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Photocatalytic oxidation of toluene in the gas phase: Modelling an annular photocatalytic reactor

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ABSTRACT

Photocatalytic oxidation of toluene in the gas phase over UV-illuminated thin layer of titanium dioxide was studied. The reaction was performed in the annular photocatalytic reactor at the room temperature and at various space times. The inlet reacting mixture consisted of air containing toluene and water vapors. Dependence of the reaction rate on various operating variables (water content, inlet toluene concentration and gas flow rate) was examined. The catalytic activity for toluene removal was evaluated by measuring the inlet and outlet toluene concentrations with GC/FID at the steady-state conditions. The additional XRD and FTIR measurements were carried out to get better understanding of the catalytic properties.

Modelling analysis was carried out to investigate effect of the key parameters on the reactor performance. To understand complex interaction between the chemical reaction and mass transfer phenomena, experimental data were analysed and compared with three different mathematical models (one-dimensional (1D) model and two-dimensional (2D) models based on ideal flow and laminar flow conditions). The proposed models were verified by comparing the computer simulation data with the experimental laboratory results. It was found out that behaviour of the annular photocatalytic reactor was mainly limited by the interphase mass transfer. Finally, the 2D heterogeneous model, based on the assumed laminar flow through the reactor, appeared to be the most suitable model for a detailed description of the annular photocatalytic reactor used for air pollution remediation.

1. Introduction

Volatile organic compounds (VOCs) represent the important class of pollutants, usually found in the atmosphere of all urban and industrial areas. Photochemical oxidation, PCO (also referred to as the advanced oxidation processes, AOP) has become increasingly popular as an alternative to VOC removal purposes [1]. The first PCO was reported by Fujishima and Honda [2] who used a photoelectrochemical cell for water splitting and rutile TiO_2 as a (photo)catalyst. TiO_2-mediated heterogeneous photocatalysis for oxidation of VOC compounds at low concentrations has been extensively studied [3–5]. While most relevant studies have dealt with photodegradation in the liquid phase, degradation of gaseous organic compounds has gained importance only recently, predominantly for air purification [3–5]. A great variety of organic compounds can be oxidized by TiO_2 photocatalysis in the presence of molecular oxygen and/or water [6,7]. Most attention is given to ethylene [8], isopropanol [9], butane [9], heptane [10], acetone [11], methanol [11], 1-butanol [12], benzene [13], toluene [9,11,14,15], acetaldehyde [16], butyl acetate [17], dimethylformamide (DMF) [18], 1-butylamine [12], trichloroethylene (TCE) [9,11,19], chloroform [19], dichloromethane [19], carbon tetrachloride [19], and dichloroacetic acid [20].

In the last decade the mechanism of heterogeneous photocatalysis has been investigated by many researchers [7,12,21]. Deactivation of photocatalysts was found to be a crucial disadvantage of this technique in practice, especially for the oxidation of aromatics [10,22]. The oxygen-bearing compounds, especially benzoic acid, can cause irreversible loss in the photoactivity of TiO_2 catalysts [22]. According to the literature this can be retarded using binary catalyst, such as titania–silica [16,22], titania–vanadia [14,15], titania–iron [23], titania–tungsten [15,17] or titania–tin mixed oxide [19].

Recently, investigation of optimal reactor configurations has become an important research area in the field of PCO. Different laboratory reactor designs are reported in the literature, e.g. fixed bed annular reactor [6,9,17], batch reactor [11], semi-batch reactor with quartz flat window [19], circulating fluidized bed (CFB)

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a	geometric surface area (m^2)
A_R	surface area of reactor (annulus) cross-section (m^2)
C_A	toluene concentration ($g\ dm^{-3}$)
D_A	molecular diffusion coefficient of toluene in air (1 bar, 20 °C) ($cm^2\ s^{-1}$)
D_g	molecular diffusion coefficient ($m^2\ h^{-1}$)
k	reaction rate constant ($kg\ m^{-3}\ min^{-1}$)
k_A	reaction rate constant (min^{-1} (Eq. (6)))
k_g	interphase mass transfer coefficient ($m\ h^{-1}$)
K_a	adsorption equilibrium constant ($kg^{-1}\ m^3$)
L	length of reactor (m)
p	pressure (Pa)
$p(H_2O)$	partial pressure of water vapor in the gas mixture (Pa)
r	radial reactor coordinate (m)
r_A	reaction rate ($mol\ h^{-1}\ kg^{-1}$)
R	diameter of reactor annulus (m)
RH	relative humidity
R/L	dimensionless geometric number
T	temperature (K)
u	fluid linear velocity ($m\ h^{-1}$)
v_0	volume flow rate ($m^3\ h^{-1}$)
V	reactor volume (m^3)
X_A	toluene conversion
z	axial reactor coordinate (m)

