

Facile synthesis of manganese oxide loaded hollow silica particles and their application for methylene blue degradation

Qingnan Meng^a, Siyuan Xiang^a, Wei Cheng^a, Qiaonan Chen^a, Pengfei Xue^a, Kai Zhang^{a,*}, Hongchen Sun^b, Bai Yang^a

^aState Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, PR China

^bSchool of Stomatology, Jilin University, Changchun 130021, PR China

ARTICLE INFO

Article history:

Received 14 February 2013

Accepted 12 May 2013

Available online 31 May 2013

Keywords:

Hollow particles

Metal oxides

Soft template

Catalysis

ABSTRACT

A facile poly acrylic acid (PAA) soft templating method was developed to fabricate manganese oxide loaded hollow silica particles (MHSPs). The synthesis involves PAA-Mn aggregation to form spherical particles and silica coating layer formation on the outer surface of the particles. Subsequent calcination in air at 500 °C removes the polymer inside the particles, and hollow silica spheres with trapped metal oxide particles are thus formed. The PAA traps the Mn ions and forms aggregates which template the silica shell formation in this process. The Mn content and the structure of the MHSPs can be tuned by changing doses of the Mn salt initially added. Moreover, decomposition of PAA during calcination endows high surface areas of the MHSPs. Catalytic oxidation of methylene blue (MB) with H₂O₂ was tested on the MHSPs. The results show that the MHSPs with hollow structure and high surface areas enhance the catalytic activity compare to the corresponding manganese oxide solid particles (MSPs). This strategy can also be used to synthesize other metal oxides (such as MgO and NiO) loaded hollow silica particles.

© 2013 Elsevier Inc. All rights reserved.

1. Introduction

Manganese oxides are known to be active catalysts for numerous chemical processes such as organic synthesis [1–4], CO and NO_x removal from waste gas [5,6], dye decomposition [7–12], and water oxidation [13]. The catalytic activity of manganese oxides has been attributed to the capability of Mn to change its valence states and to store and release oxygen selectively from its various oxide crystalline lattices [2]. Up to now, great efforts have been made to enhance the catalytic performance of manganese oxides by carefully controlling their morphology and porosity [6,10,14,15]. However, the unsupported catalysts always undergo sintering during the reactions especially at elevated temperature [16]. Immobilizing manganese oxides onto an inert support seems to have more practical significance because they can hinder the aggregating and sintering of neighboring particles and expose more active sites toward the reactants [17–19].

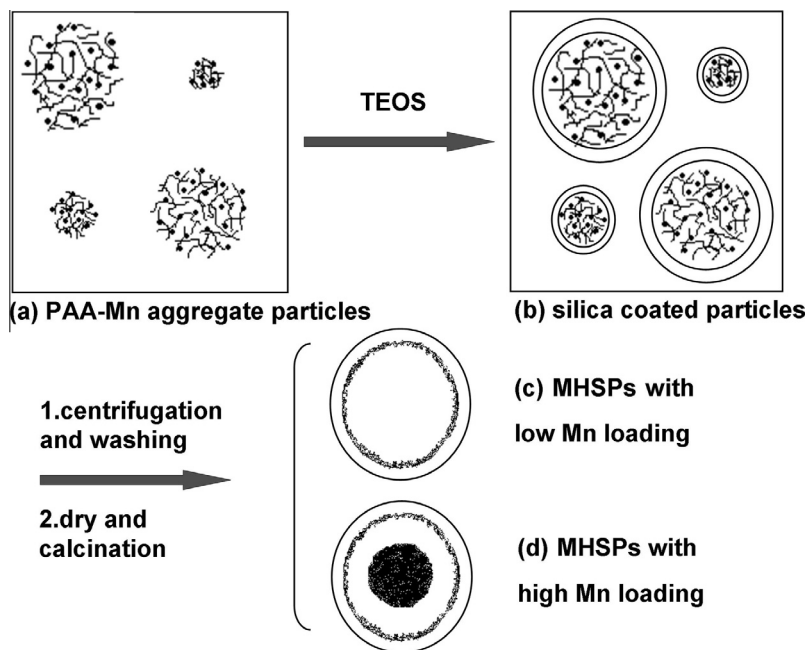
Recently, hollow silica particles are found to be promising catalyst supports due to their low toxicity, low density, and high chemical and mechanical stability [20]. The silica shell, which allows small molecules to diffuse in and out, serves as a shield for the embedded catalyst inside to be leached out during solution reactions and prevents their aggregation and sintering [21,22]. In

addition, via controlling the porosity of the silica shell with an appropriate silane coupling agent, size-selectivity toward reactants can also be improved [3,23,24]. Two strategies are commonly used to incorporate catalyst into hollow silica particles [25–33]. In the first one, hollow silica particles are prepared first and then combined either directly with the preformed catalyst (such as metal particles and enzyme) [25,26] or metal ions via impregnation, followed by converting them into a desired form (e.g., metal or metal oxide) [27–30]. Unfortunately, this method often leads to locating the catalyst outside the silica shell [28]. Moreover, the impregnation needs to be repeated several times in order to achieve the desired precursor loadings, and the catalyst often blocks the pores on the silica shell, leading to reduction in the overall surface area [29,30]. In the second one, the catalyst (always nanoparticles) is prepared first, and then, silica shell is formed outward [23,31–33]. Although the structures of the catalyst particle can be well controlled, the preparation process seems to be very tedious [32]. Multi-steps are needed for coating the catalyst particles and selectively removing of the template layer between the catalyst core and the silica shell [23].

