High Pressure Catalytic Hydrogenation of Acetone in a PDMS Based Recirculating Microreactor System

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Abstract

Mass transfer resistances often play a limiting role in gas-liquid-solid reactions. Catalytic hydrogenations are such a class of reactions where high operating pressures and mechanical stirring are used to overcome these resistances. Microreactors[1] offer the opportunity to overcome such limitations using large interfacial areas. Their low holdup volumes are advantageous when dealing with hazardous reagents[2]. Consequently, a number of researchers have looked at conducting hydrogenations in microfluidic setups[3,4].

PDMS based microreactors offer the advantages of low cost and ease of manufacture as compared to silica based microreactors[5]. Yet PDMS based microreactors lack mechanical strength and thus there have been no reports of high pressure (>100 psi) hydrogenations using such a setup.

We report the high pressure (725 psi) catalytic hydrogenation of acetone to isopropanol over Ru/C in a PDMS based microreactor. To overcome limitations of the mechanical stability of the PDMS based microreactor to high pressures, a novel arrangement was used wherein the microreactor was placed in a high pressure Parr reactor. Using Ru/C at 40°C and 650 psi hydrogen pressure, 20% acetone conversion to isopropanol was achieved with no byproduct formation.

1. Introduction

Exploratory work in our labs demonstrated that ruthenium nanoparticles supported on MCM-41 were active towards the catalytic reduction of lactic acid and glycine[6]. On a per mole ruthenium basis, the nanocatalysts exhibit an order of magnitude increase in catalytic activity towards hydrogenation as compared to carbon supported ruthenium catalysts. In continuation, this work has two main objectives, viz. to enable the study of hydrogenation kinetics in an environment where hydrogen is not the limiting reactant and to characterize the behaviour of nanoparticles in the absence of any interactions due to the support .

Mass transfer resistance leads to decreased concentrations of reactants in solvents. The solubility of hydrogen in water at 350 psi and 27 °C is 0.02 M. This value is less than the solubilities of most substrates, hence hydrogen becomes the limiting reactant. At 1050 psi and 27 °C the hydrogen solubility in water increases to 0.056 M. High operating pressures are thus used in hydrogenations, primarily to increase the concentration of hydrogen in the liquid phase.

Nanoparticles are unstable and tend to agglomerate over long durations. This tendency to agglomerate can be aggravated by high temperatures and other conditions commonly found in heterogeneous catalytic reactions. One strategy to study nanoparticle behaviour in catalytic reactions, while preventing agglomeration, is to anchor the nanoparticles on porous supports[6]. Another strategy can be to pass reaction mixture over a monolayer of catalytic nanoparticles – this removes any role a support may play in the reaction.

2. PDMS-Glass Microreactor System

PDMS (Poly DiMethyl Siloxane) based microchannel reactors of 300 μm width, 75 μm depth and 5 cm length (Figures 2 and 3) were prepared by soft lithography[5]. The microchannel was sealed by bonding a 5 mm thick glass slide to the etched face of the PDMS microreactor. To facilitate flow in and out of the microreactor, holes were drilled into the 5 mm thick glass cover slide and HPLC tubing was sealed to the glass with epoxy adhesive to ensure strong and leak proof connections.

Elevated hydrogen pressures are necessary for hydrogenation. By itself, the PDMS microchannel reactor system described above can only withstand pressures up to 0.5 MPa. Hence, a novel reactor configuration was developed that involved placing the PDMS microreactor in a high pressure Parr reactor, such that there is equal hydrogen pressure both within and outside the microreactor, A 7-ml glass vial placed in the Parr reactor was used as a reservoir (Figure 4). Reaction mixture was recirculated from the 7ml reservoir to the microreactor and back by means of an external HPLC pump. This configuration reduces the length of the flow loop, enables control over temperature and pressure in the various components of the setup, and keeps the volume of the reservoir small.

