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Shape-controlled fabrication of the porous Co_3O_4 nanoflower clusters for efficient catalytic oxidation of gaseous toluene

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ABSTRACT

Co_3O_4 nanoflower clusters were fabricated by a simple low-temperature hydrothermal method. The properties of Co_3O_4 nanomaterials were comprehensively determined by combining different analytical techniques. The self-assembled Co_3O_4 nanoflower clusters had good crystallinity and porous structure. They were utilized as the catalyst for the degradation of gaseous toluene. The experimental results showed that the catalytic activity of the as-prepared Co_3O_4 nanoflower clusters was much superior to the Co_3O_4 blocks under the same reaction conditions.

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1. Introduction

There are many techniques to remove the volatile organic compounds (VOCs), which are common air pollutants to human health. These techniques include adsorption, catalytic combustion, photocatalytic degradation and physical separation. For example, Everaert et al. [1] have utilized membrane separation techniques for the separation of gases and vapors. Among the techniques, catalytic combustion of VOCs is always a hot topic investigated by many researchers. Among various VOCs, toluene is a typical gaseous pollutant difficult to remove at moderate temperature due to its chemical stability. Everaert et al. [2] studied the $V_2O_5/TiO_2/WO_3$ catalyst for removing various VOCs. They suggested chlorinated aromatics are easier to oxidize than the pure aromatics with $V_2O_5/TiO_2/WO_3$ as catalyst.

Noble metal based catalysts are traditionally used in VOCs catalytic degradation, but they are too expensive for daily use. Transition metal oxides are an important category of catalysts in many catalytic reactions and they have served as the substitute for the transitional noble catalysts. Transitional metal oxides have been demonstrated to be active and cost effective in VOCs removal as alternatives to noble metals. It has been found that such kinds of catalysts can reduce the activation energy for the catalytic oxidation [2]. Meanwhile, there is a growing potential to promote their activity with the advance in nanotechnology. It is very attractive to investigate the nanostructured transitional metal oxides for enhanced VOCs removal performance.

Co_3O_4 is a p-type magnetic semiconductor with the normal spinel structure, where O^{2-} is cubic close packed, Co^{2+} is in a tetrahedral coordination and Co^{3+} is in an octahedral coordination. The lowest Co—O bonds strength and the highest capability of the activation of molecule oxygen play crucial roles in the catalytic oxidation systems [3]. Due to its special physical and chemical properties, Co_3O_4 is widely used in magnetism [4], photovoltaics [5,6], chemical sensors [7], homogeneous catalysis [8].

Because the structure (microstructure), size, and morphology significantly influence the material properties and application, controlling the morphology of inorganic nanomaterials through proper synthetic strategy plays a central role in obtaining nanomaterials with novel properties. The morphology of Co_3O_4 based nanomaterials is diverse and experimentally available owing to the special spinel structure. The researchers have synthesized hollow nanospheres [9,10], octahedrons [11,12], nanorods [13,14], nanosheets [15,16] as well as hollow sphere clusters [17] and arrays [18] by assembling these units. Nevertheless, it is still a hot theme to fabricate the Co_3O_4 nanomaterials with different morphologies in order to promote the performance [19–22].

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Recent reports [22–24] have demonstrated that cobalt oxide is relatively superior to other similar metal oxides in catalytic degradation of toluene. Previous researchers usually used cobalt oxide as the active component loaded on molecular sieves and other supports with large surface area [25]. The large surface area of the supports can make cobalt oxide loading uniform and well dispersed, which not only exposes more cobalt active sites but also increases the contact area between the catalyst and the gaseous toluene. In addition, some researchers prepared composites by combining the cobalt oxide with other metal oxides compound to form bi-metal or multi-metal oxides [26] in order to improve the catalytic activity. This method utilized the synergy between the cobalt oxide and other metal oxides to increase the conversion rate of toluene. However, it has rarely been reported that the catalytic oxidation of toluene could be enhanced just using Co_3O_4 as the single metal oxide catalyst by controlling the particle size and morphology.

In this paper, nanoflower-shaped Co_3O_4 was fabricated by a low-temperature hydrothermal method. The influence of the preparation conditions such as the composition of the precursor (cobalt hydroxycarbonate) on the microstructure of Co_3O_4 sample has been systematically explored. Then, a series of characterization techniques were employed to study the crystal structure, surface properties and the morphologies of the as-prepared Co_3O_4 sample. Finally, the catalytic activity of the as-prepared Co_3O_4 nanoflower clusters for degrading the toxic toluene was further studied by comparing with Co_3O_4 blocks.

2. Experimental

2.1. Preparation of catalysts

Co_3O_4 was prepared by low-temperature hydrothermal method. All chemicals were of analytical grade. In a typical procedure, 2.91 g $Co(NO_3)_2{\cdot}6H_2O$, 0.6 g $CO(NH_2)_2$ and 0.25 g polyvinylpyrrolidone (PVP; MW = 30,000) were added to 100 mL distilled water under stirring for 30 min to form homogeneous solution. The obtained mixture was transferred into the stainless steel autoclaves with a Teflon liner of 120 mL in capacity, which was then heated in an oven at 95 °C for 12 h. After the autoclave was air-cooled to room temperature, the black products were collected and washed with distilled water and absolute ethanol for several times by a centrifugation–redispersion process, followed by drying under vacuum at 60 °C. The as-prepared powder was converted into Co_3O_4 via thermal decomposition at 300 °C for 5 h in air with a ramping rate of 10 °C/min.

