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Heterogeneous photocatalytic oxidation of methyl ethyl ketone under UV-A light in an LED-fluidized bed reactor

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ABSTRACT

Photocatalytic oxidation over titanium dioxide is a promising technique for decomposition of hazardous compounds effectively. This paper reports the photocatalytic oxidation of methyl ethyl ketone (MEK) in air over three commercialized TiO_2 catalysts, namely PC500, PC50, and P25. The photocatalytic activity of catalysts was evaluated in a fluidized bed reactor under UV-A light, which was supplied by light emitting diodes (LEDs). Pure anatase titania with remarkable high surface area, PC500, yielded the highest reaction rate. The high surface area of PC500 titania compensates the faster recombination of charge carries and maintains the superior activity under steady state condition. From quantum yield calculations, the use of the most active titania under low intensity of UV light was determined as preferable condition to carry out MEK photocatalytic oxidation.

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1. Introduction

The emission of hazardous compounds from different industries into the environment is a great matter of concern. Photocatalytic oxidation (PCO) as a promising technique has the potential to be applied in decontamination of both liquid [1–6] and air streams containing organic pollutants [7]. TiO_2-mediated PCO process has been attracted the attention of researchers, due to the noticeable properties of titanium dioxide [7,8]. In PCO process, under ultraviolet (UV) radiation, which overcomes the band gap energy of TiO_2, the presence of two charge carriers (electron and hole) on the surface of catalyst is resulted in the formation of active species such as OH radicals [9].

The heterogeneous photocatalytic oxidation has been extensively studied over both commercial and laboratory made titania samples. The structural properties of TiO_2 have been demonstrated as the important determinants of overall performance [10–12]. The structural characteristics of a given catalyst (including crystallite size, phase composition, and surface area) are determined by the catalyst preparation conditions and its thermal treatment. For instance, AEROXID TiO_2 P25, as a well-known commercially available titania, is synthesized via flame hydrolysis at temperatures between 1000 and 2400 °C. The reaction conditions in P25 production are resulted in a pure and nanostructure titania containing both anatase and rutile phases [13]. Cristal Global (formerly Millennium Inorganic Chemicals) provides PC500 titania, a pure anatase titania with fine particle size, which is synthesized hydrothermally. Thermal treatment of PC500 yields other PC series (e.g. PC10, PC50, PC100) with lower surface area and larger crystallite size compared to PC500 [14].

Different types of commercial titania samples have been used to study the photocatalytic oxidation of gas phase pollutants in different configuration of reactors. The exposition of catalyst to UV light and reactants depends on the reactor geometry. In a fixed bed reactor with a thin film of catalyst on the walls of the reactor, both quality and quantity of deposited catalyst might affect the activity. Alonso-Tellez et al. have studied the photocatalytic oxidation of methyl ethyl ketone (MEK) and hydrogen sulfide (H_2S) over thin film of Hombikat UV100 and P25 catalysts in a single pass annular reactor [10]. They concluded that the higher activity of UV100 in the oxidation of both pollutants is related to its small particle size and higher UV light transmission through the catalyst coating. Similar behavior was observed in the photocatalytic destruction of gaseous diethyl sulfide over Hombikat UV100 and P25 [15]. The better performance of UV100 catalyst was attributed to the high specific surface area (SSA). Ibrahim et al. have compared the conversion of acetone over P25 and Hombikat UV-100 supported on a wire mesh placed in a batch photoreactor [16]. They have concluded that

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both catalysts provide close overall acetone photo-degradation rate at the optimum loading of catalyst. P25 has been reported more efficient than PC500 in the photo-degradation of acetylene in a batch reactor in which the powdered catalysts were irradiated without any support and binder [17].

Photocatalytic oxidation of 2-propanol was studied over different catalysts in a packed-bed reactor in which only a portion of catalysts was irradiated by external lamps [11]. The catalysts with high SSA and only anatase phase, i.e. Hombikat UV100 and Millennium PC100, showed better performance than P25 and Kemira650. The results of photocatalytic oxidation of *n*-butanol over a thin film of P25 and Hombikat UV100 were similar under black light, whereas P25 was more active than UV100 under visible (white) light [18]. The photocatalytic removal of methanol and *n*-octane has been compared among P25, PC500, and PC100 powders, which were distributed as a thin layer in a flow reactor [12]. Although the differences in photoactivity were very small, PC500 was called the most active catalyst. Photocatalytic activity of PC500 has been reported more than P25 for acetaldehyde oxidation in a reactor packed with glass bead particles coated by catalysts [19].

Generally P25, as a mixed phase titania, has been demonstrated more activity than anatase titania such as PC500 in liquid phase reactions [20]. It seems that the structural properties of catalysts do not play a major role in the aqueous phase reactions. A systematic study on the photocatalytic oxidation of 19 model pollutants in aqueous phase was carried out over eight commercial titania samples by Ryu and Choi [21]. The activity of catalysts was substrate-dependent and no correlation was found between activity and physicochemical specifications of catalysts. It has been reported that the pH of solution determines both the surface charge of catalyst and the size of aggregates [22]. In other words, the activity of a given catalyst in the aqueous phase highly depends on the acidity of solution, and hence it is pollutant-dependent [23].

