Chemical Engineering Journal 270 (2015) 309–319

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Study of the preparation of γ-Al_2O_3 nano-structured hierarchical hollow microspheres with a simple hydrothermal synthesis using methylene blue as structure directing agent and their adsorption enhancement for the dye

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HIGHLIGHTS

- The γ-Al_2O_3 were prepared using methylene blue as structure directing agent.
- The microstructure of the prepared adsorbents can be effectively controlled.
- The mechanism of the enhanced adsorption can be explained by template synthesis.

ARTICLE INFO

Article history:
Received 17 December 2014
Received in revised form 3 February 2015
Accepted 4 February 2015
Available online 16 February 2015

Keywords:
γ-Al_2O_3
Structure directing agent
Methylene blue
Adsorption property
Hydrothermal synthesis

ABSTRACT

The γ-Al_2O_3 nano-structured hierarchical hollow microspheres were prepared with a simple hydrothermal synthesis using methylene blue as structure directing agent and the structure directing agent was removed after the γ-Al_2O_3 samples were calcinated at 600 °C for 2 h. The microstructural and properties of the prepared γ-Al_2O_3 samples were characterized by X-ray diffraction (XRD), TEM, BET, FT-IR. The static adsorption of γ-Al_2O_3 for methylene blue was conducted. The results showed that when 20 mg (the molar ratio of Al^{3+} to structure directing agent was 56:1) of structure directing agent was used, the γ-Al_2O_3 samples were prepared with that the specific surface area increased by 31% and the maximum adsorption capacity for methylene blue was 8.38 mg/g, increased by 61%.

In addition, the adsorption equilibrium isotherms model and adsorption kinetics model were investigated. The adsorption of γ-Al_2O_3 for methylene blue is best fitted with Langmuir adsorption model, the kinetic process of adsorption can be described by the pseudo-second-order kinetic model.

This study demonstrates the microstructure of γ-Al_2O_3 can be effectively controlled and the adsorption properties of it is improved using template synthesis with a proper amount of methylene blue as structure directing agent.

1. Introduction

The treatment of dye wastewater is considered to be one of the most urgent subjects in industrial water pollution control. Much dye wastewater contains organic amine compounds which is carcinogenic for humans and toxic for aquatic life [1,2]. Besides, the presence of color and turbidity of dyes can interfere with the photosynthesis of aquatic plants. Therefore, it is significant to develop an efficient way for dye wastewater treatment. Over the years, many researchers have studied on the adsorption technology for dye wastewater because of its high efficiency of pollutant removal, simplicity to use and low cost [3,4] and more attention has been paid to the search for promising adsorbents for water treatment [5,6]. The characteristic of adsorbent is affected by chemical composition [7], morphology [8], micro-structure [9], specific surface area and surface density [10,11] of particles. Recent studies mainly focus on new materials with higher adsorption capacity [12] and excellent selective adsorption ability [13].

Nanometer aluminium oxides have been widely used in various fields such as adsorbents, catalysts, composite materials [14–16], humidity sensors and optical materials [17,18] because they possess many properties such as high surface area [19], large pore volume [20] and high porosity [21]. Particularly, hydrothermal

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http://dx.doi.org/10.1016/j.cej.2015.02.020
1385-8947/

Table 1
The specific surface areas and pore characteristics of the Al_2O_3 samples.

Samples	Methylene blue (mg)	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
A	0	200.23	0.672	6.72
B	10	190.91	0.659	6.90
C	20	261.37	0.660	9.71
D	40	208.66	0.670	6.42

synthetic γ-Al_2O_3 nano-structured hierarchical hollow microspheres are promising nanometer materials for wastewater treatment due to its merits of morphology-controlled synthesis, high specific surface area [22], high purity and high activity [23,24].

The method termed template synthesis is applied to synthesize a variety of micro- and nano-materials [25–27]. The advantage of this method is the possibility to control both the macroscopic morphology and the microstructure [28,29]. The general route for templated synthesis of nanostructured materials includes the following two steps: (1) directed synthesis of target materials using the structure directing agent, and (2) structure directing agent removal [30]. The template synthesis materials are an important developing direction of adsorption materials [31]. The structure tuning and improved adsorption of the adsorption materials prepared with template synthesis in hydrothermal synthesis is a new challenge.

