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Attachment of nickel oxide nanoparticles on the surface of palygorskite nanofibers

Chengli Huo, Huaming Yang*

Research Center for Mineral Materials, Central South University, Changsha 410083, China
School of Resources Processing and Bioengineering, Central South University, Changsha 410083, China

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ABSTRACT

NiO nanoparticles were assembled on the surface of palygorskite (PAL) nanofibers to produce NiO/palygorskite (NiO/PAL) composites via electrostatic attraction. The samples were characterized by thermogravimetric–differential scanning calorimetry (TG–DSC), X-ray diffraction (XRD), Brunauer–Emmet–Teller (BET), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR). The interfacial characteristics between NiO nanoparticles and PAL nanofibers were in detail investigated. The PAL nanofibers were uniformly decorated with well-dispersed crystalline NiO nanoparticles with an average size of 8 nm. The results further indicated that the interfacial binding of NiO and PAL fiber ensured the stable composite structure of NiO/PAL. The NiO/PAL composites exhibited higher photocatalytic activity than pure NiO for methyl orange photodegradation under UV-light. The as-synthesized nanocomposites showed an interesting potential application in the environmental fields.

1. Introduction

Over the past few years, great interest has been focused on the synthesis of nanosized transition metal oxides because of their extraordinary properties based on size-quantization effect and large surface area [1]. Nickel oxide (NiO), a wide band gap *p*-type semiconductor, has been extensively investigated due to its chemical and magnetic properties. There were numerous attractive applications of NiO in a variety of fields including catalysts [2], gas sensors [3], dye-sensitized solar cell [4,5], lithium ion battery [6], supercapacitor electrodes [7], and so on. Recently, NiO showed excellent resistive switching behavior and could be expected to find potential use in nonvolatile memorles [8,9]. In addition, nanocrystalline NiO with high surface area possessed better properties than that with low surface area. Therefore, it was worthwhile to synthesize NiO nanoparticles with precise control of the size and distribution in nanometer regime using a facile preparation process [10].

Until now, various synthesis routes have been developed to achieve nanostructured NiO, including sol–gel, solution-based chemical route, vapor transport growth, wet-chemical method, electrochemical deposition, and thermal decomposition of either nickel salts or nickel hydroxides [11]. Recently, there were reports about the successful synthesis of nanosized NiO via metal-etching oxidation [12], low temperature thermal oxidation [13], and fibrinogen template method [14].

Meanwhile, many efforts have also been focused on the effective control of NiO particle size and shape, such as single-crystalline nanowire arrays [12], nanotubes [13], hollow nanospheres [15,16], nanosheets [11], films [17], ordered mesoporous solids [18], and other morphologies [19]. The advent of nanostructured support materials such as carbon nanofibers, carbon nanotubes, nano-fibriform silica, and ordered mesoporous silica has provided opportunities for the novel supported metal oxide catalysts, which were indispensable for energy and chemical industries to reduce consumption of raw materials and to minimize the production of waste [20]. According to the previous reported results, control over the preparation of supported metal oxide catalysts was necessary to enhance their key properties as activity, selectivity, and thermal stability due to the well-dispersed particles and possible synergetic effect [21].

Natural clays were environmental friendly materials with crystalline structures and relatively large surface areas, which can be used as catalyst supports [22,23]. Palygorskite (PAL), a species of hydrated magnesium aluminum silicate clay mineral under the 2:1 layer composition, was characterized by a porous structure with commonly a lath or fibrous morphology. Due to its unique structure and considerable textural properties, such as high specific surface area and high adsorption capacity, natural PAL clay has been widely used as an adsorbent, catalyst, and catalyst support [24]. So far, various metals and metal oxides have been anchored onto the surface of PAL clay fibers to prepare composite catalysts, and the results demonstrated that the synthesized

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* Corresponding author at: Research Center for Mineral Materials, Central South University, Changsha 410083, China. Fax: +86 731 8871 0804.

E-mail address: hmyang@csu.edu.cn (H. Yang).

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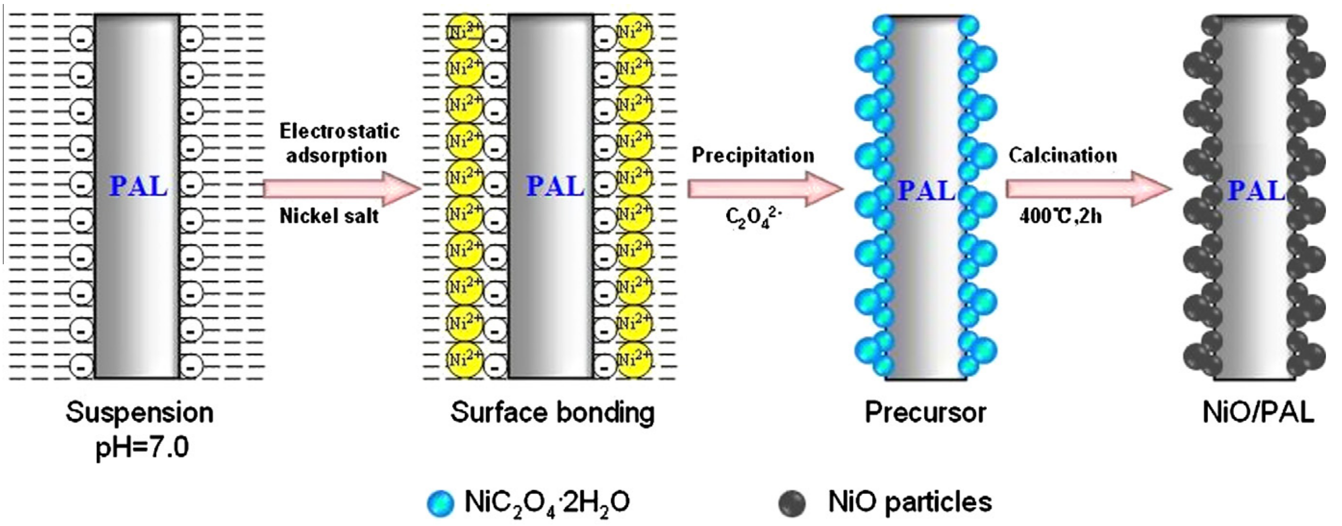

