



Zeolite incorporation in chip-based microreactors



L.A. Truter^a, V. Ordonsky^b, J.C. Schouten^{a,*}, T.A. Nijhuis^a

^a Laboratory of Chemical Reactor Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands

^b Unité de Catalyse et de Chimie du Solide, UMR 8181 CNRS, Bât. C3, Université Lille, ENSCL, Ecole Centrale de Lille, 59655, Villeneuve d'Ascq, France

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ABSTRACT

A method for the incorporation of zeolite coatings in glass chip-based microreactors has been developed. The use of a fluoride-based hydrothermal pretreatment method provides a microchannel surface with high roughness, good wettability, and a silica nutrient source in a single pretreatment step. This pretreated glass surface is ideal for the subsequent *in-situ* zeolite hydrothermal synthesis which enables the formation of zeolite coatings within the chip-based microreactor. The optimization of the zeolite precursor suspension in terms of aluminium and silica source and amount, allows for the formation of zeolite coatings which are uniform, have high surface area and high Brønsted acidity.

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1. Introduction

The application of microreactors for use in the fine chemical and pharmaceutical industries has received much attention in recent years [1–4]. The ability to produce these high-value chemicals on-site and on-demand through continuous processing gives microreactor technology a specific advantage in comparison to conventional batch-wise production of such chemicals [5–7].

Although borosilicate glass is an ideal construction material for microreactors for use in the fine chemical and pharmaceutical industries, it has been far less applied in comparison to stainless steel. Borosilicate glass microreactors have the advantage of being compact, chemically inert, corrosion resistant, and operable at high temperature and pressure [8]. However, the ability to incorporate a catalyst into such devices is challenging mainly due to the difficulty to activate the glass surface to allow for a suitably adherent coating and for the bonding between the two microchannel glass plates to not be affected by the pretreatment and coating processes [9,10].

Zeolites are advantageous materials for catalyst incorporation in microreactors since the catalyst coating can be grown onto the microchannel surface resulting in improved coating uniformity and adherence [11–17]. Currently, most methods which incorporate zeolites in glass microreactors use multiple surface pretreatments to improve the glass roughness, hydrophilicity and zeolite coverage [12,18,19]. In order to carry out these surface pretreatments, the

glass plate must first be pretreated, followed by the growth of the zeolite coating on the microchannel surface, and, thereafter, assembled together to form the microreactor. However, the more difficult bonding of the glass plates together after these pretreatment and coating procedures greatly affects the sealing which ultimately limits the temperature and pressure ratings of such devices. An alternative approach is to initially form the closed-microchannel (i.e. chip microreactor) by bonding together the two glass plates and, thereafter, perform an *in-situ* hydrothermal synthesis where the glass is used as a nutrient source to reduce the number of pretreatment steps.

The transformation of porous glass monoliths to form hierarchical ZSM-5 and TS-1 zeolite structures have effectively demonstrated the ability of the glass to act as a nutrient source and provide the scaffold for these structures [20–23]. The advantage of using the support as a nutrient source is to favour zeolite nucleation and growth on the substrate as opposed to the bulk solution [24]. However, for the support to act effectively as a nutrient source, a balance between the partial dissolution of the support to supply the silica precursors and the inclusion of these precursors into the zeolite structure needs to be found [25]. A fluoride-based hydrothermal synthesis has been demonstrated by Louis et al. to produce ZSM-5 coated filamentous glass supports [26]. The partial dissolution of the glass in the presence of the fluoride ions enabled complete coverage in less synthesis steps in comparison to the conventional hydroxide-based synthesis.

Furthermore, in microreactor applications where mass transfer is very fast and the reaction kinetics are often rate limiting, it is

* Corresponding author. Tel.: +31 40 2472850; fax: +31 40 2446653.
E-mail address: j.c.schouten@tue.nl (J.C. Schouten).

highly advantageous for the coating to have a high surface area. In conventional zeolite coatings such as membrane application, seeding is often used as a pretreatment procedure to promote the intergrowth of the zeolite crystals to form a continuous layer [27]. However, in microreactor application, a coating which consists of individual nano-sized zeolite crystals would be more advantageous. The use of a nutrient source to promote the formation of a high surface-area zeolite coating has been demonstrated for the *in-situ* hydrothermal synthesis of ZSM-5 in a microchannel by the transformation of a porous silica coating [25].

In this study, a different approach is taken for the incorporation of zeolites in chip-based microreactors in which the two glass plates are initially sealed together to form the chip-microreactor, and thereafter followed by an *in-situ* glass surface pretreatment and zeolite hydrothermal synthesis step. A glass pretreatment method is described which allows the glass microchannel surface to have a good surface roughness and wettability by a single pretreatment step. Furthermore, the main factors involved in the formation of a zeolite coated chip-microreactor are described. The composition of the zeolite precursor suspension and the *in-situ* hydrothermal synthesis conditions are optimized in order to obtain a ZSM-5 coating which has a high Brønsted acidity, good uniformity, and high surface-area coating.

