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In situ preparation of $Pd/Al_2O_3–SiO_2$ composite microspheres by combining a sol–gel process and precipitation process in a microchannel

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HIGHLIGHTS

- A novel method for the preparation of $Pd/Al_2O_3–SiO_2$ microspheres in a microchannel.
- The specific surface area of the spheres was >600 m^2/g.
- The smallest Pd particles had an average size of 3.79 nm after calcination at 550 °C.
- The sphere with the diameter of 400 μm was suitable for packing into a fixed bed.

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ABSTRACT

$Pd/Al_2O_3–SiO_2$ composite microspheres with 4 nm Pd nanoparticles were prepared in a microchannel by combining a sol–gel process with the precipitation of Pd ion. The sol of silica and alumina with Pd ion was used as the dispersed phase, and liquid paraffin-containing soluble organic amines were used as the continuous phase. The mass transfer of organic amines from the organic phase to the aqueous phase in microchannels changed the pH of the aqueous phase, which resulted in the precipitation of $PdCl_2$ in acidic solution and the faster sol–gel process of $SiO_2–Al_2O_3$. The resulting catalyst was characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and Brunauer–Emmett–Teller analyses. Experimental results showed that the prepared microspheres with a diameter about 400 μm had a special structure that was externally compact and internally, and they were suitable for packing into a fixed bed. Each microsphere had a microporous–mesoporous–macroporous structure and the specific surface area was larger than 600 m^2/g. After calcination at 550 °C, the smallest Pd particles still had an average size of 3.79 nm and were highly dispersed. These microspheres in a fixed bed also showed a high performance for the hydrogenation of cyclohexene. When the retention time was 2.2 min in the liquid phase, a conversion rate reached 0.447. This one-step in situ synthesis had the advantages of high utilization of Pd, small Pd nanoparticles with high monodispersity, and adjustability of resulting microspheres at the micron level.

1. Introduction

Noble metal catalysts have very high catalytic activity and excellent selectivity, and are thus widely used in hydrogenation and dehydrogenation in the chemical industry [1–6]. The noble metal palladium also has excellent catalytic performance and is often used for catalytic reforming in the petroleum refining, isomerization, and dehydrogenation of alkanes and aromatics, as well as in the selective hydrogenation of olefins [4,7–10]. Selvam et al. [11] prepared Pd–MCM-41 catalyst using the direct in situ hydrothermal method. This catalyst enabled the efficient hydride alkylation of various aromatic compounds containing halogens, with yields reaching over 70%. Studies revealed that the introduction of aluminum effectively increased the hydrogenation activity and palladium dispersion. Duan et al. [12] used MCM-41 catalyst as a carrier to support palladium by impregnation and characterized the hydrogenation system of sunflower oil. They found that the liquid phase yield was only 10 wt% when MCM-41 was used as the carrier, but the maximum yield reached 75 wt% when Al–MCM-41 was used as the carrier. Kawabata et al. [13] compared Si–Al–Pd catalysts prepared using direct hydrothermal synthesis and impregnation. They found that the catalyst prepared by direct hydrothermal synthesis had higher activity and that the introduction of aluminum effectively enhanced palladium dispersion. Therefore, it is a tendency to load Pd nanoparticles into a Si–Al composite materials with high pore volume and specific surface area through a in situ method.

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Another problem is that most of the synthesis catalysts loaded Pd nanoparticles in above works were powder, but not microspheres, it can not be packed in a column and was difficult to be separated from the aqueous phase. Microfluidic techniques have been widely used to prepare various microspheres and concerned for the purpose of preparing uniform microspheres through the phase separation technique [14–16]. Zhang et al. [17] reported that they had synthesized modified porous alumina spheres with Pd nanoparticles as heterogeneous catalysts for the selective hydrogenation of DMT to DMCD, but it's rarely reported that the preparation of Pd nanoparticles supported with Al_2O_3–SiO_2 as catalyst support. In our previous works [18–20], pure SiO_2 microspheres with high pore volume and specific surface area were prepared through the rapid gelation of SiO_2 sol. In a microchannel, the microdroplets of SiO_2 sol containing HCl was formed by the shearing of continuous phase containing trioctylamine, liquid paraffin, and sorbitan trioleate. These SiO_2 microspheres possessed good separation performance and high adsorption capacity for proteins. However, the one step preparation of Si–Al composite microspheres loading Palladium-based catalysts in a microchannel has never been reported. Regarding the precipitation of Pd ion and the gel process of SiO_2 sol, the pH of a solution needs to be changed from acidic to alkaline. In our preliminary experiments, when TOA was used to extract HCl to resulting in the rapid gelation of sol, Pd in the aqueous phase was also extracted, so the system in our previous work was unsuitable for the preparation of Pd/Al_2O_3–SiO_2 composite microspheres. The continuous phase must be changed.

