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Fabrication and performance of monolithic continuous-flow silica microreactors

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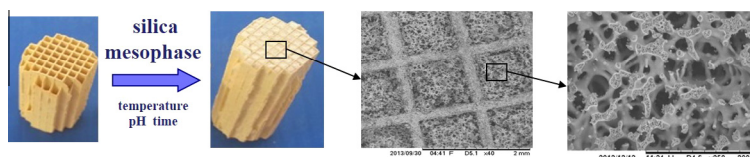
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HIGHLIGHTS

- Monolith-in-monolith topology of microreactor was realized and tested.
- Cordierite reinforcement of silica monolith facilitates its scale-up.
- Good contact of both monoliths can be achieved after a surface treatment.
- The operational viability of microreactor was demonstrated in model reaction.

GRAPHICAL ABSTRACT



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ABSTRACT

Monolith-in-monolith reactor (MiM) was obtained by embedding monolithic silica with the hierarchical pore structure into the channels of conventional honeycomb monolith made of cordierite. Surface treatment of the cordierite with alkaline and acidic solution was applied to increase its surface area and generate strong silanols, to ensure good adherence between the monoliths. Application of 10 wt% NaOH solution at room temperature for 0.5 h was found to offer the best contact between two materials. Both structure and flow characteristics of the embedded silica proved to be quite similar to those obtained for pure silica rods, considered as reference. Performance of MiM microreactor functionalised with sulphonic groups was shown to be similar to that of a single silica rod microreactor in the esterification of acetic acid with butanol. The elaboration of fabrication procedure for monolithic silica microreactors may open new venue in the engineering of cost-effective production of fine chemicals.

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1. Introduction

The mesoporous silicas have been on the forefront of research since their discovery over two decades ago. However, the separation of their fine particles, typically 10–50 μm in size, but quite often sub micrometric sizes, e.g., as obtained from the flow synthesis [1] may be a major problem. An ingenious method proposed to overcome this difficulty is to incorporate magnetic nanoparticles into their structure [1–3]. But even more effective approach is

the use of silica monoliths with the pore structure in micrometric scales similar to that displayed by the mesoporous materials. Indeed, the silica-based continuous-flow monolithic microreactors were more recently shown to be extremely promising for the cost-effective production of *fine chemicals* [4]. Owing to the unique hierarchical pore structure, in which flow-through macropores are connected to an extensive network of meso- and micro-pores [4], the back-pressure could be reduced, permeability increased and the accessibility of substrates to catalytic sites improved, giving in overall much better performance compared to packed columns [5]. The monoliths, typically obtained, feature high porosity and large surface area, but their mechanical strength is low. So far, these microreactors were fabricated by embedding the monolith

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either into a heat-shrinkable PTFE tube [4] or a polymeric body [6], which limited the scope of their operation.

To achieve more robust structure of the monoliths the concept of monolith-in-monolith (MiM) was proposed [7]. It relies on embedding silica monoliths with the hierarchical pore structure into the channels of conventional ceramic monolith, e.g. made of cordierite. The cordierite is a crystalline magnesium aluminosilicate ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) widely applied for high-temperature applications in the form of honeycomb monoliths, serving as supports in industrial catalytic systems. However, as the surface area of these monoliths is low $<0.5\text{ m}^2/\text{g}$, therefore it has to be extended and also activated, and this is achieved by a washcoat [8–10]. The acid treatment is often applied, prior to deposition of the washcoat, to increase the monolith's surface area and to improve adhesion of the coating to the support [11].

The concept of monolith-in-monolith is clear. However, it appeared somewhat difficult to fabricate it, and especially to achieve a good contact between these two materials. It is critical for the effective operation of the reactor; otherwise maldistribution of the fluid flow will follow. However, this contact is exposed to a considerable stress, caused by shrinkage of the silica monolith during drying and calcination and this poses a need for its reinforcement. The latter can be achieved by extension of the contact surface area and also the formation of strong bonds between the two solids using chemical methods.

In this paper we propose a treatment of the cordierite surface to increase the contact surface area and generate strong surface silanols for its firm binding with the siliceous monolith. The composition of the solution applied, temperature and time of the treatment were investigated. The changes in surface area, its composition and morphology were studied by nitrogen adsorption, XPS and SEM. The hydrodynamic properties of MiMs were compared with those determined for a single silica monolith. Finally, practical potentials of the MiM-type of microreactor functionalised with arenesulphonic acid groups were examined in a model reaction of acetic acid esterification with butanol to demonstrate its operational viability.

