



Preparation and catalytic property of PVDF composite membrane with polymeric spheres decorated by Pd nanoparticles in membrane pores



Zeya Wang^{a,b}, Xi Chen^{a,b,*}, Kun Li^{a,b}, Shiying Bi^{a,b}, Chenglin Wu^c, Li Chen^{a,b}

^a School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, PR China

^b State Key Laboratory of Separation Membranes and Membrane Processes, Tianjin Polytechnic University, Tianjin 300387, PR China

^c School of Pharmaceutical and Chemical Engineering, Taizhou University, Taizhou, Zhejiang Province 317000, PR China

ARTICLE INFO

Article history:

Received 12 June 2015

Received in revised form

29 July 2015

Accepted 23 August 2015

Available online 3 September 2015

Keywords:

PVDF membrane

Catalytic property

Cross-flow

Pd nanoparticle

Polymer microsphere

ABSTRACT

In this study, we prepared a novel poly(vinylidene fluoride) (PVDF) membrane with poly(methacrylic acid)(PMAA) microspheres decorated by Pd nanoparticles in membrane pores and utilized the composite membrane for the catalytic reduction of *p*-nitrophenol. First, blending PMAA microspheres with PVDF powders formed a PVDF/PMAA blend membrane with a large quantity of PMAA microspheres in membrane pores. Subsequently, immobilization of the Pd nanoparticles on PMAA microspheres resulted in the as-prepared composite membrane. The membrane was characterized by ATR-FTIR, FESEM and EDX and applied for the catalytic reduction of *p*-nitrophenol under a cross-flow model. Results indicate that the unique structure of composite membrane not only prevents the agglomeration of Pd nanoparticles, but also realizes the dream of timely separating highly purified products from reaction system without any additional process. The cross-flow model significantly enhances the accessibility of the catalytic active sites, makes the as-formed composite membrane display excellent catalytic activities for the reduction of *p*-nitrophenol to *p*-aminophenol. In a word, the novel composite membrane exhibits integrated merits of catalysis and separation, and shows a promising prospect for numerous catalytic applications.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Noble metal nanoparticles (NPs) have achieved great interests in the field of catalysis owing to their high surface area-to-volume ratios and unique surface properties compared to the corresponding bulk metals [1–3]. However, their catalytic applications still face two great challenges [4–7]. One is the high surface energy of metal NPs with diameters in the low nanometer range, which often causes the undesirable agglomeration of metal NPs, leading to a decreased catalytic activity [4,5]. The other is some surfaces of the metal nanocatalysts being covered, leading to the active sites on their surface being limitedly utilized, also causing a decrease of catalytic activity [6,7]. To prevent aggregation, the general method is immobilization of metal NPs into a suitable stabilizer such as fibrous silica nanosphere [6], halloysite nanotube [8], dendrimer [9] and graphene [10]. However, besides preparation is costly and

difficult, use and recycling are also not convenient for these stabilizers. In order to effectively utilize active sites, metal NPs are designed to be wrapped in various types of materials with porous shell constructed by silica [11,12], carbon [13–16], metal oxides [17–22], and polymers [23]. However, the pores of such porous materials are usually so small that reactants can not effectively diffuse to internal metal NPs in catalytic reactions [11]. In addition, most processes to fabricate such porous materials are complicated, time-consuming, and need strict conditions.

Porous polymeric membranes provide good prospects to overcome the above limitations, and thus are outstanding supports for metal nanocatalyst due to their excellent advantages. First, the membrane material such as PVDF is economic, readily obtained and hard to be ravaged on various conditions because of its favorable thermal stability, excellent mechanical strength, good chemical inertness, and insolubility in most organic solvents [24–27]. Second, the numerous internal pores of the membrane have a large surface area, which can provide sufficient sites to bind enormous metal NPs. Third, membrane can run continuously and recurrently because the catalyst does not need to be separated from the reaction products, and thus is more convenient for reuse and recycling than other supports [6–23]. More importantly, when

* Corresponding author at: School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, PR China and State Key Laboratory of Separation Membranes and Membrane Processes, Tianjin Polytechnic University, Tianjin 300387, PR China. Fax: +86 22 83955792.

E-mail addresses: polymerchenxi@163.com, polychenxi@gmail.com (X. Chen).

the membrane acts as reaction contactors, fluids rapidly bring the reactants to the active catalyst surface [28,29]; simultaneously, they can also constantly remove the products from the reaction zone. As a result, much faster conversion of reactants can be achieved.

Based on the above mentioned benefits, polymer membranes are considered to be ideal candidates for loading metal NPs [30–36]. However, since the general polymeric membranes such as pure PVDF membranes have no ability of stabilizing metal NPs, some researchers prepared the composite membranes by layer-by-layer adsorption of polyelectrolytes and metal NPs on the surfaces of porous membranes [30–32]. Since polyelectrolyte layers easily suffer destruction, the metal NPs maybe leak from membrane when applied for a long-time catalytic reaction [32]. In order to enhance the NPs loading, the membranes are chemically modified by complexing ligands or functional groups in advance and then retain metal ion nanoparticle precursors. Subsequently, metal NPs form in the polymeric membrane matrix by chemical reduction of metal ions [32–36]. Up to now, these methods have been successfully developed to stabilize noble metal NPs on surfaces or near surface layers of polymeric membranes [30–36].