2.2. Characterization

The X-ray powder diffraction (XRD) pattern was recorded on a Rigaku D/max X-ray diffractometer (Cu Kα radiation, λ = 0.15418 nm), and the scanning range was 10–70°. The JEOL JSM-6360LV scanning electron microscope (SEM) was used to study the size and morphology of nanomaterials. A small amount of sample was placed in a carbon-coated grid and subjected to the measurements on JEM 2100 transmission electron microscopy (TEM). Hydrogen temperature programmed reduction (H_2-TPR) was carried out in a Quantachrome Chem-BET Pulsar TPR (p/n 02139-1). The band gap of the Co_3O_4 was determined by UV–vis spectroscopy, using a UV-1100 spectrometer. The N_2 adsorption–desorption isotherm was recorded at 77 K using a Quantachrome NOVA instrument. Before the measurement, the sample was degassed at 300 °C for 4 h. The specific surface area was calculated by multipoint Braunauer–Emmett–Teller (BET) analysis of the nitrogen desorption isotherm. The Raman spectrum was taken using a micro-Raman/Photo-luminescence system with 632 nm wavelength laser. Electronic paramagnetic resonance (EPR) experiments were performed with a klystron operating in the X band (ν = 9.5 GHz) as microwaves generator. The data of Fourier transform infrared spectroscopy (FTIR) were recorded on a BRUKER VERTEX 70 spectrometer from 400 to 4000 cm^{-1} at room temperature on KBr mulls. X-ray photoelectron spectra (XPS) data was recorded by a Multilab 2000 electron spectrometer using acrochromatic Al Kα radiation (1486.6 eV).

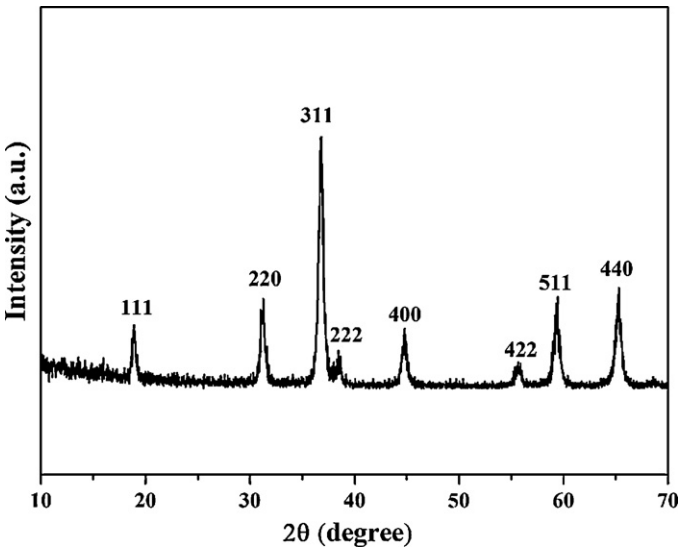

Fig. 1. XRD pattern of the as-prepared Co_3O_4 sample.

2.3. Catalytic oxidation performance

Complete oxidation of toluene was performed in a fixed bed continuous flow quartz micro-reactor under atmospheric pressure using Agilent 7890 A gas chromatograph (GC). 0.2 g (60–80 mesh) catalysts were subjected to tableting, crushing and screening and then put in the reaction tube. Before reaction, the catalysts were pretreated with O_2/Ar (33 mL/min) at 300 °C for 1 h. The reactor space velocity was 37,500 h^{-1}. Ar was employed as the carrier gas at the rate of 50 mL/min to the pure toluene in liquid phase, which was cooled by the ice water bath. The initial concentration of gaseous toluene was about 1000 ppm by detection. The inlet flow was a mixture of Ar with toluene (50 mL/min) and O_2/Ar (33 mL/min). The effluents from the reactor were analyzed with a flame ionization detector (FID) and TCD detector. The temperature range was set at 125–300 °C.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the XRD pattern of the sample prepared by calcining the cobalt precursor at 300 °C for 5 h. All the diffraction peaks can be indexed as cubic Co_3O_4 with the lattice constant (a = 0.8084 nm), which are consistent with the values in the standard card (JCPDS Card No. 43-1003). Sharp peaks suggest the sample has a good crystallinity of pure Co_3O_4 phase. No peaks from other phases are observed in this pattern.

In the FTIR spectrum of the precursor (Fig. 2), the two peaks at 1500 and 1350 cm^{-1} correspond to the symmetric and asymmetric stretching vibrations of υ (NO_3), respectively. The bands centered at about 829 and 687 cm^{-1} are assigned to the stretching vibrations of δ (CO_3) and ρ (OCO) in the carbonate anion, respectively.