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Visible-light photocatalytic denitrogenation of nitrogen-containing compound in petroleum by metastable $Bi_{20}TiO_{32}$

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ABSTRACT

Exploration of new system which selectively removes nitrogen-containing organic compounds in petroleum by photocatalytic catalysts is of great value on enriching the foundation of photocatalytic science as well as developing photocatalytic technologies in their practical applications in gasoline fuel. In this paper, tetrabutyl titanate was used as titanium source and bismuth nitrate was utilized as the source of bismuth, and $Bi_{20}TiO_{32}$ was synthesized using ultrasonic assisted impregnation method. The samples were characterized by X-ray diffraction (XRD), N_2 adsorption–desorption (BET), and X-ray photoelectron spectroscopy (XPS). To evaluate its photocatalytic denitrogenation performance, simulated gasoline feed containing a certain concentration of pyridine was used as a reference. The analysis results showed that the synthesized $Bi_{20}TiO_{32}$ was a type of tetragonal crystal system of Bi–Ti oxide in metastable phase with nanosheet at a size of about 15 nm and band gap of 2.9 eV. This system can absorb the light ranging from UV to 500 nm wavelength. Under the irradiation of visible light above 420 nm wavelength for 150 min, the conversion of pyridine by photocatalytic degradation in 50 mL simulated feed (pyridine containing 100 μg/g) using 0.05 mg the photocatalyst was up to 86.0%. The visible light removal efficiency of pyridine was directly proportional with the illumination time, and there was no noticeable oxidation degradation of the solvent.

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Introduction

The nitrogen-containing compounds (NCCs) in gasoline fuel affect the stability of products significantly, and the combustion products are likely to form acid rain [1]. With current concerns about the negative influence of nitrogen-containing compounds (NCCs) for human health, there is a pressing demand for economical and environmentally benign technology to effectively remove nitrogen-containing organic pollutants [2].

Combination of Bi_2O_3 and TiO_2 will form several crystal phases, such as $Bi_2Ti_2O_7$, $Bi_2Ti_4O_{11}$, $Bi_4Ti_3O_{12}$, $Bi_{12}TiO_{20}$, and $Bi_{20}TiO_{32}$, etc. It is reported that $Bi_2Ti_2O_7$, $Bi_4Ti_3O_{12}$, $Bi_{20}TiO_{32}$ have strong photocatalytic activities to the degradation of methyl orange in aqueous solution, which indicates that these compounds have semiconductor photocatalytic activity. The photocatalytic activity of $Bi_{20}TiO_{32}$, however, was rarely studied, because it generally exists as an intermediate in the process of preparing other phase of the bismuth titanate [3]. The hybridization between Bi 6s and O 2p states may increase the mobility of the photo-generated carriers and eliminate the recombination center [4]. This unique crystal structure is also responsible for the high photocatalytic activity of bismuth-based mixed oxides, making them promising sunlight-driven photocatalyst candidates for the degradation of aqueous organic pollutants [5].

In the present paper, we used the above synthesized bismuth-based oxides to degrade the remaining nitrogen-containing organic pollutants in a simulated gasoline feed. The prepared $Bi_{20}TiO_{32}$ was well-characterized and evaluated by various influencing factors.

Experimental

Materials

Bismuth nitrate ($Bi(NO_3)_3\cdot 5H_2O$), glacial acetic acid (CH_3COOH), tetrabutyl titanium ($Ti(OC_4H_9)_4$), nitric acid (HNO_3), ethyl alcohol (C_2H_5OH), pyridine (C_5H_5N), normal octane (C_8H_{18}) were used in the sample preparation and all chemicals were analytical grade reagents. Aqueous solutions were prepared using distilled water.

Photocatalyst preparation

The $Bi_{20}TiO_{32}$ samples were prepared using a two-step synthesis route which includes sol–gel and surface impregnation methods. In the first step, titanium dioxide was prepared using a typical process, in which a solution of 10 mL ethanol, 10 mL glacial acetic acid and 10 mL water was slowly added into another solution of 10 mL tetrabutyl titanate and 40 mL ethanol with vigorously stirring. After 2 hours of continued stirring, the above solution was transferred to a water-bath with 2 mL nitric acid added. After 3 hours, a yellow semi-transparent sol was produced. The resulting semitransparent sol was then dried at 80 °C for 18 h in an oven. After TiO_2 was synthesized in the first step, the TiO_2 powders were dispersed again into a solution containing a calculated amount of bismuth nitrate (with nitric acid added to enhance the solubility of bismuth nitrate in the solution) under ultrasonic treatment for 20 min. The resulting product was sit for 1 h and dried at 100 °C for 18 h. Finally, the $Bi_{20}TiO_{32}$ powder was obtained by thermal treatment of the above material at 400 °C for 5 h in air with a heating rate of 1 °C min^{-1}.

Characterization

X-ray diffraction (XRD) spectroscopy of the samples was measured using a Philips X'Pert MPD diffractometer with Cu Kα radiation at a tube voltage of 40 kV and a tube current of 40 mA. The Kα λ of copper target was 0.154 nm, the scanning angle (2θ) was 10°–80° with a scanning speed of 2(°) min^{-1}. The sample after surface spraying with gold for 120 s was inspected by a JSM-7500F FESEM scanning electron microscope at an acceleration voltage of 30 kV and energy X-ray of 15 keV. The morphology and particle size of nanoparticles were analyzed by a FEI Tecnai 30 HRTEM. To study the absorption spectra of the photocatalysts, UV–vis diffuse reflectance spectra was analyzed using a UV–vis spectrophotometer (CARY-500, VARIAN) with an integrating sphere attachment at room temperature and $BaSO_4$ was the reflectance standard. The spectra were recorded in the range of 200–800 nm.

Photocatalytic activity measurement

The activity evaluation of the catalyst was carried out in a self-made photocatalytic reaction device [6]. In the degradation studies, 0.05 g of catalyst was dispersed in a 50 mL of simulated feed containing pyridine at an initial mass concentration of 100 μg (pyridine) g^{-1}. This suspension was continuously stirred in dark for 30 min prior to visible light irradiation. At given time intervals (every 30 min), 5 mL of suspension was sampled and centrifuged at a proper speed to separate the photocatalyst particles from the solution. The supernatant

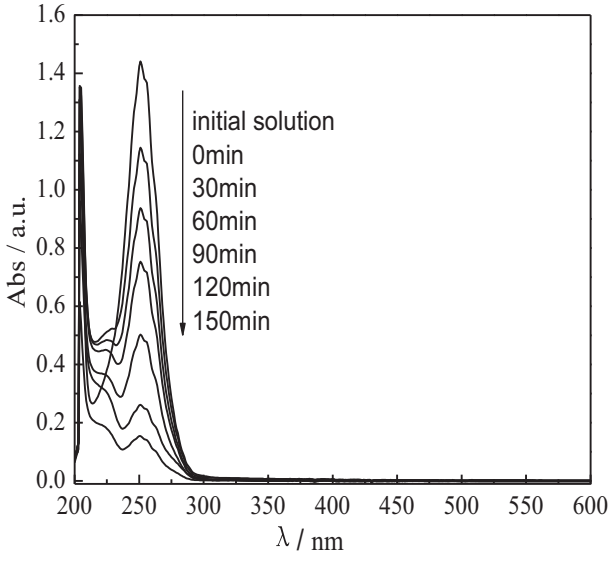

Fig. 1 – The absorbance spectra of pyridine in the presence of $Bi_{20}TiO_{32}$ under the visible light irradiation.