Liquid-Phase Hydrogenation on Palladium-Coated Silica Nanosprings™ in a Continuous Flow Reactor

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Catalytic hydrogenation processes in the liquid phase present challenges and difficulties due to the three-phase system formed by the solution, the solid-state catalyst and the gaseous hydrogen. Design of reliable experiments and analysis of the experimental data are the main points to be considered in these reactions. A continuous flow reactor (CFR) containing a film of immobilized palladium nanoparticles simplifies the study of the kinetics of liquid-phase hydrogenation processes. In addition, a CFR eliminates the post-processing work required to separate the catalyst particles from the reaction products. Palladium was selected for these hydrogenation processes because of its unique chemistry with hydrogen [1]. In the present paper, we report the results obtained in a CFR using palladium nanoparticles supported on a silica Nanospring substrate for the reduction of 4-nitrophenol with sodium borohydride and hydrogen gas.

Silica Nanosprings, shown in figure 1a, create a material with 100% open porosity. An individual silica Nanospring is actually formed by multiple silica nanowires of approximately 5 nm in diameter wrapped around each other in a helical configuration [2]. BET measurements of silica Nanospring mats show a surface area of 300 m^2/g, which is equivalent to 1500 cm^2 per cm^2 of footprint. Figure 1b shows a TEM image of palladium supported on silica Nanosprings. The particle size distribution, shown in figure 1c, indicates an average particle size for palladium between 1-3 nm. The concentration by weight of palladium deposited on silica Nanosprings used in the present work was 0.8 %. Figure 2a shows the components of the CFR used in the present investigation. The size of the film inside the reactor was 7×2 cm. Figure 2b displays the variation of the pressure drop through the reactor as a function of the flow rate.

To assess the performance of the catalytic material, a sample was attached to a microscope slide and immersed in a beaker with a solution of 4-nitrophenol (120 mL, 1 mM). Next, 50 mg of solid sodium borohydride was added to the beaker under constant agitation and the absorbance (400 nm) of the solution was monitored over time to calculate the reaction rate. The results obtained in this test are reported in figure 3a and indicate a remarkable catalytic activity for this particular process. The performance of the catalyst inside the CFR was evaluated by feeding a solution of 4-nitrophenol (0.1 mM) into the reactor at different flow rates using a stroke pump. The reducing solution of sodium borohydride (0.3125 g/L) was supplied using a syringe pump at a constant flow rate (25 mL/h). The conversion was estimated by measuring the absorbance of the liquid product at 400 nm. The space velocity was calculated by dividing the total flow rate of reactants by the volume of the reactor (0.1 mL). The results shown in figure 3b indicate that the Nanospring-based CFR displays a high performance at moderate space velocities. Palladium supported on silica Nanosprings is a highly active catalytic material for continuous liquid-phase hydrogenation and represents a flow reactor solution to a key process in the pharmaceutical industry.

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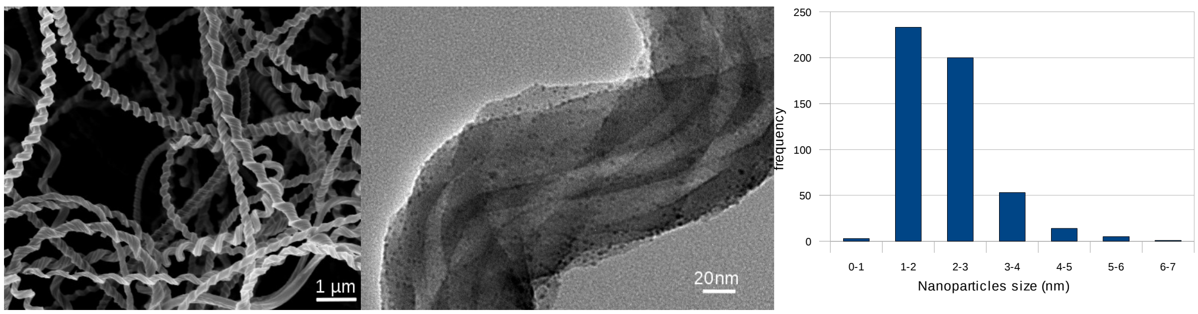

Figure 1: a) Silica Nanosprings, b) Pd coated silica Nanospring, c) Particle size distribution of Pd particles on silica Nanosprings

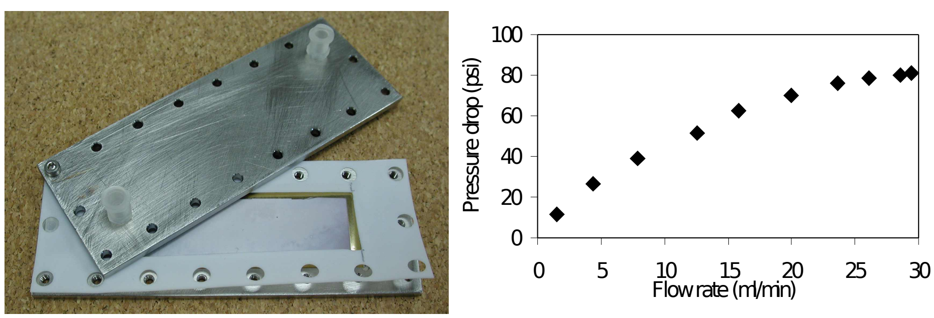

Figure 2: a) Nanospring based CFR, b) CFR pressure drop vs. flow rate

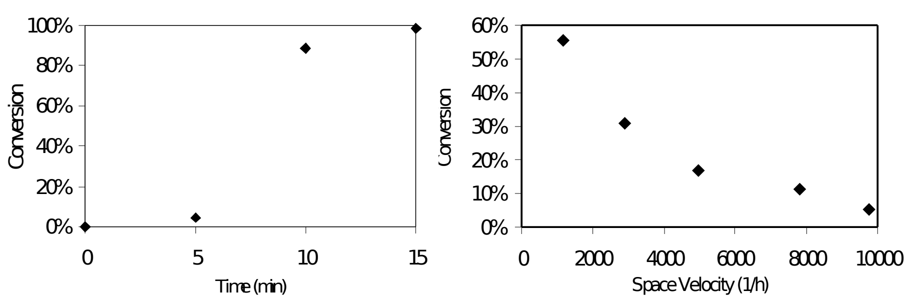

Figure 3: a) Catalytic activity test; b) CFR performance test

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