This setup allows subjecting the reaction mixture and catalyst to high hydrogen pressures while keeping the pressure within and outside the microreactor equal, preventing breakup of the microreactor. By passing water saturated with hydrogen at high pressure through the narrow channel over an immobilized catalyst, we alleviate resistance to mass transfer between gas and liquid phases. This enables study of the intrinsic kinetics of a reaction.
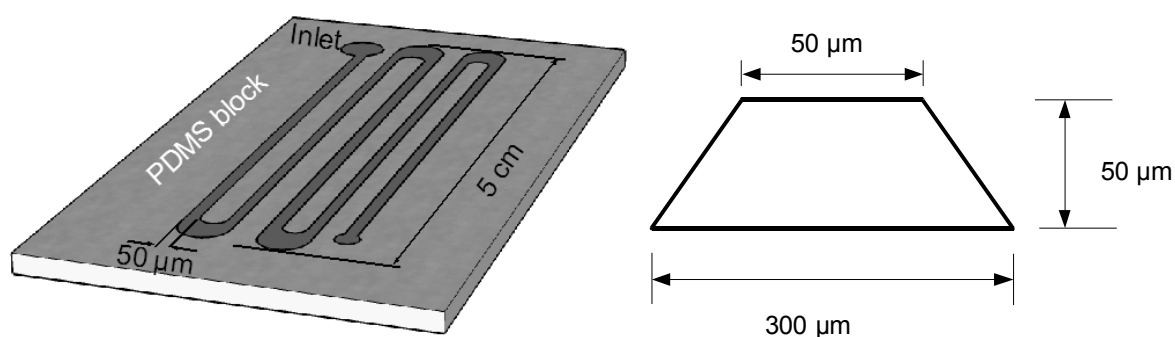

Figure 2. Schematic showing a) dimensions of microchannels engraved in a block of PDMS using soft lithography. b) Cross section of a PDMS microchannel.
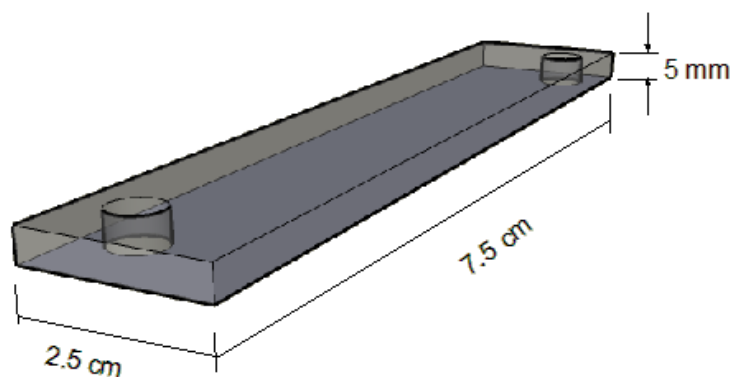
Figure 3. Dimensions of a glass slide with holes, which is plasma bonded to PDMS block engraved with microchannels to form a PDMS glass microreactor. (Schematics not to scale).

To determine the feasibility of the catalytic microreactor for reaction studies,, the proposed system was modeled as a 10 ml stirred batch reactor. With 4 micrograms of 3.5 nm ruthenium nanoparticles deposited as a monolayer onto the bottom face of the microreactor, a simple calculation showed that under typical reaction conditions 4 %per hour conversion of reactant to product was possible. Thus, the proposed system appears to be a viable tool to study reaction kinetics.
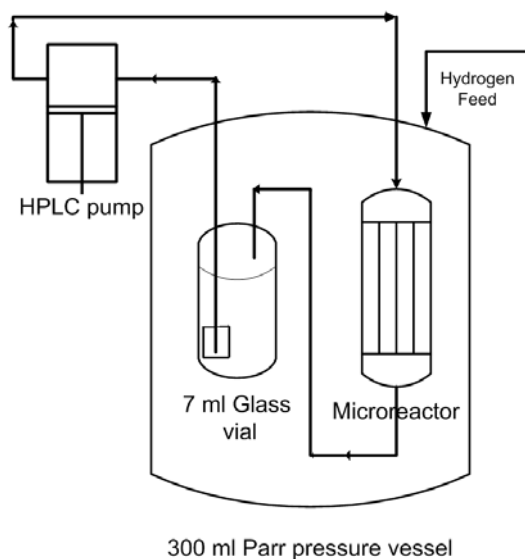

Figure 4. Schematic of modified flow loop and various components of the flow loop

3. Catalyst

Whereas the ultimate objective of this work involves immobilizing nanoparticles in the microchannels, in order to demonstrate feasibility of catalytic hydrogenation in the setup, preliminary studies were carried out using immobilized bulk Pd metal. Palladium microwires of 50 micron diameter were therefore placed in the microchannels before irreversible bonding to the glass took place. .

