



Short Communication

Facile hydrogenation of carbon-carbon double bonds using catalytic noble nanoparticles immobilized in microfluidic reactors

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ABSTRACT

Facile hydrogenation of carbon-carbon double bonds was achieved in a poly(dimethylsiloxane) (PDMS) microfluidic reactor with immobilized noble nanoparticles, using the conversion of 6-bromo-1-hexene to 1-bromo-hexane as a model reaction. The microreactor was used to measure the intrinsic catalytic activity and turnover frequencies (TOF) of palladium (Pd), platinum (Pt) and ruthenium (Ru) nanocatalysts. The TOF of reactions run with immobilized nanocatalysts in the microfluidic reactor were hundreds of times larger than those measured in identical reactions in batch reactors. The combination of well-defined nanocatalysts and microfluidics significantly enhances hydrogen diffusion to catalytic sites, thus eliminating mass transfer limitations and enabling evaluation of the intrinsic catalytic activity. The system provides an excellent platform for high throughput screening of catalysts, and for conducting mechanistic studies of reaction kinetics.

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1. Introduction

Triphasic hydrogenation with solid catalysts, molecular hydrogen, and liquid substrates plays an important role in many academic and industrial laboratories. However, mass transfer between the gas, liquid and solid phases can often be inefficient, making it difficult to get sufficient hydrogen to catalytic sites for the required reactions. As a result, triphasic hydrogenation is usually carried out under high temperature and high hydrogen pressure over long periods of time. Such harsh reaction conditions and long reaction times can lead to problems that include undesirable side reactions, lack of operational safety and high energy consumption [1,2]. It can also hinder assessment of the intrinsic reaction kinetics. An effective solution to these problems is to combine catalytic nanoparticles (which provide significantly enhanced surface areas) with microfluidics (which reduces the diffusion length for hydrogen transport). The resulting improvement in multiphase mass transfer enables high yield and selectivity under mild reaction conditions, in an efficient and environmentally friendlier manner.

Noble metallic colloidal nanoparticles under 10 nm in diameter have been shown to greatly improve catalytic efficiency for multiphase hydrogenation, due to their large surface area to volume ratios compared to their bulk counterparts [3–5]. Nanoparticles with well-controlled

particle sizes and narrow size distributions also have a high percentage of their catalytically active atoms on the surface, which enables greatly enhanced reactivities. Stabilizing ligands are required to prevent particle agglomeration, to maintain catalytic activity. For example, *n*-dodecyl sulfide (NDS) has been shown to be effective as a stabilizing ligand for synthesizing uniform palladium (Pd), platinum (Pt) and ruthenium (Ru) nanoparticles in the 2–5 nm size range [6]. The sulfur atom in the NDS molecule coordinates well with noble metal atoms, and the long carbon chains prevent particle agglomeration through steric hindrance.

With a surface area to volume ratio at least 100 times larger than in conventional batch reactors, microfluidic reactors have been used extensively for heterogeneous catalytic hydrogenation [7–10]. Mass transfer limitations are greatly reduced by the increased interfacial areas and short diffusion distances [7–9]. A microfluidic system also enables high throughput and high space-time yield, low consumption of reagents and energy as well as precise control over various reaction parameters [11]. Microfluidic systems fabricated from poly(dimethylsiloxane) (PDMS) have been used widely in biomedical research because of their biocompatibility, easy and inexpensive assembly, versatility of surface functionalization, and high hydrogen permeability compared to those constructed from silicon, glass or stainless steel. As a result of these attributes, they have been drawing increasing attention in synthetic chemistry and catalysis [7–12]. In spite of their low tolerance for temperature ($T_g \sim 125^\circ\text{C}$) and tendency to swell in non-polar organic solvents, PDMS microfluidic reactors are suitable for hydrogenation in aqueous or polar organic media under mild reaction conditions [13]. Catalysts can be immobilized evenly and robustly on the channel walls to allow catalyst reuse and recycling, and to avoid significant pressure drop across the reactor [11,14,15].

