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**Microreactor Research and Development at  
Louisiana Tech University: Fabrication of  
Silicon Microchannel Reactors for Catalyst  
Studies on Conversion of Cyclohexene as a  
Prototype and Syngas to Alkanes**

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Design and fabrication of microreactors and catalyst development of two reactions are described. A prototype reaction - gas phase conversion of cyclohexene to cyclohexane and benzene - has been studied extensively. The conversion is significantly improved ( $> 90\%$ ) using silica sol-gel impregnated catalyst. An industrially relevant reaction on syngas conversion ( $\text{CO} + \text{H}_2$ ) to alkanes using mixed metal catalysts encapsulated in alumina or silica sol-gel has also been investigated. A high conversion of CO ( $\sim 73\%$ ) in the presence of a catalyst promoter with high selectivity to propane ( $\sim 80\%$ ) has been achieved. Characterization of the catalysts, design of experiments on syngas conversion, and development of the parallel array microreactor system for fast and effective screening of catalysts are discussed in this chapter.

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## Introduction

Process miniaturization and microreaction technology provide opportunities for improving process capability and control in chemical/biochemical synthesis and can allow safer and more efficient chemical/biochemical kinetic investigations. Compared to normal scale reactors, microreactors have the following advantages: decrease of linear dimensions, increase of surface to volume ratio, fast and efficient process development, decreased potential of environmental impact, and increased safety. The large surface-to-volume ratios of the micro channels inhibit gas-phase free-radical reactions and improve heat transfer for exothermic reactions. Microreactors' narrow channels and thin walls also make them suitable candidates for studying potentially explosive reactions with reduced risks.

Microreactors, "Lab-on-a-chip" device (Figure 1), in general, consist of micro channels, with lateral dimensions on the order of micrometers, etched on metal, glass, silicon, or other substrates *via* photolithography or other techniques [1-3]. The physical design of the device can be the size of a dime containing ~ 200 or more channels depending on their width (Figure 2). Silicon is usually a material of choice because of well developed photolithography and etching techniques used in the microelectronics industry [2].

Microreactor technology is relatively new but has a greater industrial interest as judged by the number of issued patents (<100). It provides relatively simple and quick means towards commercialization of a process [4-8]. The economic production of large numbers of microreactors enables the shift from the present production paradigm of batch process and "scaling up" to a new paradigm of continuous process and "numbering up", i.e., running numerous microreactors in parallel for mass production [9] and parallel catalyst screening [10, 11]. This would lead to short lead times from laboratory catalyst development to industrial production as well as the ability to produce chemicals on demand on-site. The potential exists for every chemical process to be miniaturized to increase process safety as well as overall efficiency and productivity.

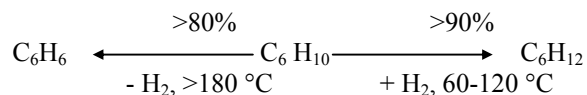
At the Institute for Micromanufacturing (IfM) of Louisiana Tech University, we have been doing microreactor research for ~ 10 years including simulation, design and microfabrication of the reactors. Initially, the conversion of cyclohexene to benzene and cyclohexane has been chosen as a model reaction [12-14]. In addition, two reactions of industrial significance are currently being investigated: Fischer-Tropsch synthesis to higher alkanes [15, 16] and preferential oxidation for CO amelioration in hydrogen fuel cell feeds. While the former is part of this paper, the latter is presented in another chapter of this book [17].

## History of Microreactors Developed at IfM

Microreactors were initially fabricated at IfM using a <110> silicon wafer by anisotropic wet etching and comprised of a system of 10 channels - 10  $\mu\text{m}$  deep, 500  $\mu\text{m}$  wide, and 50 mm long [18]. Platinum was sputtered on the channels to catalyze the gas-liquid heterogeneous reaction with a minimal conversion (9%) of cyclohexane to benzene. A finite difference model was used to determine conversion for a given length, depth, pressure drop by taking into account flow regime through Knudsen number, the reaction probability, and the number of collisions. Channel depth has a profound effect on conversion.