4. Substrate

The PDMS microreactor swells in organic solvents and has limited temperature stability[8] (373 K). Hence, test reactions should ideally be aqueous phase hydrogenation, with the substrate reactive enough to demonstrate significant conversion at low temperatures, viz. 50°C. Hydrogenation of acetone to isopropanol proceeds relatively fast under such mild reaction conditions. Additionally, the existing HPLC instruments in our laboratory are capable of analyzing acetone and isopropanol at the low concentrations being considered (1 - 200 mM). Hence hydrogenation of acetone was selected as a test reaction as shown in Figure 8.
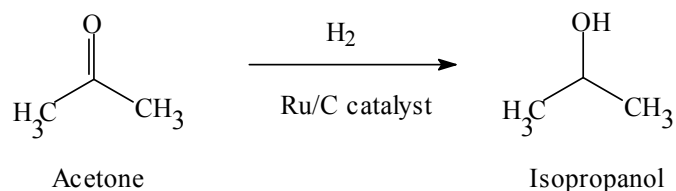

Figure 8. Hydrogenation of acetone to isopropanol

5. Results and discussion

5ml of 5mM acetone in water was subjected to hydrogenation in the microreactor setup. A typical run involved passing the reaction mixture at 1.0 ml/min through the flow loop for 20 hours. The temperature of the system was varied between 22 and 55 °C between runs, while hydrogen pressure was kept constant at 350 psi or higher. 5 mM glycerol was used as an internal standard. Table 1 summarizes results from the runs.

Table 1. Summary of results from hydrogenation runs using Pd wire immobilized in PDMS-glass microreactor

Feed	reaction conditions	catalyst	Yield to IPA
5 ml of 6mM acetone + internal standard	20 °C, 350 psi H_2, 22 h at 1 ml/min	25 cm of 50 μm Pd wire	3.5 ± 0.2 %
5 ml of 6mM acetone + internal standard	22 °C, 350 psi H_2, 22 h at 1 ml/min	**no catalyst**	0.75 ± 0.2 %
5.5 ml of 8.8 mM acetone + internal std.	**55 °C**, 725 psi H_2 22 h at 1 ml/min	25 cm of 50 μm Pd wire	6 ± 0.2 %
5.5 ml of 8.8 mM acetone + internal std.	55 °C, 725 psi H_2 **92 h** at 1 ml/min	25 cm of 50 μm Pd wire	36 ± 0.2 %
5.5 ml of 8.8 mM acetone + internal std.	55 °C, **no H_2** 21.5 h at 1 ml/min	25 cm of 50 μm Pd wire	No IPA observed

The data in Line 2 of Table 1 show that there is some background activity (metal fittings, pump parts, etc.) that results in the conversion of acetone to isopropanol in the absence of any Pd catalyst. However, it is clear that under the reaction conditions shown, the palladium wires are catalytically active and result in conversion at least 3-5 times higher than that due to background reactivity.

Conclusions

A PDMS-glass microreactor was incorporated into a 300 ml high pressure Parr autoclave reactor. A flow loop was developed which ensured equal pressure inside and outside the microreactor, overcoming limitations related to mechanical stability of the microreactor. As a result, liquid saturated with hydrogen at high pressures could be passed through the microchannels, eliminating gas-liquid mass transfer resistance, and enabling the study of intrinsic reaction kinetics under conditions where hydrogen is not the limiting reactant. Preliminary results were obtained using immobilized palladium wires. Work continues on developing an immobilization technique to deposit other catalysts in microchannels.

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