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A Simple technique for microfluidic heterogeneous catalytic hydrogenation reactor fabrication

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A simple process is described for the facile production of microfluidic reactors with 'built-in' metallic catalysts. This approach provides considerable reductions in cost and complexity when compared to existing catalytic chip designs. The process involves the sputtering of catalytic metals into the channels of microfluidic reactors prior to device bonding. The utility of such microreactors as environments for heterogenous catalytic hydrogenations was tested and demonstrated by applying them to the on-chip reduction of butyraldehyde to butanol and benzyl alcohol to benzaldehyde. The use of such 'built-in' systems as microreactors for specific processes was shown to have considerable potential for both fundamental research and industrial application.

KEY WORDS: heterogeneous Catalysis; hydrogenation; sputtering; fabrication; microreactor.

1. Introduction

In the field of chemical synthesis, the hydrogenation of a double bond is one of the most fundamental and important reactions. It is a vital stepping stone in thousands of processes both in the research laboratory and on an industrial scale. Consequently, the study of such reactions and potential catalysts is an ongoing trend in chemical research [1]. Although the basic methods in this area are virtually antique from a modern research standpoint [2], and a wide variety of works have long been available to document its wide scope [3,4], there remains ample room for development.

In particular, the control and safety of such reactions remain important issues. Hydrogenation necessarily includes the oxidation of hydrogen, a notoriously violent process. In addition, where heterogenous catalysis is employed, the need for as high a surface area of catalyst as possible leads to the use of particulate or sponge like supports. This frequently enhances the risks involved. The pyrophoric properties of, for example, Raney nickel present appreciable safety concerns [5]. It is in this area that the use of microfluidic environments for hydrogenation leads to significant gains. Enhanced control over heat dispersion and reactant delivery combined with an isolated reaction volume, massively decrease the risk of reactions running out of control. At the same time, the ultra-low instantaneous volumes of reactants in use diminish the consequences of any loss of control. Beyond this, the use of microfluidic reactors offers the possibility of faster reactions and improved yield when employed as part of a fully optimised synthesis [6].

Attempts to exploit these advantages have led to a number of microfabricated reaction systems that incorporate metallic catalysts. Foremost among the methods employed for catalyst incorporation have been 'packed-bed' chambers filled with particles [7] and catalyst membranes [8]. Recently, the group of Jensen presented a design for a packed bed chip arranged in a cross flow format [9]. These designs, though, are generally costly and complex to fabricate. The process described in this work employs sputter coating techniques to coat the channels of a microfluidic reactor with a catalytic metal during production, followed by reduction of the metal layer after completion. This involves the addition of a single, relatively simple step to the regular process of chip fabrication (photolithography, wet-eching and bonding), and a highly facile reduction process post fabrication. The result is a chip with a built in, supported heterogenous catalyst system which has immediate uses as an 'einbau' reactor for catalytic hydrogenations. Although reactive channel walls have been created for zeolite catalysis [10] the production of such devices is necessarily more time consuming.

The creation of a workable catalytic chip *via* the addition of two simple steps into the normal production process represents a considerable saving in time, cost, and complexity over existing, more elaborate designs for catalytic reactor chips. In addition, the built in nature of the catalyst eliminates many of the complexities and

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risks of conventional particulate extraction and management.

Microfluidic chips were prepared as described below. Microchannel surfaces were coated with metals known to act as catalysts in hydrogenation reactions; platinum, palladium and rhodium. The catalytic properties of each metal in the microfluidic environment were tested by the on-chip mixing of an aldehyde and hydrogen gas, and subsequent evaluation of alcohol yield. It was noted that palladium is not an optimal catalyst for the hydrogenation of aliphatic aldehydes, whereas rhodium and platinum are not optimal in the case of aromatic aldehydes [3]. Hence, the reduction of benzaldehyde to benzyl alcohol was performed on palladium coated devices, whereas the reduction of butyraldehyde to butanol was used to test platinum and rhodium coated chips.

2. Experimental

2.1. Fabrication

A fluidic channel pattern with a double inlet, single outlet and an extended delay section was designed using appropriate CAD software. Channels were fabricated using standard photolithographic procedures followed by wet chemical etching and bonding [11]. Briefly, the channel design was transferred to a positive photoresist coated chrome/glass substrate (Nanofim, Westlake Village CA.) using a direct write laser lithography system. The exposed regions of the photoresist were removed using a resist developer (Microposit 351, Shipley Europe Ltd, Coventry, UK). The exposed chromium layer was then removed using a chrome etchant (Lyodyne, Microchem Systems Ltd., Coventry). Channels were then etched into the substrate using a buffered oxide etching solution ($HF-NH_4F$) at ambient temperature. An aggressive mix ratio was used so that a rough channel surface was created. This increased the surface area available for catalyst deposition and increased catalyst adhesion. The exposed channels were then sputter coated with the selected metal under a 0.01 Torr air vacuum. A catalytic layer between 80 and 120 nm thick was deposited in each device.

