

Zirconia functionalized monolithic cores with improved hierarchical porosity for continuous-flow microreactors in cascade reactions

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Abstract

This work presents a method for the preparation of zirconia-silica monoliths with improved porosity and their application in a continuous-flow system for cascade deacetalization and Knoevenagel condensation reactions carried out in two microreactors connected in series. The post-synthesis treatment of pristine micro/macroporous zirconia-silica monoliths, obtained by one step method, with the use of ammonia and sulfuric acid solutions resulted in mesoporous materials and improved macroporosity. They showed high activity in the deacetalization reaction of benzaldehyde dimethyl acetal, despite a relatively low zirconium content, ca. 0.3 wt.%, probably due to the formation of small quantities of the zirconium sulphate superacid. The Knoevenagel condensation reaction of benzaldehyde with ethyl cyanoacetate was performed in an amine-functionalised microreactor. The cascade process resulted in an 80% yield of ethyl cyanocinnamate and a very high selectivity that reached 99%. The flow resistance and residence time distribution were determined for both reactors.

Keywords

monolithic microreactor, zirconia-silica catalyst, improved porosity, cascade process

1. INTRODUCTION

Cascade reactions are defined as series of chemical reactions in which the products of one reaction are consumed in the next reaction. They allow the generation of complex molecules in a single operation. The process can be performed in homogeneous and heterogeneous batch modes, as well as in heterogeneous flow systems (Climent et al., 2014; Let et al., 2023). Recently, a hierarchically structured bifunctionalised acid base monolithic microreactor was developed and compared with cascade and batch reactors (Ciemięga et al., 2024). In the studied tandem process, active zirconia and amine centres were involved in two consecutive reactions of deacetalization and Knoevenagel condensation, respectively. Both centres were incorporated into silica monoliths using the post synthesis method. In this work we focussed on the improvement of the structural properties of monolithic zirconia-silica materials obtained by one-step method by generating the mesopores in its skeleton. To achieve this goal, the pristine micro-/macroporous monoliths were hydrothermally treated in ammonia and sulfuric acid solutions. The structural and flow properties of monoliths were determined. The catalytic activity was examined in a deacetalization-Knoevenagel condensation cascade process.

2. METHODS

Silica-zirconia monoliths were obtained according to the procedure described in (Maresz et al., 2023) using zirconium

sulphate as a Zr source. Typical synthesis includes the following steps: mesophase formation – sol-gel/phase separation – ageing – drying – calcination. In this work, additional hydrothermal treatment was applied. The monoliths after ageing were treated with 1M ammonia solution (90 °C, 6 h) and then with 50% H₂SO₄ (90 °C, 6 h) or using only one of the specified medium. The nominal Zr content in the samples was 1.8 wt.%.

Pure silica monoliths were synthesised using a method from (Pudło et al., 2006). Here, polyethyleneglycol of average molecular weight of 100.000 was applied. Functionalisation with amine groups was performed by the grafting method. First, monoliths were embedded in the heat-shrinkable tubes and equipped with connectors to form a microreactor. The solution of [3-(2-aminoethylamino)propyl]trimethoxysilane in ethanol (0.5 mmol/g_{SiO₂}) was then passed through microreactor in a loop with a flow rate of 0.5 cm³/min for 5 h at 50 °C.

SEM images (Phenom Pure, BSD detector, 3 nm gold layer) were recorded with a magnification of 100×; voltage 5 kV and used to estimate the size of macropores. Nitrogen adsorption measurement was carried out using ASAP2020 (Micromeritics) at –196 °C. The specific surface area, size and volume of pores were calculated using BET, Dubinin-Astakhov and BJH equations. The amine concentration was determined by thermogravimetric analysis (Mettler Toledo; temp. range of 25–800 °C, air flow rate: 60 cm³/min; heating rate: 10 °C/min). The zirconia content was checked by wavelength-dispersive X-ray fluorescence (WDXRF; Spectrometer Axios mAX; Rh lamp).



