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Full Length Article

Synthesis of hierarchically porous perovskite-carbon aerogel composite catalysts for the rapid degradation of fuchsin basic under microwave irradiation and an insight into probable catalytic mechanism

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ABSTRACT

3D hierarchically porous perovskites $LaFe_{0.5}M_{0.5}O_3$-CA (M = Mn, Cu) were synthesized by a two-step method using PMMA as template and supporting with carbon aerogel, which were characterized with SEM, TEM, XRD, XPS and FT-IR spectroscopy. The as-prepared composites were used in microwave (MW) catalytic degradation of fuchsin basic (FB) dye wastewater. Batch experiment results showed that the catalytic degradation of FB could be remarkably improved by coating with CA. And $LaFe_{0.5}Cu_{0.5}O_3$-CA exhibited higher catalytic performance than $LaFe_{0.5}Mn_{0.5}O_3$-CA, which had a close connection with the activity of substitution metal ion in B site of the catalysts. The FB removal fit pseudo-first-order model and the degradation rate constant increased with initial pH value and MW powder while decreases with initial FB concentration. All catalysts presented favorable recycling and stability in the repeated experiment. Radical scavenger measurements indicated that hydroxyl radicals rather than surface peroxide and hole played an important role in the catalytic process, and its quantity determined the degradation of FB. Furthermore, both Cu and Fe species were involved in the formation of active species, which were responsible to the excellent performance of the $LaFe_{0.5}Cu_{0.5}O_3$-CA/MW system. Therefore, $LaFe_{0.5}Cu_{0.5}O_3$-CA/MW showed to be a promising technology for the removal of organic pollutants in wastewater treatment applications.

1. Introduction

With the rapid growth of industrialization, the massive discharge of hazardous organic pollutants into aquatic systems has impelled extensive attention on the treatment of wastewater [1,2]. As a promising remediation for this concern, advanced oxidation processes (AOPs) using reactive radical species (such as hydroxyl and oxygen radicals) harvested directly from the treatment train as non-selective oxidant of organic pollutant, which has received enormous attention [3–6]. However, traditional AOPs technology still exist some fatal drawbacks remained to be resolved, such as the complexity of experimental equipment, dependency upon excess oxidants, requirements of high temperature and pressure, long treatment time before complete mineralization and leading to incomplete degradation during the stepwise oxidation processes [7,8]. Consequently, it is urgent and critical importance to develop new technologies or improve old processes to dispose organic pollutants efficiently and rapidly.

In recent years, microwave-induced catalytic oxidation (MICO) has been exploited as one of the most efficient AOPs. Due to the properties of internal and volumetric heating (dipole rotation and/or ionic conduction), microwave (MW) irradiation has advantages of simple reaction condition, rapid selective heating, high heating rate and improved energy efficiency [9]. It has been reported that MW irradiation through heating and non-heating effect combined with some MW-absorbing materials including conductive polymer, carbon, metals and metal oxides will be selectively heated and form active "hot spots" and reactive center, which are responsible for the enhanced degradation of organic pollutants [10].

Perovskite-type oxide with ABO_3 structure, where A and B are cations with coordination numbers 12 and 6, respectively, are shown to be effective in catalytic, energy and environmental applications [11]. Generally, perovskites have several key properties that facilitate their good catalytic activity towards oxygen reduction reaction: flexibility in the valence state of transition metals

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leading to the generation of redox couples, structural defects for oxygen excess or vacancy, high oxygen ionic conductivity, and fast kinetics of oxygen exchange [12]. Ion substitution in A or B site can result in a distortion of perovskite structure and induce B site valence transformations, therefore creating oxygen vacancies in the perovskite structure and increasing catalytic oxidation activity [13,14]. La is widely used in the A-site due to its appropriate ionic radius that enables easy construction of the cubic ABO_3 lattice [15]. Substituting B-site with a reducible early transition metal such as Co, Mn, Ni, Fe, Cu provides redox active sites that facilitates catalytic reaction. Synergistic effect, which is due to combination of two different ions at B-site leads to enhanced catalytic activity. The partial substitution of Mn in Fe-based perovskites, as an example, was observed to induce a weakening of M—O bond strength leading to a strongly catalyst activity[16]; Li et al. [17] reported that in $LaFeO_3$, Fe^{3+} partial substitution byCu^{2+} or Pd^{2+} in B-site also induced greatly improved selective redox ability.

However, the nanoscale perovskite can be easily lost during degradation, resulting in lower efficiency and stability. Meanwhile, MW energy can be transferred rapidly from the low-loss supports to the organic pollutants due to what has been broadly termed "hot-spot effects" [18]. Thus, distributing perovskites on suitable supports can present remarkable catalytic activity. Carbon aerogels (CA) with high porosity, absorbability and electrical conductivity are considered as a good catalyst support, which can act as a MW receptor together with the catalyst to promote the reaction [19]. In our previous study [20], we have confirmed that carbon xerogel supported perovskite showed the complete degradation of humic acid under MW irradiation within 10 min, suggesting it as an effective and promising catalyst in water treatment.