Therefore, soluble organic amines replacing TOA were used to change the pH of the aqueous phase because these organic amines dissolve in the aqueous phase during the flowing. A variety of water-soluble organic amines were tested, and diethanolamine was ultimately chosen to control the pH of the aqueous phase. Moreover, it was very interesting that $PdCl_2$ was not completely dissolved in the silica sol, but after $AlCl_3$ was added into the silica sol the solution sol became transparent, it meant that Pd was completely dissolved, it was very helpful for getting Pd nanoparticles. Meanwhile, microfluidic techniques can be used to achieve a rapid gelation of silica sol containing $AlCl_3$ and $PdCl_2$. As the pH and temperature of aqueous phase droplets have an important influence on the the process of gel, Pd/Al_2O_3–SiO_2 composite microspheres were prepared changing both the temperature and the pH of solution. (Fig. 1). The precipitation of $PdCl_2$ and gelation of SiO_2 simultaneously occurred, thereby realizing the one-step synthesis of Pd/Al_2O_3–SiO_2 composite microspheres. These microspheres were characterized by SEM, TEM and BET, and the catalytic performance was test by using a cyclohexene hydrogenation system.

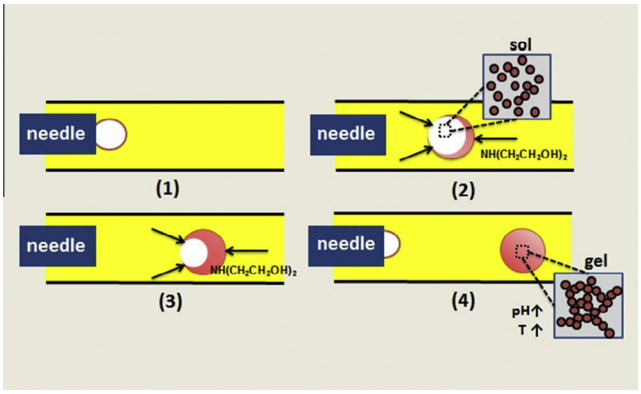

Fig. 1. Schematic of the gel process in a microchannel.

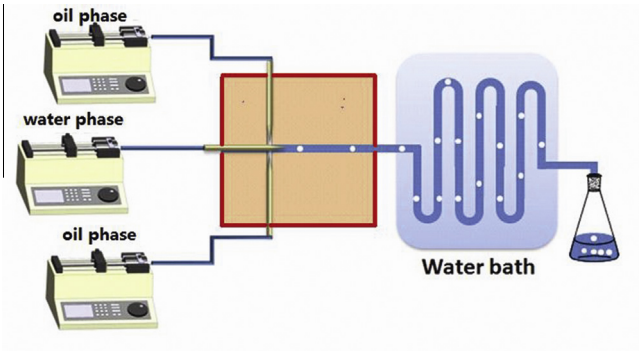

Fig. 2. Schematic of the microfluidic device.

Table 1
Preparation conditions for samples S1–4.

Sample	Si/Al mole ratio	Amount of tetraethylorthosilicate (g)	Amount of $PdCl_2$ (g)	Amount of $AlCl_3{\cdot}6H_2O$ (g)
S1	∞	2.5	0.01	0
S2	20	2.5	0.01	0.145
S3	15	2.5	0.01	0.193
S4	10	2.5	0.01	0.290

2. Experimental

2.1. Materials

Tetraethyl orthosilicate was obtained from Xilong Chemical Co. (Shantou, China). Aluminum chloride, palladium chloride, hydrochloric acid, and diethanolamine were purchased from Beijing Chemicals Co. (Beijing, China). Liquid paraffin was purchased from Bodi Chemicals Co. (Tianjin, China). Sorbitan trioleate (Span 85) was obtained from China Medicine Group Shanghai Chemical Reagent Corporation (Shanghai, China). Poly(ethylene glycol) (PEG20000) was obtained from YiliFine Chemical Co. (Beijing, China). Methylcellulose was produced by Sigma–Aldrich Corporation (USA).

2.2. Preparation of Pd/Al_2O_3–SiO_2 microspheres

The microfluidic device (Fig. 2) included a polytetrafluoroethylene tube (4 m long, 1.5 mm i.d., 2.0 mm o.d.) embedded in the

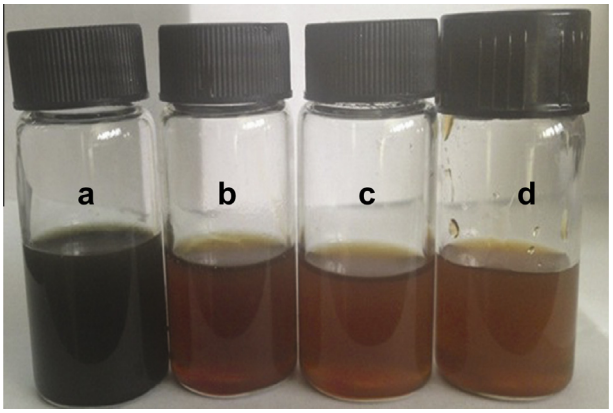

Fig. 3. Changes in sol colors: (a) S1, sol without $AlCl_3$; (b) S2, Si/Al mole ratio = 20; (c) S3, Si/Al mole ratio = 15; and (d) S4, Si/Al mole ratio = 10.