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In the present work, we report the combination of nanocatalysts and microfluidics for improved reaction efficiency in a model triphasic hydrogenation reaction. We used a PDMS microfluidic reactor with immobilized metallic noble nanoparticles for high throughput assessment of intrinsic catalytic activity. The simple and robust immobilization protocol is based on our previously reported scheme [10]. The model reaction, hydrogenation of 6-bromo-1-hexene to 1-bromo-hexane (Scheme 1), is important in the synthesis of pharmaceutical intermediates where the selective reduction of carbon-carbon double bonds can be carried out without affecting the halogen atom.

2. Experimental

2.1. Synthesis of NDS-stabilized nanoparticles

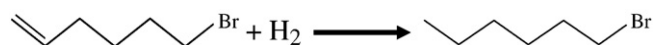
Pd, Pt and Ru nanoparticles were synthesized by thermal decomposition, using the parameters given in Table 1. Briefly, a 1:5 molar ratio of the metal precursors and stabilizing ligands were mixed and heated to the respective decomposition temperature, followed by acetone washing and centrifugation [6]. NDS is highly soluble in toluene, so it was used as the solvent in the synthetic procedures for Pd and Ru. Since Pt precursors have a higher decomposition temperature than both Pd and Ru, we used phenyl ether as the solvent for Pt synthesis because of its higher boiling point (259 °C vs. 111 °C for toluene).

2.2. Design and fabrication of microfluidic reactors

A PDMS microfluidic reactor with a Y-shaped inlet was fabricated by soft lithography [8,16] using the protocol shown in Fig. 1a. A serpentine reactor pattern on a silicon wafer was transferred to a PDMS block, and irreversibly bonded to a microscope glass slide to form rectangular channels with dimensions (W, H, L) of 500 μm, 100 μm and 30 cm, respectively (Fig. 1b). To prevent swelling of the PDMS, the nanoparticles were redispersed in compatible solvents following synthesis. *In situ* nanoparticle immobilization was achieved by sequential infusion of a mixture of 3-aminopropyltrimethoxysilane (APTMS, Sigma, St. Louis, MO) and nanoparticles into the oxygen plasma-treated microfluidic reactors at a flow rate of 0.025 mL/min for several hours, followed by curing at 60 °C for 1 h in an oven. The aminosilanization process deposits primary amine groups (–NH₂) on all microfluidic channel surfaces already rich in hydroxyl groups following oxygen plasma treatment. The sequential introduction of Pd, Pt or Ru nanoparticles into the channel enables coordination with the primary amine groups on the channel surfaces [10], thus inducing immobilization (Fig. 2). A similar immobilization procedure was carried out on 1 cm by 1 cm pieces of glass and PDMS surfaces, for the purpose of characterization.

2.3. Hydrogenation of 6-bromo-1-hexene in batch and microfluidic reactors

Hydrogenation of 6-bromo-1-hexene was conducted in both blank and microfluidic reactors with immobilized catalysts. The microfluidic reactors were pretreated by flowing hydrogen through the system at 100 °C for 1 h before reactions. All reactions were conducted at room temperature (25 °C). Hydrogen at a pressure of 1 atm. and reactant solutions of 1, 5, and 10 mM were introduced independently into the microfluidic channel through the Y-shaped inlet using a mass flow controller (Bronkhorst F-201CV-020-AGD-



Scheme 1. The hydrogenation of 6-bromo-1-hexene to 1-bromo-hexane was used as a model reaction to assess catalytic activity.

