



Development of gas flow reactor with on-line monitoring system for nitrogen dioxide removal



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ARTICLE INFO

Article history:

Received 13 August 2017

Received in revised form 11 September 2017

Accepted 11 September 2017

Available online 13 September 2017

Keywords:

Flow analysis

Griess-Saltzman reaction

Nitrogen dioxide removal

Photocatalyst efficiency

Titanium dioxide photocatalyst

ABSTRACT

In this work, a new flow system was developed for investigating the efficiency of synthesized TiO₂ photocatalysts for NO₂ degradation. The system consists of two parts: the gas flow reactor and an on-line NO₂ monitoring system. The latter is based on the conversion of NO_{2(g)} to NO_{2⁻(aq)} with subsequent spectrophotometric detection of the nitrite anion by the Griess-Saltzman reaction. Simplex optimization was employed to obtain the required sensitivity for the NO₂ monitoring. The developed flow system was employed to measure the catalytic efficiency of photodegradation of NO₂ by various types of TiO₂-based synthesized photocatalysts and a commercial TiO₂ photocatalyst, 'P25'. The TiO₂ photocatalysts were synthesized using titanium isopropoxide (TTIP), tetrabutyl orthotitanate (TBOT) and titanium oxysulfate (TiOSO₄) as precursors. Glass beads, coated with the TiO₂ photocatalyst, were packed in a quartz tube reactor. Standard NO₂ gas mixture (50 ppmv) was continuously flowed through the reactor under UV radiation. Residual NO₂ from the outlet of the reactor was measured using the on-line NO₂ monitoring system which employs a gas diffusion unit and an acceptor stream of triethanolamine solution. The NO_{2(g)} was converted into NO_{2⁻(aq)} which was measured spectrophotometrically at 540 nm using the Griess-Saltzman reaction. The photocatalytic efficiency of the synthesized photocatalysts was compared. The effects of oxygen and humidity were also studied in order to investigate the mechanism of photodegradation of NO₂ by the TiO₂ catalyst. We observed that at low humidity (12% RH), the OH[•] radical generated from moisture plays an important role for photooxidation process of NO₂.

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1. Introduction

Nitrogen dioxide (NO₂) emission is one of the most serious environmental problem worldwide. NO₂ is a very reactive gas with a suffocating odor and highly toxic. Epidemiological studies have provided evidence that long-term NO₂ exposure decreases lung function and increases the risk of respiratory symptoms [1,2]. Besides health impact, NO₂ also has an effect on the environment. It decomposes in contact with water and generates acid rain which can destroy plants, trees, and man-made structures (buildings or bridges). Moreover, NO₂ causes photochemical smog when it reacts with hydrocarbons in the presence of sunlight. This smog reduces aerial visibility. Owing to its hazard both to the human health and the environment, effective methods for monitoring and removal of NO₂ are required.

There are several methods available for NO₂ measurement. Ion chromatography is the most published method for analysis of NO₂. NO_{2(g)} is usually collected in a solution of triethanolamine (TEA) as the absorbing reagent which converts the gas to NO_{2⁻(aq)} prior to analysis by ion chromatography [3,4]. Although this technique is a sensitive technique, the method takes long analysis time and may not be appropriate for continuous detection of NO₂. Semiconductor electrochemical sensors with rapid response have been employed for NO₂ detection [5–7]. However, these NO₂ sensors only work at high temperature (500–600 °C). Thus, they are not effective detectors of NO₂ at ambient temperature. Another technique is laser-induced fluorescence detection which can measure NO₂ in air [8]. However, the instruments are sophisticated and expensive.