The flow resistance was measured using a pressure controller (UNIK 5000, Ex-Calibra) in the flow rate range of 0.03–7 cm³/min. The mean residence time distribution for zirconia-silica and amine-silica microreactors was determined using the pulse input method, where octane was selected as a tracer molecule. The efflux was analysed by GC. The $E(t)$ and $F(t)$ curves were constructed and the mean residence time RTD was calculated. The experimental RTD data were compared with the space time value $\tau = V_{\text{pore}}/F$, where V_{pore} is the total pore volume of the monolith [cm³] and F -flow rate [cm³/min].

The Zr-microreactor was tested in the deacetalization reaction of benzaldehyde dimethyl acetal, the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate was performed in the amine modified reactor, and both microreactors were used in the cascade process to obtain the final product: ethyl cyanocinnamate. Reaction conditions: substrates: equimolar concentration; temperature: 50 °C; flow rate: 0.03–0.12 cm³/min; solvent: toluene:ACN (4/1 v/v). The reaction mixture was delivered by a syringe pump, and the temperature was maintained by a thermostatic oil bath.

3. RESULTS

The silica monoliths were characterised by mesopores with a bimodal pore size distribution of 3 and 20 nm and macropores with a diameter of approx. 80 μm (Fig. 1). The incorporation of zirconium during synthesis gave the monolith different structure parameters (Fig. 2). In this material channels of diameter ca. 10 μm were detected, while micropores with average size of 1.5 nm were present in the skeleton. The hydrothermal treatment of these materials using sulfuric acid or ammonia solution resulted in the generation of mesopores with narrow size distribution and average diameters of 4 and 8 nm, respectively. The mesopore volume increased three times compared to the untreated material. The double treatment allowed to obtain materials with the largest mesopores of about 11 nm and pore volume comparable to the volume of the pure silica material. The additional synthesis step also influenced the macropore structure. The largest impact on the pore size was found in the sample treated with 1M ammonia solely. The channels of diameters of approx. 15 μm were observed. In acid treated materials, the formation of the skeleton with larger struts was detected. All monoliths were characterised by large specific surface area, and the largest value, equal to 921 m²/g, was determined in sample treated in H₂SO₄ solution (Table 1). The treatment of pristine Zr-monoliths with base and acid solution caused a leaching of zirconium, and its final concentration was found to be ca. 0.3 wt.%. However, despite such a low content, they showed high activity in the hydrolysis reaction of acetal, probably due to formation of small quantities of zirconium sulphate superacid (Grecea et al., 2012).

The post synthesis modification of SiO₂ monolith with amine groups resulted in a decrease in the specific surface area and pore volume. The concentration of amine centres, ca.

0.5 mmol/g_{silica}, was confirmed by thermogravimetric analysis. All results discussed below were obtained for Zr-monoliths treated in ammonia and sulphuric acid solution.

The flow resistance strongly depended on the flow-through pore size in the monoliths (Fig. 3). Pressure drop in the Zr-SiO₂ and NH₂-SiO₂ microreactors was measured over a wide range of flow rates. In both cases, a linear relationship was obtained. The laminar flow is a characteristic feature of microreactors. A higher flow resistance was recorded in the zirconia modified monolith, and it was approximately 35 times larger, which correlates well with Darcy's law (Whitaker, 1969).

The residence time distribution was evaluated for the 1 cm long Zr-SiO₂ reactor and the 4 cm NH₂-SiO₂ microreactor, for the flow rates applied in the catalytic tests. For the Zr-SiO₂ reactor, the residence time corresponded well to the theoretically determined value. However, for the NH₂-SiO₂ core, t_{RTD} was equal to τ only for flow rate of the 0.03 cm³/min and its decrease was recorded with increasing flow rate (Fig. 4). Detailed studies of mass transport in microreactors will be the aim of further research.