Holes were drilled into the substrate to allow access to the fluidic network below. The remaining photoresist was then removed using dimethyl formamide (DMF) and the chrome layer removed using chrome etchant. The substrate was then washed sequentially in methanol, DMF followed by immersion in H_2SO_4 for 1 h. The substrate was washed with ultra-pure water at ambient temperature, and dried with N_2 gas. Finally, a cover plate was thermally bonded to the substrate by heating the assembly at 550 °C for 1 h, 580 °C for 5 h and 555 °C for 1 h. The completed device was then allowed to cool for at least 8 h. A typical device is shown in figure 1 and the production sequence is described in figure 2.

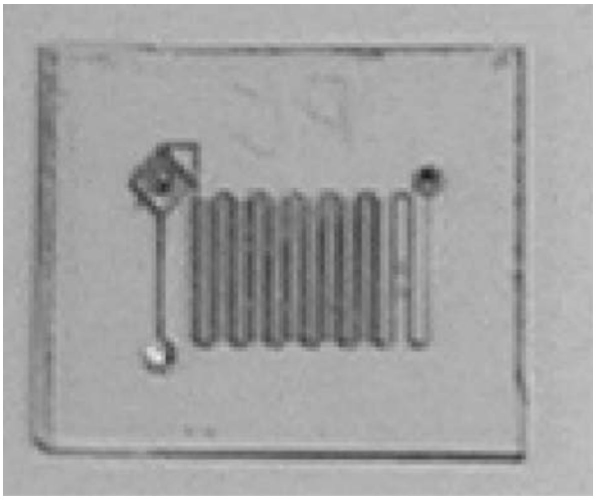


Figure 1. Photograph of a chip sputtered with Pt.

Reduction of the metal layer was achieved by passing hydrogen through the completed channels for 25 min at 60 °C. It should be noted that this procedure represents only a slight deviation from standard procedures for the preparation of non-catalytic chip [9].

2.2. Reactions

Subsequent to completion, each chip was tested *via* the reduction of an aldehyde to an alcohol. In the case of

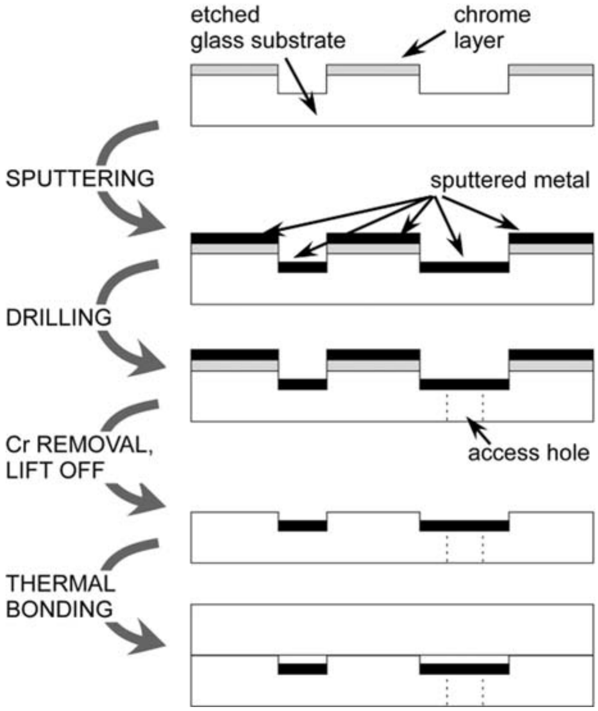
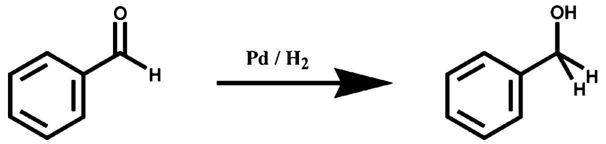
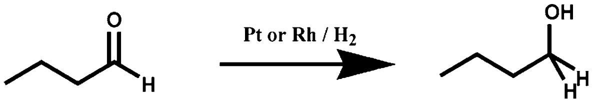


Figure 2. The chip fabrication process was adapted slightly by incorporating a metal sputtering step after etching of the substrate. Access holes were drilled and subsequently the chromium layer was removed, resulting in lift off of any catalyst metal outside of the channel structure.

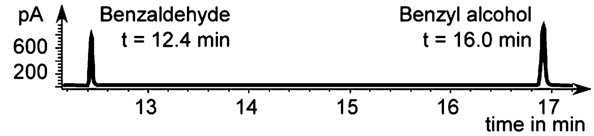


Scheme 1. Reduction of Benzaldyhyde to Benzyl alcohol.

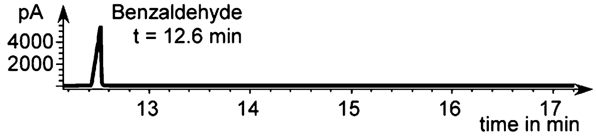


Scheme 2. Reduction of Butyraldehyde to Butan-l-ol.

