



Visible-light-induced photocatalytic oxidation of nitric oxide and sulfur dioxide: Discrete kinetics and mechanism



Yinghui Han ^{a, b, *}, Junjun Zhang ^c, Yi Zhao ^a

^a School of Mathematics & Physics, North China Electric Power University, Baoding, Hebei 071003, China

^b State Key laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China

^c Fujian Shuikou Power Generation Group Co. LTD, Fujian, Fuzhou 350000, China

ARTICLE INFO

Article history:

Received 31 March 2015

Received in revised form

19 October 2015

Accepted 6 December 2015

Keywords:

Photocatalysis

Visible light induction

Desulfurization

Denitration

Kinetics

Mechanism

ABSTRACT

A new photocatalyst was prepared using doped titanium dioxide (TiO₂) with active species for the removal of nitric oxide (NO) and sulfur dioxide (SO₂) under visible light irradiation. Nitrogen (N-), zirconium (Zr-), and nickel (Ni-) tridoped TiO₂ was found to possess higher photocatalytic activity than single Ni-doping, single Zr-doping, bimetallic doping or un-doping TiO₂. X-ray diffraction patterns and ultraviolet–visible spectra suggest that N-, Zr-, and Ni-tridoped TiO₂ is a mixed-crystal structure that enhances absorption in the visible light region. Kinetic experiments on the removal of NO and SO₂ by N-, Zr-, and Ni-tridoped TiO₂ under visible light irradiation were carried out in a self-designed photocatalytic reactor respectively. The effects of various operation factors on the reaction rates were evaluated. The reaction rates were successfully expressed by Langmuir–Hinshelwood model. Based on ion chromatography analysis, a visible light induced photocatalytic removal mechanism has been proposed based on N-, Zr-, and Ni-tridoped mixed-crystal TiO₂.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Nitrogen oxide (NO_x) and sulfur dioxide (SO₂) generated from coal combustion lead to significant pollution, including acid rain [1] and photochemical smog [2]. Abatement of these pollutants is an urgent task for sustainable global development [3], especially for those countries [4] heavily reliant on coal as their primary energy source. Many FGD (flue gas desulfurization) technologies, including wet limestone–gypsum process [5], flue gas CFB (circulating fluidized bed) process [6], sea water desulfurization process [7] and others [8], have been adopted in power plants, among which the wet limestone–gypsum technology is most commonly used. However, FGD cannot be used for the efficient removal of NO_x, due mainly to the low solubility of nitric oxide (NO) [9]. Commonly, additional denitration equipment, such as SCR (selective catalytic reduction) or SNCR (selective non-catalytic reduction), has been considered for installation at either the front or back end of desulfurization equipment. But such fractional removal technology has many drawbacks with regard to space requirements and

operating costs, among other factors [10]. The development of the emerging high-efficiency and environmentally friendly technology available for synchronous removal of NO_x and SO₂ has therefore become an inevitable trend.

The linchpin of synchronous removal of NO_x and SO₂ techniques is to oxidize nitric oxide (NO) into nitrogen dioxide (NO₂) rapidly in the flue gas [11], as the latter is readily dissolved in water. There have been several studies on the rapid oxidation of NO, however, some strong oxidizer were not only economically infeasible during industrial application, but also tended to introduce heavy metal, such as cobalt [12] etc., and other secondary pollution, e.g. chloride ion exceeding discharge standard [13].

As one of the most promising environment-friendly catalysts, titanium dioxide (TiO₂) has many advantages, including high catalytic activity [14], good chemical and thermal stability [15], absence of secondary pollution [16], safety, and non-toxicity, etc., and has been studied extensively in wastewater [16,17] and air treatment. TiO₂-based photocatalysis was recently reported in flue gas purification for emission control of sulfur dioxide [18–20], nitrogen oxide [20–22], elemental mercury [23,24] and carbon dioxide [25–27]. However, there are problems in the application that need further study, one of the largest being the shift of the band gap of TiO₂ from the ultraviolet to the visible spectral range. As is well

* Corresponding author. School of Mathematics & Physics, North China Electric Power University, Baoding, Hebei 071003, China. Tel.: +86 312 752 5093.

