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Enhanced photocatalytic degradation of VOCs using Ln^{3+}–TiO_2 catalysts for indoor air purification

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Abstract

Two types of lanthanide ion-doped titanium dioxide (Ln^{3+}–TiO_2) catalysts including La^{3+}–TiO_2 and Nd^{3+}–TiO_2 were prepared by a sol–gel method. The effects of the lanthanide ion doping on the crystal structure, surface area, adsorption properties, pore size distribution, and surface chemical state of the catalysts were investigated by means of XRD, BET, and XPS. As results, the crystal size decreased significantly, while the specific surface area, *t*-plot total surface area, micropore volume, and the total pore volume increased owing to the lanthanide ion doping. The nitrogen adsorption–desorption isotherms of the catalysts showed that the N_2 adsorption ability of the Ln^{3+}–TiO_2 catalysts was better than the TiO_2 catalyst. Among them, the 0.7% Ln^{3+}–TiO_2 catalysts demonstrated the highest adsorption ability. The photocatalytic activity of the catalysts was investigated in the experiments of the photocatalytic degradation of benzene, toluene, ethylbenzene and *o*-xylene (BTEX) in a gaseous phase. The photocatalytic efficiency of the TiO_2 catalysts with the lanthanide ion doping was remarkably enhanced by BTEX removal. The 1.2% Ln^{3+}–TiO_2 catalysts achieved the highest photocatalytic activity. The enhanced photodegradation of BTEX is possibly due to the improved adsorption ability and the enhanced electron–hole pairs separation due to the presence of Ti^{3+} on the surface of Ln^{3+}–TiO_2 catalysts and the electron transfer between the conduction band/defect level and lanthanide crystal field state.

Keywords: BTEX; Indoor air purification; Lanthanide ion; Photocatalysis; TiO_2

1. Introduction

Indoor air quality (IAQ) within buildings is a critical concern, since many metropolitan generally spend more than 80% of time in an indoor environment. Recently the sick building syndrome has been paid great attention especially in some urban cities such Hong Kong and other major cities in China (Roberts and Nelson, 1995). Indoor air pollutants mainly include nitrogen oxides (NO_x) and volatile organic compounds (VOCs), which can cause adverse health impacts on occupants (Jones, 1999). VOCs are primarily composed of BTEX (benzene, toluene, ethylbenzene, and *o*-xylene) and halogenated hydrocarbons (Maroni et al., 1995). These indoor air pollutants are emitted from different sources such as combustion byproducts, cooking, construction materials, office equipment, consumer products, and

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nearby traffic vehicles. BTEX is one group of major VOCs found in the indoor environments in Hong Kong and Mainland of China. In these areas, the concentration of BTEX was found in the range of 10–100 ppbv (Ao et al., 2003a). For example, recent studies in Hong Kong determined that the maximum concentration of BTEX in several selected shopping malls was 13.2, 78.1, 17.2, and 8.49 ppbv, respectively, while that in the selected office buildings was 2.51, 5.68, 6.40, and 13.0 ppbv, respectively. These studies indicated that the concentration of benzene in the shopping malls exceeded the criteria of IAQ in good class (5 ppb for benzene, HKEPD, 2003).