2. Materials and methods

2.1. Support

Borosilicate glass chip-microreactors were purchased from Chemtrix (The Netherlands) with outer dimensions of $22.5 \times 22.5 \times 1.4$ mm (Fig. 6a). The microchannel was 420 μm diameter, 190 μm depth, and 30 cm in length. To further characterize the zeolite coating on the glass, borosilicate glass plates or bulk synthesised powder were used in some cases for comparison.

2.2. Glass pretreatment

The glass pretreatment procedure was conducted before the zeolite hydrothermal synthesis within the confines of the chip microchannel. A 0.7 M NH_4F solution was inserted into the chip and the chip inlet and outlet sealed. 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. Catalyst preparation

The fluoride precursor suspension was prepared according to the method described by Louis et al. [26] Tetrapropylammonium bromide (TPABr, 99% Merck) and ammonium fluoride (NH_4F , 99%, VWR) were dissolved in distilled water. In the case when tetraethylorthosilicate (TEOS, 99%, Merck) was used in the synthesis, the solution was left for 4 h to hydrolyse. Finally, the pH was adjusted to 7 by adding some drops of concentrated hydrofluoric acid (48 wt %, Merck). A typical suspension had the following composition 1 SiO_2 : 0.07 TPABr: 0.9 NH_4F : 0.012 NaAl_2O_3 : 80 H_2O .

Two methods were used for the preparation of the hydroxide precursor suspension. In the first method, aluminium isopropoxide (99.9%, Sigma–Aldrich) and TEOS were used. The aluminium isopropoxide and tetrapropyl ammonium hydroxide (TPAOH, 40% aq. sol., Merck) were mixed together at 0 °C for 4 h. After the solution turned clear, TEOS 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 the hydrolysis, when

the solution turned clear, the solution was filtered with 0.2 μm syringe filters (0.2 μm PTFE membrane filters, VWR).

In the second method, sodium aluminate (NaAlO_2 , Merck) was used as the aluminium source and colloidal silica (40% colloidal suspension in water, Ludox AS-40, Sigma–Aldrich) as the silica source. The NaAlO_2 was added together with the NaOH solution. The TPAOH was added to the colloidal silica and stirred, followed by the addition of a solution containing the NaAlO_2 , NaOH, and water. The use of colloidal silica resulted in the precursor suspension to form a gel which prevented the final suspension being filtered.

2.4. Hydrothermal synthesis

After preparation of the precursor suspension, hydrothermal synthesis was conducted. This was carried out to pretreat the glass microchannel surface and to form a zeolite coating.

In the *in-situ* hydrothermal treatments, the precursor suspension was injected into the chip-microreactor and the inlet and outlet sealed by use of a PEEK chip-holder (Chemtrix, The Netherlands). The ZSM-5 hydrothermal synthesis was conducted to form (i) coating in the chip microreactor, (ii) coating on the borosilicate glass plate, (iii) bulk-synthesised powder. For coating of the borosilicate glass or preparation of the bulk-synthesised powder, the precursor suspension and the glass plate were inserted into teflon-lined autoclaves. Hydrothermal synthesis was conducted for 24–48 h at 150–175 °C. After the hydrothermal synthesis, the excess solution was removed from the chip-microreactor, washed with distilled water, and dried at 120 °C for 24 h. Calcination was conducted in air at 500 °C for 2 h at a heating rate of 1 °C/min to remove the organic template.

In the fluoride-based synthesis, the ZSM-5 was in the NH_4 - form, however, for the hydroxide-based synthesis, an ion exchange step was necessary to convert the Na-ZSM-5 to NH_4 -ZSM-5. A 0.5 M NH_4NO_3 solution was either flowed through the chip-microreactor or stirred with the ZSM-5 powder for 2 h at 80 °C. Thereafter, the calcination step was repeated.

2.5. Incorporation of other zeolites by washcoating method

To ascertain the extendibility of the coating method to other zeolites and heterogeneous catalysts, titanium silicalite-1 (TS-1) was incorporated by the hydrothermal synthesis method, as well as ZSM-5 by a washcoating method.

The ZSM-5 washcoating was incorporated into the chip-microreactor by the use of the bulk-synthesised ZSM-5 powder described earlier. After the fluoride pretreatment step was applied to the chip-microreactor to improve the surface properties of the glass microchannel surface, a suspension containing 30% ZSM-5, 10% pluronic F127 (BASF), in ethanol was inserted into the chip-microreactor. The ZSM-5 suspension was displaced from the chip-microreactor using a 50 ml/min N_2 flow with a 5 bar back pressure. The back pressure was necessary to ensure that the N_2 linear velocity was constant throughout the length of the chip-microreactor.

The TS-1 coated chip-microreactor was prepared using the hydrothermal synthesis method. Initially, the glass surface was pretreated using the fluoride pretreatment, followed by a TS-1 seeding coating. A suspension containing 30% TS-1 seeds and 10% pluronic F127 in ethanol was washcoated into the chip-microreactor. The TS-1 seeds were prepared using a precursor suspension of 0.43 TBOT:10 TEOS:5 TPAOH:7 IP: 697 H_2O for 12 h at 150 °C. Thereafter, the *in-situ* hydrothermal synthesis method was conducted using the same methodology as described previously [28]. A precursor suspension was prepared by mixing anhydrous isopropyl alcohol

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