Composite membranes with noble metal NPs in membrane pores as catalysts have a number of unique advantages. Besides metal NPs are very stable and can be long used, they also have a good resistant for fouling due to the filtration of membrane surface. When reaction is carried out by membrane catalyst, reactants can rapidly reach to and products can rapidly run off from metal NPs, contributing to a rapid conversion of them, and thus such a composite membrane favors a large-scale reaction. More importantly, due to highly enriched metal NPs in membrane pores, reactants can be directly transformed into products when they penetrate through the composite membrane. Thus, it can really realize reaction of reactants and timely separation of products under a cross-flow operation. Meanwhile, the penetrative flow will lower the competition between products and reactants for active sites of the catalyst, leading to a decreased possibility of undergoing side reactions and poisoning catalyst surface. In addition, due to leaving out the additional steps for separating products and/or nanocatalysts from reaction mixture, operations of the composite membrane for catalysis and recover are convenient, economical and environmentally-friendly. However, much less is known of creating noble metal NPs only in membrane pores. Evidently, before forming noble metal NPs, the noble metal compound must be firmly immobilized in the membrane pore and at the same time be prevented from immobilizing onto the membrane surface. Hence, it is important to construct a suitable membrane having a well-defined pore and surface structure for such a requirement. To our best knowledge, few studies devote to the composite membranes with noble metal NPs in membrane pores.

Herein we present the first systematic study of preparation and catalytic behavior of a PVDF membrane bearing PMAA microspheres decorated with Pd NPs in membrane pores. Firstly, a mixture of PVDF powders and PMAA microspheres forms membranes by a solution phase-transition method. After membrane formation, PMAA microspheres were enriched in the membrane pores. By converting carboxylic acids of PMAA microspheres into the carboxylates and then reacting with palladium chloride, the immobilized metal compound was subsequently reduced to metal NPs in membrane pores. The novel composite membrane was applied to the catalytic reduction of *p*-nitrophenol under a cross-flow operation. Catalytic behavior was investigated under various experiment conditions such as temperature, pressure and Palladium loadings. The catalytic reaction kinetics and long-term maintenance of Pd NPs were also investigated.

2. Experiment

2.1. Materials

Methacrylic acid (MAA), dimethyl formamide (DMF), acetonitrile, and sodium borohydride (NaBH_4) were gained from Tianjin Kemiou Chemical Reagent Co, Ltd. Azodiisobutyronitrile (AIBN) was obtained from Tianjin Yingda Rare Chemical Reagents Factory. Palladium chloride (PdCl_2) was purchased from Tianjin Mascot Chemical Limited Corporation. Ethyleneglycol dimethacrylate (EGDMA) was obtained from J&K Scientific. Poly(vinylidene fluoride) (PVDF) powders ($M_w=3.52 \times 10^5$ g/mol, $M_w/M_n=2.3$, Solvay Company, Belgium, Solef 1010) were used as received. Ethyl alcohol was obtained from Tianjin Bodi Chemical Engineering Limited Corporation. *p*-nitrophenol was purchased from Tianjin Guangfu Fine Chemical Engineering Institute. All the chemical reagents and chemicals were analytical grade and directly utilized without any further purification.

2.2. Preparation of PVDF/PMAA blend membrane

2.2.1. Preparation of PMAA microsphere

PVDF/PMAA blend membranes were prepared by blending PVDF powders with PMAA microspheres, synthesized through distillation-precipitation polymerization [37] with AIBN as initiator and EGDMA as cross-linking agent. In a 250 mL three-neck flask, a solution was formed by mixing MAA (0.023 mol), EGDMA (0.011 mol), and AIBN (0.48 mmol) in 160 mL acetonitrile. Subsequently, the solution was rapidly heated to 80 ± 2 °C and simultaneously stirred for 120 min. The PMAA microspheres were obtained by centrifuging (10,000 r/min, 10 min) the reaction mixture, and then washing the obtained sediments from centrifugation with ethyl alcohol and deionized water for several times, and finally drying the sediments in a vacuum oven at 60 °C. The obtained PMAA samples were spherical in morphology (Fig. S1A) with an average size of about 151.4 nm in the size range of 80.9–223.1 nm (Fig. S1B).

2.2.2. Preparation of PVDF/PMAA blend membrane

PMAA microspheres (5.0 wt%) were dispersed in DMF(83.4 wt%). After that, PVDF powders(11.6 wt%) was added to the mixture and vigorously stirred for 6 h at 60 °C to form solution. After vacuum degassed, the solutions were cast on a glass plate with a steel knife, and then the glass plate was immersed in a coagulation bath of deionized water at room temperature. When peeled off from the substrate, the nascent membranes were rinsed with deionized water thoroughly to remove the residual solvent and then stored in deionized water until use. The blend membranes prepared from the blends of PVDF powders and PMAA microspheres were denoted as M10; by contrast, pure PVDF membranes were labeled as M00.

2.3. Immobilization of Pd nanoparticles in membrane pores

Immobilization of Pd NPs in PVDF/PMAA blend membrane pores is shown in Fig. S2. Briefly, Pd NPs were formed by the first ion exchange of Pd^{2+} with PMAA microspheres in membrane pores, and then by hydrogenation reduction with NaBH_4 . Before ion exchange, the PVDF/PMAA membrane was impregnated in 100 mL of sodium hydroxide solution (0.1 M) for 12 h to convert the carboxylic acid ($-\text{COOH}$) of PMAA into carboxylate ($-\text{COONa}$). Subsequently, the membrane was rinsed by deionized water to remove the excess sodium hydroxide, and then shaken in 100 mL of palladium chloride solution (4 mM) at pH 4 for 48 h. In this process, Pd^{2+} was bound to the PMAA microspheres in the membrane pores by ion exchange with Na^+ . After excess palladium chloride was removed by washing the membrane with deionized water, the Pd NPs on PMAA spheres in the membrane pore were formed by immersing the membrane into 200 mL of the

Download English Version:

<https://daneshyari.com/en/article/632854>

Download Persian Version:

<https://daneshyari.com/article/632854>

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