



# Highly effective continuous-flow monolithic silica microreactors for acid catalyzed processes

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## ABSTRACT

This work reports the performance of a new monolithic silica microreactor, activated with sulphonic acid groups in the continuous-flow synthesis of *n*-butyl acetate and *n*-butyl lactate. A reactive core of the reactor was made of a single silica rod with bi-continuous structure, containing flow-through pores with diameter in the range of 20–50 μm and mesopores of ca. 20 nm localized in silica struts. This structure resulted in low pressure drop, even at flow rates large enough to eliminate external mass transfer effect on the reaction kinetics. The microreactor functionalized with 0.65 mmol/g of –SO<sub>3</sub>H groups showed high activity and productivity in both esterification reactions carried out in temperatures up to 140 °C. Structural and catalytic stability of the microreactor was confirmed to demonstrate its process viability.

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## 1. Introduction

Synthesis of most fine chemicals is typically carried out in a liquid phase and batch operation. Their replacement by continuous processes using microreactor-based technologies can make them more effective, safer and to give products with stable properties. Catalysts beads, currently applied as column reactor packings in fine chemicals' synthesis, are usually of 50–100 μm diameter. Therefore, their application often leads to serious operational problems; excessive backpressure results in a maldistribution of fluids, and thus formation of stagnant zones and hot spots, which in addition to a fairly long diffusion path, leads to lower yields, poorer selectivity and reduced catalyst life [1]. Continuous-flow monolithic polymeric microreactors show important advantages: defined system of flow-through pores and facile modification of the surface using ample arsenals of chemical tools [2,3]. But their thermal sensitivity and propensity to swell are serious drawbacks [4]. Typical ceramic (e.g. cordierite) monoliths, which feature bunch of channels of 1–5 mm sizes, connected with smaller ones of ca. 0.1–1.0 mm, are aimed at gas-phase reactions [5].

Silica-based continuous-flow monolithic microreactors, first proposed by the Montpellier group, appeared to be extremely promising for the cost-effective production of fine chemicals [6]. This stems from a unique, bi-continuous structure of the monoliths in which flow-through macropores are connected to an extensive network of meso- and micro-pores present in the silica skeleton [6–8]. In effect, pressure drops are fairly small, even at considerable throughputs, whereas easily accessible large surface area offers very large concentration of active sites per unit volume. Initially, such microreactor was made of a single monolith–MonoSil, the surface of which was functionalized with –NH<sub>2</sub> or –HSO<sub>3</sub> groups [6]. Control of its meso- and macro-porosity was obtained by combining phase separation method, elaborated by Nakanishi [9–11], with pseudomorphic synthesis [12,13], to obtain an ordered mesoporosity of the silica skeleton. But more importantly perhaps, the productivity of MonoSil microreactors in Knoevenagel reaction and acid transesterification was shown to be 13 and 18 times larger than in the corresponding batch processes.

The original Nakanishi method was later modified [14,15] to give silica monoliths with notably larger macropores (30–50 μm) and more isotropic structure. Their pore structure was not destroyed after immobilization of ionic liquids and the catalysts obtained from the crushed monoliths were very active, selective and stable in the Baeyer–Villiger reaction and also in aerobic oxidation of primary alcohols [16–18].

The up to date methods of silica modification [19] offer huge potentials to develop microreactors with the structure

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purposely designed to meet specific catalytic and process engineering demands. Most recently these monoliths were successfully converted into a miniaturized multichannel enzymatic reactor [20] which could operate at flow rates up to about 20 cm<sup>3</sup>/min at backpressure not exceeding 2.5 bar. Worth noting, the sucrose hydrolysis catalysed by invertase appeared to proceed in this microreactor with maximum rate over 1000 times faster than in the MCF-based slurry system, and the enzyme confined in mesopores showed notably larger affinity to substrate than the native one, a clear signature of hyperactivity effect.

For this reason we deemed it important to test the potentials of continuous-flow microreactors made of similar silica monoliths with ultra large (20–50 μm) macropores, but activated with sulphonic acid groups, in the esterification of acetic acid and lactic acid with *n*-butanol. While considered here as model reactions [21–25], they are both of a major practical interest. The *n*-butyl acetate is commonly used as a solvent in the manufacturing of lacquer, artificial perfume, photographic films, plastics and safety glass, and also as synthetic fruit flavouring in foods [26]. Typically, the esterification of lactic acid is applied to recover and purify the acid obtained by bacterial fermentation of carbohydrates [27,28]. But as all previous experiments with the reactors of this type were carried out in relatively benign conditions [7,20], we considered it also important to test whether they can effectively operate at elevated temperature.

## 2. Experimental part

### 2.1. Synthesis of silica monoliths

Silica rods of 4.5 mm diameter were synthesized using Nakanishi method [9–11] with the modifications described in [15,16]. In brief, 0.91 g of polyethylene glycol (PEG 35000) was dissolved in 10.5 cm<sup>3</sup> of 1 M HNO<sub>3</sub>, next 7.6 cm<sup>3</sup> of TEOS was added slowly, followed by addition 0.4 g of cetyltrimethylammonium bromide (CTAB). The solution was mixed at room temperature for 1 h and then polypropylene tubes (5.7 mm i.d.) were filled with the sol. After gelation at 40 °C (12 h) they were aged at the same temperature for seven days. Then the samples were treated in 1 M ammonia aqueous solution at 90 °C for 9 h and after washing with water the monoliths were dried at 40 °C for three days and finally calcined at 550 °C for 5 h. During the processing shrinkage of about 20% of the size of mold was observed.

