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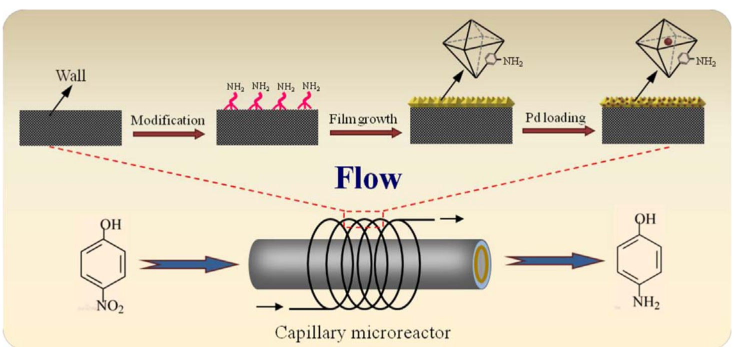
Flow fabrication of a highly efficient Pd/UiO-66-NH_2 film capillary microreactor for 4-nitrophenol reduction

Jing Li[a], Feichao Wu[a], Lu Lin[a], Yu Guo[b,*], Haiou Liu[a], Xiongfu Zhang[a,*]

[a] State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China
[b] School of Chemical and Environmental Engineering, Liaoning University of Technology, Jinzhou 121001, China

GRAPHICAL ABSTRACT



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ABSTRACT

A novel Pd/UiO-66-NH_2 film quartz capillary microreactor was fabricated by a flow method in which fine control of the film thickness and metal loading could be readily achieved by adjusting flow time. Firstly, UiO-66-NH_2 film as the catalyst support layer was synthesized on the inner wall of the quartz capillary employing a two-step procedure including surface modification with 3-aminopropyltriethoxysilane (APTES) and the subsequent flow growth of UiO-66-NH_2 film. Secondly, Pd nanoparticles (NPs) were uniformly and firmly immobilized in the UiO-66-NH_2 film as active catalysts using the same flow method. Such Pd/UiO-66-NH_2 film capillary microreactor was applied as catalyst for the reduction of 4-nitrophenol (4-NP) to produce 4-aminophenol (4-AP) under continuous flow conditions. Nearly 100% conversion was achieved under mild conditions in a short residence time. Importantly, no deactivation was observed for this microreactor during the continuous flow reaction of 100 h, indicating its excellent stability due to the firm immobilization of active Pd NPs in UiO-66-NH_2 film.

1. Introduction

Membrane/film microreactors, fabricated by assembling membranes/films in catalytic configurations with channels below 500 μm in diameter, have attracted increasing interest as highly efficient heterogeneous catalysts [1–5]. First of all, microreactor itself can offer enhanced catalytic performance due to its intrinsically higher mass and heat transfer rate [6]. Then, the introduction of membrane/film in microreactors can realize the immobilization and uniform dispersion of catalytic active components, and achieve supra-equilibrium conversions, resulting in intensified production processes and greatly improved reaction efficiency [7,8]. Furthermore, the coated membrane/film, as a protective layer, can also prevent metal nanocatalysts from deactivation by avoiding aggregation and leaching of active

* Corresponding authors.
E-mail addresses: guoyulnut@163.com (Y. Guo), xfzhang@dlut.edu.cn (X. Zhang).

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nanoparticles [9,10]. Such membrane/film-based microreactors can generally be synthesized either by static method or under flow condition. The latter approach is preferred over the former one because of its merits in achieving continuous and uniform membrane/film layers on the inner surface of the microreactors with huge ratio of length to diameter.

Metal organic frameworks (MOFs), constructed by the periodic coordination of metal ions/clusters and ligands, possess uniform microporous structure, large surface areas and even some acidic or basic sites [11,12]. These advantages have inspired researchers to explore their potential as membrane/film substrates for loading catalytically active components. For example, Mao et al. [9] firstly employed HKUST-1, a MOF material, in the form of film to immobilize various functional particles (metal nanoparticles, inorganic, polymers, proteins and so on) for catalysis and bio-activity application. Zamaro and co-workers [10] achieved ZIF-8 films on microchannel copper foils to support Ag nanoparticles and then conducted the composite films as high-performance catalysts in the CO oxidation. Despite the efforts have been devoted, much work still needs to be done on more types of appropriate MOFs to explore their potential as membrane/film supports in microreactors. The UiO-66 family, composed of $Zr_6O_4(OH)_4$ cluster and carboxylate ligands, exhibits exceptional chemical and thermal stabilities [13,14]. Besides, UiO-66 and its derivative materials are also widely used as supports to encapsulate active catalytic species [15–18]. Therefore, these Zr-based crystalline materials may serve as a promising candidate for membrane/film substrates. However, to the best of our knowledge, there are few reports about the coating of UiO-66 series MOFs on microchannels as membrane/film microreactors for catalytic application.

