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Preparation of polyvinylidene fluoride–nickel hollow fiber catalytic membranes for hydrogen generation from sodium borohydride

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HIGHLIGHTS

- PVDF hollow fiber catalytic membranes prepared by in situ reduction of metal ions.
- CMs and membrane modules were used as catalyst for hydrogen production.
- 16 PVDF hollow fiber catalytic membranes showed good reusability for H₂ production.
- A module achieved integration of catalytic H₂ generation and gas–liquid separation.
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ABSTRACT

Polyvinylidene fluoride hollow fiber catalytic membranes (CMs) are prepared by in situ reduction of nickel salt with sodium borohydride (NaBH₄). The CMs and their membrane modules are both used for hydrogen generation from alkaline NaBH₄ solution. Characterization of this nickel-based catalytic membrane is carried out by using various techniques, such as scanning electronic microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The rate of hydrogen generation from catalytic hydrolysis of alkaline NaBH₄ solution is determined by varying the temperature, concentration of NaBH₄ and sodium hydroxide (NaOH), and content of catalyst. In general, the rate of hydrogen generation is about 388.8 mL min⁻¹ m⁻² CMs in 20 mL of 1.0 wt.% NaBH₄ and 0.5 wt.% NaOH aqueous solution at 30 °C. It can be efficiently cycled and reused more than six times without significant loss of the catalytic activity. The optimum treated conditions for CMs are 20 wt.% NaOH, 0.2 M NiCl₂, and 1 M NaBH₄ aqueous solution. The activation energy of NaBH₄ hydrolysis reaction is noticed about 55.3 kJ mol⁻¹.

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49 1. Introduction

50 With increasing requirement for low-carbon, green growth of economy, hydrogen has become more and more attractive as an 51 alternative energy resource. Therefore, safe, low cost and high effi-52 cient storage and releasing of hydrogen has been the focus of many 53 researches. Chemical hydrides, combining the optimum properties 54 for hydrogen supply and storage, due to their capability in produc-55 ing highly pure H₂ and their larger H₂ storage capacity, are prom-56 ising materials to meet the goal of U.S. Department of Energy for 57 9 wt.% hydrogen capacity by 2015 [1]. Among chemical hydrides, 58 59 sodium borohydride (NaBH₄) is a favorable material for hydrogen 60 supply and storage because of its high hydrogen storage capacity 61 (about 10.9 wt.%), great stability in alkaline solution [2], pure 62 hydrogen generation [3], recycling of the by-products [4–6] and

http://dx.doi.org/10.1016/j.fuel.2014.10.022 0016-2361/© 2014 Published by Elsevier Ltd. non-flammability. It was often applied in controlled generation of hydrogen with specific catalysts.

Many reports on development of suitable catalysts for the hydrogen production from hydrolysis of NaBH₄ solutions have appeared in recent years. These catalysts included rhodium [7], platinum [8], ruthenium [9], cobalt [10–12] and nickel [13,14]. Recently, considering the high cost of noble metals such as rhodium, platinum and ruthenium, numerous researchers have focused on development of nickel catalysts. Nickel based catalysts have been shown to be a better prospect due to their lower cost and higher catalytic activity in production of hydrogen by hydrolysis of NaBH₄ in alkaline solutions [15]. Various nickel-based catalysts have been synthesized for hydrogen production by hydrolysis of NaBH₄. For example, approximately 100 nm Ni nanoparticles generated in situ inside the networks of 2-acrylamido-2-methyl-1-propansulfonic acid hydrogel were prepared by Ozav et al. [15]. Nickel-boride-silica nanocomposite catalyst, in which the formed Ni-B particles attached to the amine-modified silica nanoparticles,

