Contents lists available at ScienceDirect

Chemical Engineering Research and Design

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

Multilayered Pd nanocatalysts with nano-bulge structure in a microreactor for multiphase catalytic reaction

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ARTICLE INFO

Article history:
Received 1 April 2018
Received in revised form 4 July 2018
Accepted 16 August 2018
Available online 24 August 2018

Keywords:
Microreactor
Multilayered Pd nanocatalyst
Nano-bulge structure
Multiphase catalytic reaction
Durability

ABSTRACT

Microreactors are promising for fine chemistry and value-added chemical synthesis, but the small dimension places significant challenges in catalyst layer fabrication. Meanwhile, enhancing catalyst dispersion to obtain smaller particle size are of great interests. We proposed a multilayered Pd nanocatalysts with nano-bulge structure inside a microreactor for multiphase catalytic reaction. The unique bulged nanostructure can provide more accessible sites for precursor ($PdCl_4^{2-}$) adsorption, and extend the available area to reduce the Pd nanoparticle size. Experimental results show rugged Pd catalyst layer with the nano-bulge structure was prepared, and both the precursor utilization rate and Pd nanocatalysts dispersion were enhanced, resulting in 35.4% higher catalyst loading and 4-fold smaller particle size. Benefitting from these advantages, compared with conventional Pd coated polydopamine catalyst layer, the proposed multilayered Pd nanocatalyst can significantly intensify the reaction rate and obtain an order of magnitude longer durability in nitrobenzene hydrogenation. This versatile and convenient fabrication method can be used in fabricating high performance and durable catalyst layers in microreactors.

1. Introduction

Metal nanoparticles are usually used as catalysts due to high activity in various reactions (Cárdenas-Lizana et al., 2013; Kataoka et al., 2012; Mo and Kawi, 2014; Qiao et al., 2011). To ensure efficient and economic usage, metal nanoparticles are generally supported on substrates with high surface area. In this respect, both the dispersity and stability of the deposited metal species could be improved, providing more catalytic active sites expose to the reactants adsorption and reaction (Liu et al., 2017b). When such supported metal catalysts are employed in gas–liquid–solid reactions (Borg et al., 2007; Davis et al., 2013; Taylor et al., 2016), the mass transfer resistance between the phases is somewhat predominated because of the sluggish mass transfer between the phases (Kataoka et al., 2012). To address this issue, these multiphase reactions are generally operated at high pressure and/or temperature with vigorous stirring, which not only aggravated the financial burden but also induced more potential safety and environmental issues (Alaimo, 2001). To overcome these defects, Kobayashi et al. (2004) designed a new microfluidic device and proved that efficient multiphase catalytic reaction could be achieved by using such micro-system as a result of its intrinsic large specific surface area and high mass transfer rate and precise microenvironment control. As a result, an increasing number of attentions have been focused on the microreactor system because of its competitive advantages in vari-

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https://doi.org/10.1016/j.cherd.2018.08.026
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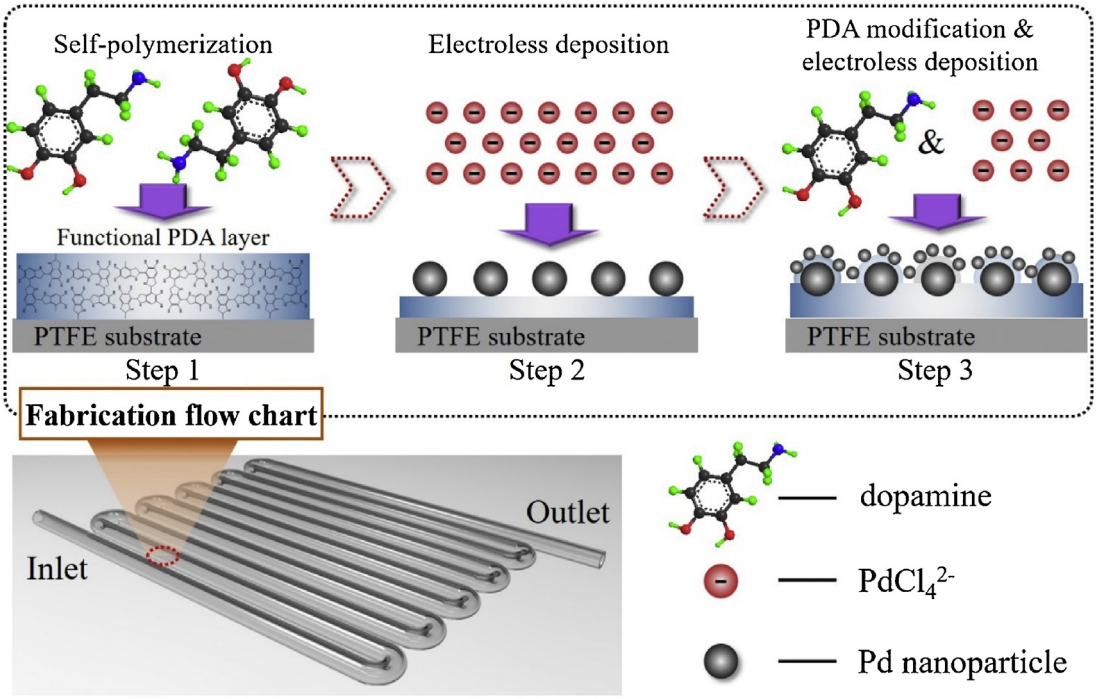

Fig. 1 – Schematic of the fabrication of the multilayer Pd catalyst with nano-bulge structures in the microreactor.

ous industrial applications (Li et al., 2013, 2014, 2018; Liu et al., 2016; Yoshida, 2015; Zhang et al., 2016).