(a) Output from Pd-Chip



(b) Benzaldehyde Standard



(c) Benzyl alcohol Standard

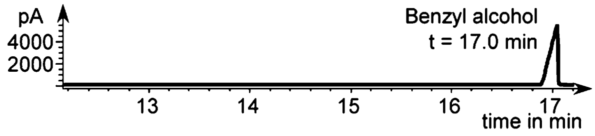


Figure 3. GC traces of (a) chip effluent for the reduction of benzaldehyde to benzyl alcohol in the palladium chip, (b) benzaldehyde standard, (c) benzyl alcohol standard.

the palladium-coated chips, benzaldehyde was reduced to benzyl alcohol (scheme 1). With the devices heated to 80 °C, hydrogen was passed through the chips (generating a pressure of 1.5 bar) *via* one inlet and mixed with a solution of benzaldehyde in xylene (5% by volume). The liquid output from the chip was collected under a reducing atmosphere (H_2).

In the case of the platinum and rhodium coated chips, the reduction of butyraldehyde to butan-l-ol was enacted (scheme 2). This was executed as above with the following modifications: the reaction temperature was 100 °C, and it was not judged to be necessary to hold the product under a reductive atmosphere.

Butyraldehyde and benzaldehyde were purchased from Lancaster Synthesis (Morcambe, UK) and used as received.

3. Results and discussion

Samples collected from each chip were analysed *via* Gas Chromatography (GC) (HP Innowax column, FID detector. Samples were injected *via* an HP 6890 autosampler to eliminate operator effects). Integration readings were calibrated by means of a series of GC standards of known concentration solutions of butyraldehyde (reactant) and butanol (product) in xylene, or benzaldehyde and benzyl alcohol for the appropriate reduction. Butanol was purchased from Lancaster Synthesis, Morcambe, UK and used as received. Benzyl alcohol was purchased from BDH Ltd., Poole, UK, and used as received.

The mean residence lifetime of reactants was calculated as 125 s for the palladium chip, 77 s for the platinum chip and 265 s for the rhodium chip. The highest conversion rates were obtained from the palladium coated chips, which gave 64% conversion, and a corresponding conversion rate of 1.25×10^{-6} mol s^{-1}, or $0.51^{-1}\%\ s^{-1}$. This compares highly favourably with 7.64×10^{-7} mol s^{-1} ($0.0027\%\ s^{-1}$ as given by traditional macroscale methods for the hydrogenation of aldehydes [4]. Both platinum and rhodium chips gave acceptable conversion rates of 3.9×10^{-7} mol s_{-1} ($0.71\%\ s^{-1}$) and 1.12×10^{-7} mol s^{-1} ($0.28\%\ s^{-1}$) respectively. This represents a desirable combination of greatly increased efficiency and negligible safety risks. These data are displayed in table 1. Typical GC traces of the effluent from a palladium coated chip is shown in figure 3. Furthermore, GC traces of pure benzaldehyde and pure benzyl alcohol in xylene are shown for comparison.

Beyond obvious research applications, these initial results indicate a potential role for such catalytic reactors in industrial scale production. A simple calculation shows that an array of two platinum coated chips as employed here would equal the output of a traditional macroscale reactor over comparable time periods [10]. By extension, the use of a larger array of such chips to replace a typical plant-sized reactor is certainly possible,

Table 1
Comparison of residence times, conversion rates and yields for catalytic hydrogenation performed on-chip and on the macroscale.

Method	Residence lifetime in s	Yield in %	Conversion rate in 10^{-7} mol s^{-1}	Relative conversion in % s^{-1}
Pd-chip	125	64	12.5	0.51
Pt-chip	77	55	3.9	0.71
Rh-chip	265	74	1.12	0.28
Macroscale [4]	36,000	97	7.64	0.0027

and even desirable. However, potentially the most direct application of microreactors in this area will be in highthroughput screening, where systems variables such as temperature and reactant concentration may be varied across parallel arrays of catalytic channels.

It was noted that the sputtering of platinum or palladium in air, followed by heating to 580 °C during bonding led to the formation of black, oxidised films. The subsequent reduction of these oxides with hydrogen produced a rough and porous structure. Rhodium, however, underwent far less oxidation and smooth, reflective films were produced. Hence, the rhodium-coated devices would have had a catalytic layer with less of a porous structure and consequently a smaller active surface area. This may explain the lower efficacy of the rhodium devices compared to the palladium and platinum devices.

4. Conclusions

This work demonstrates that by a simple modification to the conventional chip fabrication process it is possible to produce low cost and yet highly effective microreactors with incorporated metallic catalysts. These devices can be used to run hydrogenation reactions under conditions of improved safety and yield-pertime, thereby exploiting the economies of reduced scale available in the microfluidic environment. This fabrication method can be readily applied to bulk manufacture and it is ideally suited to the scale out of many microfluidic reaction processes.

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