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Preparation of TiO_2 ultrafine nanopowder with large surface area and its photocatalytic activity for gaseous nitrogen oxides

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ABSTRACT

TiO_2 nanopowder with a large surface area and high crystallinity was synthesized by a thermal decomposition process. The physicochemical properties of the prepared powders were examined by X-ray diffraction, transmission electron microscopy and nitrogen adsorption–desorption isotherms. The nanocrystallites of the prepared powers were considerably smaller than those of the commercial photocatalyst (Degussa, P25), and the particles had a dense polyhedral structure. In addition, the particles had a mainly disordered mesoporous structure with a pore volume that varied according to the pore size in the range of 2–20 nm. The photocatalytic activity of the prepared photocatalyst was obviously higher than that of P25 on the photodegradation of gaseous nitrogen oxides under $UV_{254+185\ nm}$ lamp irradiation. Above 40% relative humidity, the NO_x removal efficiency of the prepared photocatalyst was 10% higher than that of P25. Furthermore, a suitable relative humidity and longer residence time were found to enhance the photocatalytic oxidation of gaseous nitrogen oxides by $UV_{254+185\ nm}$ lamp irradiation and TiO_2 nanoparticles.

1. Introduction

In a recent publication [1], TiO_2 nanoparticles prepared via a thermal decomposition process were investigated systematically for the photocatalytic degradation of methylene blue. The photocatalytic performance was found to vary according to the crystallite size and crystallinity. In particular, it was suggested that the photocatalytic activity could be improved by optimizing the surface area and crystallinity through control of the synthesis conditions (synthesis temperature and precursor heating temperature). However, the photocatalytic activity of the resulting particles for air pollutants was not described earlier, which is the primary goal of the present paper.

Nitrogen oxides (NO, NO_2, and N_2O), which are representative air pollutants, are emitted from the combustion of coal, thermal power plants and automobile exhaust, and cause a range of environmental problems. For example, NO_x is an indirect cause of acid rain and photochemical smog, which causes diseases of the human respiratory system [2,3]. Many studies of NO_x removal technologies have been carried out over the last few decades. The selective catalytic reduction (SCR) of NO_x with ammonia has attracted particular attention. However, the SCR process requires an expensive catalyst and ammonia. Other problems include secondary pollution by the reducing agent, as well as poisoning and the loss of expensive catalyst [4].

Photocatalytic oxidation (PCO) on TiO_2 is a promising method for destroying NO_x and can be carried out at room temperature and atmospheric pressure. Hashimoto et al. [5] reported the PCO of NO with TiO_2 and zeolite to remove NO_x from the atmosphere. Devahasdin et al. [6] reported the transient behavior of PCO in removing NO. In addition, some studies showed that irradiation with ultraviolet-light from an ozone producing UV lamp decomposes organic compounds photochemically on TiO_2 catalysts [7,8]. Wang et al. [9] reported that the ozone formed could have a positive effect by reactivating the deactivated catalyst. The photocatalytic oxidation process can remove NO by OH radicals. NO is converted to HNO_3 through photooxidation via a NO_2 intermediate [10–13].

Unfortunately, the above mentioned studies focused on the removal of NO_x after a sufficient residence time using a commercial photocatalyst (Degussa, P25). Therefore, it is essential to develop more efficient ways of enhancing the photocatalytic decomposition of NO at a less than optimal residence time. In general, a large surface area and good crystallinity are beneficial to TiO_2-based photocatalysis in the gas phase [5,6,14].

The thermal decomposition process is one of the best techniques for preparing TiO_2 nanoparticles with the desired size, shape and homogeneity in composition as well as crystallinity [1,15–19]. The thermally decomposed TiO_2 nanoparticles are typically produced in a process that involves the introduction of a titanium precursor into a furnace in vapor form or as very small droplets. In this process, an inert carrier gas is bubbled through the liquid precursor that transports the molecules into the high temperature furnace zone. The high temperature process promotes very rapid gas-phase chemical reactions that

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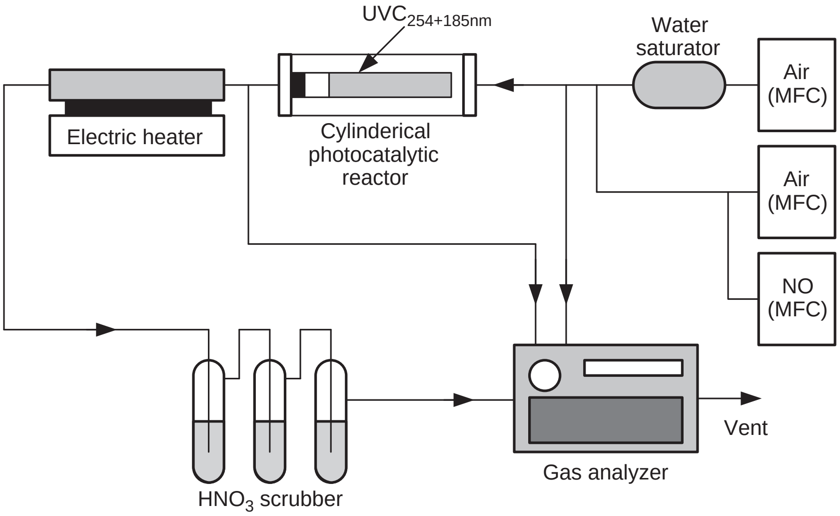

