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Effects of catalyst characters on the photocatalytic activity and process of NiO nanoparticles in the degradation of methylene blue

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ABSTRACT

By a hydrothermal method combining a subsequent calcination process, series of nano-scale NiO samples with different morphologies and sizes were synthesized and characterized. The effects of synthesis conditions including using different alkali reactants and being calcined at different temperatures on the characters of NiO samples have been investigated. In these characters the integrality of crystal structure and the crystallinity of NiO were found to become the determinative factors which affect the photocatalytic activity and process of NiO catalyst in the degradation of methylene blue (MB). The NiO sample which has a good crystallinity and small particle size ($\leq$100 nm) possesses more shallowly trapped holes to react with chemisorbed oxhydryl OH^- or H_2O to generate $OH^\bullet$ radicals, exhibiting a high photocatalytic activity, furthermore, in this UV/NiO suspension the photocatalytic oxidation process of MB occurrs via the attack by $OH^\bullet$ radicals. The NiO sample which has a higher crystallinity and bigger particle size (>200 nm) possesses more deeply trapped holes (h^+_{vb}) to react directly with physisorbed organism, exhibiting a low photocatalytic activity, therefore, in this system the MB is oxidized by direct reacting with holes (h^+_{vb}).

1. Introduction

In the past two decades, photocatalytic degradation organic pollutant by semiconductor oxide such as TiO_2, ZnO, NiO, SnO_2, Cu_2O, and In_2O_3 has attracted public concern due to their high photocatalytic efficiency, low cost and low toxicity, high physical and chemical stability, especially, strong ability of fully decomposing organic pollutant into harmless species (e.g. CO_2, H_2O, etc.) [1–6]. The photocatalytic degradation mechanism of organic pollutant has been widely demonstrated that when the semiconductor oxide is illuminated with UV or visible light, an electron excites out of its energy level to the conduction band and consequently leaves a hole in the valence band to give a electron (e^-)–hole (h^+) pair. The potential of hole (h^+) is positive enough to react with the adsorbed OH^- or H_2O on oxide surface to generate hydroxyl radicals ($^\bullet OH$), and the potential of electron (e^-) is negative enough to reduce molecular oxygen into superoxide ion ($^\bullet O_2{}^-$). These active species have capable to degrade toxic compounds into harmless species. Synchronously, the holes (h^+) and electrons (e^-) rapidly recombine each other, inducing the decrease of photocatalytic activity [7–9].

In these semiconductor oxides TiO_2 as a photocatalyst has been widely investigated. NiO is also used as a photocatalyst to decompose organic pollutant. Some studies have attempted to exploit NiO for the capability of efficiently using solar light or visible light [10–12]. Other studies attempted to extend the probability of electron–hole separation to enhance the photocatalytic activity by composing a p–n junction heterogeneous NiO catalyst [13–15]. It has been known that preparation methods of photocatalyst as well as post-treatment conditions strongly affect the characters of catalyst and the photocatalytic performance in the degradation of organic pollutant. In the characters of catalyst, such as morphology and surface peculiarity, particle size, specific surface area, crystallinity and crystal quality, and optical property, which one is a determinative factor in the degradation of organic pollutant and how to affect on photocatalytic activity and mechanism become our concerned issues. To the best of our knowledge, there are few detailed investigations about the effects of catalyst characters on the photocatalytic activity and process of NiO catalyst in the degradation of organic dye.

In present work, for the purpose of obtaining series of NiO catalysts with different morphologies and sizes we chose four kinds of alkalis (namely sodium hydroxide NaOH, ammonia solution $NH_3{\cdot}H_2O$, urea $CO(NH_2)_2$, and triethanolamine $N(CH_2CH_2OH)_3$) to react with nickel nitrate $Ni(NO_3)_2$ to obtain NiO precursors and calcined the precursors at various temperatures to obtain NiO samlpes

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with different characters. With the help of SEM, XRD, BET, UV–vis, and PL analysis techniques, the effects of synthesis conditions on the characters of NiO samples were investigated. As a pholocatalyst in the degradation of methylene blue under UV-light irradiation, the effects of catalyst characters on the photocatalytic activity and degradation process of organism have been discussed extensively and the results possibly guid the purposive synthesis of catalyst.

2. Materials and experimental methods

2.1. Raw materials

The analytical reagents, nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$], sodium hydroxide (NaOH), ammonia solution ($NH_3 \cdot H_2O$), urea [$CO(NH_2)_2$], and triethanolamine [$N(CH_2CH_2OH)_3$] were purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China). Methylene blue (MB, ≥98.5%) and silver nitrate ($AgNO_3$, A.R.) were purchased from Tianjin Fine Chemical Development Centre (Tianjin, China). Methanol (MeOH) and anhydrous acetonitrile (CH_3CN) are of HPLC grade quality and purchased from Aladdin's Reagent Company Limited (Shanghai, China). All the chemicals in this study were used directly without further purification.