Greek letters

η	dynamic viscosity ($m^2\ s^{-1}$)
θ	coverage of TiO_2 surface with toluene
Θ	Bragg angle (°)
κ	ratio of inner and outer reactor diameter
μ	kinematic viscosity ($kg\ m^{-1}\ s^{-2}$)
ρ	density ($kg\ m^{-3}$)
τ	space time (min)

Dimensionless parameters

Re	Reynolds number (modification for annular reactor), $Re = (2R(1-\kappa)u_m\rho)/\eta$
Sc	Schmidt number, $Sc = D_g\rho/\mu$
Sh	Sherwood number, $Sh = 0.705[Re(d/L)]^{0.43}Sc^{0.56}$

Subscripts

g	in the bulk gas phase
m	mean value
s	on the catalytic surface
u	inner
0	inlet

Superscript

*	saturation

reactor [24], microchannel reactor [14], honeycomb monolith reactor [25], TiO_2-coated fibre-optic cable reactor [26], annular venturi reactor (photo-CREC–air) [27], etc. However, further work is necessary to accurately model the PCO reactors and to find a kinetic model which gives a reliable description of experimental results.

In this work photocatalytic degradation of toluene, used as a model VOC, was performed with the catalytic TiO_2 layer coated on the annular reactor walls. The rate of toluene removal was investigated at different reaction conditions. The appropriate kinetic model was proposed. Finally, in order to describe behaviour of the annular PCO reactor different mathematical models have been developed and the results discussed.

2. Experimental

2.1. Catalysts preparation and characterization

The commercial TiO_2 powder catalyst was supplied by *Degussa* (*Aeroxide* P-25). Average diameter of the catalyst particles was 30 nm. Crystal structure was primarily based on anatase (70% anatase and 30% rutile). The surface area was 50 $m^2\ g^{-1}$ (BET). The TiO_2 layer was coated on the internal glass surface of the outer tube of the annular reactor. TiO_2 isopropanol slurry was used for this purpose. Homogeneous suspension (1 g TiO_2/100 ml isopropanol) was prepared using the ultrasound bath (to break particle agglomerations) and homogenizer. The suspension was poured into a rotating tube and simultaneously dried in the hot air. Coating was repeated several times to a desired thickness of the catalytic layer. The TiO_2-coated tube was heated at 110 °C for 2 h. TiO_2 loading density was 22.3 $\mu g\ cm^{-2}$. The catalyst was characterized by X-ray powder diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. XRD experiments were carried out on a *Philips®* PW1730. The Cu Kα radiation was performed at 40 kV and the 30 mA current. Sample scans were collected between 3° and 75° (step 0.02°, integration time 2 s). FTIR spectroscopy experiments were performed on a *PerkinElmer®* Spectrum One FTIR spectrometer. Sample scans were collected between 4000 and 450 cm^{-1} with step 4 cm^{-1}.

2.2. Experimental apparatus and procedures

High purity synthetic air (20.5% O_2 in N_2, *Messer*) was gas carrier. Ultra-pure water and maximum purity grade toluene (*Aldrich*) were used to prepare the reaction mixtures. The appropriate concentration of toluene and water was obtained by vaporization of organic compound and water at the specified airflow rate and regulation with the mass flow controllers (*Cole Palmer*). The temperature of liquid-containing saturators was maintained at 20 °C. Then the secondary airflow was introduced into the mainstream to obtain desired concentration of the reactants. Relative humidity, RH, was varied from 0.06 to 0.61. Inlet toluene concentrations were in the range from 1.0 to 9.9×10^{-3} $g\ dm^{-3}$. Total flow rate of the reaction mixture was varied from 2.4 to 24.6 $dm^3\ h^{-1}$. The airflow rate was set and the reaction mixture was passed through the dark photoreactor (without UV light) to reach the adsorption equilibrium. Then the UV light was turned on. Toluene concentrations were measured using gas chromatography and a FID detector. Conversion, X_A, was calculated with respect to toluene concentration. Space-time in the reactor was varied by changing total flow rate at the constant reactor volume.

2.3. Design of the annular photocatalytic reactor

The annular photoreactor was constructed using a Pyrex glass tube. The reactor was 265 mm long. The outer tube diameter was 53.8 mm, and the inner tube diameter was 23.8 mm. Total volume of the reactor, V, was 0.485 dm^3. Illumination of the reactor was provided by an 8 W fluorescent black light blue lamp which efficiently emitted UVA light at 315–400 nm, with a maximum wavelength at 352 nm and 368 nm (*Sylvania®*). The UV lamp was