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS, 99%, ABCR) was used as a silica precursor. Polyethylene glycol (PEG 35000, Fluka) induced phase separation during monoliths synthesis and acted as a matrix of macropore structure. Nitric acid (65%, Avantor Performance Materials) was used as the catalyst for hydrolysis and condensation of TEOS. Cetyltrimethylammonium bromide (CTAB, Aldrich) was applied as a mesopores template. Ammonia aqueous solution (25%, Avantor Performance Materials) was employed during post-synthesis treatment of monoliths. The precursor of acidic groups was 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CSPTMS, 50% in methylene chloride, ABCR). Cordierite honeycomb monolith (Corning) with channel dimension of 1.1 mm and wall thickness of 0.17 mm was used as support for monolithic silica. Sodium hydroxide and piranha solution ($\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$) (Avantor Performance Materials) were applied for a cordierite treatment. Acetic acid (99.5%) and n-butanol (99.5%), both from Chempur were applied as reactants in evaluation of the catalytic performance. All the chemicals were used without further purification.

2.2. Fabrication of microreactors

The monolith-in-monolith structure was obtained by filling the cordierite honeycomb rods ($12 \times 40\text{ mm}$) with a silica sol. First, the

cordierite rods were treated with sodium hydroxide solution (10, 20, and 30 wt%) or piranha for 30, 60 or 120 min, at different temperature. After treatment, they were washed with excess of deionised water and dried at $110\text{ }^\circ\text{C}$ overnight. Next, silica sol was prepared using a modified Nakanishi method [6]. Briefly, mixture of TEOS, PEG and nitric acid (1 M) was stirred in an ice bath for 1 h, followed by addition of CTAB. Molar ratio of TEOS:PEG: HNO_3 : H_2O :CTAB was 1:0.53:0.26:14:0.0275. Then the honeycomb channels were filled with the transparent sol, which was left to gel and age at $40\text{ }^\circ\text{C}$ for 7 days. After that, the MiM was treated in a 1 M ammonia solution at $90\text{ }^\circ\text{C}$ for 9 h. Finally, organic templates were decomposed during calcination at $550\text{ }^\circ\text{C}$ for 6 h. The weight ratio of silica to cordierite was 0.32. For comparison, pure silica rods of the same length were synthesized using the procedure described above.

The single MiM piece was embedded into a heat-shrinkable polytetrafluoroethylene tube (PTFE, DSG-Canusa), equipped with connectors [12]. To impart catalytic properties to the microreactor the arenesulphonic groups were incorporated into silica surface. The functionalization was performed by passing (and recycling) the solution of CSPTMS dissolved in dry ethanol for 48 h at $60\text{ }^\circ\text{C}$. The amount of functional groups (determined by thermogravimetry) was 0.6 mmol/g.

2.3. Characterization

Scanning electron microscopy (SEM, TM 3000 Hitachi) was used to examine the macroporous structure and morphology of the monoliths, and the surface of the cordierite before and after the treatment with sodium hydroxide and piranha solution. The specific surface area, mesopore volume and pore size distribution were determined from the low temperature nitrogen adsorption (ASAP Micromeritics 2010). The size distributions of pores larger than 50 nm and total pore volume of silica monoliths were measured by a mercury porosimetry (Quantachrome, PoreMaster 60). The surface composition of cordierite was determined by XPS technique. The spectra were recorded by a VG Scientific ESCALAB-210 photoelectron spectrometer using a non-monochromatized Al $K\alpha$ ($E_{hv} = 1486.6\text{ eV}$) radiation (14.5 kV; 20 mA). The binding energy (E_b) scale was calibrated against the position of C 1s ($E_b = 284.6\text{ eV}$). The analysis chamber was operated under an ultrahigh vacuum with a pressure of $5 \times 10^{-7}\text{ Pa}$. The spectra were recorded with 0.4 eV resolution and deconvolution was made using AVANTAGE programme (Thermo Electric ver. 4.84), the background was fitted by a Shirley's model.

The esterification of acetic acid with butanol was carried out at $75\text{ }^\circ\text{C}$, for substrates ratio 1:1, and using the flow rate of $0.03\text{ cm}^3/\text{min}$ in all reactors. Concentrations of the substrates and product were measured using gas chromatography (Agilent 7890A, FID detector, HP-5 column). Error of the evaluated activities was smaller than 3%. The pressure drop was measured using a pressure controller (UNIK 5000, Ex-Calibra).

3. Results and discussion

As it can be seen from Fig. 1, the proposed concept can indeed be realized by filling the channels of the cordierite honeycomb with silica monoliths to obtain a monolith-in-monolith type of structure.

As already mentioned, the surface of the honeycomb was treated with sodium hydroxide solutions of different concentration and also piranha solution prior to introduction of the silica sol. Fig. 2 shows SEM images of its surface after such treatment for 0.5 h at $20\text{ }^\circ\text{C}$. Appreciable changes in surface morphology can be observed. The edges and corners of the pristine crystalline structure were

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