E-mail address: yinghuihan@ncepu.edu.cn (Y. Han).

known, under ordinary temperature and pressure, TiO₂ has three crystal types, viz. anatase, brookite and rutile, with anatase considered the most promising form. Nevertheless, anatase TiO₂ possesses a relatively wide band gap ($E_g = 3.2$ eV), resulting in an absorption wavelength of less than 387.5 nm, which leads to the need for the ultraviolet region for photocatalytic activation. However, ultraviolet light accounts for only 5% of total solar energy. Moreover, as the photon efficiency of TiO₂ is no higher than 20%, the total utilization rate of solar energy is, consequently, only about 1%, dramatically limiting its application [28]. By contrast, energy in the visible spectral region is as high as 45%. The challenge—and thus the research “hotspot”—therefore becomes how to reduce the width of the forbidden band of TiO₂ in order to promote the optical response of TiO₂ under visible light exposure or indoor room lighting, thus improving its photocatalytic activity. The doped TiO₂ becomes an effective way to achieve this goal. While earlier studies [29] concentrated on metal-ion doping, the introduced metal ions easily captured large numbers of electrons and holes, consequently accelerating the formation of carrier recombination centers that reduced the photocatalytic activity of TiO₂ instead of enhancing it. Ever since the breakthrough discovery that the band gap values of TiO₂ decreased and its absorption exhibited the visual light shift by introducing nitrogen, non-metal dopants, especially nitrogen-doped (N-doped) [30], have garnered much attention. Recently, successive researchers have discovered that the addition of small amounts of metal species (e.g. Ce [31], Ag [32], Fe, Cu, Zr, Ni, B, V, Sn, Mn) to N-doped TiO₂ markedly enhances photocatalytic activity, in which nitrogen-zirconium (N/Zr) [33] or nitrogen-nickel (N/Ni) [34] doped into TiO₂ are two of the most characteristic approaches. Although these studies on how to improve the photocatalytic activity by the doped TiO₂ have mushroomed, the reaction mechanism is still unclear and the photocatalytic removal technology is also not mature. In particular, no systematic research on the photocatalytic kinetic for the removal of SO₂ and NO under visible light irradiation were reported, even for separate removal process.

In this research, the multi-element nitrogen (N-), zirconium (Zr-), and nickel (Ni-) tridoped TiO₂ photocatalyst was synthesized and loaded to the quartz sand, followed by measurement of the discrete kinetics of the photocatalytic abatement of NO and SO₂ under visible light irradiation. Although the end goal of this research is to simultaneously abate NO and SO₂, in view of the complexities of multi-factors influence during the gas–solid reaction, the two gases were treated separately in this work. Simultaneous removal will be the subject of future work. The roles of various factors in the removal process of SO₂ and NO were established as well. Based on analysis of the removal products, the mechanism of SO₂ and NO removal by N-, Zr-, and Ni-tridoped TiO₂ photocatalysis was proposed. This work is not only the prerequisite and foundation for the further studies on the mass-transport and kinetics of the synchronous removal of multi-pollutants, but also it is important for elucidating the removal mechanism by TiO₂-based photocatalytic oxidation, in turn to be benefit for designing a practical industrial reactor to make full use of the solar energy.