According to aforementioned gas phase studies over different photocatalysts, it seems that the structural properties of catalysts control the reaction rate in gas phase. In other words, the photocatalytic activity of a given catalyst in gas phase is not pollutant dependent and a trade-off between physical characteristics determines the overall activity. In the current study, therefore, three commercialized TiO_2 samples with different structural properties were chosen to study their photocatalytic activity. In addition, the possible synergism between rutile and anatase phases of P25 was discussed in both gas and liquid phase reactions.

PCO of MEK, a typical malodorous substance chosen as model pollutant, was studied, both in fixed and fluidized bed photoreactors [24–26]. In all cases, only traditional UV lamps were used as light sources for the photoreactors. Nowadays, light emitting diodes (LEDs) are replacing UV lamps in many applications, owing to the much higher efficiency in light-electricity conversion. Further advantages of LEDs derive from the small dimensions, robustness, and the long lasting (hundred thousands of hours compared to thousands of hours in the case of classical lamps) [27]. Up to now, no papers regarding the simultaneous use of a fluidized bed reactor and UVA-LEDs as light sources were developed for studying the photocatalytic treatment of gaseous stream containing MEK. For this reason, the aim of this work is to evaluate PCO of MEK in a fluidized bed reactor under UV-A light, supplied by LEDs (LED-FBR).

2. Experimental

2.1. Catalysts and their characterization

Photocatalytic tests were carried out over P25, PC50 and PC500 photoactive powders. P25 and two PC series catalysts were supplied by Evonik (formerly Degussa) and Cristal Global Companies, respectively.

Optical and physical properties of catalysts were determined by several techniques. In order for band gap energy calculation, UV–vis reflectance spectra (UV-vis DRS) of catalysts were recorded by a Perkin-Elmer spectrometer Lambda 35 using a RSA-PE-20 reflectance spectroscopy accessory (Labsphere Inc., North Sutton, NH). SSA of catalysts was measured on a Costech Sorptometer 1040 by nitrogen adsorption at −196 °C after samples pretreatment at 150 °C for 30 min under He flow. X-ray diffraction (XRD) patterns were obtained by an X-ray micro diffractometer Rigaku D-max-RAPID, using Cu-Kα radiation. Thermo-gravimetric (TG) analyses of samples were carried out in air flow ($Q = 100\ \mathrm{Ncm^3/min}$) with a thermo balance (SDT Q600, TA Instruments) in the range 20–1000 °C at 10 °C $\mathrm{min^{-1}}$ heating rate.

2.2. Fluidized bed reactor and photocatalytic tests

The schematic picture of LED-FBR is illustrated in Fig. 1 [28–34]. The reactor (realized by Officina Elettromeccanica Elena Mormile, Naples, Italy) has been made of two parallel quartz windows incorporated in an AISI 304 stainless steel frame with dimensions of 23, 4 and 0.6 cm in height, width and thickness, respectively. A bronze filter (mean pore size 5 μm) was used to provide a uniform distribution of the fed gas, a particle disengagement zone (5 cm × 5 cm) at the top of reactor was designed to minimize the elutriation of bed particles and a specifically designed cyclone is located at the outlet of the reactor. The peak wavelength of UVA-LEDs (provided by Nichia Corporation) was centered at 365 nm and irradiation flux was easily adjusted using a DC power supply. The LEDs were inserted into two 8 × 5 cm arrays and were positioned in contact with each quartz windows. Each array consisted of 40 pieces of UVA-LEDs. In this way, the irradiated reactor volume was 20 $\mathrm{cm^3}$.

The temperature of reaction was measured and controlled by a temperature sensor (type J thermocouple) and electrical heating system, respectively. The sensor and heating system were positioned in the reactor bed and were connected to a proportional-integral-differential (PID) controller (TLK 38, ASCON TECNOLOGIC). To study the influence of light intensity (I_0) on the PCO reaction, the temperature of bed was set on the fixed value of 50 °C through the use of the PID controller. Quantum yield (QY) of photocatalysts was evaluated as the ratio between the number of MEK molecules reacted per second and the number of photons entering the reactor per second [35]. The latter was calculated at reactor walls through an UV meter with its probe positioned in correspondence of the irradiated window and able to measure UV light intensity emitted by UVA-LEDs.

Desired concentrations of MEK and water vapor in air were achieved using saturated vapor pressure calculations for water and MEK by Antoine's law; two mass flow controllers (Brooks Instruments) were used to flow air through the both MEK and water containing saturators, placed in a thermostatic bath. The diluting air passing through the third mass flow controller was mixed with humidified and MEK polluted air streams and it was fed into the reactor with flow rate of 50 NL/h. MEK concentration (C_{MEK}) was in the range 250–1000 ppm, while water vapor concentration (C_{H_2O}) was equal to 1000 ppm.

Titania powders were physically mixed with 20 g glass beads (particle size of 70–110 μm, provided by Lampugnani Sandblasting HI-TECH) to improve the quality of fluidization. The photocatalytic tests were started by switching on LEDs after the completion of adsorption in dark. The gas composition was continuously analyzed using an online quadrupole mass detector (Trace MS, ThermoQuest). The concentrations of CO_2 and CO were continuously

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