Single rods (1, 2 and 4 cm long) were embedded into a heat-shrinkable PTFE tubes (DSG-Canusa), equipped with connectors to obtain microreactors suitable for a continuous-flow operation. Then these microreactors were functionalized under flow (48 h, 60 °C) with arenesulphonic acid groups using solutions of 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CSPTMS; 50 wt% solution in CH<sub>2</sub>Cl<sub>2</sub>) dissolved in anhydrous ethanol (99.6%) to prevent uncontrolled hydrolysis.

### 2.2. Characterization of materials

Macropore structure of the monoliths thus obtained was investigated by mercury porosimetry (Quantachrome, PoreMaster 60), and by scanning electron microscopy (SEM, TM 30000 Hitachi). Low temperature nitrogen sorption (ASAP Micromeritics 2010) was applied to evaluate specific surface area (*S*<sub>BET</sub>), mesopore volume and mesopore size distribution using desorption branch of isotherm and BJH method. Before analysis the samples were degassed for 24 h at 200 °C. The incorporation of functional groups was confirmed by FT-IR analysis (samples were prepared by KBr technique). Thermal properties and an amount of incorporated active groups were determined by thermogravimetric method

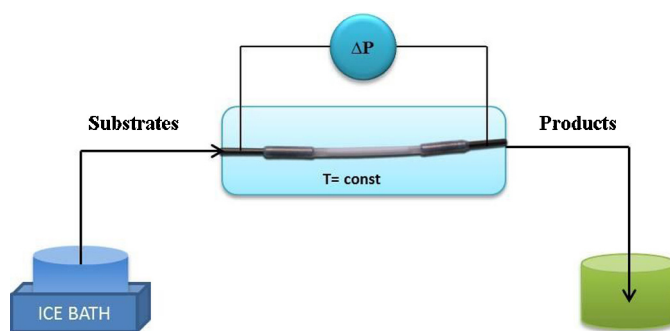


Fig. 1. Scheme of microreactor setup.

(Mettler Toledo STAR 850). The weight loss and thermal effects during heating with ramp of 10 deg/min and air flow of 60 cm<sup>3</sup>/min were recorded in the range of 25–800 °C. Additionally, drop pressure was measured in the continuous reaction conditions using pressure controller (UNIK 5000, Ex-Calibra).

### 2.3. Catalytic measurements

The microreactor was tested in esterification of acetic acid and lactic acid with *n*-butanol (pure p.a, Chempur, Poland). The reactor setup is shown schematically in Fig. 1. The substrates solution was stored in ice bath to prevent any further reaction.

The experiments with acetic acid were performed for the molar ratio of substrates 1:1, at 75 °C using flow rates of 0.03, 0.06 and 0.09 cm<sup>3</sup>/min. Esterification of lactic acid was carried out at 120 °C and 140 °C (measured with accuracy of ±0.1 °C) with flow rates of 0.03–0.4 cm<sup>3</sup>/min. The molar ratio of lactic acid to *n*-butanol was 1:12, 1:6 and 1:1. The reaction progress was evaluated from the amount of acetic/lactic acid in the mixture. Acid concentration at the inlet and outlet of the microreactor was measured by titration method and additionally confirmed by gas chromatography (Agilent 7890 A, FID detector, HP-5 column).

Productivity of the microreactor and residence time was calculated from Eq. (1) and (2) [29]:

$$P = C_0 \times \text{Conv} \times \frac{V_T}{\tau} \quad (1)$$

$$\tau = \frac{V_T \times m}{F} \quad (2)$$

where *C*<sub>0</sub> is initial concentration of substrate [mmol/cm<sup>3</sup>], Conv is the conversion coefficient, *V*<sub>T</sub> is the total pore volume [cm<sup>3</sup>/g], *τ* is the residence time [min], *m* is the mass of monolith [g], *F* is the flow rate [cm<sup>3</sup>/min]. The esterification of acetic acid was also carried out in batch reactor using round bottom flask (75 cm<sup>3</sup>) equipped with a heating jacket and condenser. The reaction was performed under agitation at 1000 rpm using the same temperature and molar ratio of substrates as in the continuous process. The functionalized monolith was crushed and particles of ca. 50 μm were applied as catalyst at concentration of 0.74 wt%.

## 3. Results and discussion

Crack free silica rods displayed in Fig. 2 featured three types of pores detected by mercury porosimetry, nitrogen adsorption and scanning electron microscopy: (i) small mesopores with diameters ca. 3 nm and larger ones with maximum at 20 nm, originating from the presence of CTAB micelles, applied as soft pore templates, and a hydrothermal treatment of monoliths in ammonia solution, and (ii) ultra large macropores (flow-through channels) with diameters in the range of 20–50 μm (Figs. 3 and 4) obtained by

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