Supporting Information

Synthesis, Assembly and Reaction of a Nanocatalyst in Microfluidic Systems: A General Platform

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Experimental methods

(1) Synthesis of magnetic silica particles

In the synthesis of magnetic silica spheres, magnetic nanoparticles ($\gamma$-Fe$_3$O$_4$, EMG 304, Ferrotech) were first dispersed in the mixture of water, ammonium hydroxide, and ethanol. Then tetraethoxyorthosilicate (TEOS, Sigma Aldrich) was injected continuously using a syringe pump (Harvard Apparatus) with a controlled infusion rate (20~40 $\mu$L/min). The obtained magnetic silica suspension was then centrifuged at 9000 rpm for 10 min and washed with ethanol and milli-Q water. The washing step was repeated for 6 times to completely remove impurities. Afterwards, the particles were re-dispersed in ethanol with a mass ratio of 4:1 (ethanol:magnetic silica nanospheres). The surfaces of the magnetic core-shell NPs were then functionalized with 10 mM aminopropyl trimethoxysilane (APTMS, TCI America) under vigorous stirring at 80 °C for 3 h. The amine grafted magnetic core-shell nanospheres were then washed 4 times with absolute ethanol. Finally these particles, with an average size of 85 nm (Fig. 2a Left) were re-suspended in Milli-Q water.

(2) Immobilization of platinum nanoparticles

For the immobilization of Pt-NPs onto silica particles, the reactants were introduced through three separate inlets (see Fig. 1a and S1a for the experimental setup). High pressure syringe pumps (Harvard
Apparatus) were used to inject the three reactants: amine grafted magnetic core-shell silica suspension (Fig. 2a), Pt precursor (dipotassium tetrachloroplatinate(II)) and the reducing agents. The ratio of the flow rates of the core-shell NPs to Pt precursor was carefully controlled to get 5 wt% loading of the Pt catalyst. Polyvinyl pyrrolidone (PVP, MW = 55000, Sigma-Aldrich) was used as a stabilizing agent, and the molar ratio of PVP-monomer/Pt remained constant at 250. Two different reducing agents were used to synthesize Pt-NPs on the magnetic nanosphere surface: ascorbic acid (AA, Sigma-Aldrich) and ethylene glycol (EG, Sigma-Aldrich). A back-pressure regulator (Jasco, Model BP-1580) maintained a set pressure inside the reactor while enabling samples to be collected in a continuous mode without depressurizing the system. Synthesized PMS-NPs were then washed with acetone by centrifugation at 9000 rpm for 10 min and re-dispersed in the aqueous phase. Since the bound NPs on the support stay stable against ultrasonic radiation for 10 min as well as the flow and pressure fluctuations, they are suitable for the flow systems including microfluidic reactors.

(3) Self-assembly of PMS particles

The microfluidic droplet generator was fabricated using concentric assembly of two microtubes (Fig. 1b): an inner glass capillary and an outer FEP capillary. Fine inner capillaries with 100~150 μm inner diameters were made by heating and then pulling glass tubes (VWR, I.D. = 500 μm). The outer FEP capillaries were used as purchased (Upchurch, I.D. = 500 μm). The capillaries were connected via flexible tubing to syringes that were driven by syringe pumps (Harvard). The PMS-NP suspension was ejected from the inner capillary with a flow rate of 40 μL/min. From the outer capillary, hexadecane (Sigma-Aldrich) with 0.8 wt% of surfactant (ABIL, EM 90) was injected with a flow rate of 100 μL/min. The emulsions containing PMS-NPs were collected onto a Teflon dish whose hydrophobic surface helped to maintain the spherical shapes of the drops. Then, the dish was kept in a convection oven at 70 °C for 6 h to evaporate the aqueous phase from the emulsions. To remove residual surfactant molecules from the PMS-supraballs, the supraballs were washed with hexane, ethanol and n-butyl acetate, repeatedly.

(4) Catalytic reaction in a packed bed microreactor

Studies on the activities of different catalytic materials were conducted in a continuous flow system using a single-channel silicon-Pyrex microreactor. The slurry of the as-prepared PMS-supraballs was directly loaded into the channel using a syringe to form a packed-bed of catalyst. Since the amount of the PMS-supraballs produced took only 15% of the reactor volume, 85% of the space was filled with inert glass beads with an average diameter of 75 μm. Two commercial catalysts, Pd/C-5wt% and Pt/Al2O3-5wt% were loaded into the reactor until it was completely full. At the downstream of the reactor, an array of pillars was fabricated with 25 μm intervals to hold all the materials inside against the flow. The 4-isopropyl benzaldehyde (IBA) solution (Sigma-Aldrich, 1.5 M in n-butyl acetate, 4~6 μL/min) and molecular oxygen (0.2~0.3 sccm) were introduced into the microreactor by a syringe pump and a mass flow controller, respectively. The temperature of the reactor was monitored using a K-type thermocouple that was inserted into a small hole on the side of the packaging chuck and was controlled by a PID controller (Omega, Model CN7833) connected to the heating cartridge inserted into the chuck. The outlet of the reactor was connected with a 6-way valve to collect product samples for chemical analysis. A high-pressure stainless steel vessel was used to provide back pressure (30~60 psi) as well as collect waste materials.
Figure S1. Scheme of the experimental setups for the synthesis, self-assembly and reaction of PMS particles. a) Experimental setup for the synthesis of PMS-NPs. b) Experimental setup for the self-assembly of PMS-NPs into PMS-supraballs. c, d) Experimental setups for the oxidation reaction catalyzed by PMS-supraballs in the semi-batch and continuous systems, respectively.
Figure S2. Platinum-magnetic core-shell particles obtained using ascorbic acid as the reducing agent. a-b) Residence time 20 s; temperature 125°C. c-d) Residence time 90 s; temperature 160°C.
Figure S3. The PMS-NP synthesized using the polyol method at 160 °C with a residence time of 90 s. Pt-NPs were well distributed on the surface of the magnetic silica nanospheres.

Figure S4. TEM image of a commercial catalyst with embedded Pt-NPs (Pt/Al₂O₃-5wt%).