In addition, it is reported that catalysts containing both interconnected macoporous and mesoporous structure exhibit enhanced catalytic activity by combing the accessible mass transport pathway of macoporous tunnel with high surface area [21]. The porous materials prepared usually by templates method. For example, $SrTiO_3$ perovskite with three-dimensionally (3D) macroporous microstructure using polymethyl methacrylate (PMMA) and polystyrene (PS) microspheres as the template has been obtained by Feng et al. [22], and exhibited notably enhanced activity due to the slow photon effect. Thus, it is theoretically expected that perovskite with hierarchically porous and loaded on carbon aerogel as a MW catalysts will have dramatic catalytic activity for degradation of organic pollutants.

Therefore, in this work, we have demonstrated a two-step method for synthesis of 3D hierarchically porous$LaFe_{0.5}M_{0.5}O_3$ (M = Mn, Cu) loaded carbon aerogel composite catalyst using PMMA as template. And cellulose hydrogel was used as precursor in preparing carbon aerogel for it has a unique cross-linked 3D network, low density, large specific surface area, and mainly contains C and O elements, which is suitable for utilize as carbon template. Furthermore, being a green renewable resource, cellulose holds more advantages, such as environmental friendliness and harmlessness [23]. The $LaFe_{0.5}M_{0.5}O_3$ and $LaFe_{0.5}M_{0.5}O_3$-CA were developed for the MW induced degradation of Fuchsin Basic (FB) which is a kind of typical commercial triphenylmethane dye as a representative target compound in aqueous solution. The catalytic activities of the four catalysts were compared, the reaction condition for degradation of FB by the MICO process was optimized, active species generation mechanism in presence of catalysts under MW was explored, and the possible MW catalytic reaction mechanism was revealed. We believe that this synthetization has been found to be extremely facile and effective, and the practicability of this route will encourage water purification from environmental contamination resulting from toxic organic compounds.

2. Materials and methods

2.1. Chemicals and materials

Acrylamide (AM), ammonium persulfate (APS) and N,N′-Methylenebisacrylamide (MBA)were of analytical grade and purchased from Sigma-Aldrich. $La(NO_3)_3·6H_2O$, $Fe(NO_3)_3·9H_2O$, $Cu(NO_3)_2·3H_2O$, $Mn(NO_3)_2·4H_2O$, carboxymethyl cellulose(CMC), methanol (MeOH), polyethylene glycol (PEG, MW = 400 g/mol), triphenylmethane dye (Fuchsin Basic, FB) used in catalyst studies were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without further purification. Deionized water was used in all experiments and the pH of solution was adjusted using dilute NaOH and HCl solution.

2.2. Preparation of $LaFe_{0.5}M_{0.5}O_3$ and $LaFe_{0.5}M_{0.5}O_3$-CAcatalysts

The 3D hierarchically porous $LaFe_{0.5}M_{0.5}O_3$-CA (M = Mn, Cu) were prepared using the PMMA-templating strategy. The well-arrayed hard template PMMA microspheres with an average diameter of ca. 300 nm were synthesized according to the literature method [24].

Firstly, the stoichiometric amounts of $La(NO_3)_3·6H_2O$, $Fe(NO_3)_3·9H_2O$, and $Cu(NO_3)_2·3H_2O$ or $Mn(NO_3)_2·4H_2O$ aqueous solution were dissolved in 7.0 mL of MeOH and 3.0 mL of PEG at room temperature under sonication for 0.5 h to obtain a transparent solution. Then, 2.0 g of the PMMA template was added into the metal nitrate containing transparent solution under stirring for 5 h. After the mixture was filtered, the obtained wet PMMA template was dried in air to obtain the perovskite precursor. Meanwhile, the precursor solution of cellulose hydrogel was prepared by simply dissolving 0.3 g of carboxymethyl cellulose (CMC), 1.0 g of acrylamide (AM), 0.15 g of ammonium persulfate (APS) and 0.05 g of N,N′-Methylenebisacrylamide (MBA) in 20 mL deionized water, vigorous stirring for about 1 h simultaneously (denoted as S1). The perovskite precursor was then mixed homogenously with solution S1 to obtain the composite gel-forming solution at room temperature. Finally, the gel was freeze-dried overnight and then stored in a Teflon crucible and transferred into muffle furnace calcined in air at 600 °C for 3 h. The schematic diagram for preparation of the catalysts has been illustrated in Scheme 1.

For comparison purposes, the bulk $LaFe_{0.5}M_{0.5}O_3$ samples were also prepared by the same procedure described above except for adding the cellulose hydrogel precursor solution (S1).

2.3. Characterization of prepared catalysts

The morphologies of catalyst samples were evaluated using scanning electron microscopy (SEM, S-4800, Hitachi, Japan) operating at 5 kV and transmission electron microscopy (TEM, FEI Tecnai G20, USA) with high resolution transmission electron microscope (200 kV). Brunauer Emmett Teller (BET) surface areas, pore diameter, and pore volume of catalysts prepared were measured using an Quantachrome autosorb-iQ-2MP. The crystal structure was scanned by X-ray diffraction (XRD, Bruker D8, Germany) using Cu Kα radiation (λ = 0.1541 nm) at 40 kV and 40 mA. The chemical states and proportions of the elements on the surface of the perovskites were carried out by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, U.K.). The functional groups of samples were characterized using Fourier transform infrared spectroscope (FT-IR, Nicolet iS10, USA) in the range of 4000–400 cm^{-1} with ATR technique.

2.4. Procedure of degradation experiment

Microwave chemical reactor (MCR-3, Beilun Co. Ltd., China) was used for the MICO experiments. In each experiments, the catalysts