Chemiluminescence (CL) method has been widely used for NO₂ detection due to its high sensitivity. Maeda et al. [9] described NO₂ determination using the CL method based on luminol reaction. The CL reaction between NO₂ gas and liquid luminol phase took place in a special vessel which does not require any metal ions as catalyst. However recalibration of system is necessary due to the limited stability of

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luminol. Another published work on CL determination of NO₂ was reported based on ozone (O₃) reaction [10,11] in the gas phase. The NO₂ is measured indirectly by first reducing the NO_{2(g)} to NO_(g) and then reacting the resultant NO with O₃ to produce electronically excited state of NO₂ (NO₂^{*}) and O₂. The NO₂^{*} immediately decays to the ground state with emission of a photon. The light intensity from the reaction is related to NO₂ content in the sample. The method provides rapid response. It is now commercially available, known as 'NO/NO_x chemiluminescent analyzer'. However, this technique requires expensive complex instrument.

Another widely employed and cost effective method for NO₂ measurement is the spectrophotometric detection based on the reaction with Griess-Saltzman reagent [12]. The NO₂ gas is usually collected by direct introduction into absorbing reagent of triethanolamine (TEA) or by diffusion onto absorbent materials impregnated with solution of TEA. The nitrite anions are then reacted with sulfanilamide (SA) and *N*-(1-naphthyl)-ethylenediamine dihydrochloride (NED), to generate a stable pink azo compound product. Several flow-based systems coupled with gas collection of NO₂ and subsequent detection by Griess-Saltzman reaction have been reported [13–15]. Toda et al. [13] proposed a membrane-based microchannel scrubber as the NO₂ gas collection unit. The method was applied for analysis of NO_{2(g)} for environmental monitoring and on-site medical treatment. Wei et al. [14] reported the use of flow injection analysis (FIA) with a chromatomembrane cell (CMC) as an on-line preconcentration unit for continuous monitoring of polluting NO₂ in air sample. Owing to the advantages of flow-based analysis and simple spectrophotometric detection, flow systems have been developed for automated and mobile monitoring of NO₂ gas in various applications.

With regards to NO₂ removal, many researchers have tried to produce an economical and environmental friendly NO₂ gas treatment technology. Photocatalytic oxidation (PCO) of NO₂ using titanium dioxide (TiO₂) has been reported as one of the technology for NO₂ degradation [16,17]. TiO₂ is inexpensive, safe and a very stable catalyst showing high photocatalytic efficiency [18,19]. Due to these properties, many researchers have used TiO₂ to remove NO₂ and study its efficiency. Various designs of photoreactors and systems have been employed for investigation of the photocatalytic efficiency of NO₂ removal [20–24]. Nevertheless, chemiluminescent method is the most popular detection system for on-line monitoring of NO₂ and/or NO since it is commercially available. For example, Komazaki, et al. [20] employed an annular diffusion scrubber reactor for the treatment of NO_{2(g)}. The reactor consists of two concentric quartz tubes and a black light which is installed inside the tube reactor. The TiO₂ is coated in the inner wall of outer tube where the NO_x is destroyed. The reactor is connected with the NO_x chemiluminescent analyzer for analyzing the residual NO_x after treatment. In 2014, Nguyen and Bai [24] designed a photoreactor using an acrylic resin-type material on which titania nanotubes (TNTs) catalyst was coated. The photocatalytic reactivity of TNTs was studied by monitoring the residual NO and NO₂ using commercial NO_x chemiluminescent analyzer. Even though chemiluminescent detection is convenient because of its commercial availability, the instrumental setup involves handling of gas phase reaction (reaction between O_{3(g)} and NO_(g)) which makes for difficulty in the operation of the system. Therefore, detection in aqueous phase is more favorable since it does not require sophisticated instruments.

In this work, we present a new simple flow system for investigation of the efficiency of synthesized TiO₂ photocatalysts for NO₂ degradation. The flow system consists of a gas flow reactor and an on-line NO₂ monitoring system. The detection of NO₂ is based on the conversion of NO_{2(g)} to NO₂⁻(_{aq}) with subsequent spectrophotometric detection using the Griess-Saltzman reaction. The developed system was applied to evaluate the efficiency of synthesized TiO₂ catalysts in the photodegradation of NO₂ gas.