In the present work, a facile flow method was developed to fabricate a highly efficient capillary quartz microreactor based on Pd nanoparticles (NPs) immobilized in UiO-66-NH_2 film (named as Pd/UiO-66-NH_2 film) for 4-nitrophenol reduction. As shown in Fig. 1, the method involves a two-step procedure including the growth of a continuous UiO-66-NH_2 film on the inner surface of quartz capillary, followed by immobilizing active Pd species inside the UiO-66-NH_2 film. The thickness of the UiO-66-NH_2 film and the loading content of Pd NPs could be conveniently optimized by adjusting the operation time to achieve highly efficient capillary microreactor. This method covered three key points: 1) APTES was employed to chemically modify the inner surface of the quartz capillary with active nucleation and growth sites for the formation of a continuous and uniform UiO-66-NH_2 film; 2) porous UiO-66-NH_2 film was selected as the support for fixing Pd species because UiO-66-NH_2 has functional amino groups to immobilize Pd NPs without agglomeration and leaching through metal coordination chelation [17,19]; 3) all procedures including the preparation of the Pd/UiO-66-NH_2 film catalyst and reaction of 4-nitrophenol reduction were conducted under flow conditions, which was simple and scalable. The reduction of 4-nitrophenol with $NaBH_4$, a part of the catalytic hydrogenation of aromatic nitro compounds, is usually served as the standard of testing nanostructured catalysts and exploiting for the study of catalytic activities [20–21]. This reaction can not only be carried out under ambient conditions without by-products, but also can be facile analyzed by UV–Vis spectroscopy [22]. Moreover, *p*-aminophenol is also an important intermediate [23].

2. Experimental

2.1. Materials

The quartz capillaries (O. D: 630 μm, I. D: 530 μm, length: 250 mm) were purchased from Dalian Zhong Hui Da Instrument Corporation. 3-aminopropyltriethoxysilane (APTES), Zirconium tetrachloride ($ZrCl_4$), *N,N*-Dimethylformamide (DMF), 2-aminoterephthalic acid (NH_2-H_2BDC), acetic acid (99.5%) were obtained from Sigma Aldrich. 4-nitrophenol (4-NP), sodium borohydride ($NaBH_4$), hydrochloric acid (HCl), sodium hydroxide (NaOH) and ethyl alcohol were supplied by Sinopharm Chemical Reagents Co. Ltd. (Beijing, China). Palladium chloride ($PdCl_2$) was obtained from Shanghai Jiuling Chemical Co. Ltd. (Shanghai, China). All the chemical reagents were used as received without further purification. The used deionized water (DI water) was home-made.

2.2. Fabrication of Pd/UiO-66-NH_2 film microreactors by the flow method

2.2.1. Synthesis of UiO-66-NH_2 film on the inner wall

The quartz capillary was used as a microchannel for the flow growth of UiO-66-NH_2 film including chemical surface modification of the internal surface of the quartz capillary and then the growth of UiO-66-NH_2film. As shown in Fig. 2, a homemade device was employed for the film growth. At first, the quartz capillary was successively pre-treated with 1.0 M HCl and 1.0 M NaOH at 348 K, and then APTES was grafted on the surface of the wall by pumping the mixture solution of APTES and ethyl alcohol (1:30 v/v) at a velocity of 1 mL/h for 3 h at 348 K.

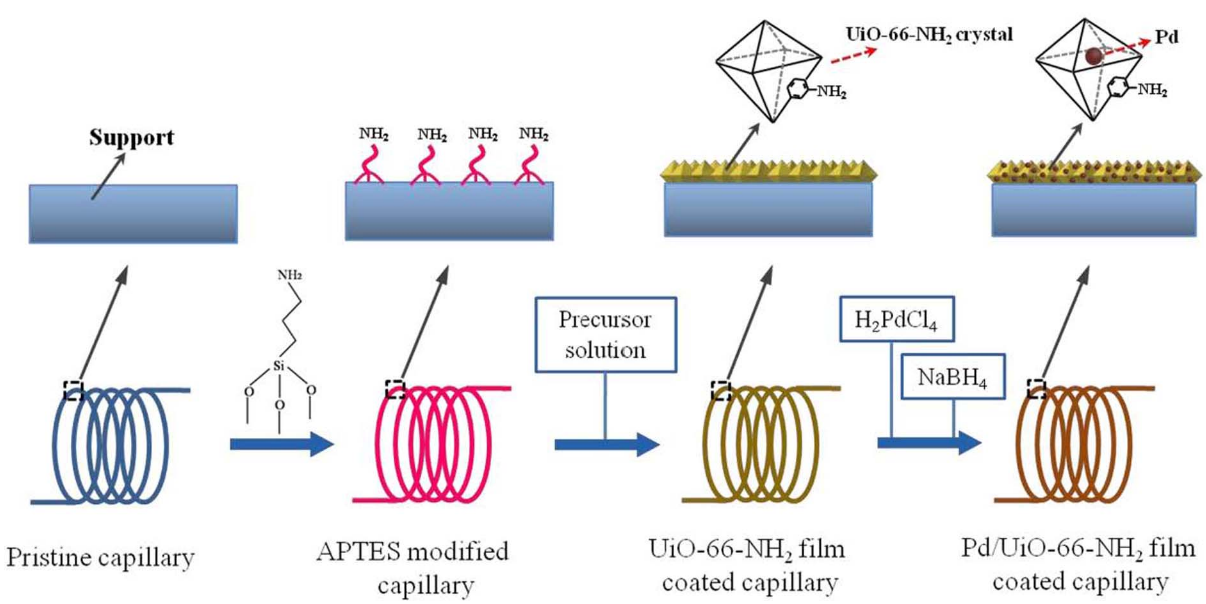

Fig. 1. Schematic representation of the fabrication process.