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81 was synthesized by Chen and Kim [16]. A novel Ni/Ag/silica nano-82 composite and a highly stable, active nickel boride catalyst (NixB) 83 was prepared by Dong et al. [17]. Ni@zeolite, a highly active cata-84 lyst, was prepared by Zahmakiran et al. [18]. However, these cata-85 lysts probably need complicated processing for their preparation. 86 Besides, the catalytic activity also could be reduced and was not 87 easy to recover due to formation of sodium metaborate (NaBO₂) 88 on the catalyst. Hence, simple preparation and high stability of catalysts are significant for CMs, and highly uniform distribution of the 89 catalyst is the key for excellently catalytic activity. 90

91 Hollow fiber membranes are good candidate for serving as car-92 riers for catalysts due to their high surface area and ease to assembly a membrane module. Several catalytic membrane reactors 93 supported by polymeric hollow fiber membranes were established 94 95 in literature. For instance, bimetallic PVP-Pd-0.5Co/cellulose ace-96 tate (CA) hollow fiber membrane reactor was synthesized by Liu 97 et al. [19]. There was a remarkable synergic effect of palladium and cobalt reduced by NaBH₄, which resulted in a 97.5% conversion 98 of cyclopentadiene and a 98.4% selectivity for cyclopentene. Poly-99 mer-stabilized metal nanoparticles inside functionalized poly-100 101 meric membranes were prepared by Macanás et al. [20], and the 102 catalytic performance has been evaluated by reduction of nitro-103 phenol to aminophenol with sodium borohydride. Van der Vaart 104 et al. [21] demonstrated that palladium could be deposited on a 105 hydrophobic porous polypropylene hollow fiber membrane by 106 use of an electroless deposition method while maintaining the 107 membrane's hydrophobic nature. Palladium catalyst-supported chitosan hollow fibers were investigated by Peirano et al. [22] 108 and the catalyst was used for the continuous catalytic hydrogena-109 110 tion of nitrotoluene into o-toluidine.

111 In the present work, polyvinylidene fluoride (PVDF) hollow fiber membranes were used for preparation of CMs and membrane 112 modules. The hollow fiber membrane was used as support for 113 nickel catalyst both for static catalysis (3 cm in length) and mem-114 115 brane module catalysis (30 cm in length). In static catalysis, the 116 catalytic membrane used as general catalyst for hydrolysis of 117 sodium borohydride. While in membrane module, the catalytic 118 membrane played roles both as catalyst and separation media. 119 The most important point for using PVDF membranes is that the 120 hydrophobic PVDF hollow fiber membranes and membrane mod-121 ules just permit the generated hydrogen to permeate through the membrane while block the reaction liquid. Thus the membrane 122 module can separate hydrogen from the aqueous solution. It 123 124 achieved integration of catalytic hydrogen production and gas-125 liquid separation. The external surface of CMs loaded with metal 126 nickel nanoparticles, which is formed by in situ reduction of nickel 127 salt with NaBH₄. The surface and cross-sectional morphology of the 128 CMs were characterized by FESEM. In addition, the content of ele-129 ment was tested by XPS. Furthermore, the hydrogen generation 130 rate and catalytic stability were also measured with water dis-131 placement method.

132 **2. Materials and methods**

133 2.1. Materials

PVDF hollow fiber membrane (outer diameter, 1.30 mm, wall 134 thickness, 0.18 mm, pore size, 0.1 µm, and surface water contact 135 136 angle, 95°) was received from Tianjin Motimo Company. Pure eth-137 anol, sodium hydroxide (NaOH) and nickel chloride 6-hydrate 138 (NiCl₂·6H₂O) were purchased from Tianjin Fengchuan Chemical Reagent Technology Co, Ltd. Sodium borohydride (NaBH₄) and 139 140 polyethylene glycol 6000 (PEG 6000) were obtained from Tianjin 141 Guangfu Fine Chemical Research Institute. All chemicals were pur-142 chased and used without further purification.