Fig. 1. Schematic illustration of the synthesis process of NiO/PAL composites.

composite catalysts showed the enhanced activity with the PAL clay as support [25–27].

This paper focused on the use of environmental-friendly natural clay fibers with a high specific surface area as support material while using adsorption precipitation for the preparation of supported nickel oxide composites. An illustration of the process for preparing NiO-decorated PAL nanofibers was shown in Fig. 1. Firstly, the natural PAL fibers were activated with HCl to provide a higher surface activity and a stronger ability to combine with secondary phases, simultaneously functionalized the surface of PAL with –OH groups and equipped more negative charge, which facilitated the adsorption of Ni^{2+} by electrostatic attraction. The NiO/PAL composite was synthesized by calcination of the precursor, which was obtained using an adsorption precipitation on the surface of PAL nanofibers. We hope that the combination of nickel oxide nanoparticles and PAL nanofibers can reduce the agglomeration of NiO particles and thus increase the specific surface area and number of reactive sites, with a corresponding improvement in photocatalytic activity.

2. Experimental

Palygorskite (PAL) clay used in this work was obtained from Jiangsu, China. The PAL clay was first activated using 3 M hydrochloric acid at 110 °C for 2 h to improve proton acidity, followed by washing with distilled water until the pH reached 7.0. The acid-activated PAL clay was selected as support in this experiment. In a typical synthesis, the acid-activated PAL was dispersed in a 150 mL 0.026 g/mL $Ni(NO_3)_2$ alcohol–water mixed solution at room temperature for 2 h. Because of the electrostatic attraction, the Ni^{2+} cation can be adsorbed onto the surface of PAL clay fibers. Then, 50 mL alcohol solution that dissolved in 3.28 g oxalic acid was slowly added into the above mixture under continuous stirring to form the precursor solution and kept stirring at 400 rpm for 2 h. Subsequently, the precursor was obtained by vacuum filtration and dried at 60 °C for 4 h. Finally, the obtained catalyst was denoted as NiO/PAL after it has been calcined at 400 °C for 2 h. For comparison, NiO nanoparticles was prepared by the same method and calcined at 400 °C for 2 h.

Thermogravimetry–differential scanning calorimetry (TG–DSC) was performed in air using a TA SDT Q600 thermal analyzer from 20 °C to 800 °C at a heating rate of 10 °C/min. X-ray diffraction (XRD) patterns were recorded on a D8 Advance Bruker diffractometer using Cu Kα radiation (λ = 1.5406 Å). The morphology of the products was observed with a Transmission Electron Microscopy (TEM, JEOL JEM-2100F), fitted with an EDAX data analyzer, using 200 kV accelerating voltage. FTIR spectra of the samples were collected on a Nicolet Nexus 670 FTIR spectrometer using KBr disks in the range of 4000–400 cm^{-1}. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Fisher Scientific K-Alpha 1063 spectrophotometer with the Al Kα radiation. The zeta-potential of the pristine palygorskite was determined by a Zeta Meter System (Backmen–Coulter Delsa 440SX, USA) to indicate the charges at the surface of the clay mineral fibers. Specific surface area was measured at 77 K with a micromeritics (Quantachrome Autosorb-I) equipment. All samples were first dehydrated at 523 K for 4 h before analysis. The specific surface area was calculated from the nitrogen isotherms using the Brunauer–Emmet–Teller (BET) equation.

The photocatalytic activities of pure NiO nanoparticles and NiO/PAL composite were investigated by the photodegradation of methyl orange (MO). The photodegradation experiments were performed in a glass beaker at room temperature, under UV light with 2 × 15 W UV tube predominantly emitting at 365 nm. The reaction was carried out with 50 mg of catalyst dispersed in 100 mL of 25 ppm MO aqueous. The initial pH value of solution was constant at 6.5 for all experiments. Absorbance variations of MO aqueous before and after photocatalyse for different times were measured on spectrophotometer (Model: 756P, Shanghai, China). The percentage degradation ratio was calculated as follows: Degradation (%) = $(A_0–A_t)/A_0 \times 100\%$, where A_t is the absorbance of the contaminant solution at reaction time, t, and A_0 is the absorbance of the initial MO solution.

3. Results and discussion

The thermal analysis of NiO precursor/PAL composite was shown in Fig. 2. Three obvious weight-loss steps were observed according to the TG–DSC results. The weight loss of about 6% was observed below 150 °C, which was due to the removal of adsorbed water and part of zeolitic water filling tunnels. The endothermic peak between 160 and 300 °C at a maximum of 210 °C with a weight loss about 13% corresponded to the elimination of the remaining zeolitic water and crystallization water of the precursor. The sharp exothermic peak observed at 337 °C with a total weight loss of around 30% was assigned to the decomposition of