Table 1

Conditions used for synthesis of palladium (Pd), platinum (Pt) and ruthenium (Ru) nanoparticles, along with the resulting average particle sizes.

| Sample | Stabilizing ligand | Precursor | Molar ratio of ligand to precursor | T (°C) | Time (h) | Solvent | Particle size (nm) |
|--------|--|--|------------------------------------|--------|----------|--------------|--------------------|
| NDS-Pd | [CH ₃ (CH ₂) ₁₁] ₂ S | Pd(OAc) ₂ | 5:1 | 95 | 3 | Toluene | 3.0 ± 0.3 |
| NDS-Pt | [CH ₃ (CH ₂) ₁₁] ₂ S | Pt(C ₅ H ₇ O ₂) ₂ | 5:1 | 180 | 1 | Phenyl ether | 3.3 ± 0.7 |
| NDS-Ru | [CH ₃ (CH ₂) ₁₁] ₂ S | Ru(cod)(cot) | 5:1 | 60 | 1 | Toluene | 3.5 ± 0.4 |

20-V, Ruurlo, Nederland) and a syringe pump (Harvard apparatus PHD 2200, Holliston, MA). The gas and liquid flow rates were adjusted to produce an annular flow pattern in which the gas travelled in the

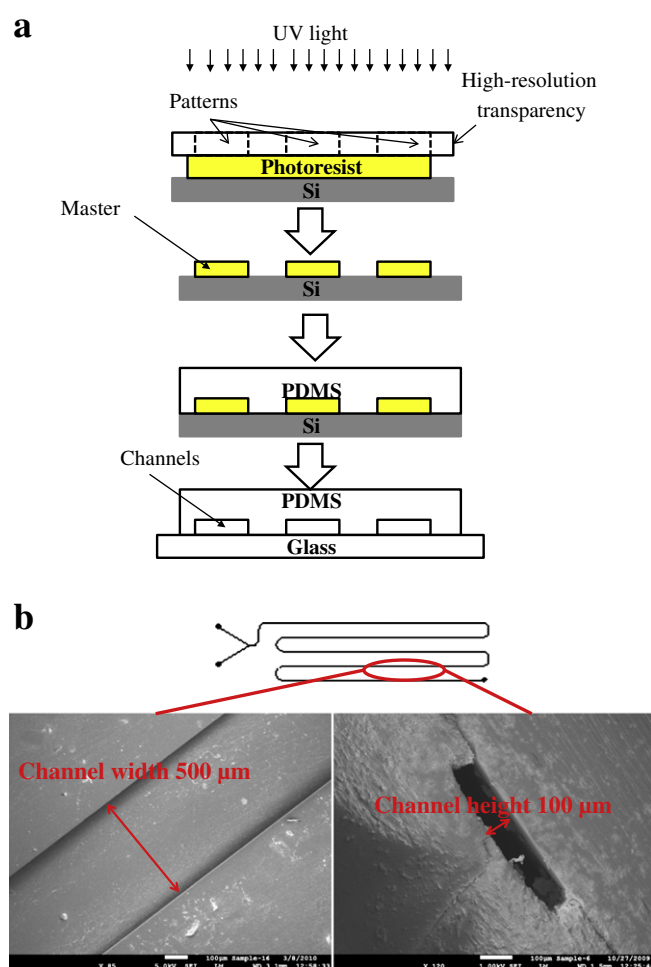


Fig. 1. (a) Step-by-step soft lithography procedure for fabrication of microfluidic channels in PDMS [8,16]. The channel pattern was designed by Adobe illustrator and printed on a dark high resolution transparency on which only the pattern is transparent. The pattern was first transferred to a silicon wafer coated with photoresist by exposure to UV light, creating a positive master. A mixture of PDMS precursor and cross-linker was poured onto the positive master and cured to form a PDMS block containing the negative pattern. Sealed microfluidic channels were then created by using oxygen plasma treatment to irreversibly bond the PDMS block to the microscope slide. (b) Serpentine microfluidic channel with a Y-shaped inlet for independent transport of hydrogen and reactants into the microreactor. The SEM image on the lower left is the top view of the microfluidic channel. The SEM image on the right is the cross-section of the microfluidic channel, with the PDMS block to the left and the glass slide to the right. The channel width and height are 500 μm and 100 μm, respectively. The channel length in this setup is 30 cm, and can be controlled by the number of loops.

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