Applied Surface Science 256 (2010) 3031–3034

Contents lists available at ScienceDirect

Applied Surface Science

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

Preparation of cross-linked copolymer microspheres 4VP/St and cobalt tetraphenylporphyrins supported on it

Ruixin Wang, Weizhou Jiao, Baojiao Gao *

Department of Chemical engineering, North University of China, Taiyuan 030051, People's Republic of China

ARTICLE INFO

Article history:
Received 12 September 2009
Received in revised form 20 November 2009
Accepted 20 November 2009
Available online 26 November 2009

Keywords:
4-Vinylpyridine
Suspension polymerization
Cross-linked microsphere
Cobalt tetraphenylporphyrins
Immobilization

ABSTRACT

The cross-linked microspheres 4VP/St made of 4-vinylpyridine (4VP) and styrene(St) were prepared with suspension copolymerization method using ethyl glycol dimethacylate (EGDMA) as cross-linker and polyvinyl alcohol (PVA) as disperser. The cobalt tetraphenylporphyrins (CoPs) were immobilized on 4VP/St microspheres via the axial coordination reaction between CoPs and the pyridine groups of 4VP/St microspheres, resulting in the functional microspheres CoP-4VP/St. The chemical structure of 4VP/St and CoP-4VP/St were characterized with infrared spectrum and their morphologies were observed with the scanning electron microscope. The experimental results show that via controlling the various reaction conditions of the suspension copolymerization, the 4VP/St microspheres with excellent sphericity and narrow particle diameter distribution can be gained. In addition, CoPs are successfully immobilized on 4VP/St microspheres by means of Co–N bonds, on which the immobilized content of CoPs goes up to 10.7–17.5 μmol/g.

1. Introduction

4-Vinylpyridine is usually copolymerized with other monomers to obtain various functional polymer microspheres for the active pyridine functional groups. Also, the pyridine groups on polymer microspheres could be easily modified to be the hydrophilic groups, the acidic groups, alkaline groups, amphoteric groups, or join with the ligand. Thereby, the polymer microspheres with the pyridine groups have been used extensively and successfully in various applications, such as the immobilization of the enzyme [1], the supports of catalysts [2], adsorption resins [3], the supports of medicaments, and so on.

In the field of the catalytic oxidation of hydrocarbons to oxygenic compounds, much attention has recently been focused on metalloporphyrins (MPs) [4,5], which could effectively and selectively catalyze the transfer of an oxygen atom from a great variety of oxidizing agents into hydrocarbon molecules under the lower temperature. Recently, from both academic and applied point of view, the MPs immobilized on the supports, including polymers (e.g. polystyrene, chitosan, ion-exchange resin, etc. [6–8]) and the inorganic particles (e.g. silica [9,10], zeolite [11], motmorillonite [12], etc.), are significant particularly. The supported MPs would not only improve the stability of MPs and make it have the reusability, but also deal with the industrial rubbish and not pollute environment. So the supported MPs would replace the conventional MPs, which are being used in industry now.

Recently, highly cross-linked polymer resins with pendant pyridine functional groups have been reported for immobilization of ytterbium triflate and dirhodium tetracarboxylates [2,13]. The immobilization was considered to be owing to both ligand coordination and physical encapsulation. These examples led us to speculate that cross-linked microspheres 4VP/St could serve as potential supports for MPs. Herein, we describe the synthesis of a series of cross-linked poly(4-vinylpyridine/styrene) microspheres, and immobilization of MPs on these microspheres. This study is evidently significant for immobilizing MPs on the cross-linked polymer resins and preparing the heterogeneous biomimetic catalysts.

2. Experimental

2.1. Materials and instruments

4-Vinylpyridine (4VP) and styrene (St) were purchased from Aldrich and Tientsin Denfen Chemical Reagent Co. respectively, and were freshly distilled under vacuo prior to use; Azodiisobutyronitrile (AIBN, Shanghai Chemical Reagent Plant, Shanghai City, China) was of analytical purity grade and was twice recrystallized from ethanol; Cobalt tetraphenylporphyrin (CoPs) was self-synthesized according to the literature [10]; All the reagents were of analytical grade.

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* Corresponding author. Tel.: +86 351 3921414; fax: +86 351 3922118.
E-mail address: gaobaojiao@126.com (B. Gao).

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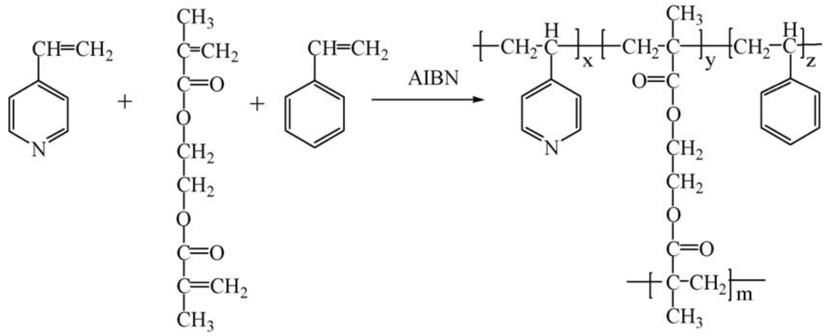
doi:10.1016/j.apsusc.2009.11.068



Scheme 1. Schematic express of process to prepare 4VP/St microspheres.

The instruments used in this study were as follows: PerkinElmer 1700 infrared spectrometer (IR, PerkinElmer Company, USA), A 438VP scanning electron microscope (SEM, LEO company, UK), Thermo SOLAAR atomic absorption spectrometer (AAS, Thermo Company, USA).