Using the same microreactor, dehydrogenation of cyclohexane to benzene is an endothermic reversible reaction with an equilibrium conversion of 18.9% at 200°C. However, the conversion can be driven beyond equilibrium to 99%, if the hydrogen is selectively removed from the system using a palladium membrane (Figure 3) [19]. This structure allowed for 50% exposure of the palladium membrane (3 to 6  $\mu\text{m}$  thick) with the rest being supported by silicon braces. The model, mentioned above [18], showed that the efficacy of the membrane was also sensitive to channel depth, operating pressures and catalyst activity.

After successful fabrication of 500 $\mu\text{m}$  wide channels, 100  $\mu\text{m}$  and 5 $\mu\text{m}$  wide channels with 100 $\mu\text{m}$  depth were subsequently developed using ICP (Inductively Coupled Plasma) dry etching (Figure 2). The high resolution and anisotropy of ICP etching has produced microchannels with high surface-to-volume ratio and vertical channel walls [20]. Using these reactors, hydrogenation and dehydrogenation of cyclohexene (see below), as a prototype reaction, have been investigated. The conversion of cyclohexene with sputtered Pt is over 95% with high selectivity to cyclohexane and benzene [21,22].



## Microreactor Design and Fabrication

Microreactors with different dimensions and geometry, with a very high depth to width (aspect) ratio, have been developed over the years [15, 16]. Recently, we have performed microfluidic modeling studies in different micro channels using CoventorWare software to understand the effect of surface area on catalysis and the residence time of reactants in the micro channels. Figure 4 shows the effect of channel geometry on fluid flow in 5  $\mu\text{m}$  straight and zigzag channels. Under the condition of similar inlet flow rates, the flow velocity in

straight channels is much greater than the zigzag channels, yielding a lower residence time as compared to zigzag channels. Also, the velocity vector in Y direction is much higher in zigzag channels yielding higher surface fluid interaction.

Fabrication follows simulation of a desired design. Currently, the microreactors are made from a four-inch diameter, 500  $\mu\text{m}$  thick, double side polished silicon wafer using two main processes: photo-lithography and ICP etching. The lithography process used to make the microreactor is much like the one used in the integrated circuit (IC) industry [23]. The details of this procedure is described elsewhere [24]. Besides straight and zig-zag channels, column and novel sinewave channels have also been fabricated.

The fabricated microreactor is 3.1 cm x 1.6 cm, with a reaction area of 1.3 cm x 1.2 cm and consists of via (the holes through the wafer), feed inlet, product outlet and numerous micro channels of 5-50  $\mu\text{m}$  width and have a depth of 100  $\mu\text{m}$  (Figure 1). After the channels are coated with the catalyst (described later), the reactor is covered with the Pyrex glass 7740 by anodic bonding. [25-27].

### Experimental Apparatus

For a typical reaction in a microreactor, additional peripheral equipment are needed for control of flow, temperature, and pressure, and for the acquisition of the product distribution of the effluent stream (Figure 5). The silicon reactor chip interfaces to a steel holding block fitted with an O-ring sealed gas connections to the inlet and outlet openings on the bottom side of the chip. The block also has resistive heating elements and a thermocouple for temperature control. Gases are fed to the block by mass flow controllers. Digital pressure sensors are situated in the inlet and outlet streams to monitor pressure drops. Experiments with liquid reactants, such as cyclohexene, were conducted by bubbling a carrier gas, such as argon. The flow and reactor temperature settings were monitored and controlled by a PC running LabView software.

The reactant gases flow through the *via* into the inlet area and the microchannels with the effluent leaving the reactor through another *via* where it is diluted with helium (He) gas. The effluent is then analysed using a Stanford Research Systems mass spectrometer where the progress of the reaction is monitored.

### Catalyst Study

The development of the catalyst and its support is an important area of our research [15]. Higher surface area materials such as sol-gel prepared alumina

increase the catalyst activity by increasing the number of active sites located on the surface of pure metal.

General: We have used both physical and chemical methods for the preparation of the catalysts/catalyst supports. While the physical method involved sputtering, the chemical procedure included sol-gel and ion impregnation techniques. The chemical methods are preferred to increase the surface area of the catalyst and to lower deposition cost compared to that of sputtering. The catalyst supports were prepared using alumina and silica sol-gel precursors.

