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The application of palladium and zeolite incorporated chip-based microreactors

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ABSTRACT

The ability to successfully incorporate heterogeneous catalysts into chip-microreactors is demonstrated in the application of a Pd/ZSM-5 and Pd/silicalite chip-based microreactor for the synthesis of methyl-*iso*-ketone (MIBK) and the hydrogenation of 3-methyl-1-pentyn-3-ol. The bifunctional Pd/ZSM-5 chip-microreactor provides a high selectivity (>90%) to MIBK due to the incorporation of palladium and high Brønsted acidity while demonstrating the ability to regenerate and reuse the Pd/ZSM-5 chip-microreactor. The Pd/silicalite chip-microreactor illustrated the advantage of improved control of residence time in the microreactor to obtain high alkene yields. In addition, the design of chip-holders which are operable at high temperature, pressure and have a high chemical resistance further extend the operability of chip-based microreactors for use in the special chemical industry.

1. Introduction

The advent of lab-on-a-chip technology in recent years has seen its application across a broad spectrum of scientific disciplines such as biology [1], medicine [2,3], physics [4,5], chemistry [6], material science [7], energy [8], and pharmaceuticals [9–12]. However, the use of chip-based microreactors in heterogeneous catalysis in comparison to other fields is relatively small. This is surprising since the use of microreactor technology in chemical synthesis has shown to provide notable improvements such as better heat and mass transfer, control over residence time and temperature, safety, and portability [13]. Furthermore, glass chip-based microreactors provide distinct advantages for use in the fine chemical and pharmaceutical industries where this material is chemically inert, corrosion resistant, and operable at relatively high temperatures and pressures [14]. One of the main reasons for the limited use of chip-based microreactors in heterogeneous catalysis is the lack of suitable methods to incorporate the catalysts in these reactors [15].

Zeolites as catalysts offer various advantages for incorporation in microreactors [16]. These silica/alumina microporous structures contain uniform nano-sized pores with high surface area, which is advantageous when used as a support for metal deposition; have tunable catalytic properties such as acid-sites; and have the ability to be grown as a highly uniform and adherent layer on the microchannel surface. In addition, zeolites have shown to be effective heterogeneous catalysts in fine chemical synthesis [17–19]. Typical methods for incorporating zeolites in microreactors require the microchannel plate to be immersed in the precursor solution, followed by hydrothermal synthesis [20–27]. After the formation of the zeolite coating, the two plates are assembled together to form the microreactor [28]. In the case of chip-based microreactors, the highly alkaline precursor solution is detrimental to the chemical integrity of the microchannel plate and thus requires pretreatment procedures to prevent the dissolution of the side walls and plate bottom [29,30]. Furthermore, the assembly step can be greatly affected by the deposition of the coating or dissolution of the plate area where sealing should occur resulting in poor bonding and limiting the temperature and pressure ratings of such devices [31].

While there have been numerous studies on zeolite incorporation in stainless steel microreactors by the hydrothermal synthesis method, less examples have been applied for chip-microreactors. The incorporation of a mesoporous silica thin film (500 nm) and a zeolite-beta coating (1–2 μm) onto borosilicate microstructured glass was carried out [30,32]. However, these coatings were not evaluated in a reaction to assess their catalytic activity possibly due to the formation of coating in the areas typically required for bonding, making it impossible to convert the coated plates to a closed microreactor.

Recently, a method for incorporating zeolites into a chip-microreactor has been described [33]. A fluoride-based in-situ hydrothermal treatment was used to pretreat the glass chip's

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microchannel surface to improve the surface wettability and roughness, avoiding the need of multiple surface pretreatment steps. The subsequent in-situ zeolite hydrothermal synthesis within 30 cm chip-microreactors resulted in a well adherent and uniform zeolite coating.

In this work, the glass surface pretreatment and in-situ zeolite hydrothermal synthesis coating method is scaled-up to a 1 m length chip-microreactor and used to coat microchannels of various dimentions. Custom-designed chip-holders have been fabricated to withstand the various operating conditions required for the coating preparation and catalytic reaction.

The palladium and zeolite incorporated chip-based microreactors have been applied in two test reactions in order to assess the catalytic activity and coating properties. These reactions are the (I) the production of methyl-*iso*-butyl-ketone over a bifunctional Pd/ZSM-5 coated chip-microreactor and (II) the hydrogenation of 3-methyl-1-pentyn-3-ol over a Pd/silicalite coated chip-microreactor. The use of the MIBK test reaction provides a means to assess the acidity of the ZSM-5 coating synthesized, and the ability to accurately incorporate palladium in the microreactor in order to form a bifunctional catalyst. Methyl isobutyl ketone (MIBK) is one of the most widely used aliphatic ketones in paintings, protective coatings, various plastics and resins. Most commercial MIBK processes (one-step from acetone) use the liquid phase reaction in a trickle bed reactor over palladium impregnated cation exchange resin [34]. In order to achieve a high selectivity to MIBK, a fine balance between the acid and hydrogenating metal function is required [35–39]. The rate-limiting step is the aldolization of the acetone to mesityl oxide where the subsequent hydrogenation step to form MIBK is much faster [40]. If the acid strength of the catalyst were to be significantly lower, this would result in less formation of the intermediates, diacetone alcohol and mesityl oxide, resulting in less MIBK to form. Conversely, if the Pd loading or particle size were to be too high or non-uniformly dispersed, there would either be an over hydrogenation of acetone leading to the formation of lighter side-products such as propane, pentane and isopropanol or MIBC [41,42]. Alternatively, a palladium concentration which is too low would result in insufficient hydrogenation, leading to the formation of mesityl oxide, and isophorone, one of the main compounds leading to the catalyst's deactivation [37,43,44]. Furthermore, if the two active sites are in the correct concentration but in different locations, mass transfer effects could result in a low MIBK selectivity due to the formation of side products or consecutive reactions. It is therefore important to ensure good mass transfer, active sites in close proximity of one another, and an accurate residence time distribution.