Zr-SiO₂ and NH₂-SiO₂ monoliths were used as cores of flow-through microreactors (Fig. 5). First, the dependence of the conversion of acetal and benzaldehyde vs. the flow rate was determined separately for each reaction to find the optimal flow conditions for the cascade process. In the first reaction, 91% of acetal conversion was obtained for a flow rate in the range of 0.03 to 0.08 cm³/min. A decrease in conversion of approximately 7% was observed when the flow rate was increased to 0.12 cm³/min. In the condensation reaction, the highest yield was obtained for 0.03 cm³/min. Based on these results, the cascade process was carried out at a flow rate of 0.03 cm³/min. The isolated yield of the final product, ethyl α -cyanocinnamate was 78%, and the selectivity achieved a value of 99%, while in the bifunctional microreactor (Ciemięga et al., 2024) it was only 88% with comparable efficiency. The higher selectivity was due to a lower reaction rate of acetal hydrolysis in the Zr-microreactor studied (data not shown here), which was caused by a low concentration of zirconium in the microreactor.

4. CONCLUSIONS

A method for the preparation of zirconia-silica monoliths with mesoporous skeleton and improved macroporosity was proposed. A one-step monolith synthesis followed by hydrothermal treatment in ammonia and sulfuric acid solutions resulted in materials with mesopores and macropores of 11 nm and 15 μm in diameter, respectively. They showed high activity in the deacetalization reaction of benzaldehyde dimethylacetal, probably because of the formation of small quantities of the zirconium sulphate superacid. Conversion of up to 91% was achieved for a residence time of 90 s. Amine-functionalised silica monoliths were obtained by a post-synthesis grafting

method and used as a microreactor in the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate. Both microreactors were verified in the cascade deacetalization-condensation process. A high yield, of ca. 80% of the product, ethyl cyanocinnamate, was obtained with 99% selectivity. The flow resistance and residence time distribution were determined for both reactors.

