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Magnetically separable core–shell structural γ-Fe_2O_3@Cu/Al-MCM-41 nanocomposite and its performance in heterogeneous Fenton catalysis

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HIGHLIGHTS

- A novel core–shell magnetic nanocomposite γ-Fe_2O_3@Cu/Al-MCM-41 was synthesized.
- Cu in higher amounts results in less order structure of mesoporous silica.
- Al incorporation helps to retain a high surface area and ordered mesopores.
- The catalyst displayed efficient Fenton-like catalytic activity for phenol removal.

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ABSTRACT

To target the low catalytic activity and the inconvenient separation of copper loading nanocatalysts in heterogeneous Fenton-like reaction, a core–shell structural magnetically separable catalyst, with γ-Fe_2O_3 nanoparticles as the core layer and the copper and aluminum containing MCM-41 as the shell layer, has been fabricated. The role of aluminum has been discussed by comparing the copper containing mesoporous silica with various Cu contents. Their physiochemical properties have been characterized by XRD, UV–vis, FT-IR, TEM, nitrogen physisorption and magnetite susceptibility measurements. Double content Cu incorporation results in an improved catalytic activity for phenol degradation at the given condition (40 °C, initial pH = 4), but leads to a declined BET surface area and less ordered mesophase structure. Aluminum incorporation helps to retain the high BET surface area (785.2 m^2/g) and the regular hexagonal mesoporous structure of MCM-41, which make the catalyst possess a lower copper content and even a higher catalytic activity than that with the double copper content in the absence of aluminum. The catalysts can be facilely separated by an external magnetic field for recycle usage.

1. Introduction

Cost-effective water treatment methods are urgently demanded to deal with recalcitrant organic pollutants in wastewater or surface water bodies. Compared with other advanced oxidation technology, Fenton reaction is favorable and regarded as a promising approach due to the low cost of H_2O_2 and the efficient hydroxyl radical generation [1–3]. However, the homogeneous reaction brings the notorious iron oxides precipitation and a low pH requirement for dynamically feasible reactions [4,5]. In the recent years, heterogeneous Fenton or Fenton-like catalysis has attracted increasing attention. Decomposing H_2O_2 over iron-containing heterogeneous catalysts could be an alternative technology to avoid above drawbacks in the homogeneous reaction. These catalysts include iron compounds such as α-Fe_2O_3, Fe_3O_4, green rust and $BiFeO_3$ [6–10], and iron immobilized zeolites, clays, Nafion, and carbon materials [11–15].

The rate and efficiency of H_2O_2 catalytic decomposition over catalysts is the control factor for organic pollutant removal in wastewater. Nanoparticles, inherently characterizing high surface areas, could be favorable supports to offer much more anchoring sites for the active transition metal ions, so as to result in an efficient catalytic activity for wet peroxidation [4]. MCM-41, a molecular sieve with a broad spectrum of mesopore sizes (2–10 nm) and a large specific surface area (>1000 m^2/g), has drawn considerable attention in the fields of catalysis [16,17]. By chemical interactions between the silanol groups and transition metal ions, various metal elements can be incorporated into the hexagonally arranged framework of silica and enable it to possess catalytic activity for

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Abbreviations: a_0, unit cell parameter (Å); $d(1\,0\,0)$, the interplanar spacing of (1 0 0) (Å); S_{BET}, BET specific surface area (m^2/g); K_{app}, apparent first order rate constant (min^{-1}).

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H_2O_2 decomposition. Such modified MCM-41 demonstrates to be superior to other support-based catalysts due to its excellent stability, mass transfer characteristic and easy immobility of metals. Cu/MCM-41 has been widely studied for the transformation of organic compounds with the presence of H_2O_2 [18–20]. Only in the latest, it was reported that compared to Fe/MCM-41, Cu/MCM-41 is more pH-insensitive in the Fenton reaction [21]. This suggests that as a Fenton-like catalyst it can work even in a neutral condition, and this is very important for practical applications. Normally, it could be a way to improve the catalytic activity by increasing the amount of metal ions. However, it is difficult to incorporate high content copper into the silica framework by traditional impregnation, ion-exchange and hydrothermal method. Although according to a sol–gel method [22], copper content could reach as high as 30 wt%, the mesophase structure was wrecked and the surface area was significantly decreased. Therefore, novel strategies are required to further improve the catalytic activity of Cu/MCM-41 with a low amount of copper, so as to possess unaltered mesoporous structure. The incorporation of Al into MCM-41 has been widely employed to create Brønsted acidity sites and facilitate divalent cation entering the silica skeleton [23,24]. Moreover, it was found recently that the presence of aluminum in MCM-41 framework could improve the catalytic activity of iron loading MCM-41 [8,25]. Although the mechanism on this is still requiring more effort, it could be a possible way to synthesize high active catalyst with a low content of active metal ions and an undestroyed mesoporous structure [25,26].

It is a big challenge to separate pulverous nanocatalysts from aqueous solutions for recycling in practical applications. The technology of magnetic separation, based on core–shell structural nanocomposites with superparamagnetic cores of Fe_3O_4 and γ-Fe_2O_3 nanoparticles, has found wide applications in adsorption, enzyme immobilization, drug delivery and heterogeneous catalysis [27]. With the development of assembly chemistry of multifunctional magnetic nanocomposites, heterogeneous Fenton nanocatalysts with facile recyclable magnetically separable properties becomes a popular and promising field for the scale up application in wastewater treatment [4,9–11]. In this paper, we successfully developed an efficient magnetically separable Fenton catalyst with γ-Fe_2O_3 core and Cu/Al-MCM-41 silica shell. The physicochemical properties and catalytic activity for phenol mineralization were also discussed through the comparison with the copper containing MCM-41 with different copper contents.