Our interest is to develop a facile synthesis method without the drawbacks mentioned above to fabricate manganese oxide loaded hollow silica particles with high surface areas for catalysis. We employed a poly acrylic acid (PAA) soft templating method, and the synthesis process is schematically illustrated in Scheme 1. It has been reported that PAA forms aggregate particles in an

* Corresponding author. Fax: +86 431 85193423.

E-mail address: zk@jlu.edu.cn (K. Zhang).



Scheme 1. Schematic illustration of the formation of MHSPs.

ammonia–ethanol solution, which provides template for the synthesis of hollow silica particles [34,35]. In the present work, we found that PAA could chelate Mn ions and stabilize them in the ammonia solution. By dropping the solution into ethanol, we obtained PAA-Mn aggregate particles. We then coated the as-prepared particles with a layer of silica via in situ hydrolysis of TEOS. After collecting the PAA-Mn@SiO₂ particles by centrifugation and calcining them at 500 °C in air, the polymer was removed, and the trapped manganese ions were transformed into manganese oxide inside the silica shell.

Our method has the following features: (1) the metal oxides are mainly located inside the hollow silica particles. This is because the metal ions are trapped by the PAA aggregate template; (2) the metal oxide particle and the hollow structure form simultaneously; so multi-steps as in the other methods [32] are no longer needed; (3) the Mn content as well as the morphology of MHSPs can be easily tuned by changing the initial dose of the Mn salt; and (4) more importantly, the released gas molecules such as H₂O, CO₂ and CO during the PAA decomposition facilitate the porous structure formation of the MHSPs. We tested the MHSPs as catalyst for catalytic oxidation of methylene blue (MB), an important reaction for wastewater treatment [8]. The MHSPs showed superior catalytic activity than the corresponding manganese oxide solid particles (MSPs) catalyst obtained without silica shell protection and a porous Mn₃O₄ nanorod catalyst reported in the literature [10].

2. Experiment

2.1. Chemicals

Tetraethoxysilane (TEOS, 27 wt%), ammonia solution (28%), absolute ethanol (99.5%), Mg(Cl)₂·6H₂O, NiCl₂·6H₂O, and H₂O₂ were all purchased from Beijing Chemical Factory. Methylene blue trihydrate (MB·3H₂O) and Mn(CH₃COO)₂·4H₂O were purchased from Sinopharm Chemical Reagent Co. Poly (acrylic acid) (PAA, M.W. = 1800) was obtained from Aldrich. Deionized water with an electrical resistance of 18 MΩ cm was made in the lab using Millipore and used in all experiments.

2.2. Preparation of MHSPs

In a typical synthesis, a certain amount (0.1, 0.2 and 0.3 mmol) of Mn(CH₃COO)₂ was first dissolved in 0.2 mL water and then injected into 2 mL ammonia solution containing 120 mg PAA under sonication. Next, the as-prepared solution was dropped into 90 ml absolute ethanol under vigorous magnetic stirring and then continued to stir for at least 15 min to form a stable colloidal dispersion. The silica coating was performed by adding 0.75 mL of TEOS into the colloidal dispersion. The reaction was promoted by ultrasound for 2 h (40 KHz, 150 W) while keeping the reaction temperature below 35 °C by changing water in the sonicator. The silica coated particles were collected by centrifugation (8500 rpm, 15 min), washed with absolute ethanol, and sequentially dried at 60 °C. Finally, MHSPs were obtained by calcination at 500 °C for 5 h. MHSPs-*n* was used to denote the manganese oxide loaded hollow silica particles prepared with different amount of manganese acetate added in the first step (*n* = 1, 2, 3 for 0.1, 0.2, and 0.3 mmol Mn(CH₃COO)₂ added).

By changing the Mn(CH₃COO)₂ solution with Mg(Cl)₂ or NiCl₂ solution (both containing 0.2 mmol metal salt), MgO and NiO loaded hollow silica particles (MgO@HSPs and NiO@HSPs) were synthesized via the same method.

2.3. Catalytic oxidation of methylene blue (MB) with H₂O₂

The catalytic oxidation of MB with H₂O₂ was chosen as a modal reaction to test the catalytic activity of the MHSPs. The catalytic reaction was carried out in a 250 mL glass flask that contains 50 mL MB aqueous solution (100 mg/L), 50 mL distilled water, and 10 mg MHSPs. After adding 20 mL 30 wt% H₂O₂ aqueous solution, the mixture was allowed to react at 80 °C with continuous stirring. For a given time interval (10, 20 or 30 min), 1 mL of the mixture solution was taken out and put into a volumetric flask and then quickly diluted with distilled water to 25 mL for the UV–Vis measurement. And the degradation of the MB was evaluated as the method described elsewhere [8,10].

Download English Version:

<https://daneshyari.com/en/article/607630>

Download Persian Version:

<https://daneshyari.com/article/607630>

[Daneshyari.com](https://daneshyari.com)