant of pharmaceutical origin) and inactivation of Escherichia coli bacteria under visible ($\lambda > 430$ nm) and UVA ($\lambda = 365$ nm) radiation, respectively.

The PCO over nitrogen-modified TiO₂ nanotubes was also investigated for the conversion of methylethylketone (MEK) and hydrogen sulfide (H₂S). MEK showed high resistance to photocatalytic degradation over these materials, but a high photocatalytic activity towards H₂S degradation under UVA ($\lambda = 365$ nm) radiation and moderate photocatalytic activity under solar light radiation were observed.

Finally, based on lab-scale experimental data, modelling simulations and predictions of PCO of pure-targeted VOCs, a pilot-scale annular photoreactor ($r = 32.8$ mm, $L_{\text{catalytic bed}} = 144$ cm) was designed and manufactured. The photoreactor features a CPC to capture both direct and diffuse solar radiation and/or UVA lamps, in order to work continuously day and night. The PCO of n-decane ($C_{\text{dec, feed}} = 10$ ppm, $Q_{\text{feed}} = 2$ L min⁻¹, $\tau = 44$ s) over cellulose acetate monolithic structures coated with different TiO₂-based photocatalytic films (P25, PC500 and photocatalytic paint) was studied under solar and artificial UVA radiation. Conversions up to 100 %, were attained using P25 or PC500 films under solar irradiances of 15 WUV m⁻² (morning, increasing temperature) and 3 WUV m⁻² (afternoon, decreasing temperature). The photocatalytic paint film promoted up to 45 % of n-decane conversion under 48 WUV m⁻² in both periods of the day. The excess of photons reaching the photocatalytic bed seems to favour the direct reaction pathway of CO₂ production. The PCO of n-decane under artificial UVA radiation was 29 % higher using the PC500 film in comparison with the P25 film (resulting in 100 % of conversion), while over the photocatalytic paint film no more than 25 % of n-decane was converted. Results suggest that a 24 h continuous PCO process towards the removal of n-decane can be accomplished by combining both radiation sources (artificial UVA and solar).