2. Experimental

2.1. Materials

Ferrous sulfate ($FeSO_4{\cdot}7H_2O$), cupric nitrate ($Cu(NO_3)_3{\cdot}3H_2O$), aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$) and tetraethyl orthosilicate (TEOS) were obtained commercially from Sinopharm Chemical Reagent Co. Ltd. Hydrogen peroxide (H_2O_2) and ammonia were purchased from Pinghu Chemical Reagent Factory. All chemicals used in this study were of analytical grade and used as received. All solutions were prepared with deionized water.

2.2. Syntheses of catalysts

The magnetic γ-Fe_2O_3 nanoparticles were synthesized by a previously reported method [28]. Briefly, 80 mL aqueous solution of KOH (0.5 mol/L) and KNO_3 (0.5 mol/L) was obtained. $FeSO_4$ solution (0.525 mol/L, 20 mL) was added dropwise to above solution while vigorous stirring. After a further reaction at 90 °C for 4 h under vigorous stirring, the resulting suspension was filtered, washed thoroughly and dried overnight at 80 °C. Finally, the black powder was oxidized in an oven at 180 °C for 24 h to obtain γ-Fe_2O_3 nanocrystals.

To prevent the γ-Fe_2O_3 nanocrystals from aggregation in the solution, and to offer anion positions for electrostatic self-assembling cationic surfactant molecules over the surface of the magnetic core, trisodium citrate modified γ-Fe_2O_3 nanocrystals (TFN) were prepared by treating them in trisodium citrate solution (0.5 mol/L) at 60 °C for 12 h. Magnetically separable catalysts were synthesized by a modified nano-assembling method in our previous report [11]. In a typical synthesis, 0.2 g TFN was dispersed in 60 mL absolute ethanol by ultrasonication. Meanwhile, an aqueous solution of 0.9 g cetyltrimethylammonium bromide (CTAB) in 70 mL water was prepared. Two solutions above were mixed and stirred rapidly for 1 h. Then the same molecules (2.95×10^{-4} mol) of $Cu(NO_3)_3$ and $Al(NO_3)_3$ previously dissolved in 10 mL water was added into the mixture followed by the dropwise addition of 2 mL tetraethyl orthosilicate (TEOS). After stirring for 1 h, 3.4 mL ammonia was added to the mixture to form a sol, and the suspension was kept vigorous stirring for 9 h. The products were filtered, washed and dried at 120 °C. Finally, the products were calcined at 823 K for 6 h with a rate of 1 K/min. The magnetically separable catalyst γ-Fe_2O_3@Cu/Al-MCM-41 was assigned as MSACM, in which the theoretic weight ratios of Cu and Al are 3.2 wt% and 1.4 wt% to SiO_2, respectively. The control samples of MSCM, MS2CM and MSM were prepared without the addition of $Al(NO_3)_3$, but with the same, the double amount, and none of $Cu(NO_3)_3$, respectively.

2.3. Characterization and analysis

A powder X-ray diffraction instrument (XRD, D8 Advance, Bruker-AXS, Germany, Cu K_α radiation) was employed to determine the mesoporous phases of the samples, at the range of 0.8–6° with the scanning speed of 0.5° per minute. Large diffraction angle patterns were also obtained at the range of 10–60° with a scanning speed of 5° per minute to analyze the crystal phase of catalysts. A high resolution-transmission electron microscopy (HRTEM, JEM-2100F, JEOL, Japan) was used to observe the micro-morphology of catalysts. A Nicolet 6700 Infrared-Raman Spectroscope (ThermoFisher Co., USA) was used to record FTIR spectra of samples in the range of 4000–400 cm^{-1}. BET specific surface area, pore volume and pore size distribution were obtained on a gas sorption analyzer (Micromeritics ASAP 2010 M+C, USA) at a liquid nitrogen temperature. Prior to measurement, samples were outgassed at 473 K for 3 h. The coordination environment of metal elements in the catalysts was examined by measuring their diffuse reflectance UV–vis spectra (UV/Vis Spectrometer, Lambda 950, PerkinElmer, USA), and the reflectance was converted to absorption values according to the Kubelka–Munk method. Magnetite susceptibility measurements were carried out at room temperature on a physical property measurement system (PPMS, PPMS-9T, Quantum Design, USA).

2.4. Catalytic activity

Phenol degradation in a heterogeneous suspension was carried out to assess the catalytic activity of as-prepared catalysts. In a typical test, 0.06 g catalyst was added to 60 mL phenol solution (initial concentration 80 mg/L, initial pH 4.0) in a flask (100 mL). The variation of pH value is less than 1 unit during the degradation in the unbuffered catalytic systems. The suspension containing the catalyst and phenol was kept at 40 °C in the dark for 15 min to achieve adsorption equilibrium. Then 3 mL H_2O_2 (3 wt%) was added to the suspension to start the degradation reaction. Samples were taken out at 0.5 h intervals. The supernatant solution was collected by centrifugation for TOC measurements using a TOC-V-TN analyzer (multi N/C 3000, Analytic Jena, Germany). The