2. Experimental section

2.1. Material and photocatalytic fabrication

High purity (>90%) white quartz sand (3–5 mm) was purchased from Henan Maofahe Commerce Trade Co. Ltd. and used for coated substrates. Titanium (IV) butoxide (97%, Sigma–Aldrich, USA), acetic acid (99.9%, Dongwan Qiaoke Chem. Co, China) and ethanol (99.9%, Tianzheng Fine Chem. Co. Tianjin, China) were used to prepare the TiO₂ catalyst. Analytical-grade triethylamine, zirconium nitrate and nickel nitrate for use as dopants were purchased

from Nanjing Chem. Regent Co. LTD, China. All the other reagents used were analytical grade and purchased from Huaxin Chemical Reagents Co. (Baoding, China). The photocatalyst was fabricated through the sol–gel spin coating of codoped TiO₂ on quartz sand substrates. The first step is to obtain solutions A and B. Solution A was prepared by mixing titanium (IV) butoxide and ethanol in a suitable molar ratio and then placing it in a separating funnel for use; meanwhile, solution B was obtained by mixing deionized water, ethanol and acetic acid. The second step is to add a certain amount of pipetted triethylamine, zirconium nitrate and nickel nitrate to solution B, stirring until thoroughly mixed. Next, solution A is added drop by drop to solution B and stirred constantly, until forming a transparent homogeneous sol; the scrubbed quartz sand of uniform particle sizes is then spread in a single layer in a 2 L beaker, followed by adding the prepared sol to completely submerge the quartz sand particles. After aging at room temperature for two days, the gel is obtained and then oven-heated at 85 °C for 12 h. Finally, through calcinations at different temperature, the doped TiO₂ photocatalyst supported on quartz sand is obtained.

2.2. Apparatus and procedure

Fig. 1 shows the schematic diagram of the experimental system's three units: inlet flue gas simulation, photocatalytic reactor, and outlet gas analysis and treatment, corresponding to parts 1–6, 7–14, and 15–17. The inlet gas consisted of four streams, i.e., nitrogen (1a), nitric oxide (1b), sulfur dioxide (1c), and oxygen (1d) (Beiyang Special Institute Co. LTD, Beijing, China), controlled by a mass flow controller (2, MFC, Model. FMA 5400/5500, Omega Engineering, Inc., Stamford, CT). The inlet gas was then mixed with water steam produced by the high pressure water pump and boiler (3 and 5, 100PSI DC 12 V 5 L/min, Shenzhen) to obtain the simulated flue gas. The temperature was monitored with thermocouples (6) and controlled with heat tape, and the pressure was adjusted with pressure-regulating equipment (4, 7 and 8). Heat-traced stainless steel tubing (9) and fittings were employed to connect all parts of the apparatus. Downstream, the simulated flue gas entered a photocatalytic reactor (10) fabricated by the research team. A linear fluorescent lamp (11a, Philips, USA) used as a light source was placed vertically in the innermost photocatalytic reactor, which was covered by a cylindrical tube of fused quartz 72 mm inside diameter, 80 mm outside diameter and 1.4 m in height, respectively, and with the outside covered by a heating insulation layer (13). The power of the fluorescent lamp was 40 W, with a wavelength range from 400 nm to 650 nm. There was a 2 cm gap from the inner wall of the reactor to the outer wall of the fluorescent lamp, which was packed with supported TiO₂ photocatalyst (10). Nitrogen, as carrier gas, confines the flow rate 0.60 m³/h; accordingly, the residence time is 5.7 s. The inlet and outlet concentrations of SO₂ and NO were continuously measured using a flue gas analyzer (15, MRU Instruments Inc., Germany), respectively, and recorded (16). The removal efficiencies were calculated by

$$\eta = \frac{C_{i,in} - C_{i,out}}{C_{i,in}} \quad (E1)$$

where $C_{i,in}$ represents the concentration of NO or SO₂ at the inlet of the reactor and $C_{i,out}$ represents the concentration of NO or SO₂ at the outlet of the reactor. The exhaust gas was sent through a scrubber (17) and vented.

Download English Version:

<https://daneshyari.com/en/article/8073928>

Download Persian Version:

<https://daneshyari.com/article/8073928>

[Daneshyari.com](https://daneshyari.com)