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Effect of Fe on the photocatalytic removal of NO_x over visible light responsive Fe/TiO_2 catalysts

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ABSTRACT

We synthesized different Fe/TiO_2 catalysts and studied the influence of Fe on the structure and performance of Fe/TiO_2 as a photocatalyst to remove gaseous NO in air under visible light. The electron paramagnetic resonance results revealed that Fe ions substituted the Ti ions of TiO_2 prepared by co-precipitation and homogeneous precipitation method. More Fe ions were incorporated into the crystal lattice of TiO_2 prepared by co-precipitation method than that prepared by homogeneous precipitation method. No Fe ions were incorporated into the crystal lattice of TiO_2 prepared by conventional wet impregnation method. Furthermore, Fe doping influenced the UV–vis absorption and photoluminescence of TiO_2. The higher photocatalytic activity of Fe/TiO_2 prepared by co-precipitation method was attributed to the synergistic effects of more visible light absorption and minimum electron hole recombination caused by the Fe ions incorporated into the crystal lattice of TiO_2. Density functional theory calculations further confirmed the role of Fe on the electronic structure of TiO_2.

1. Introduction

Nitrogen oxides (NO_x), mainly produced from combustion of fossil fuels, are considered as a major contributors to atmospheric environmental problems, such as urban haze, photochemical smog, acid rain, and so on [1,2]. NO_x concentration in the atmosphere has greatly increased over the past few decades because of the increased number of coal burning, motor vehicles, and industrial emission [1]. The conventional approaches, such as selective catalytic reduction (SCR), wet scrubbing, adsorption, biofiltration, and catalytic decomposition can remove NO_x from emission sources; however, they are not economically feasible for the removal of NO at parts per billion (ppb) levels in urban environments [3,4]. Semiconductor photocatalysis, as a "green" technology, which utilize natural sunlight to purify air pollutants of low concentration at ambient conditions, has been used to remove NO_x [5–13].

Since the discovery of photocatalytic splitting of water on a titanium dioxide (TiO_2) electrode in 1972 [14], TiO_2 has long been a promising candidate for photocatalysis applications due to its strong photocatalytic oxidation performance, photostability, natural abundance, and nontoxicity [15]. However, the relatively large band gap of TiO_2 (3.0–3.2 eV) limits its application in the visible light region ($400\,nm < \lambda < 750\,nm$), which accounts for 43% of incoming solar energy [3,16]. Therefore, developing visible light-responsive photocatalysts with high efficiency and stability are desirable and has become one of the most important topics in environmental photocatalysis [17,18]. Metal/nonmetal elements doping, narrower band gap semiconductor coupling, hydrogen treatment and photosensitization with dyes have been applied to enhance the visible light activity of TiO_2 [19–27].

Metal element doping is one of the typical approaches to extend the spectral response of TiO_2 to the visible-light region. Some metal elements, such as Fe, V, Co, Mo and Cr have been employed to tune the electronic structure and enhance the photocatalytic activity of TiO_2 [21,28–32]. Among these elements, Fe has attracted special attention as the ionic radius of Fe^{3+}(0.64 Å) is similar to that of Ti^{4+}(0.68 Å), resulting in easier insertion of Fe^{3+} into the crystal structure of TiO_2 [33]. As a dopant, however, the role of Fe^{3+} is still controversial. Some authors have suggested that the detrimental effect of Fe^{3+} as a promoter increases the rate of charge recombination, while other authors have reported on the beneficial effects of Fe^{3+} in the separation of photogenerated electrons and holes and in the shift of the absorption edge into the visible-light range with the narrowing of the band gap, thus increasing photocatalytic activity [31,34,35]. It is known that the role of Fe is determined by doping levels. The solubility limit of Fe in TiO_2 is

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1.0%, with separate α-Fe_2O_3 or Fe_2TiO_5 phases forming above this limit [36]. A separate Fe_2O_3 phase is detrimental to oxygen activation and photocataltic activity [35]. Therefore, high Fe doping levels may decrease photocatalytic activity. On the other hand, surface or bulk doping may also influence the role of Fe. It is difficult for photogenerated holes or electrons trapped at bulk-doped Fe ions to migrate to the surface without recombination [37]. Experimental and theoretical computation results suggest that Fe ions on the surface may increase photocatalytic activity, while Fe ions in bulk may have a negative effect [37].

Although the state of Fe has great influence on photocatalytic activity, it has not been systematically investigated. We synthesized different Fe/TiO_2 catalysts and studied the influence of Fe on the structure and performance of Fe/TiO_2 as a photocatalyst to remove gaseous NO in air under visible light.

2. Experimental

2.1. Materials preparation

The Fe/TiO_2 catalysts were synthesized by facile co-precipitation method using $Fe(NO_3)_3{\bullet}9H_2O$ (≥98.5%) as a Fe precursor and $Ti(SO_4)_2$ (≥96%) as a Ti precursor (the molar content of Fe was 0.1%, 0.3%, 0.5%, 0.7% and 1%) and 25 wt% $NH_3{\bullet}H_2O$ as precipitator. After the pH of the mixed solution rose to 10 in the co-precipitation process, the precipitate cakes were first filtrated and washed by distilled water, and then desiccated at 100 °C for 12 h and calcined at 400 °C for 6 h under air conditions (the heating rate kept at 5 °C/min). The catalysts was signified by Fe*x*%T(*x* means the molar content of Fe). Pristine Fe_2O_3 and TiO_2 were synthesized using $Fe(NO_3)_3{\bullet}9H_2O$ and $Ti(SO_4)_2$ as precursors, respectively.

