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Microreactor containing platinum nanoparticles for nitrobenzene hydrogenation

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ABSTRACT

Pt nanoparticles were immobilized inside a microreactor to catalyze the hydrogenation of nitrobenzene to aniline. Catalyst support layers were provided on the inner wall of the microreactor to enhance the adsorption and reaction of the Pt nanoparticles. Using this immobilization method, the Pt nanoparticles inside the microreactor exhibited a good catalytic activity and also were easily regenerated even after they were deactivated. During a 14-h continuous experiment, the average yield of aniline was higher than 92% for 50 mM initial nitrobenzene concentration with the retention time of 12 s. This is equivalent to a turnover frequency of 3200 h^{-1}. The deactivation mechanism of the Pt nanoparticles was also discussed in a long-time reaction.

1. Introduction

Metal nanoparticles are known to exhibit high catalytic activity in various reactions stemming from their size and shape [1–3]. When nanoparticles embedded in support media are employed in gas–liquid–solid reactions as catalysts, the accessibility of gas molecules to the nanoparticle surface is somewhat limited because of the low mass transfer between the phases. To overcome this problem, such multiphase reactions using nanoparticle catalysts are generally performed under high pressure to increase the amount of dissolved gases [4–6]. However, the handling of these high-pressure experiments requires special care because of the increased potential for explosion, especially when catalysts have high activity [7]. Therefore, if gases can be supplied efficiently to the nanoparticle surface in a safe manner, the nanoparticles can be more effectively employed in gas–solid–liquid chemical syntheses.

Microreactors have proven to be a useful tool for fine chemical syntheses [8–10]. They generally have a large interfacial area per unit volume, which particularly facilitates multiphase reactions including gas–liquid–solid catalytic reactions [11–16]. In these reactions, both gaseous and liquid reactants are in good contact with the surface of solid catalysts coated on the inner wall of microreactors. Therefore, such catalytic reactions can rapidly proceed even under ambient conditions. In addition, since small amounts of gaseous and liquid reactants coexist inside, the explosive risk can be minimized [10]. For these reasons, the use of microreactors is well suited for gas–liquid–solid reactions using nanoparticle catalysts.

To prevent their aggregation in solutions, nanoparticle catalysts are generally supported on porous solids and/or polymers [17,18]. It is well known that these support media greatly influence on their catalytic activity. When nanoparticles are immobilized inside microreactors, the choice of support media is a key to achieving effective multiphase reaction. In the past, several attempts have been made to immobilize metal species inside microreactors: Pd catalyst was impregnated on a γ-alumina on the wall of a microchannel [11]; Pd catalysts encapsulated in polymers were chemically bonded to the wall of a microreactor [12]; Ag and Pd nanoparticles were formed in a polymer brush on the wall of a microreactor [19]; Pt nanoparticles were immobilized inside carbon nanotubes on the inner wall of a microreactor [20]. In these attempts, good catalytic activity was exhibited; however, the resulting deactivation of the catalysts was not clearly discussed. Since reactions inside microreactors are generally conducted in a continuous flow manner, the catalyst deactivation causes a continual decrease in product yields. Furthermore, since deactivated nanoparticles are immobilized in the confined space of a microreactor, methods for regenerating them are quite limited. Unless they are regenerated, expensive equipments would be discarded after a single use. Therefore, the regeneration of immobilized nanoparticles should be included in the design of microreactor.

In this study, we immobilized Pt nanoparticles inside a microreactor and performed the hydrogenation of nitrobenzene. In order to facilitate the adsorption of the nanoparticles inside the microreactor, thin films (mesoporous silica, mesoporous titania, and titania)

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