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Hierarchical porous $ZnWO_4$ microspheres synthesized by ultrasonic spray pyrolysis: Characterization, mechanistic and photocatalytic NO_x removal studies

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ABSTRACT

Solar-light-driven photocatalysts with porous structure are preferred for gaseous pollutants removal at low concentration levels. In this study, hierarchical porous $ZnWO_4$ microspheres were synthesized by a facile ultrasonic spray pyrolysis method for the first time. The as-prepared $ZnWO_4$ samples were composed of microspheres with diameter ranging from 0.1 to 2 μm and it was revealed that these microspheres are formed by the self-assembly of nanoparticles. The photocatalytic performances of these microspheres were evaluated by the degradation of gaseous NO_x under simulated solar light irradiation. It was found that the $ZnWO_4$ batch synthesized at 700 °C exhibited superior photocatalytic activity to those synthesized at 650 °C and 750 °C as well as Degussa TiO_2 P25. Both $^{\bullet}OH$ and $O_2^{\bullet-}$ radicals were found to be the major reactive species involved for NO_x degradation as identified by electron spin resonance spectroscopy (ESR) method, which was consistent with the theoretical analysis. The excellent catalytic activity of ZWO-700 was attributed to its special hierarchical porous structure, which facilitated the separation/diffusion of the photogenerated charge carriers and the diffusion of intermediates and final products of NO_x oxidation. The photocatalytic NO_x removal mechanism over $ZnWO_4$ samples was also proposed. This study suggests that ultrasonic spray pyrolysis is a facile and scalable process to fabricate $ZnWO_4$ porous microspheres which are promising photocatalytic materials for gaseous pollutants purification.

1. Introduction

Nitrogen oxides (NO_x, the sum of NO and NO_2) are mainly emitted from combustion-related processes, and are one of the most important precursors for secondary organic aerosols (SOAs) formation which contribute 22–77% of the $PM_{2.5}$ mass concentrations in China during serious haze episode [1]. Therefore, it is essential to control and reduce NO_x concentrations to mitigate the air pollution problems in China. Various techniques have been developed for NO_x abatement, including selective catalytic and non-catalytic reduction [2,3], three-way catalysis [4], wet scrubbing and biofiltration [5,6], and adsorption [7]. However, most of these approaches have been hindered in application because they either need high temperature to initiate the catalytic conversion reactions or cause secondary pollution. Hence, novel and practical strategies for reducing atmospheric NO_x to levels that could improve the environment are urgently needed.

Photocatalysis is an effective and promising technique for environmental NO_x removal at ambient temperature, and it has attracted considerable attention in the past few decades [8]. $ZnWO_4$, with a wolframite structure, is one of the most important metal tungstates that has high potential applications in various fields as well as utilized for photocatalytic degradation of organic pollutants [9–13]. As it is well known, the crystallinity,

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dimensions and morphology of photocatalysts are crucial to improve their catalytic performance [14,15]. Therefore, to enhance the photocatalytic activity of $ZnWO_4$, various methodologies including conventional solid-state reactions, microwave-assisted precipitation, and hydro/solvothermal methods have been adopted to prepare $ZnWO_4$ photocatalysts with different microstructures and tunable properties [10,11,14,16–20]. For example, $ZnWO_4$ nanoparticles and nanorods were successfully synthesized via kinetic and thermodynamic control processes by hydrothermal method, and it was demonstrated that the perfect crystallinity of $ZnWO_4$ nanorods can enhance the photocatalytic activity [10]. $ZnWO_4$ with cubic morphology [16], nanocrystals [21], yolk-shell microspheres [20], nanorods with different aspect ratio [22] were also synthesized for photocatalysis application in recent years. The effects of morphology on the photocatalytic activity of $ZnWO_4$ are also discussed in several studies. Photocatalysts with porous structures could possess high surface areas to facilitate the mass transfer of reactants, which is crucial for the efficient elimination of gaseous pollutants at low concentration levels [23]. However, there was no reported study about porous structured $ZnWO_4$ fabrication and application in photocatalysis for air purification.

Ultrasonic spray pyrolysis (USP) method is a low-cost and environmentally benign process, which has been used to synthesize various nanostructured materials, such as mesoporous nickel ferrites [24], hollow $BiFeO_3$ microspheres [25], and amorphous metal oxide catalysts [26]. In our previous studies, we adopted USP to fabricated a series of microsphere photocatalysts, including core-shell microspherical Ti_{1-x} Zr_xO_2 solid solutions [27], B-Ni-codoped TiO_2 solid and hollow microspheres [28], Bi_2WO_6 [29], and $PbWO_4$ [23]. Compared with other conventional methods for fabrication of porous structured catalysts, USP is a template-free method which can produce products with high purity. Most recently, Overcash and coworkers reported the fabrication of high surface area iron oxide microspheres of different morphologies, sizes, and crystallinities via USP method [30]. Wolframite $ZnWO_4$, however, has not been previously prepared with hierarchical porous structure through USP method.