Photocatalytic oxidation has proven to be a promising technology for air purification and may be more cost-effective than other conventional techniques such as activated carbon adsorption and chemical scrubbers, because semiconductors are inexpensive and capable of mineralizing most organic compounds effectively. However, this technique is still in the developmental stage for VOCs removal from indoor air (Fu et al., 1995; Ku et al., 2001; Feitz et al., 2002; Kim and Hong, 2002; Li et al., 2004). The bottle-neck is the development of a better catalyst. A good photocatalyst depends strongly on the efficiency of electron–hole pair separation and the adsorption ability of gaseous VOCs. To effectively eliminate the electron–hole recombination in the photocatalytic reaction, TiO_2 catalysts can be improved by doping some metal ions, coupling with other semiconductor oxides or depositing noble metals (Choi et al., 1994; Li et al., 2001). However, some literature have proved that the incorporation of lanthanide ions such as La^{3+}, Eu^{3+}, Pr^{3+}, Nd^{3+}, and Sm^{3+} into TiO_2 matrix could promote the chemical or physical adsorption of organic substrates on the catalysts surface in an aqueous phase (Ranjit et al., 2001a,b; Xu et al., 2002). In the meantime, this lanthanide ion doping could also improve the photochemical properties by increasing the photocurrent response and the incident monochromatic photon to current conversion efficiency in the light wavelength of 300–400 nm (Wang et al., 1999). The increase of photocurrent implies the effective separation of electron–hole pairs. In fact, the transient absorption decay spectra showed more effective separation of charge carriers for Gd^{3+} or Sm^{3+}-doped TiO_2 than for naked TiO_2 (Xu et al., 2002). However, the relevant information regarding the application of lanthanide ion-doped TiO_2 catalysts in gaseous reaction has been hardly reported based on the best of our knowledge. In reality, indoor air often contains BTEX with NO together (Jones, 1999). Concurrent photodegradation of BTEX and NO was also conducted. This study was aimed at applying the photocatalytic oxidation using the lanthanide ion-doped TiO_2 catalysts to remove VOCs from a gaseous stream for indoor air purification.

2. Experimental methods

2.1. Preparation of Ln^{3+}-TiO_2 catalysts

Two types of lanthanide ion-doped TiO_2 (Ln^{3+}–TiO_2) catalysts were prepared by doping La^{3+} or Nd^{3+} onto TiO_2 using a sol–gel process. 17 ml of tetra-*n*-butyl titanium (Ti(O-Bu)$_4$) was dissolved in 80 ml of absolute ethanol and the Ti(O-Bu)$_4$ solution was added drop-wise under vigorous stirring into 100 ml of a mixture solution containing 84 ml of 95% ethanol, 1 ml of 0.1 M Ln^{3+} $La(NO_3)_3 \cdot 6H_2O$ or $Nd(NO_3)_3 \cdot 6H_2O$, or 15 ml of acetic acid (>99.8%). The resulting transparent colloidal suspension was stirred for 2 h and aged for 2 days till the formation of gel. The gel was dried at 353 K under vacuum and then ground. The powder was calcined at 773 K for 2 h, and eventually the Ln^{3+}–TiO_2 catalysts were obtained in a nominal atomic doping level of 0.2% abbreviated as 0.2% Ln^{3+}–TiO_2. Other lanthanide ion-doped TiO_2 samples prepared according to the above procedure with the dosage of 0.7%, 1.2%, 1.6%, and 2.0%, respectively. In the meantime, pure TiO_2 as a blank catalyst was also prepared in the same way without doping lanthanide ions.

2.2. Characterization of Ln^{3+}–TiO_2 catalysts

To determine the crystal phase composition of the prepared Ln^{3+}–TiO_2 catalysts, X-ray diffraction (XRD) measurement was carried out at room temperature using a Rigaku D/MAX-IIIA diffractometer with CuKα radiation ($\lambda = 0.15418$ nm). The accelerating voltage of 35 kV and emission current of 30 mA were used. The specific surface area, *t*-plot total surface area, *t*-plot surface area, monolayer volume, micropore surface area, and total pore volume of all samples were measured by the Brunauer–Emmett–Teller (BET) method, in which the N_2 adsorption at 77 K was applied and a Carlo Erba Sorptometer was used. To study the valance state and chemical state of the catalysts, X-ray photoelectron spectroscopy (XPS) was recorded with the PHI quantum ESCA microprobe system, using the MgKα line of a 250-W Mg X-ray tube as a radiation source with the energy of 1253.6 eV, 16 mA × 12.5 kV and a working pressure of lower than 1×10^{-8} N m^{-2}. As an internal reference for the absolute binding energies, the C (1s) peak at 284.80 eV of hydrocarbon contamination was used. The fitting of XPS curves was analyzed with a software package (Multipak 6.0A). To study the recombination of electrons and holes, the photoluminescence (PL) emission spectra of the samples were measured with the following procedures: at 77 K, a 325 nm He–Cd laser was used as an excitation light source; The light from the sample was focused into a spectrometer (Spex500) and detected by a photo-multiplier tube (PMT); The signal from the PMT was input-