2.2. Synthesis of NiO nano-catalyst

By a hydrothermal process combining subsequent calcination the NiO catalysts were synthesized through the reactions of nickel nitrate with one of four kinds of alkalis, namely NaOH, $NH_3 \cdot H_2O$, $CO(NH_2)_2$, and $N(CH_2CH_2OH)_3$, respectively. Typically, 80 mL of 1.2 mol L^{-1} alkali solution was slowly added into 80 mL of 0.6 mol L^{-1} $Ni(NO_3)_2$ solution at room temperature under stirring magnetically, afterwards the pH of cloudy suspension was adjusted to 8.0 by using HNO_3 or NaOH solution. The suspension was transferred into a 200 mL Teflon-lined stainless steel autoclave, sealed, then heated at 185 °C for 24 h in a furnace. After the reaction was complete, the steel autoclave was air-cooled down to room temperature. The resulting solid product was filtrated and washed with deionized water several times to remove the impurities. The product was dried in an oven at 80 °C for 24 h to obtain the precursor of NiO. These precursors are thermally treated at 400, 600, 800, and 1000 °C in air for 3 h, respectively, thus the NiO samples with various morphologies and particle sizes were obtained. The precursors obtained by using alkali reactants of NaOH, $NH_3 \cdot H_2O$, $CO(NH_2)_2$, and $N(CH_2CH_2OH)_3$, respectively, were named A, B, C, and D. The NiO samples obtained by calcining A∼D precursors at 400, 600, 800, and 1000 °C, respectively, were named (A∼D)400, (A∼D)600, (A∼D)800, and (A∼D)1000 NiO.

2.3. Photocatalytic activity testing

In order to evaluate the photocatalytic activity of NiO, we use methylene blue (MB) as a model contamination to characterize the photocatalytic activity and process. A 125 W low-pressure mercury lamp predominantly emitting at 254 nm wavelength (produced by Philips Electronics Ltd.) was chosen as a irradiation source because the excited energy must higher or equal to the band gap E_g of NiO (about 3.5 eV). For each condition, 0.1 g of NiO catalysts were dispersed in 100 mL of 10 mg L^{-1} MB aqueous solution in darkness for 30 min to establish the adsorption equilibrium of MB. The initial pH of solution was adjusted at 6.5 for all experiments. The 250 mL beaker containing reactive solution was placed in a water bath which maintain temperature at 35 ± 0.2 °C. The photocatalytic reaction was carried out under UV-light irradiation from a 125 W UV lamp, which was positioned vertically 16 cm awary from the liquid surface in the beaker. After given time intervals, about 2 mL suspension was withdrawn by a syringe and filtered with a micropore filter (0.45 μm pore size). The filtrate was diluted and measured the absorbance at 655 nm wavelength (the maximum absorption wavelength of MB) on a UV–vis spectrophotometer to obtain the degradation rate of MB.

2.4. Analytic technique

The morphology and size of NiO sample were obtained by a field emission scan electron microscopy (JSM-6700F, Electron Company, Japan), and the crystal structure was determined by a XRD powder diffraction instrument (AXS D8-Advance, Bruker Company, Germany). The UV–vis absorption spectrum was measured on a UV–vis spectrophotometer (UV-1700, Shimadzu Corporation, Japan). The specific surface area of NiO sample was calculated from the BET adsorption equation and measured by the accelerated surface area porosimetry instrument (ASAP2010, Micromerities Company, USA) at liquid nitrogen temperature (77.4 K). Photoluminescence spectrum of NiO sample was obtained at room temperature on a fluorescent spectrometer (FLS920, Edinburgh Instruments, UK) with a xenon lamp as an excitation source.

3. Results and discussion

3.1. Effect of synthesis condition on the characters of NiO sample

3.1.1. Phase structure and particle size of NiO sample

The SEM images of as-prepared NiO samples A600, B600, C600, and D600 are shown in Fig. 1. A600 NiO obtained by using NaOH as a alkali shows a short rod shape, and the mean diameter and length are estimated at about 29 and 80 nm, respectively. B600 NiO obtained by using $NH_3 \cdot H_2O$ as a alkali shows a wafer shape, and the mean diameter and length are estimated at about 250 and 350 nm, respectively. C600 and D600 NiO samples obtained by using $CO(NH_2)_2$ and $N(CH_2CH_2OH)_3$ as alkali reactants, respectively, show a cotton- and a flower-like shapes. These results implied that the chemical composition and base strength of alkali reactants observably affect both the compositions and morphologies of the obtained precursors, inducing the differences of as-prepared NiO samples in morphologies and sizes. In the reaction of Ni^{2+} ion with NaOH the concentration of OH^- in local region was correspondingly high due to the complete dissociation of NaOH, the crystal nucleus of the precursor [$Ni(OH)_2$] formed more rapidly and sufficiently, and the growth of $Ni(OH)_2$ crystallite was fast, then the precursor $Ni(OH)_2$ was obtained with a small size. In these NiO samples B600 exhibits the biggest particle size, good dispersity, high crystallinity, and smooth surface. When $NH_3 \cdot H_2O$ solution was droped into $Ni(NO_3)_2$ solution, the $Ni(NH_3)_6{}^{2+}$ complex ions were formed firstly, then the decomposition of $Ni(NH_3)_6{}^{2+}$ ions at 185 °C induced the formation and growth of the precursor [$Ni(OH)_2$] slowly and regularly, so the $Ni(OH)_2$ with a bigger particle size and higher crystallinity was obtained. By calcining the precursor $Ni(OH)_2$ at 600 °C the B600 NiO sample with a wafer shape was obtained. The similar phenomenon has been found in the synthesis of D600 NiO sample because of the formation of $[Ni(OH)(N(CH_2CH_2OH)_3)]^+$ complex ion in the mixed solution of Ni^{2+} ion and $N(CH_2CH_2OH)_3$ alkali. Our experiments have proved that the precursor of urea ($CO(NH_2)_2$) reacting with Ni^{2+} ion at 185 °C was basic nickel carbonate $Ni_2(CO_3)(OH)_2$ and it decomposed ceaselessly from 50 to 550 °C to form NiO sample with a cotton-like when calcined the precursor at 600 °C. The particle size of NiO sample increase with increasing calcination temperature. When the precursor was calcined up to 800 °C, the obtained NiO sample began to melt, then totally melted and agglomerated each other at 1000 °C (the SEM images not been shown).

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