In this study, wolframite $ZnWO_4$ with porous structures were prepared using the continuous, scalable process of ultrasonic spray pyrolysis at different preparation temperature for the first time, and the photocatalytic performance of the material were evaluated by gaseous NO_x degradation under simulated solar light irradiation. The physical and chemical properties of the resulting products were fully characterized and the photocatalytic degradation mechanism of NO_x over the as-prepared porous $ZnWO_4$ was elucidated in detail.

2. Experimental

2.1. Synthesis of hierarchical porous $ZnWO_4$

Zinc (II) nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), tungstic acid (H_2WO_4), and ammonia were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals used for synthesis were of analytical grade and used without further purification. Deionized water was provided by Millipore® Milli-Q water purification system (Merck Millipore, Darmstadt, Germany). Hierarchical $ZnWO_4$ samples with porous structures were synthesized through ultrasonic spray pyrolysis (USP) method. For the preparation of $ZnWO_4$ microspheres, 10 mmol of zinc nitrate ($Zn(NO_3)_2$) and 10 mmol of tungstic acid were first dissolved in 10 mL of deionized water and 10 mL of concentrated ammonia solution, respectively. Subsequently, the tungstic acid/ammonia solution was added into the $Zn(NO_3)_2$ aqueous solution and stirred for about half an hour. Finally, the mixed solution was diluted to 100 mL with deionized water. The aqueous solution was nebulized using an ultrasonic nebulizer at 1.7 MHz ± 10% (YUYUE 402AI, Shanghai, China). Aerosol droplets generated were carried through a tube furnace at 700 °C (OTF-1200X, Hefei, China) by an air flow. $ZnWO_4$ microspheres were also prepared at 650 °C and 750 °C under other identical conditions with the sample at 700 °C. The $ZnWO_4$ products were collected by percolators at the end of the tube furnace. The obtained products were washed with ethanol and deionized water several times, and then dried at 70 °C in air. The resulting $ZnWO_4$ product obtained from USP at finance temperature of 650 °C, 700 °C, and 750 °C was denoted as ZWO-650, ZWO-700, and ZWO-750, respectively.

2.2. Characterization

The crystalline structure of the as-prepared $ZnWO_4$ samples was characterized through X-ray powder diffraction (XRD; PANanalytical, X'pert, Almelo, the Netherlands) using a Cu Kα radiation source (λ = 1.5406 Å) at a scanning rate of 0.04° 2θ/s in the 2θ range of 10°–80°. The morphology of the samples was investigated through field-emission scanning electron microscopy (FE-SEM; JEOL Model JSM-6700F, Tokyo, Japan). The transmission electron microscopy study (TEM; JEOL Model JEM-2100HR) was performed on a JEOL JEM-2100HR electron microscopy instrument. The samples for TEM were prepared by dispersing the $ZnWO_4$ powders in ethanol, followed by dropping onto carbon-coated copper grids. A Varian Cary 100 Scan UV–vis system equipped with a labsphere diffuse reflectance accessory was used to obtain the reflectance spectra of the catalysts over a range of 200–800 nm. Labsphere USRS-99-010 was employed as a reflectance standard. The spectra were converted from reflection to absorbance by the Kubelka–Munk method. Photoluminescence (PL; F-7000, Hitachi, Japan) was used to investigate the optical properties of the as-prepared samples. The Brunauer–Emmett–Teller (BET) surface area and pore structure of $ZnWO_4$ samples were obtained from N_2 adsorption/desorption isotherms at 77 K by using an ASAP 2020 automatic analyzer (Micromeritics Instrument Corp., Norcross, GA, USA). The samples for electron spin-resonance spectroscopy (ESR; ER200-SRC, Bruker, Germany) were prepared by mixing 0.05 g of the as-prepared photocatalyst in a 25 mM 5,5′-dimethyl-1-pirroline-N-oxide (DMPO) solution with a 50 mL aqueous dispersion for DMPO–•OH or a 50 mL methanol dispersion for DMPO–$^{\bullet}O_2^-$, respectively, under irradiation with 254 nm ultraviolet (UV) light. After the photocatalytic activity test was completed, the intermediate and final products (nitrate and nitrite ions) remaining on the catalyst powders were extracted by immersing the powders into deionized water (6 mL) and measured with a Dionex-600 Ion Chromatograph (Dionex Inc., Sunny-vale, CA, USA) equipped with an IonPac AS14A column. The mobile phase was composed of a mixture of 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ at a flow rate of 1.20 mL min^{-1}, and the injected sample volume was 20 μL. The detection limit for NO_2^- and NO_3^- is 15 mg L^{-1}.

2.3. Photocatalytic activity test

The photocatalytic activity of $ZnWO_4$ microspheres was investigated by degradation of NO at ppb levels in a continuous flow reactor at ambient temperature under simulated solar-light irradiation. The reaction chamber was made of a rectangular stainless steel vessel (30 cm L × 15 cm W × 10 cm H) and covered with a quartz window. The simulated solar-light, which supplied by a 300 W Xenon lamp with the wavelength range from 200 to 1100 nm (Perfect Light MICROSOLAR 300, Beijing, China) and the spectral composition of the light source is shown in Fig. S1. The light beam vertically passed through the quartz window. For each photocatalytic activity test experiment, one sample dish (with a diameter of 12 cm) containing the photocatalyst powders was placed in the