Fe0.1%T catalyst was also prepared by the homogeneous precipitation method. The aqueous solutions of $Fe(NO_3)_3{\bullet}9H_2O$ (≥98.5%) as Fe precursors and $Ti(SO_4)_2$ (≥96%) as Ti precursors were mixed with required molar ratios. Excessive urea aqueous solution was then added into the mixed solution. The solution was heated to 90 °C and held there for 12 h under vigorous stir. After filtration and washing with deionized water, the resulting precipitant was dried at 100 °C overnight and subsequently calcined at 400 °C for 6 h in air condition (the heating rate kept at 5 °C/min). The catalyst was signified as Fe0.1%T-h. We also prepared Fe0.1%T catalyst using conventional wet impregnation method for comparison. The precursor was commercial anatase (Degussa). The catalyst was signified as Fe0.1%T-i.

2.2. Catalytic measurements

The photocatalytic experiments for the removal of NO were similar to our previous work [38], and are fully described in SI. Briefly, a 500 W commercial xenon arc lamp (Beijing TrusTech Science and Technology Co., China) was used as the light source. Two optical filters were used to obtain light in the 420–700 nm range, and the integrated light intensity was 35.8 mW/cm^2 (FZ-A, radiometer, Photoelectric Instrument Factor of Beijing Normal University). The weight of the photocatalyst used for each experiment was kept at 0.05 g. The initial concentration of NO was diluted to about 400 ppb by the air stream. The desired humidity level of the NO flow was controlled at 55% by passing the nitrogen streams through a humidification chamber. The total flow rate was controlled at 1.2 $L\,min^{-1}$. The concentration of NO, NO_2 and NO_x was continuously measured by a chemiluminescence NO_x analyzer (Thermo Environmental Instruments Inc., Model 42i), which monitors NO, NO_2, and NO_x (NO_x represents NO + NO_2) with a sampling rate of 0.7 $L\,min^{-1}$.

In the data analysis, the NO conversion, NO_2 selectivity, and NO_x conversion were defined as follows:

$$\text{NO conversion} = \frac{[\text{NO}_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}}$$

$$\text{NO}_2\text{ selectivity} = \frac{[\text{NO}_2]_{\text{out}}}{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}$$

$$\text{NO}_x\text{ conversion} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}_x]_{\text{out}}}{[\text{NO}]_{\text{in}}}$$

Since NO_2 is more toxic than NO, the photocatalyst performance should be evaluated by the NO_x conversion, or the NO conversion in conjunction with the NO_2 selectivity.

2.3. Catalyst characterization

The actual ratio of Fe in Fe/TiO_2 products was detected using inductively coupled plasma optical emission spectrometer (ICP-OES).

The surface area of the catalyst was determined with a physisorption analyzer (Autosorb-1C-TCD, Quantachrome) by N_2 adsorption–desorption at 77 K. The surface area (S_{BET}) was determined by applying the Brunauer–Emmett–Teller (BET) method to the adsorption isotherm in the partial pressure range of 0.05–0.35.

The crystalline structure of the catalysts was determined by a powder X-ray diffractometer (XRD; X'Pert PRO, PANalytical, Netherlands) using Cu Kα (λ = 0.15406 nm) radiation at 40 kV and 40 mA. The data of 2θ from 20° to 80° were collected at 8°/min with the step size of 0.07°.

Raman spectra of the catalysts were recorded at room temperature on a UV resonance Raman spectrometer (UVR DLPC-DL-03), which consisted of three optional exciting lasers (244, 325, and 532 nm), a three-stage grating spectrograph, and a CCD detector cooled by liquid nitrogen. The instrument was calibrated against the Stokes Raman signal of Teflon at 1378 cm^{-1}. A 325-nm He–Cd laser was also used as an exciting source for the measurement of UV Raman. The spectra resolution was 2.0 cm^{-1}. All Raman spectra used in the paper were original and unsmoothed.

The UV–vis diffuse reflection spectra of the catalysts over the range of 200–800 nm were recorded at room temperature with a diffuse reflectance UV–vis spectrophotometer (U-3310, Hitachi), using $BaSO_4$ as reflectance standard.

The photoluminescence (PL) spectra were measured in a home-built laser induced luminescence spectrograph. The photoluminescence signal was collected with an ellipsoidal collecting mirror and focused onto a 320 mm monochromator (Jobin-Yvon Triax 320) by passing through a filter with cutoff wavelength below 360 nm. A charge-coupled device (Jobin-Yvon Spectrum One CCD 3000) was mounted at the focal plane in the exit of the monochromator to detect the luminescence signal. Prior to the experiments, the wavelength calibration of this setup was carried out with a mercury lamp. A 325-nm He–Cd laser was used as the exciting source for the measurement of photoluminescence spectra.

The X-band electron paramagnetic resonance (EPR) spectra were recorded at room temperature using a Bruker A300-10/12 EPR spectrometer.

The XANES of Fe K and Ti K edges were measured in a transmission mode at room temperature on BL-7C beam line, Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (IMSS-KEK), Japan. Fe foil, FeO, magnetite Fe_3O_4 and hematite Fe_2O_3 were used as reference samples. The storage ring was operated at 2.5 GeV with 300 mA as an average storage current. The synchrotron radiation beam line was monochromatized with a Si (1 1 1) double crystal monochromator,