Fig. 1. Schematic diagram of the experimental apparatus for the catalytic testing.

lead to rapid nucleation. The particles then grow by Brownian coagulation, resulting in highly crystalline titanium dioxide particles in an aerosol form, which is finally trapped in a filter or a condenser. The titanium dioxide nanoparticles produced are mostly 3–150 nm in diameter and the product is typically an anatase–rutile mixture [15–21].

In this study, TiO_2 nanopowder was synthesized by a thermal decomposition process [1]. The photocatalytic activity of the prepared photocatalyst was evaluated for the photodegradation of gaseous nitrogen oxides under $UV_{254+185\ nm}$ lamp irradiation. The physicochemical properties of the prepared TiO_2 nanoparticles were fully characterized, and the relationship between the physicochemical properties and photocatalytic activity was discussed.

2. Experimental

2.1. Catalyst preparation

The detailed experimental apparatus for TiO_2 nanoparticles preparation was described previously [1]. Titanium tetraisopropoxide ($[(CH_3)_2CHO]_4Ti$, TTIP, Aldrich, >97%) was used as the precursor. In a recent publication [1], the photocatalytic activity of TiO_2 nanoparticles prepared at a TTIP heating temperature of 95 °C and a synthesis temperature of 900 °C was the highest of the TiO_2 photocatalysts examined. Therefore, in this study, the synthesis conditions were 95 °C and 900 °C. The powder samples were labeled “P25-TiO_2” for the commercial catalyst (Degussa, P25) and “TD-TiO_2” for the synthesized catalyst (thermal decomposition process).

2.2. Characterization of catalysts

The X-ray diffraction (XRD) patterns of the catalysts were recorded on a DMAX-2500 (Rigaku Inc; focal spot size: 5 mm^2) diffractometer using a Cu rotating anode with a scan rate of $2°min^{-1}$. The anatase content, f_A, was determined from the integrated intensity of the anatase phase diffraction line, I_A, and that of the rutile phase diffraction line, I_R, using the following equation [22].

$$f_A = \frac{0.79 I_A}{I_R + 0.79 I_A}$$

For scanning transmission electron microscopy (TEM), the materials were deposited onto a carbon foil supported by a copper grid. TEM analysis was carried out using a CM-30 microscope (Philips; operated at 300 kV, image resolution <0.23 nm). The powder specific surface area (SSA, $m^2\ g^{-1}$) was determined by nitrogen adsorption (>99.999%) at 77 K on a Micromeritics Tristar 3000 apparatus using the Brunauer–Emmett–Teller (BET) method. The pore volume distribution was determined from the desorption isotherms (Micromeritics ASAP 2010 Multigas system) using the Barrett–Joyner–Halenda (BJH) method. Assuming monodisperse, spherical primary particles, the BET-equivalent particle diameter (d_{BET}) was calculated using the formula, $d_{BET} = 6/(\rho \times SSA)$, where ρ is the particle density.

2.3. Catalytic testing

Fig. 1 gives a schematic diagram of the photocatalytic test for NO_x. The system consisted of the following: a NO gas feeding unit, water saturator, $UVC_{254+185\ nm}$ lamp, photocatalytic reactor, electric heater, HNO_3 scrubber and gas analyzer. Simulated gas was fed into the photocatalytic reactor through a mass flow controller (3660, KOFLOC Co. Ltd.). Water vapor was obtained by passing dried air through a bottle containing deionized water at room temperature. The relative humidity of the simulated gas was measured at the inlet of the photocatalytic reactor using a humidity measuring instrument (Testo 625, Testo Co. Ltd.).

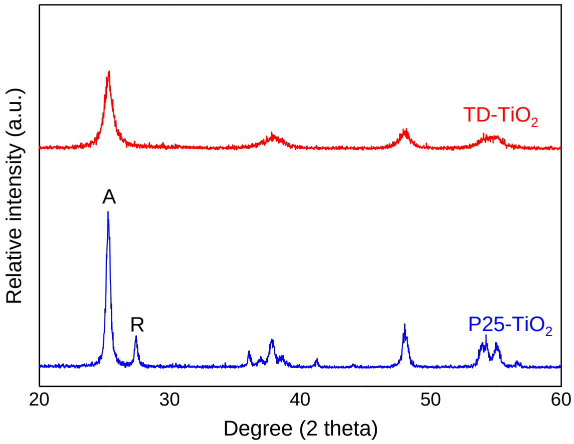

Fig. 2. X-ray diffraction patterns of the as-synthesized TiO_2 (TD-TiO_2) and commercial catalyst (P25-TiO_2). The symbols ‘A’ and ‘R’ indicate anatase and rutile, respectively.