Three sol-gel methods - dip coating, spin coating, and drop coating - have been used for the catalyst and support coating inside microreactor channels [24]. Lithography technique is used to perform selective deposition of sol-gel to the desired regions of the microreactor [22]. The catalyst/support is deposited in the microchannels either by mixture of the support with catalyst precursors or by the sol-gel coating followed by catalyst deposition (sputtering or impregnation). The properties of the sol-gel matrices are significantly affected by the experimental conditions such as calcination temperature and the time of aging.

### **Cyclohexene Conversion Reaction**

The prototype reaction on conversion of cyclohexene was studied in the presence of platinum catalyst at different reaction temperatures to compare the efficiency of two types of catalyst preparation. For sol-gel impregnation, tetraethoxysilane ( $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) was chosen as the precursor of silica because of its ease of preparation and compatibility to microfabrication [28-31]. The silica sol-gel was prepared in an acidic medium as the surface area was expected to be approximately ten times higher than that obtained in a basic environment [30]. Platinum was then deposited on the catalyst support in the form of  $\text{Pt}^{+2}$  by ion impregnation followed by reduction in an hydrogen atmosphere to  $\text{Pt}^0$  [23, 33].

The specific surface area of silica supported Pt catalyst using BET (Brunauer-Emmett-Teller) method is  $\sim 292 \text{ m}^2/\text{g}$ . The high surface area is due to porous structure of the silica sol-gel particle with an average size of 50-80 nm in diameter as observed using Atomic Force Microscopy (AFM). Also, the X-ray Photoelectron Spectroscopy (XPS) sputter depth profiling of the catalyst/support film indicates uniform Pt concentration to a depth of at least 5  $\mu\text{m}$  thickness of the film.

A series of experiments were designed and performed in 100  $\mu\text{m}$  wide channels reactors to compare the performance of sputtered catalyst with that of impregnated sol-gel catalyst. The temperature and flow rates for reactants were varied as shown in Table 1. Cyclohexene conversion on impregnated Pt remains same ( $\sim 90\%$ ) at all flow and temperature settings compared to that obtained using sputtered Pt (Figure 6). The sol-gel method increases the surface area of

the catalyst and improves significantly the overall conversion of the reaction. And also, the other experiment results indicate that cyclohexene is converted to cyclohexane in sol-gel support situation above 150 °C, and to benzene on unsupported Pt [24]. These results show that easy catalyst screening and desired product distribution are the benefits of the microreactors compared to the normal scale reactors.

**Table 1. Different Reaction Conditions for Testing Platinum Catalyst Using Cyclohexene Conversion Reaction.**

<i>Design point</i>	<i>Temp (°C)</i>	<i>H<sub>2</sub> (sccm)</i>	<i>Ar with cyclohexene (sccm)</i>	<i>Contact time (sec)</i>
1	62.5	0.82	0.28	5.659
2	62.5	0.82	0.82	3.795
3	62.5	0.28	0.82	5.659
4	125	0.55	0.55	5.659
5	187.5	0.28	0.28	11.115
6	187.5	0.82	0.28	5.659
7	187.5	0.82	0.82	3.795

#### Syngas to Alkanes (Fischer-Tropsch Synthesis)

After a thorough investigation of the prototype reaction of cyclohexene to cyclohexane and benzene, we have started our catalyst studies on the Fischer-Tropsch synthesis of higher alkanes from syngas (CO+H<sub>2</sub>).



*Catalyst used* : Fe, Co; *Catalyst support*: Alumina or Silica sol-gel

As the sol-gel support improves cyclohexene conversion (shown above), our current studies have focussed on sol-gel matrix for catalyst deposition. For syn-gas reaction, aluminum tri-sec butoxide and tetraethylorthosilicate are used as the precursors for the preparation of alumina and silica sol-gel, respectively. The basic step involves acid hydrolysis followed by polycondensation to form a highly porous sol-gel network [34]. Iron nitrate and cobalt nitrate were incorporated into alumina or silica sol- gel solution for the desired composition. The mixture of sol- gel and catalyst is deposited into the microchannels of the reactor by wash coating and reduced to the metallic form in an atmosphere of H<sub>2</sub>.

