Journal of Alloys and Compounds 585 (2014) 667–673

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Synthesis of three coordination polymer microspheres and their application in hydrogen storage

Yubiao Sun, Haojie Yu *, Li Wang *, Wenbin Ding, Jing Ji, Yongsheng Chen, Fujie Ren, Zhifei Tian, Yulai Zhao, Liang Huang, Pengfei Ren, Rongbai Tong

State Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, PR China

ARTICLE INFO

Article history:
Received 14 August 2013
Received in revised form 26 September 2013
Accepted 29 September 2013
Available online 11 October 2013

Keywords:
Coordination polymer microspheres
Hydrogen uptake capacity
Metal ions
Adsorption enthalpy

ABSTRACT

In this paper, three coordination polymer microspheres based on different metal ions have been fabricated via solvothermal method by using 1,1′-ferrocenedicarboxylic acid as organic linker. The as-synthesized samples are of high local crystalline ordering, as confirmed by powder X-ray diffraction patterns. These materials cannot only remain stable up to nearly 400 °C, but also have improved hydrogen storage capacity, reaching 1.60 wt%, 2.12 wt% and 1.22 wt% at 163 K, 5 MPa. The influence of metal ions on hydrogen uptake capacity has investigated and the corresponding adsorption enthalpy has been calculated. The comparison between these three microspheres indicates that the impact of metal ions follows the trend of $Zn^{2+} < Mn^{2+} < Co^{2+}$, which is a useful conclusion for future material design.

1. Introduction

The design and construction of coordination polymer microspheres (CPMs) is a flourishing field of research in contemporary chemistry. Generally, CPMs are made by the coordination-chemistry-induced assembly of metal ions and organic building blocks. In view of the self-assembly, the great tailorability via the wide choice of metal connectors and organic precursors makes the design of new CPMs readily. For example, Li used hydrothermal self-assembly to produce hierarchically flower-like nanospheres [1]. Moreover, Min took advantage of the self-assembly of 3-aminobenzoic acid and metal cations to get a novel material with enhanced-photoluminescence emission property [2]. According to the most recent researches, CPMs assembled for particular functions have gained growing applications in various fields, such as in electronics, magnetics, catalysis, drug delivery system, sensing, and hydrogen storage, purification and separation, nonlinear optic and lithium-ion batteries [3–13].

For many years, considerable efforts have been undertaken to generate heteropolynuclear organometallic compounds, and among them ferrocenyl coordination polymers have received great attention for their excellent electrochemical, magnetic, and optical and non-linear optical properties [14–22]. As is known, ferrocene derivatives, on the basis of the conformational flexibility of the ferrocenyl rings, tend to form coordination polymers with interesting assembled structures [23]. For instance, we had previously synthesized hollow iron-based ferrocenyl coordination polymer microspheres with microporous shell using a template-free method and discussed the Ostwald ripening mechanism of the microspheres [24]. This mechanism has also been confirmed in the fabrication of hollow ZnSe microspheres [25]. According to the previously reported papers, versatile methods have been developed to enhance gas storage capacity; for instance, Liu used nanosized Cu-MOFs to increase the material's gas adsorption capacity. Particularly, an effective method is the incorporation of coordinately unsaturated metal sites within absorbents, which can facilitate the binding of absorbents with H_2, thus an improvement in H_2 adsorption becomes available [26–28].

But up to date, there are limited research papers that unambiguously compare the roles of different coordinating metal ions on H_2 adsorption [29]. Herein we focus on designing new coordination compounds based on the same organic linker by merely varying the coordinated metal ions. Specifically, a new class of micrometer scale spherical polymers named as Mn-CPM, Co-CPM, and Zn-CPM have been constructed by taking advantage of 1,1′-ferrocenedicarboxylic acid as the organic linker. The hydrogen storage capacity of CPMs has been investigated and their isosteric heats of adsorption have been calculated. The different isosteric heats of adsorption are attributed to the kind of metal ions, indicating that the relative strength of interaction of M^{2+}–H_2 consequently leads to the variation in hydrogen storage capacity.

* Corresponding authors. Fax: +86 571 8795 1612.
E-mail addresses: hjyu@zju.edu.cn (H. Yu), opl_wl@dial.zju.edu.cn (L. Wang).

0925-8388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jallcom.2013.09.195

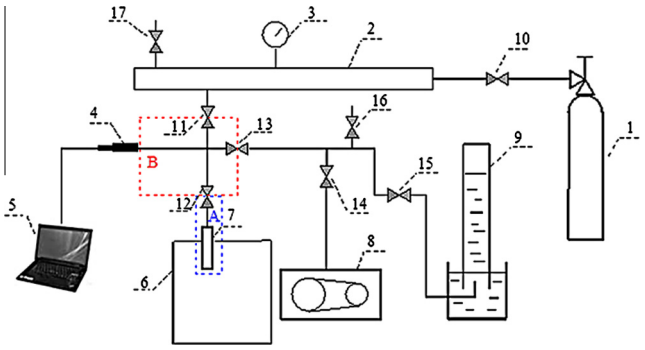

Fig. 1. Schematic representation of Sievert's apparatus for hydrogen adsorption.

2. Experimental

2.1. Chemicals

Before usage, 1,1′-ferrocenedicarboxylic acid (Shanghai Chemical reagent Co., Ltd.) was purified via dissolution in sodium hydroxide solution, filtration, precipitation with hydrochloric acid and drying under vacuum. N,N′-dimethylacetamide (DMF, Sinopharm Chemical Reagent Co., Ltd., AR) was used directly without further treatment. Other reagents and chemicals were at least analytical reagent grade.