2.2. Pretreatment of the hollow fiber membranes

PVDF hollow fiber membranes were tailored to about 4 cm (for 144 static catalysis) or 30 cm (for membrane modules) in length. Pre-145 treatment of the PVDF hollow fiber membranes began by immers-146 ing them in 50 mL ethanol for 15 min. Then, the hollow fiber 147 membranes were transferred into NaOH aqueous solutions (15, 148 20, and 25 wt.%) for 3 min. After pretreatment, the PVDF hollow 149 fibers membranes were washed with distilled water for several 150 times 151

2.3. Preparation of PVDF–Ni hollow fiber CMs and membrane modules

Hollow fiber CMs were prepared by adsorption-reduction 153 method. The pretreated hollow fiber membranes were immersed 154 in NiCl₂ (0.04, 0.06, 0.1, 0.2, and 0.25 M) and PEG 6000 (0, 10, 155 and 400 g L^{-1}) mixed aqueous solution for 30 min. Ni compound 156 was formed by reducing NiCl₂ after immersing the hollow fiber 157 membranes in NaBH₄ aqueous solution (0.2, 0.3, 0.5, 1.0, and 158 1.25 M). The adsorption and reduction of NiCl₂ procedures was 159 repeated for six times. They were then washed with distilled water 160 for several times. Finally, the hollow fiber membranes were dried 161 in vacuum oven at room temperature. The pretreatment and the 162 preparation of CMs were both done at room temperature. The hol-163 low fiber CMs with length of 30 cm were treated as the above. After 164 that, catalytic membrane modules were fabricated by sealed both 165 ends of the fibers (3-5 fibers) with silicon rubber and fixed in a 166 polyurethane plastic pipe with epoxy. The fibers was bent into 167 U-loop type and the end of the plastic pipe was cut after solidifica-168 tion of the epoxy to connect the bore of the fibers to air. The effec-169 tive length of catalytic membrane fiber was the number of fibers 170 times the length of fiber immersed in the reaction solution (52, 171 81, and 115 cm for this study). 172

2.4. Characterization

Surface and cross-sectional morphologies of the PVDF hollow 174 fiber CMs were examined using FESEM (S-4800, Hitachi) under 175 3.0 kV or 5.0 kV. The samples were sprayed with gold before test-176 ing. Elemental content on the surface of the CMs was characterized 177 by X-ray photoelectron spectroscopy (XPS) (Perkin-Elmer PHI) and 178 Al_{Ka} was the radioactivity source. The specific surface areas (S_{BET}) 179 were carried out at 77 K on a Quantachrome QuadraSorb SI instru-180 ment by nitrogen adsorption/desorption. Prior to analysis, the sam-181 ples were degassed at 100 °C for 4 h to remove the adsorbed 182 species. The S_{BET} was determined from the linear part of the BET 183 curve. Mass gains of the membranes were obtained with an ana-184 lytic balance (ACCULAB ALC-210.3) with a resolution of 0.1 mg. 185

2.5. Hydrogen generation with hollow fiber CMs and membrane modules

Static catalytic performance of the hollow fiber CMs for hydro-188 gen production was measured by immersing the hollow fiber CMs 189 (0.103, 0.206, 0.310, and 0.413 g) (containing 25, 50, 75, and 190 100 mg of catalyst) into 20 mL aqueous solution containing NaBH₄ 191 (0.5, 1.0, 2.5, 5.0, and 7.5 wt.%) and NaOH (0.5, 2.5, 5.0, and 192 7.5 wt.%). The volume of hydrogen production was measured with 193 water displacement method. The outlet tube of the reactor (50 mL) 194 was connected to a flask (2000 mL) for collecting produced hydro-195 gen. Gradually produced hydrogen from the reactor traveled to the 196 flask full of water and pushed out the water into a measuring cyl-197 inder (200 mL). The volume of produced hydrogen was the same as 198 the volume of displaced water. For the measurement of catalytic 199 activity, the reaction was done in a glass reactor with magnetic 200 stirring bath at various temperatures (25, 30, 35, 40, 45, and 50 °C). 201

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