2.2. Preparation of cross-linked microspheres 4VP/St

We performed the reaction using a 250 ml round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, and a nitrogen inlet. Firstly, we dissolved poly(vinyl alcohol) (PVA, 2 g) and NaCl (5 g) into de-ionized water (100 ml) in the flask under a N_2 atmosphere, forming water phase as continuous phase. A mixture of 4VP (3 ml), St (4 ml) and EGDMA (2 ml), constituting oil phase as dispersion phase, was added to the water phase. The system was stirred sufficiently under a nitrogen atmosphere so as to fully disperse the oil phase into the water phase. After 30 min, the content was heated to 75 °C, and 0.05 g of AIBN was added. The suspension copolymerization was carried out at 75 °C for 2 h with stirring under N_2 atmosphere, and then the temperature was enhanced to 85 °C, performing the reaction for another 2 h. After the reaction, we separated the cross-linked copolymer microspheres by filtration, washed with alcohol and de-ionized water, and then we dried them to constant weight under a reduced pressure at room temperature. Finally, the transparent cross-linked microspheres 4VP/St were obtained. Their structure was characterized by FTIR and their morphology and size was examined with SEM. The process to prepare 4VP/St microspheres can be expressed schematically in Scheme 1.

2.3. Immobilization of CoPs on 4VP/St microspheres

0.2 g of 4VP/St microspheres was placed in 50 mL vial containing 0.1 g of CoPs. 30 mL of DMF solvent was added to the vial. After being tightly capped, these vials were shaken for 24 h at 30 °C. The microspheres were then washed in a Soxhlet apparatus for 10 h with $CHCl_3$ of 100 mL, in order to remove the weakly adsorbed CoPs on the microspheres. Finally, the wine-colored microspheres were dried under reduced pressure to give the functional microspheres CoP-4VP/St. The structure of CoP-4VP/St was characterized with FTIR and the immobilized content (μmol/g) of CoPs on CoP-4VP/St sample was determined by means of an atomic absorption spectrometer (AAS).

3. Results and discussion

3.1. Characterization of two microspheres

3.1.1. IR spectra

Fig. 1 gives the FTIR spectra of microspheres 4VP/St and the functional microspheres CoP-4VP/St. In the FTIR spectrum of 4VP/St, some characteristic bands that are directly related with the 4VP and St units of 4VP/St microspheres are shown: the band at 1550 cm^{-1} responds to the vibration of C=N in pyridine groups, and the bands at 1456 cm^{-1} and 1417 cm^{-1} are the absorptions of C=C in pyridine groups; the band at 1601 cm^{-1} is related to the skeletal vibration of benzene, the bands at 3024 cm^{-1}, 2910 cm^{-1} and 1502 cm^{-1} to the absorption of C–H in benzene, and the band at 698 cm^{-1} shows that the benzene is mono-substituted; the band at 1739 cm^{-1} is the absorption of ester-carbonyl in EGDMA, and the band at 1107 cm^{-1} is the vibration of C–O–C in EGDMA. In the spectrum of CoP-4VP/St, not only the main characteristic absorptions of 4VP/St have been displayed, but also the characteristic absorptions of CoPs appear clearly. The band at 1358 cm^{-1} is ascribed to the absorption of C=N bond of porphyrin ring, 1045 cm^{-1} and 996 cm^{-1} are corresponding to the absorptions of the skeletal vibration of porphyrin ring. Also, the characteristic absorptions of C=N in pyridine groups at 1550 cm^{-1} is red-shifted obviously to 1538 cm^{-1} owing to the decreased force constant of C=N bond of pyridine after the axial coordination between CoPs and microspheres 4VP/St. Moreover, the bands of 2910 cm^{-1}, 821 cm^{-1}, 758 cm^{-1} and 698 cm^{-1} are both strengthened owing to the immobilized CoPs. The above band changes reveal that CoPs have been immobilized on the 4VP/St microspheres via the axial coordination reaction of CoPs and pyridine groups, forming the functional microspheres CoP-4VP/St.

3.1.2. SEM observation

Fig. 2 displays the SEM photographs of 4VP/St and CoP-4VP/St microspheres. It can be observed that the sphericity of 4VP/St microspheres is fine and the size is almost uniform. The 4VP/St

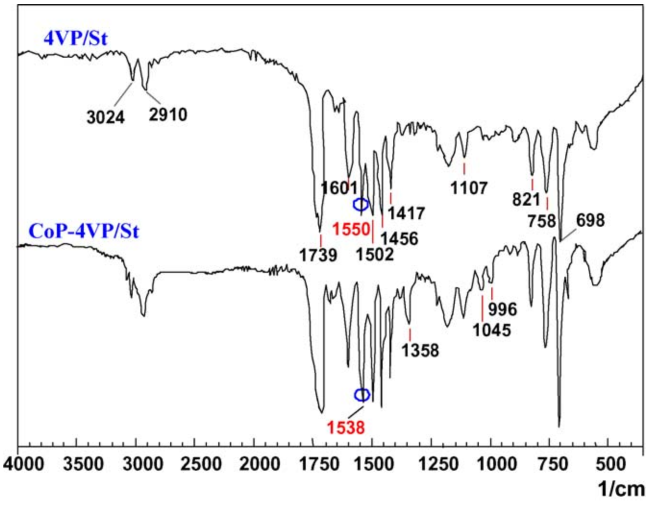


Fig. 1. FTIR spectra of 4VP/St and CoP-4VP/St microspheres.