2.2. Preparation of coordination polymer microspheres

2.2.1. Preparation of Mn-CPM

0.3981 g (2 mmol) $MnCl_2{\cdot}4H_2O$ and 0.5480 g (2 mmol) ferrocenedicarboxylic acid ($Fc(COOH)_2$) were dissolved separately in a mixture of H_2O/DMF (16 ml, 1:1, v/v). Then, these two different solutions were mixed together in a 23-mL polytetrafluoroethene bottle and then the bottle was sealed in a stainless steel autoclave. The sealed pressure bomb was heated slowly (2 °C/min) from room temperature to 120 °C in an isothermal oven, allowed to react solvothermally for 12 h yielding precipitates and then cooled to room temperature. The precipitates were collected by centrifugation, washed with DMF and $CHCl_3$ repeatedly until the upper solution became clear, and then the product was dried in a vacuum oven at 60 °C for 48 h, removing the remaining solvent.

2.2.2. Preparation of Co-CPM

0.4278 g (1.8 mmol) $CoCl_2{\cdot}4H_2O$ and 0.4938 g (2 mmol) ferrocenedicarboxylic acid were dissolved separately in a mixture of H_2O/DMF (18 ml, 1:1, v/v). The following procedures are the same to the corresponding steps in the synthesis of Mn-CPM except that the heating temperature changed to 125 °C.

2.2.3. Preparation of Zn-CPM

0.1775 g (0.6 mmol) $Zn(NO_3)_2{\cdot}6H_2O$ and 0.1653 g (0.6 mmol) ferrocenedicarboxylic acid were dissolved separately in a mixture of H_2O/DMF (16 ml, 1:1, v/v). The following procedures are the same to the corresponding steps in the synthesis of Mn-CPM except that the heating temperature changed to 180 °C.

2.3. Characterization

Scanning electron microscopy (SEM) measurements were made on a FEI SIRION-100 scanning electron microscope at an accelerating voltage of 20 kV, equipped with a GENESIS4000 energy-dispersive X-ray analyzer. The sample for SEM measurements was prepared by firstly placing a drop of microsphere suspension in absolute ethanol on a brass substrate and drying at room temperature, and then being sputter-coated with a conductive gold thin layer to improve the electrical conductivity. SEM images with ~100 particles were selected to determine the size distribution of the particles by manual counting using Nano Measurer 1.2.5 software.

Fourier transform infrared spectroscopy (FT-IR) was recorded on a JASCO FT-IR 700 spectrometer as KBr pellets in the 400–4000 cm^{-1} range.

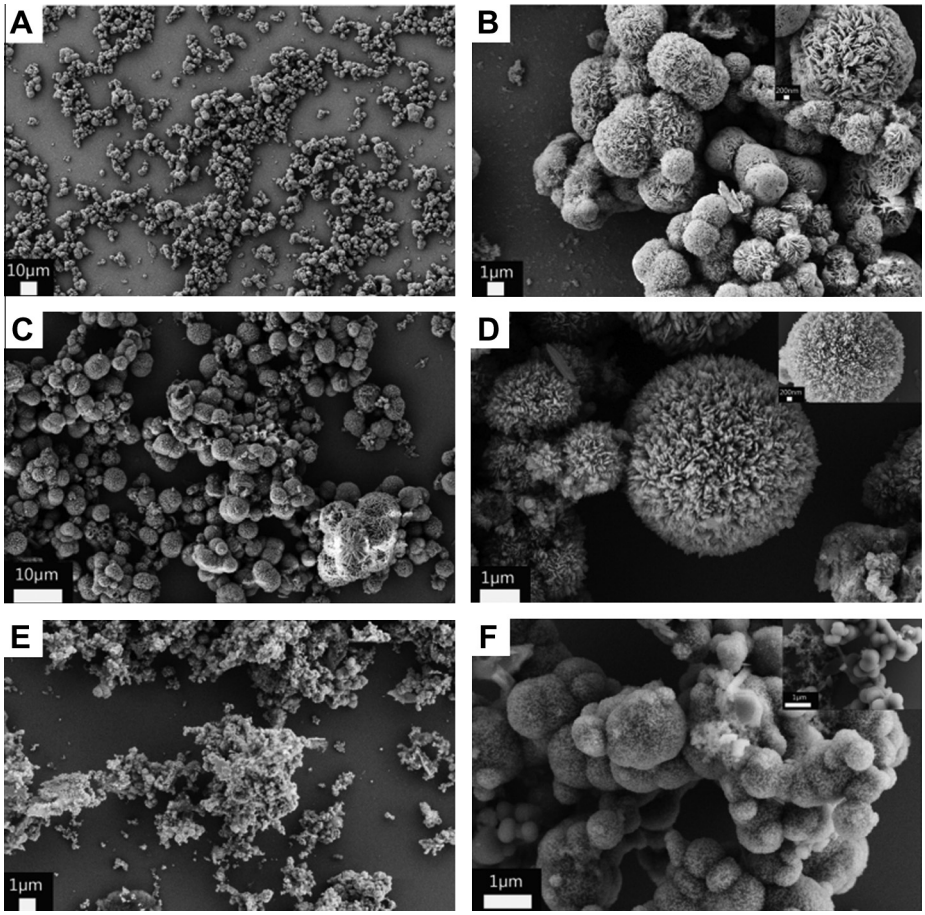

Fig. 2. SEM images of Mn-CPM, Co-CPM, and Zn-CPM. Low-magnification (A) and high-magnification (B) images of Mn-CPM (inset is a local magnification); low-magnification (C) and high-magnification (D) images of Co-CPM (inset is a local magnification); Low-magnification (E) and high-magnification (F) images of Zn-CPM (inset is a local magnification).