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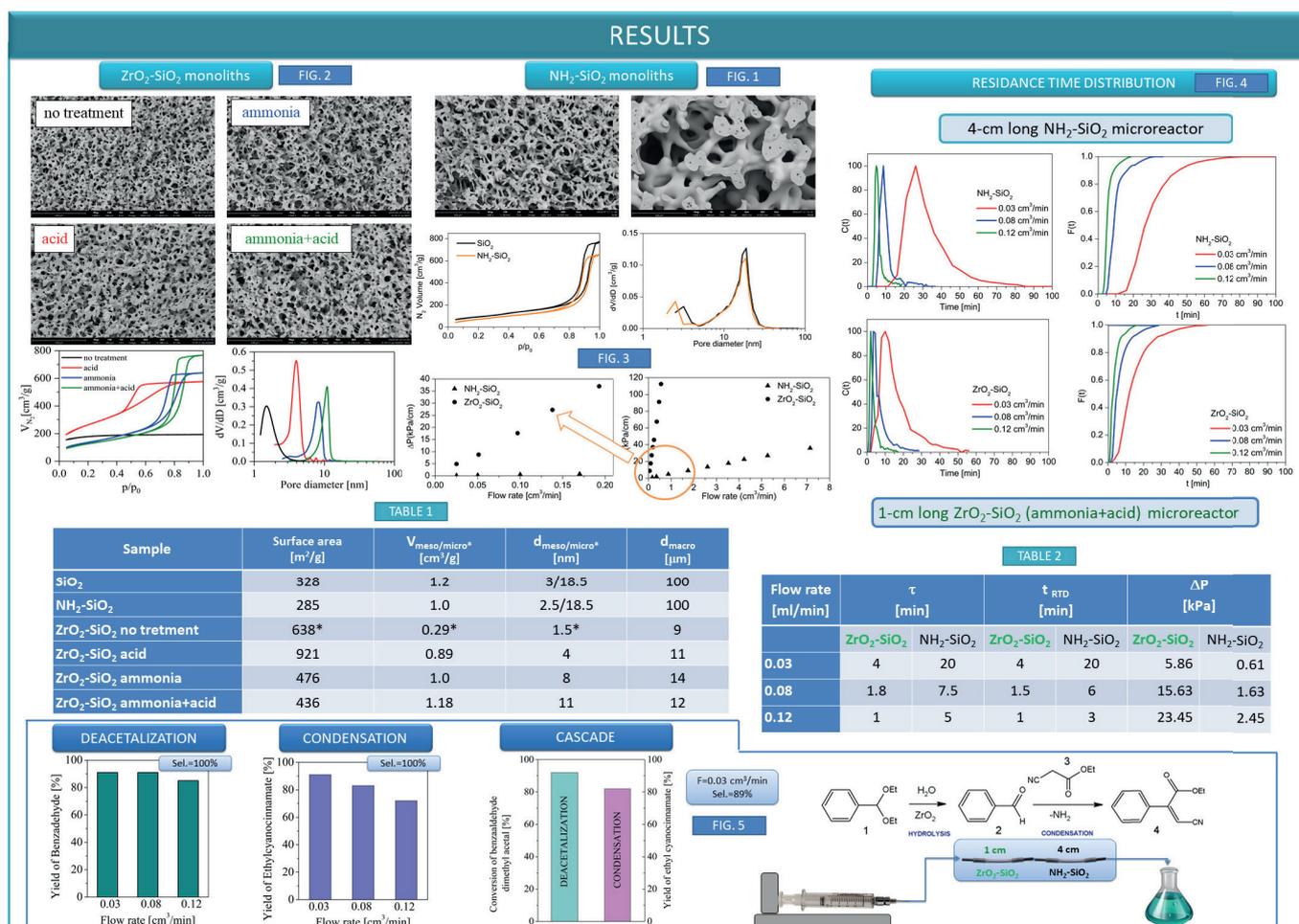
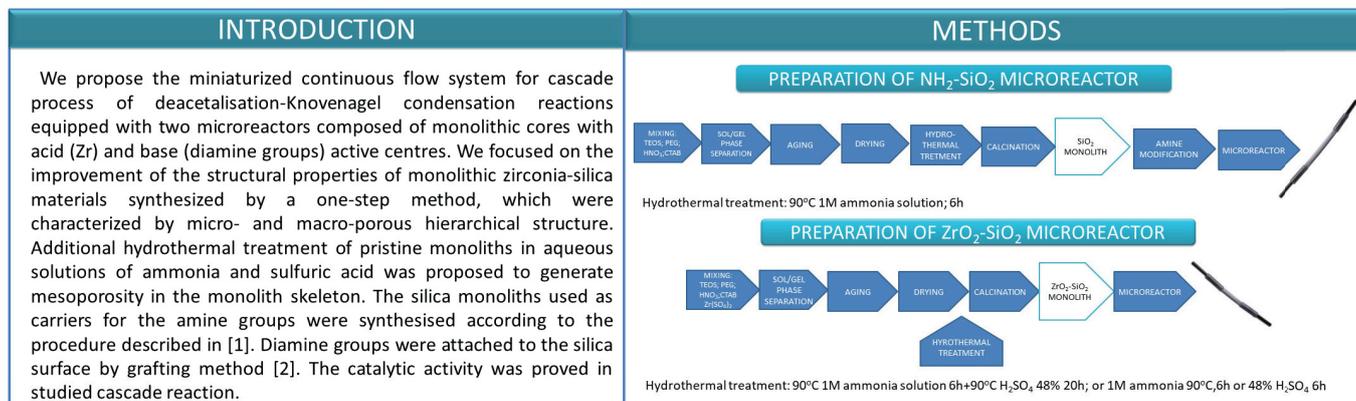
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CONCLUSIONS

- Improved one-step synthesis method was proposed to obtain mesoporous/macroporous zirconia-silica monoliths.
- These monoliths used as a core of flow microreactor demonstrated good catalytic activity in deacetalization reaction.
- The ZrO₂-SiO₂ and NH₂-SiO₂ microreactors applied in cascade process of deacetalization-Knoevenagel condensation showed high catalytic activity and good selectivity.
- Residence Time Distribution vs. flow rate was determined.

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