Generally, the prepared catalyst layer inside the microreactor is crucial for the catalytic activity and stability. To prevent the aggregation and acquire a well-dispersed metal nanocatalysts, support media like solid oxides (such as Al_2O_3, SiO_2, TiO_2) (Guan et al., 2008; Kataoka et al., 2008, 2012) and polymers (polydopamine, polyelectrolytes, etc.) (Dotzauer et al., 2006; Feng et al., 2016; Hornung et al., 2010) are usually fabricated preferentially inside the microreactor for the further metal catalysts (Pd, Pt, Au, Rh, etc.) deposition (Dotzauer et al., 2006; Feng et al., 2016; Haywood and Miller, 2014; Hornung et al., 2010; Kobayashi et al., 2004). Although those solid oxides support media can provide a large surface area for the nanocatalyst deposition with good dispersion and activity, calcination is typically required to improve the binding between the catalyst and supporting materials/substrates, making it restricted to certain materials, and also increasing the manufacturing costs (Bartholomew and Farrauto, 2005). Thus, polymer-supported metal nanocatalysts have attracted a wide attraction as a result of the

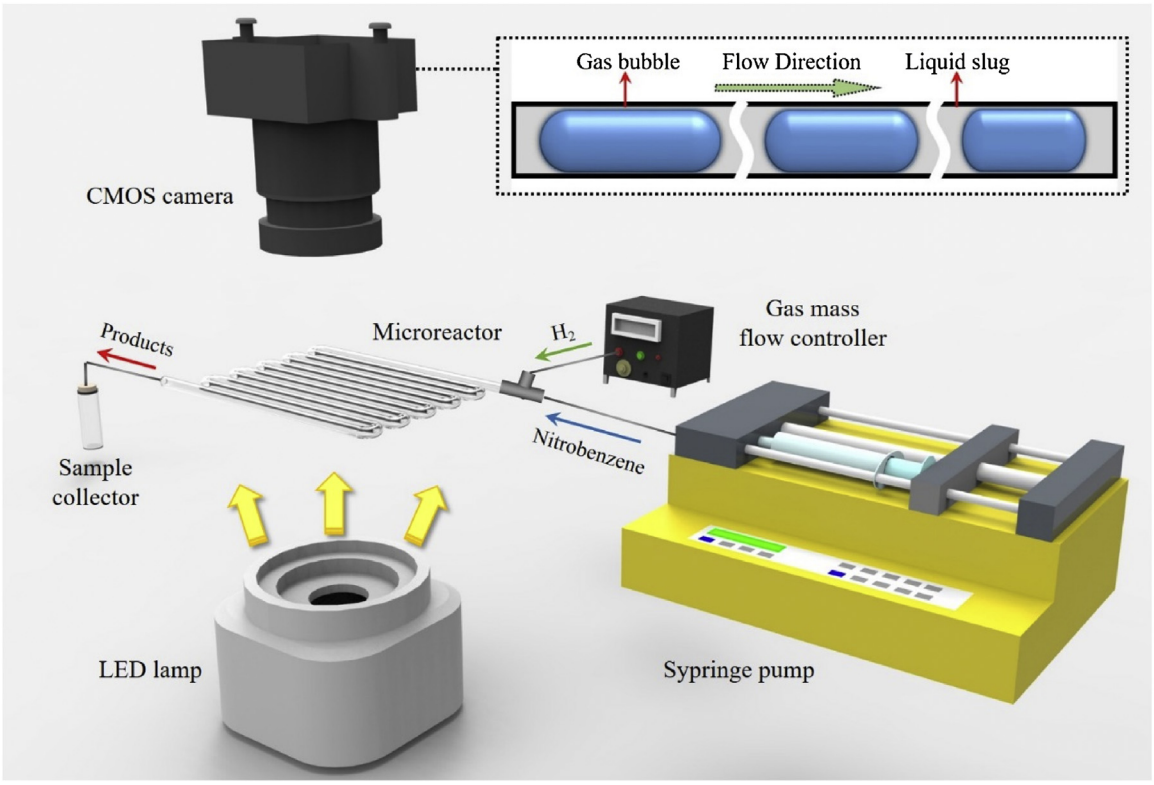

Fig. 2 – Schematic of the experimental setup.