### *Characterization of the Catalyst and its Support*

The BET surface area measurements were performed for sol-gel encapsulated Fe/Co catalyst as described above for cyclohexene reactions. The sol-gel encapsulated catalysts yield an average specific surface area of 285 m<sup>2</sup>/g for alumina and ~ 300 m<sup>2</sup>/g for silica. This high surface area is due to the high porosity of alumina and silica sol-gel observed in their AFM images (Figure 7 and Figure 4 of the other chapter in this book). It can also be inferred from Figure 7 that the diameter of the alumina sol-gel granules is ~ 50- 100 nm. It is expected that the diameter of encapsulated metallic Fe and Co particles would be less than 50 nm.

To optimize the sol-gel preparation and deposition process in the microchannels of the reactor, SEM studies were performed as shown in Figure 8. We have noticed that the sol-gel is deposited evenly in the 25 μm channel reactors compared to the narrow 5 μm channels (not shown). An Energy Dispersive X-ray (EDX) spectrometer coupled with the SEM was used to study the elemental composition of sol-gel encapsulated catalyst (Fe and Co) deposited in the reactor. Although the intended metal composition of Fe and Co in the reaction is 24 % (12% each), the EDX results indicate that only 5-7 % of total metal catalyst is loaded onto sol-gel prepared from metal nitrate solution. However, the metal loading can be improved significantly to around 16-18% using commercially available nanoparticles of iron oxide (10-40 nm) and synthesized cobalt oxide (15-30 nm) as the catalyst precursors [15]. The EDX data suggest that the metal loading using nitrates is quite less compared to the direct use of oxide nanoparticles.

### *Conversion of CO to Alkanes*

Conversion of CO to alkanes has been studied both in alumina and silica sol-gel coated in 5 μm and 25 μm channel reactors. As we have found that the sol-gel deposition in the 5 μm channels reactors is not uniform, we have done most of our studies in 25 μm channel reactors [35]. The conversion of CO is ~ 53 % in 25 μm channel reactors containing Fe-Co-Al<sub>2</sub>O<sub>3</sub> at 230°C, H<sub>2</sub>: CO ratio of 3:1, total flow rate of 0.8 sccm and contact time of 0.994 second. Similar studies were done with silica sol-gel encapsulated in 25 μm channel reactors in the presence of Ru-promoter to yield ~62 % conversion (Figure 9). We have achieved CO conversion around 73 % using ruthenium promoter under different reaction conditions that will be reported elsewhere [35]. However, the selectivity for alkanes is not affected by the channel geometry and the type of catalyst support. Propane has been the major product with a selectivity of ~ 80% under all reaction conditions.

To determine the nature and activity of the catalyst at different stages, magnetization studies were performed using Vibrating Sample Magnetometer (VSM). The magnetic behavior of the sol-gel encapsulated Fe-Co catalyst coated microreactors after calcination, after reducing and after syn-gas (CO+H<sub>2</sub>) reaction is shown in Figure 10. The catalyst in as-deposited reactor shows paramagnetic behavior mostly coming from the iron and cobalt oxides. As Fe and Co oxides are reduced to pure metals, ferromagnetic behavior is observed. The saturation magnetization of the ferromagnetic component can be used to estimate a lower limit of ~ 40 % for the reduction efficiency at higher temperatures. The ferromagnetic behavior, however, diminishes in the post catalytic reaction sample, as Fe and Co are forming inactive compounds. The magnetic data indicate that about 85% of the catalyst has become inactive after 25 hrs of catalytic reaction.

#### *Comparison to Macroscale Reactions*

In parallel to the microreactor research at the IfM, Chemistry Program is also involved in the macroscale synthesis of higher alkanes from syngas. The process involves a modified sol-gel/oil drop method [36] to prepare Co/Fe/Cu nanoparticles which are incorporated into mesoporous  $\gamma$ -alumina and silica granules. The surface areas of the sol-gel encapsulated nano-catalysts are 250-350 m<sup>2</sup>/g similar to that observed in the microchannels. This suggests that the alumina and silica granules are mesoporous in nature [37].

The efficacy of CO/H<sub>2</sub> conversion was investigated with the Co/Fe (12%) metal loaded  $\gamma$ -alumina granules in both gas and slurry phase reactors. At higher flow rates (40 cc/hr), the conversion of CO is higher in the slurry phase (~80 %) compared to that observed in the gas phase (~30%) within 15 hrs of the reaction. In the gas phase, we have observed a variety of hydrocarbons such as CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, isoC<sub>4</sub>H<sub>10</sub>, C<sub>4</sub>H<sub>10</sub>, isoC<sub>5</sub>H<sub>12</sub>, C<sub>5</sub>H<sub>12</sub> with very little benzene. It is not clear, at this stage, why alkanes higher than propane are not observed in our reactions in the microreactors coated with the Fe/co catalyst. Perhaps, the presence of copper in the macroscale reaction has a significant effect on the formation of higher alkanes.