2. Experimental

2.1. Chemicals and reagents

Chemicals used in this work were all analytical reagent (AR) grade. Deionized-distilled water (18.0 MΩ cm⁻¹, Millipore Corp., USA), was employed for the preparation of all aqueous solutions. Titanium isopropoxide (TTIP), tetrabutyl orthotitanate (TBOT) and titanium oxysulfate (TiOSO₄) were purchased from Sigma-Aldrich (USA). The commercial titanium dioxide (TiO₂; P25) was purchased from Aerioxide (Japan). All chemicals were used without additional purification.

Standard 100 ppmv nitrogen dioxide gas (NO₂) was from BOC Scientific (Thailand). The carrier gas, nitrogen (N₂), and oxygen (O₂), were purchased from TIG (Thailand).

A solution of 5 × 10⁻² mol L⁻¹ triethanolamine (TEA) was prepared by dissolving 4.64 g TEA (Merck, Germany) in 500 mL of deionized water. A 0.6 × 10⁻² mol L⁻¹ sulfanilamide (SA) solution was prepared by dissolving 0.52 g SA (Sigma-Aldrich) in 500 mL of 0.5 mol L⁻¹ hydrochloric acid. *N*-(1-naphthyl)-ethylenediamine dihydrochloride (NED) solution, 1 × 10⁻³ mol L⁻¹, was prepared by dissolving 0.13 g NED (Sigma-Aldrich) in 500 mL of deionized water.

2.2. Synthesis of TiO₂-photocatalyst

TiO₂ was synthesized by the hydrothermal technique [25]. This process provides mono-dispersed and highly homogeneous nanoparticles without the use of additional solvent and high temperature calcination step. TiO₂ photocatalysts were synthesized using three types of titanium precursors: titanium isopropoxide (TTIP), titanium orthotitanate (TBOT) and titanium oxysulfate (TiOSO₄). Each titanium precursor (3 g) was dissolved in 30 mL of deionized water. The resultant solution was then transferred into a 100 mL Teflon-lined autoclave and kept at 160 °C for 12 h. After the hydrothermal treatment, the autoclave was cooled naturally at room temperature. The white precipitate of TiO₂ formed was filtered and washed with deionized water. The material was then dried overnight at 120 °C prior to further study.

2.3. Deposition of TiO₂-photocatalysts on glass (SiO₂) beads

Deposition of the synthesized TiO₂-photocatalysts (TTIP, TBOT and TiOSO₄) and commercial TiO₂ (P25) on glass beads (5 mm diameter, Sigma-Aldrich) was carried out by spray coating method. A suspension of 2% (w/v) TiO₂ was prepared by mixing 2 g of TiO₂ with 0.3 mL TritonX-100 (Sigma-Aldrich) and 3 mL polyethylene glycol-400 (PEG-400, Sigma-Aldrich) in 100 mL of pure water. The mixture was then sonicated for 20 min. The TiO₂ suspension was lightly sprayed on the glass beads and then dried using hot air from an electric hair dryer. This step was repeated several times until satisfactory coating on the entire surface of glass beads was achieved. The coated glass beads were further calcined in a furnace (Vecstar, USA) at 400 °C for 2 h. The amount of TiO₂ deposited was determined by weighing the glass beads before and after coating with TiO₂.

2.4. Apparatus and instrumentation

The system was constructed as shown in Fig. 1. The flow manifold consists of (a) gas flow reactor which was connected to (b) NO₂ detection system for measurement of residual NO_{2(g)}. The gas flow reactor consists of two mass flow controllers (MFC, Bronkhorst High-Tech B.V., Netherlands and Sierra, USA) for controlling the flow rate of the NO₂ and N₂ gases, 3-way selection valves (Upchurch, USA) for selecting the direction of gas stream, cylindrical shaped quartz reactor (15 cm length and 2 cm i.d.) for packing the coated glass beads and a UV light source (Philips 6 × 18 watt lamps, 350–390 nm, Netherlands). The valves SV1 and SV2 were utilized for allowing gas stream to flow either to the humidifier or directly to the reactor. Valve SV3 was employed for

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