The hydrogenation of 3-methyl-1-pentyn-3-ol over a Pd/silicalite is the second reaction considered in the coated chip-microreactor. Catalytic, selective hydrogenations are a common class of reactions carried out in the fine chemical industry where multiphase batch reactors are most commonly applied but often are affected by the effects of heat and mass transfer limitations [45,46]. One such example is the selective hydrogenation of acetylene alcohols to form the semi-hydrogenated alkene where this reaction demonstrates the incorporation of palladium in the chip-microreactor, the effectiveness of the silicalite coating to act as a support, and the advantage of the microreactor when applied to fast reactions which are often mass transfer limited.

2. Materials and method

2.1. Chip microreactor and holder

Borosilicate glass chip-microreactors were purchased from Chemtrix (The Netherlands) having outer dimensions of $45 \times 22 \times 1.4$ mm and containing a semi-circular microchannel. Two different microchannel dimensions were used. Chip-A has a 420 μm diameter, 190 μm depth, and 1 m length while Chip-B has a 260 μm diameter, 110 μm depth, and 1 m length. Most results are obtained using Chip-A unless explicitly stated otherwise.

Custom-designed chip-holders were used for the coating steps, the catalytic reaction (Fig. 1a), and the high temperature calcination step (Fig. 1b).

The maximum operating conditions of the respective chip-holders are summarised in Table 1. It should be noted that despite the high chemical resistance of the borosilicate chip-microreactor, as well as the high thermal and pressure stability; the applicability of these devices is often limited by the material of construction used to manufacture the chip-holder where low temperature materials (150 °C) such as PEEK are commonly used. For this reason, custom-designed chip-holders were required to be designed for the specific application and manufactured in order to further extend the applicability of such glass chip-microreactor devices.

Chip-holder I was used for the coating preparation and chemical reaction. In the coating preparation step, the inlet and outlet were sealed using o-rings (Kalrez 6375, Eriks) and 1/16″ stainless steel rods which contained a specific internal volume. For the larger, Chip-A, the internal volume was 3.6 mm^3 and in the smaller, Chip-B, the internal volume was 0.5 mm^3. This internal volume was necessary to allow for the expansion of the liquid at elevated temperature to prevent over pressurization. During the catalytic reaction, the stainless steel rod was replaced with 100 μm i.d. stainless steel tubing.

Chip-holder II was used for the high temperature calcination and regeneration steps where a flow of air through the microchannel at temperatures up to 500 °C was required. The holder was constructed from brass and a movable brass block held the chip-microreactor in place, allowing no o-rings to be required.

2.2. Microchannel pretreatment

The inner surface of the microchannel was modified by a hydrothermal treatment to improve the surface wetability and roughness [33]. A 0.7 M NH_4F solution was inserted into the chip and the chip inlet and outlet sealed using the chip-holder I instrumentation depicted in Fig. 1a. The hydrothermal treatment was done at 150 °C for 48 h. After the pretreatment, the excess solution was removed from the microchannel, washed with distilled water, and dried for 24 h at 120 °C.

2.3. Preparation of Pd/ZSM-5 coating

A ZSM-5 coating was incorporated into the chip-microreactor using an in-situ hydrothermal synthesis method. [33] A precursor suspension was prepared by mixing aluminium-isopropoxide (99%, Sigma-Aldrich), and tetrapropyl ammonium hydroxide (TPAOH, 40% aq. sol., Merck) at 0 °C for 4 h. After the solution turned clear, tetraethylorthosilicate (TEOS, 98%, Sigma-Aldrich) was added dropwise. After 4 h a solution of sodium hydroxide (NaOH, 99%, Sigma-Aldrich) and distilled water was added dropwise. After the completion of hydrolysis, when the solution turned clear, the solution was filtered with 0.2 μm syringe filters (0.2 μm PTFE membrane filters, VWR). The optimized precursor suspension had a molar composition of 1 SiO_2: 0.22 TPAOH: 0.13 NaOH: 65.5 H_2O: 0.033 AlO_2.

The precursor suspension was inserted into the pretreated chip-microreactor and the inlet and outlet of the chip sealed using chip-holder I. Hydrothermal synthesis was conducted at 175 °C for 24 h and repeated. After the hydrothermal synthesis, the excess solution was displaced with air, washed with distilled water, and