In contrast to gas phase reactor, the ratio of CO/H<sub>2</sub> seems to affect the alkane distribution in the slurry phase reactor. At low CO/H<sub>2</sub> ratio, the major product is methane. With an increase in CO/H<sub>2</sub> ratio, higher alkanes are produced. We have not yet observed hexane in the product mixture and speculate that it is converted to benzene. We also notice that CO/H<sub>2</sub> ratio of 1:1 produces wider distribution of alkanes and may be suitable for fuel production with nanoparticles of Co/Fe encapsulated in alumina [38]. Currently we are investigating alkane distribution when alumina is gradually replaced by silica in the granules.



*Empirical Modeling and Statistical Analysis for Syngas Conversion in a Microreactor*

In order to have a better understanding of surface catalysis and to optimize conversion of CO in microreactors, we have considered design of experiments using response surface methodology developed by Box and Wilson in 1951 [39,40]. The main goal of the Fischer-Tropsch (F-T) synthesis experiment, based on central composite design, [41] is to obtain higher CO conversion with greater propane ( $C_3H_8$ ) selectivity.

Three independent variables or factors were considered important for this reaction: the total flow rate ( $x_1$ ),  $H_2 : CO$  ratio ( $x_2$ ), and temperature ( $x_3$ ). Here, total flow rate relates to residence time and the  $H_2 : CO$  ratio relates to the stoichiometry of the chemical reaction. The conversion of CO ( $Y_1$ ), and the selectivity to  $C_3H_8$  ( $Y_2$ ) were considered as the dependent variables. The purpose of using experimental design is to find the treatment combination  $\mathbf{x}=(x_1, x_2, x_3)$  for which the conversion of CO and the selectivity of  $C_3H_8$  are maximized.

First order regression models were fitted to conversion and selectivity of experimental data based on the cube portion of the central composite design. Results of the analysis showed no quadratic lack-of-fit of the linear model for CO conversion, but did show a quadratic lack-of-fit for propane selectivity. This indicates that the surface of CO conversion is planar, but the surface of selectivity for propane ( $C_3H_8$ ) is not. As a result, a second-order regression for propane selectivity was fitted to the full second-order central composite design (shown below). It shows that  $H_2 : CO$  ratio ( $x_2$ ) has the largest effect on propane selectivity. Canonical analysis on the second-order model of propane selectivity shows that the total flow rate,  $H_2 : CO$  ratio, and temperature combination at the point (0.60, 4.51, and 218.16) give a maximum selectivity of propane ( $C_3H_8$ ) equal to 88.25%. Additional experiments are underway to verify this prediction.

$$Y_4 = 0.841 + 0.035BL_1 - 0.014BL_2 - 0.014x_1 + 0.04x_2 + 0.011x_3 - 0.005x_1^2 - 0.013x_2^2 - 0.028x_3^2 + 0.004x_1x_2 - 0.005x_1x_3 - 0.011x_2x_3$$

### Parallel Array of Micro-reactors

So far we have described all reactions using a single microreactor. We are currently developing a parallel array reactors to screen catalysts simultaneously as well as scale up microreactions [42]. Precise process control, flexible experiment operations and low operation/maintenance cost will provide distinct advantages of this system. This procedure can hasten catalyst development with automatic control and data acquisition.

### Conclusions

Microreactor technology based on silicon has been successfully developed at IfM of Louisiana Tech University over past ~ 10 years. Microreactors with different geometries and channel structures have been microfabricated using general photo-lithography, wet/dry etching (ICP etching) and anodic bonding. A micro reaction system has been built with flexibility and compability to different microscale reactions. A prototype reaction, catalytic hydrogenation and dehydrogenation of cyclohexene has been studied extensively with different preparation of the catalyst and its deposition. Industrially significant reaction such as syngas conversion to higher alkanes have been realized with ~70% conversion of CO and ~80% selectivity to propane. Other commercialization opportunities using microreactor technology are currently being explored.

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