In this paper, we presented a simple hydrothermal synthesis of the controlled microstructure of using methylene blue as structure directing agent. The adsorption properties of the γ-Al_2O_3 nano-structured hierarchical hollow microspheres was evaluated by removal of methylene blue from aqueous solution. The effects of structure directing agent on the morphology and microstructure of the γ-Al_2O_3 nano-structured hierarchical hollow microspheres as well as its enhanced adsorption performance were investigated.

2. Material and methods

2.1. Materials and reagents

Reagents: Aluminum ammonium sulfate hydrate, trisodium citrate, urea, absolute alcohol, methylene blue, sodium hydroxide and hydrochloride were analytic grade without further purification. Deionized water was used throughout the synthesis and treatment processes.

Instruments: JEM2010 High Resolution Transmission Electron Microscopy (JEOL); D/MAX-RB rotating target X-ray diffractometer (Japanese RIGAKU company); NEXUS Fourier transform infrared spectrometer (American Thermo Nicolet company); Nova200e BET N_2 Brunauer–Emmett–Teller (American Quantachrome company).

2.2. Preparation of γ-Al_2O_3 microspheres

1.7 mg of urea and 10 mL absolute alcohol were added into a solution prepared with a certain amount of $AlNH_4(SO_4)_2{\cdot}12H_2O$ and 0.258 g of trisodium citrate dissolved in 50 mL of deionized water, followed by adding different amounts of methylene blue into the mixture.

The mixed solution was magnetically stirred for half an hour, then transferred into a 100 mL Teflon-lined stainless autoclave and heated at 180 °C for 3 h. The solution cooled to room temperature and the solid precipitate was collected by centrifugation and washed for several times with deionized water and absolute ethanol, respectively. After the washed samples was dried at 80 °C for 12 h. The γ-Al_2O_3 nano-structured hierarchical hollow microspheres were gained by the dried powders were calcined at 600 °C for 2 h.

As shown in Table 1, the Al_2O_3 samples prepared with different amount of methylene blue (0, 10, 20, 40 mg) were labeled as A, B, C and D, respectively.

2.3. Characterization methods

X-ray diffraction (XRD) patterns were performed with a Rigaku D/MAX-RB rotating target X-ray diffractometer with Cu Ka irradiation. Transmission electron microscopy (TEM) was performed by a JEM2010 (200 kV) electron microscope.

Nitrogen adsorption isotherms were measured at liquid N_2 temperature (77 K), and N_2 pressures ranging from 10^{-6} to 1.0 P/P_0 with Micromeritics ASAP 2020 nitrogen adsorption apparatus (US). Surface area was calculated according to Brunauer–Emmett–Teller (BET) method and the pore size distribution was obtained according to the Barret–Joyner–Halenda (BJH) method [32].

The Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Thermo Nicolet NEXUS Fourier transform infrared spectrometer using KBr pellets.

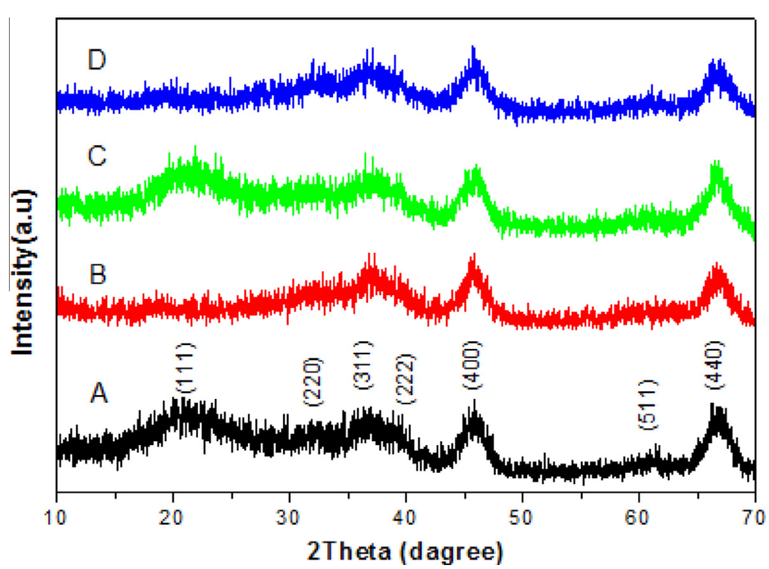

Fig. 1. XRD patterns of the Al_2O_3 samples with different structure directing agent amount.